

SYNTHESIS AND CHARACTERIZATION OF 3d TRANSITION METAL COMPLEXES  
WITH 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 Honors (Resource Chemistry)

Faculty of Resource Science and Technology  
UNIVERSITI MALAYSIA SARAWAK

2011

## **Acknowledgement**

I would like to take this opportunity to express my gratitude to all of the people who helped to make this work possible. Foremost, I am deeply appreciative and grateful to my supervisor Associate Professor Dr. Md. Abu Affan for his valuable guidance, comments, motivation and patient in accomplishing this project. I would also like to express my sincere thanks to my co-supervisor, Miss Maya Asyikin for her guidance and help throughout this research. Furthermore, this work would not be completed without the assistance of technical staff of the Faculty of Resource Science and Technology, Universiti Malaysia Sarawak. I would also like to express my billion thanks to my lab mates, Miss Dayang Norafizan, Miss Norrihan and Mr. Salam for their guidance and precious comment. My final and greatest debt is to my supportive family for being my constant companion throughout this study. Thank you very much everyone with your unceasing encouragement, that have made this thesis become a reality.

## Table of Contents

Acknowledgement	II
Declaration	III
Table of Contents	IV
List of Tables	VI
List of Figures	VII
Abstract	IX
1.0 Introduction	1
1.1 Objective	3
2.0 Literature Review	4
2.1 Transition metal(II) complexes with their Schiff base ligands	4
3.0 Materials and Method	9
3.1 Physical measurements	9
3.2 Synthesis	10
3.2.1 Synthesis of Schiff base ligand (1)	10
3.2.2 Synthesis of Schiff base ligand (2)	11
3.2.3 Synthesis of transition metal (II) complexes with Schiff base ligands (1-2)	12
3.2.3.1 Synthesis of [Ni(C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> )] (3)	12
3.2.3.2 Synthesis of [Cu(C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> )] (4)	13
3.2.3.3 Synthesis of [Fe(C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> )] (5)	14
3.2.3.4 Synthesis of [Co(C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> )] (6)	14
3.2.3.5 Synthesis of [Co(C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> ).H <sub>2</sub> O] (7)	15
3.2.3.6 Synthesis of [Fe(C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> ).H <sub>2</sub> O] (8)	16
3.2.3.7 Synthesis of [Cu(C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> ).H <sub>2</sub> O] (9)	16
3.2.3.8 Synthesis of [Zn(C <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> ).2H <sub>2</sub> O] (10)	16
4.0 Results and Discussion	17
4.1 Physical data of Schiff base ligands (1-2) and their metal complexes (3-10)	17
4.2 Infrared Spectroscopy	19
4.2.1 Infrared spectra of Schiff base ligand (1) and its metal complexes (3-6)	19

4.2.2 Infrared spectra for Schiff base ligand (2) and its metal complexes (7-10)	23
4.3 UV-Vis Spectroscopy	27
4.4 <sup>1</sup> H NMR Spectra	31
4.4.1 Schiff base ligand (1) and its metal complexes (3-6)	31
5.0 Conclusion	34
Reference	35

## LIST OF TABLES

DESCRIPTIONS	PAGES
Table 1      Physical and elemental analysis of Schiff base ligands (1-2) and their transition metal complexes (3-10)	18
Table 2      IR spectra for Schiff base ligand (1) and its metal complexes (3-6)	19
Table 3      IR spectra for Schiff base ligand (2) and its metal complexes (7-10)	23
Table 4      Electronic spectra data for Schiff base ligand (1) and its metal complexes (3-6)	27
Table 5      Electronic spectra data for Schiff base ligand (2) and its metal complexes (7-10)	27

## LIST OF FIGURES

DESCRIPTIONS	PAGES
Figure 1      Formation of imine	1
Figure 2      Structure of 2-hydroxy-N-[(1E)-1-(pyridine-2-yl)ethylidene] benzohydrazide	4
Figure 3      Structure of 2-hydroxy-N'-[(E)-phenyl(pyridine-2-yl) methylidene]benzohydrazide	5
Figure 4      Structure of N,N'-(pyridine-2,6-diyldiethene-1,1-diyl) dipyridin-2-diamine	5
Figure 5      Structure of 2- {[ (1E,2Z)-2-(3-aminophenyl)but-2-en-1-ylidene] amino } -N-(2-oxopropyl)acetamide	6
Figure 6      Structure of N- ( {[ (1E)-1-(pyridine-2-yl)ethylidene] amino } methyl)benzamide	6
Figure 7      Structure of N- ( {[ (1E)-1-(pyridine-2-yl)methylidene]amino } methyl)benzamide	6
Figure 8      Structure of 2-hydroxy-N'-[(E)-pyridin-2-ylmethylidene] benzohydrazide	7
Figure 9      Structure of 2-hydroxy-N'-[(1Z)-1-(2-hydroxyquinolin-3-yl) ethylidene]benzohydrazide	7
Figure 10     Structure of 3- {(Z)-[2-(1,3-benzothiazol-2-yl)hydrazinylidene] methyl} quinolin-2-ol	8
Figure 11     Structure of 2- {(E)-[(1-hydroxybutan-2-yl)imino]methyl} -6-methoxyphenol	8
Figure 12     Structure of 2- {(E)-[(2-hydroxyethyl)imino]methyl} -6-methoxyphenol	8
Figure 13     Synthesis of Schiff base ligand (1)	10
Figure 14     Synthesis of Schiff base ligand (2)	11
Figure 15     Synthesis of Ni(II) complex with Schiff base ligand (1)	13
Figure 16     Synthesis of Co(II) complex with Schiff base ligand (2)	15
Figure 17     IR spectrum of C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> (1)	21

Figure 18	IR spectrum of $[\text{Cu}(\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2)]$ ( <b>4</b> )	22
Figure 19	IR spectrum of $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$ ( <b>2</b> )	25
Figure 20	IR spectrum of $[\text{Cu}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2) \cdot \text{H}_2\text{O}]$ ( <b>9</b> )	26
Figure 21	Electronic spectra for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2$ ( <b>1</b> ) and $[\text{Co}(\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2)]$ ( <b>6</b> ) in chloroform solution	29
Figure 22	Electronic spectra for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$ ( <b>2</b> ) and $[\text{Cu}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2) \cdot \text{H}_2\text{O}]$ ( <b>9</b> ) in chloroform solution	30
Figure 23	$^1\text{H}$ NMR spectra for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2$ ( <b>1</b> )	32
Figure 24	$^1\text{H}$ NMR spectra for $[\text{Ni}(\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2)]$ ( <b>3</b> )	33

# Synthesis and Characterization of Transition Metal Complexes with Schiff Base Ligands

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## Abstract

There are two kinds of Schiff base ligands have been synthesized and characterized in this research project work. The first ligand was derived by the condensation reaction of benzoylacetone and ethylenediamine, whereas the second ligand was derived by the condensation of benzyhydrazide and 2-hydroxy-1-naphthaldehyde. Both Schiff base ligands have been reacted with metal(II) ions such as Fe(II), Ni(II), Cu(II), Co(II) and Zn(II) ions, respectively. Two Schiff base ligands and their metal complexes have also been characterized by UV-visible, FTIR and  $^1\text{H}$  NMR spectroscopic techniques. The first ligand was acted as dinegative tetradentate nature while the second ligand was acted as dinegative tridentate nature towards metal(II) ions, respectively. All the metal complexes have coordination number of four (4). All metal complexes are non electrolyte in nature.

*Keywords:* Schiff base ligands, transition metal, spectroscopic study

## Abstrak

*Terdapat 2 jenis ligan Schiff bes yang telah disintesis dan dicirikan dalam kajian ini. Ligan Schiff bes yang pertama dihasilkan daripada benzoaseton dan etelindiamin, manakala ligan Schiff bes yang kedua dihasilkan daripada benzihidrazi dan 2-hidrosi-1-nataaldehik. Kedua-dua ligan Schiff bes ini telah bertindak balas dengan ion logam(II) seperti Fe(II), Ni(II), Cu(II), Co(II) dan Zn(II). Kedua-dua ligan Schiff bes dan kompleks logamnya telan dicirikan dengan menggunakan teknik spektroskopi UV, IR dan  $^1\text{H}$  NMR. Ligan Schiff bes yang pertama bertindak sebagai dinegatif tetradentat manakala ligan Schiff bes yang kedua bertindak sebagai dinegatif tridentat. Kesemua kompleks logam mempunyai nombor koordinasi 4 dan tidak bersifat elektrolit.*

*Kata kunci:* Ligan Schiff bes, logam peralihan, kajian spekstroskopi

## 1.0 Introduction

Schiff base is a class of derivatives that formed by the condensation reaction of an aldehyde or a ketone with primary amine. The general formula is  $R'-R''C=N-R'''$ . This formula contains a carbon-nitrogen double bond with nitrogen atom connected to an alkyl or aryl group which makes a Schiff base is a stable imine.

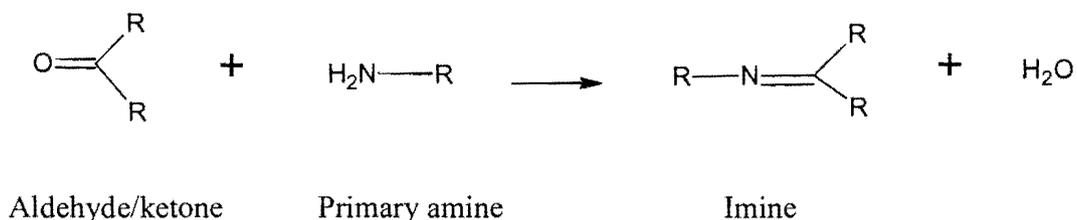


Figure 1: Formation of imine.

The Schiff base ligand can exist in monodentate, bidentate, tridentate and so on. Metal complexes of multidentate Schiff base ligand have been extensively studied because such ligand can bind very stably with one, two or more heavy metal ions centers involving various coordination modes and allow successful synthesis of homo and/or heteronuclear metal complexes with interesting stereochemistry (Atwood, 1997).

Schiff base ligand can form a very stable complexes compare to other ligands as polydentate Schiff base ligand have the chelating properties which make the coordination system resistant to the attack of non-chelating ligand. Polydentate ligand such as bidentate and tridentate which have more than one site of attachment to the same metal ion are often called chelating ligand. The chelate effect is the enhanced stability of a complex containing chelating ligand compared with similar complex formed from the corresponding monodentate ligand.

Schiff base ligands have played a special role as chelating ligand in main groups and transition metal coordination chemistry because of their stability under a variety of redox conditions and because imine ligand are border line Lewis bases. The complexes containing the chelate rings are almost 100 times more stable than the complexes that have no chelate rings. It has also been known that the complexes containing chelating ligand are more stable thermodynamically.

Schiff base metal complexes have been studied extensively due to the synthetic flexibilities of these Schiff base ligand and their selectivity as well as sensitivity towards the transition metal ions.

The Schiff base ligands are one of the most widely used ligand 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. In the area of bioinorganic chemistry, Schiff base ligand complexes has centered on the role in providing synthetic models for the metal-containing sites in metallo-proteins and metallo-enzymes (Tarafer *et al.*, 2001).

There are some research have been done on the Schiff base ligand and their transition metal complexes, but metal complexes with tridentate Schiff base ligand having a ONO donor set has been studied less. The main objective of this research proposal is to synthesize a new tridentate Schiff base ligands and investigate their coordination behavior with transition metal(II) ions.

## 1.1 Objectives

The main goals of this project involved the syntheses and characterization of *3d* metal(II) complexes. The specific objectives of this research are:

1. to synthesize Schiff base ligands.
2. to study the coordination behavior of the Schiff base ligands with *3d* transition metal(II) ions.
3. to characterize the Schiff base ligands and their metal(II) complexes by using CHN elemental analyzer, FTIR, UV-visible, and <sup>1</sup>H NMR spectral studies.
4. to determine the molar conductivity of the synthesized *3d* metal(II) complexes.

## 2.0 Literature review

### 2.1 Transition metal(II) complexes with their tridentate Schiff base ligands

The most common form of polydentate ligand is bidentate, that is having two possible points of attachment to a metal ions. Tridentate ligand are less common compared to bidentate and tetradentate ligand. However, they are quite useful for binding with metal ions that can form stable 5-coordination complexes with sufficiently bulky partner ligand or indeed the Schiff base ligand itself.

Schiff base ligands are the most commonly used ligand to form metal complexes. This is because of their capability to form very stable metal complexes to other ligand. Schiff base ligand complexes are considered to be among the most important stereochemical models due to their synthetic flexibilities and structural varieties. There are a lot of research have been done to determine the characteristics and properties of these ligands.

In 2009, Shit. S *et al.*, have been successfully synthesized three new coordination complexes of Mn(II), Co(III) and Cu(II) ions obtained from two N,N,O-donor hydrazone ligands. These two ligands were obtained by condensation reaction of 2-acetylpyridine with salicyloylhydrazide and 2-benzoylpyridine with salicyloylhydrazide. These three new coordination complexes exhibited different chemical and magnetic properties.

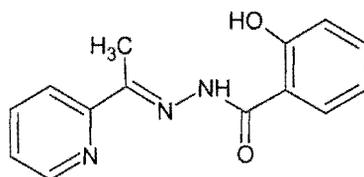


Figure 2: 2-hydroxy-*N*-[(1*E*)-1-(pyridin-2-yl)ethylidene]benzohydrazide

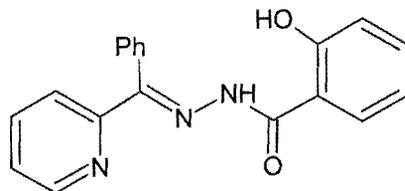


Figure 3: 2-hydroxy-*N*-[(*E*)-phenyl(pyridin-2-yl)methylidene]benzohydrazide

Gudasi. K *et al.*, 2005 state that the synthesis of a tridentate ligand, *N,N'*-bis(2-pyridinyl)-2,6-pyridinedicarboxamide is described together with its Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes which were characterized based on elemental analysis, conductivity measurements, spectral, magnetic and thermal studies. The IR spectral studies showed that all the complexes exhibited a similar feature which are the ligating nature of the ligand to the metal ions and claimed that the ligand has coordinated through the nitrogens of the deprotonated amides and the central pyridine.

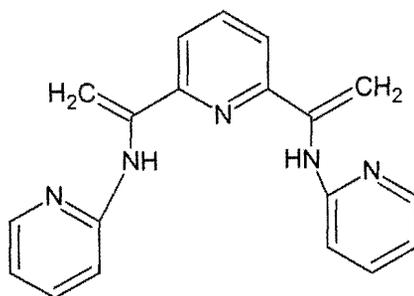


Figure 4: *N,N'*-(pyridine-2,6-diyl)diethene-1,1-diyl)dipyridin-2-amine

Joseyphus. R. S *et al.*, 2010, reported the synthesis of tetrahedral geometry for Co(II) and Ni(II) complexes and square planar geometry for Cu(II) complexes with tridentate Schiff base ligand. The Schiff base ligand was derived from the condensation of indole-3-carboxaldehyde and glycylglycine in absolute ethanol under reflux condition. The Schiff base ligand complexes were characterized by elemental analysis, mass spectrum,

IR and  $^1\text{H}$  NMR spectral studies. From this research, the magnetic measurements show weak ferromagnetic behavior for Co(II) and Ni(II) complexes and paramagnetic behavior for Cu(II) complexes.

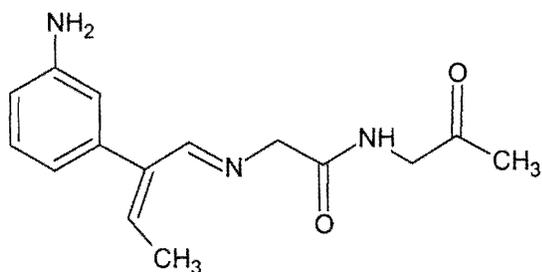


Figure 5: 2-(((1E,2Z)-2-(3-aminophenyl)but-2-en-1-ylidene)amino)-N-(2-oxopropyl)acetamide

Ray. A *et al.*, 2008 reported that three new coordination complexes of Zn(II) and Mn(II) have been synthesized using two different tridentate N,N,O donor hydrazone ligand, Hpbh and Hacpbh. The ligand Hpbh and Hacpbh were prepared by the condensation of pyridine-2-carboxaldehyde and 2-acetylpyridine with benzhydrazide respectively.

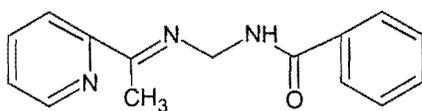


Figure 6: N-(((1E)-1-(pyridin-2-yl)ethylidene)amino)methyl)benzamide

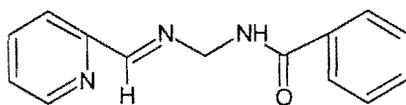


Figure 7: N-(((E)-pyridin-2-yl)methylidene)amino)methyl)benzamide

Tridentate Schiff base ligand with NNO donor sites are well known to coordinate with various metal ions such as Ni(II), Co(II) and Zn(II). The NNO-donor ligand have been derived from the condensation of pyridine-2-carboxylaldehyde and salicylhydrazide. The result showed that all the metal complexes in this research were in octahedral coordination number ( Samanta. B., 2007).

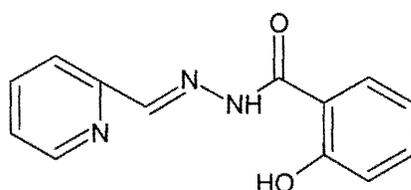


Figure 8: 2-hydroxy-*N'*-[(*E*)-pyridin-2-ylmethylidene]benzohydrazide

Kurdekar. G. S *et al.*, 2010 reported that a series of Co(II), Ni(II), Cu(II) and Zn(II) complexes of tridentate Schiff base ligands have been prepared. The ligands are synthesized by the condensation reaction of 2-hydroxy-3-formylquinoline with salicyloylhydrazide and 2-hydrazinobenzothiazole in absolute ethanol. The coordination behavior of Schiff base ligands is proven in tridentate manner with NOO and NNO-donor sites. The geometry of these metal complexes was found to be an octahedral.

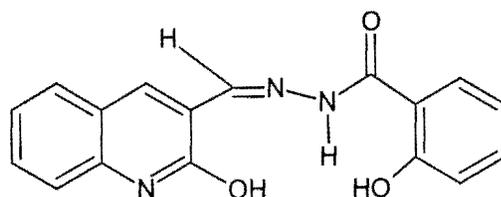


Figure 9: 2-hydroxy-*N'*-[(1*Z*)-1-(2-hydroxyquinolin-3-yl)ethylidene]benzohydrazide

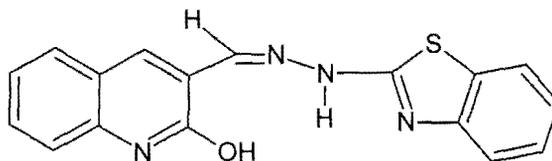


Figure 10: 3-((Z)-[2-(1,3-benzothiazol-2-yl)hydrazinylidene]methyl)quinolin-2-ol

There are two tridentate Schiff base ligands have been successfully synthesized from 2-hydroxy-3-methoxybenzaldehyde with 2-aminoethanol and 2-aminobutan-1-ol by Zhang, Y *et al.*, 2010. These two ligands are then react with nickel chloride, azide or thiocyanate to give rise to two dinuclear complexes.

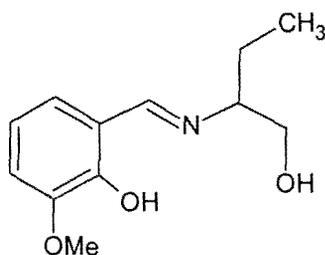


Figure 11: 2-((E)-[(1-hydroxybutan-2-yl)imino]methyl)-6-methoxyphenol

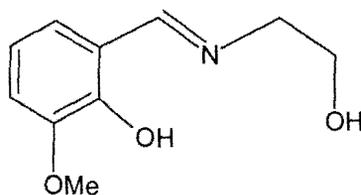


Figure 12: 2-((E)-[(2-hydroxyethyl)imino]methyl)-6-methoxyphenol

### 3.0 Material and Method

#### 3.1 Physical measurements

The research was conducted in Inorganic Research Laboratory at UNIMAS. All chemicals were purchased from Fluka, Aldrich or J.T Baker. Schiff base ligands and their transition metal complexes were characterized by C,H,N analyses, UV-visible, FTIR and  $^1\text{H}$  NMR spectra analyses. The C,H,N analyses were recorded with Flash EA 1112 Series CHN elemental analyzer at UNIMAS. Infrared spectra were recorded as KBr disc using Perkin Elmer Spectrum GX Fourier-Transform Spectrometer ( $4000 - 400 \text{ cm}^{-1}$ ).  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3/\text{DMSO}-d_6$  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 measurements of the transition metal complexes were done in  $1 \times 10^{-4}$  M solution of a DMF/DMSO at room temperature using a Jenway conductivity meter in Inorganic Laboratory at UNIMAS.

## 3.2 Synthesis

### 3.2.1 Synthesis of Schiff base ligand (1)

The Schiff base ligand (1) was prepared by the condensation reaction of benzoylacetone (0.1202 g, 2 mmol) and ethylenediamine (0.6488 g, 4 mmol) in absolute ethanol (10 mL). A few drops of glacial acetic acid were added to fasten the reaction. The mixture was stirred and heated under reflux condition for 3-4 hours in 1:2 mole ratio. After 3-4 hours, the mixture was allowed to cool to room temperature. The white precipitate was filtered and washed several times using ethanol. The crystalline white solid was recrystallized from ethanol and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. Yield: 0.596 g, 77 %, melting point: 183-185 °C.

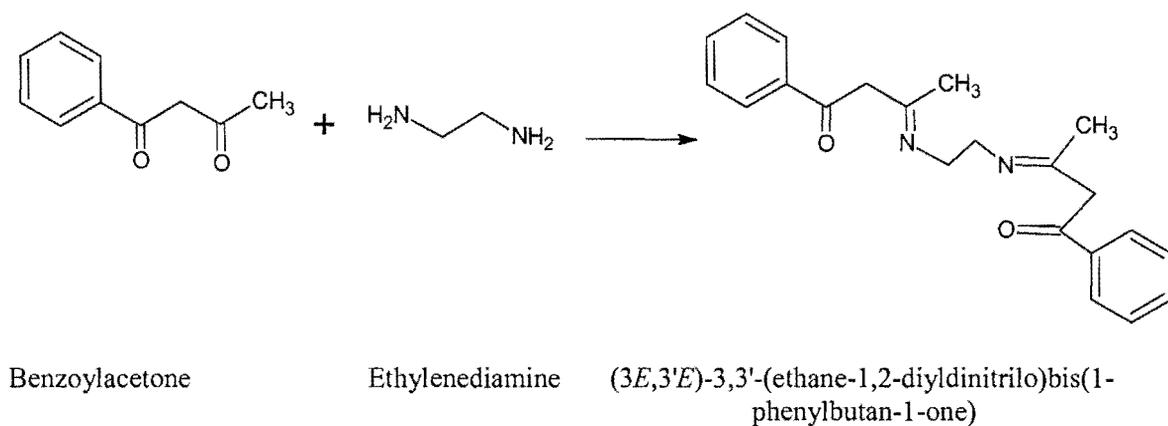


Figure 13: Synthesis of Schiff base ligand (1)

### 3.2.2 Synthesis of Schiff base ligand (2)

Benzyhydrazide (1.00 g, 7 mmol) and 2-hydroxy-1-naphthaldehyde (1.25 g, 7 mmol) were dissolved in absolute ethanol (10 mL). A few drops of glacial acetic acid were added to fasten the reaction. The mixture was refluxed for 1 hour under constant stirred condition. Then, the volume of the mixture was reduced using rotary evaporator until obtain the creamy color precipitate. The creamy color precipitate was filtered and washed several times using ethanol. The creamy color ligand was recrystallized from ethanol. The precipitate was dried in *vacuo* over P<sub>2</sub>O<sub>5</sub>. Yield: 1.420 g, 63 %, melting point: 218-220 °C.

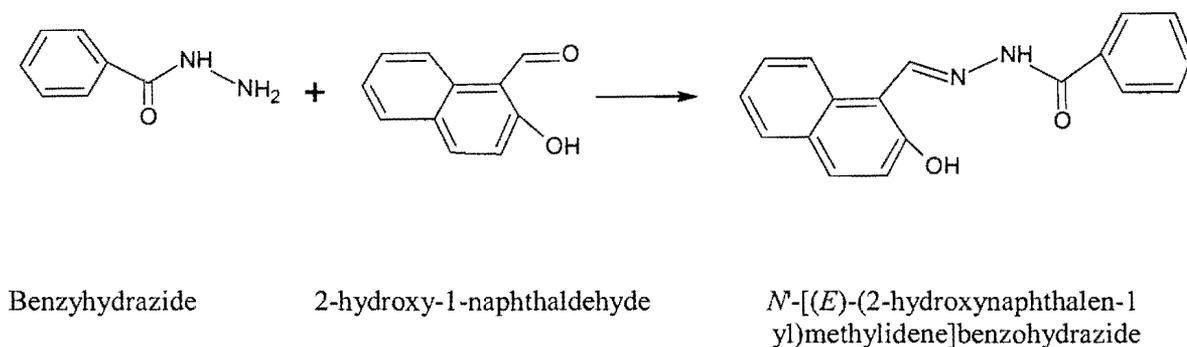
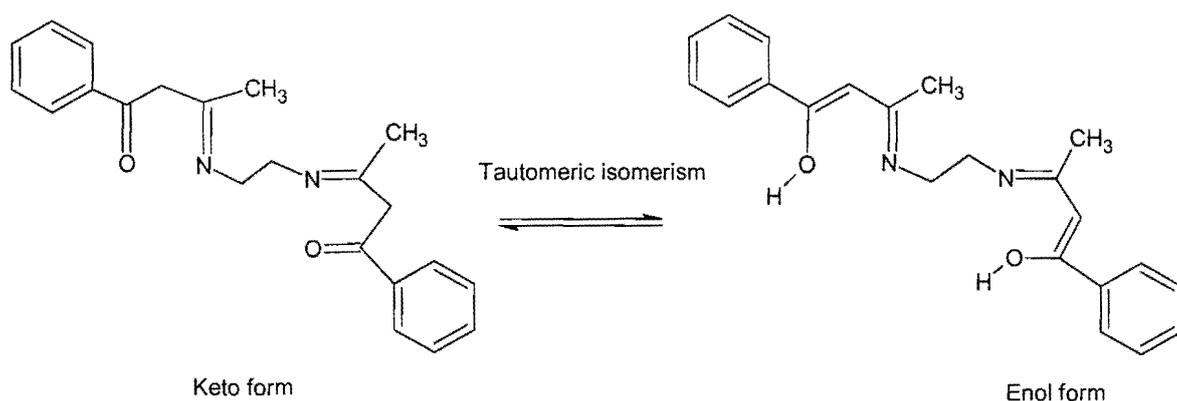


Figure 14: Synthesis of Schiff base ligand (2)

### 3.2.3 Synthesis of transition metal(II) complexes with Schiff base ligands (1-2)

#### 3.2.3.1 Synthesis of $[\text{Ni}(\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2)]$ (3)

Nickel(II) complex was prepared by direct reaction of the Schiff base ligand (1) (0.696 g, 2 mmol) with  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  (0.475 g, 2 mmol) in metal to ligand ratio 1:1 in absolute methanol in the presence KOH (0.112 g, 2 mmol). The mixture was refluxed for 4-5 hours under stirred condition. The brown color precipitate was formed after refluxed for 4-5 hours. The brown color precipitate was filtered and washed several times using ethanol. The brown color complex was recrystallized from ethanol. The precipitate was dried in *vacuo* over  $\text{P}_2\text{O}_5$ . Yield: 0.685 g, 53 %, melting point: 300-320 °C.





### 3.2.3.3 Synthesis of [Fe(C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>)] (5)

The preparation of Fe(II) metal complex was same as described in (3). FeCl<sub>2</sub>.6H<sub>2</sub>O (0.540 g, 2 mmol) was used to prepare this metal complex. The black color precipitate was filtered and washed several times using ethanol. The black color complex was recrystallized from ethanol. The precipitate was dried in *vacuo* over P<sub>2</sub>O<sub>5</sub>. Yield: 0.855 g, 63 %, melting point: 308-310 °C.

### 3.2.3.4 Synthesis of [Co(C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>)] (6)

The preparation of Co(II) metal complex was same as described in (3). CoCl<sub>2</sub>.6H<sub>2</sub>O (0.476 g, 2 mmol) was used to prepare this metal complex. The red color precipitate was collected by vacuum filtration and washed several times using ethanol. Ethanol was used as the recrystallisation solvent. The precipitate was dried in *vacuo* over P<sub>2</sub>O<sub>5</sub>. Yield: 0.815 g, 63 %, melting point: 282-283 °C.

### 3.2.3.5 Synthesis of $[\text{Co}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2) \cdot \text{H}_2\text{O}]$ (7)

Cobalt(II) complex was prepared by direct reaction of the Schiff base ligand (**2**) (0.29 g, 1 mmol) with the  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.238 g, 1 mmol) in metal to ligand ratio 1:1 in absolute methanol in the presence of KOH (0.056 g, 1 mmol). The mixture was refluxed for 1-2 hours under stirred condition. Brown color precipitate was obtained. The precipitate was filtered and washed several times with ethanol. Ethanol was used to recrystallize the precipitate. The precipitate was dried in *vacuo* over  $\text{P}_2\text{O}_5$ . Yield: 0.405 g, 69 %, melting point: 350-352 °C.

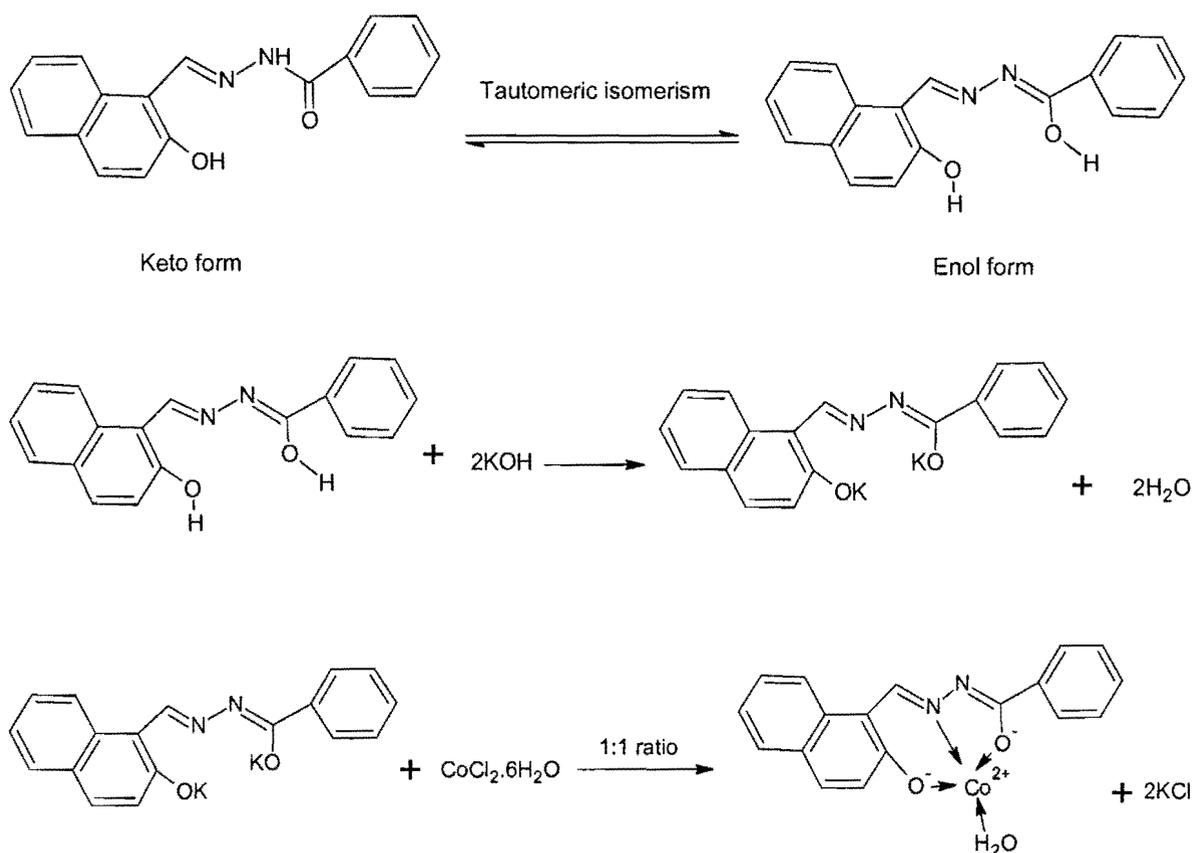


Figure 16: Synthesis of Co(II) complex with Schiff base ligand (**2**)

### 3.2.3.6 Synthesis of $[\text{Fe}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2)_2 \cdot \text{H}_2\text{O}]$ (8)

Synthesis of Fe(II) complex was same as described in (7).  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  (0.27 g, 1mmol) was used instead of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . Black color precipitate was obtained. The precipitate was filtered and washed several times with ethanol. The black color precipitate was recrystallize from ethanol. The precipitate was dried in *vacuo* over  $\text{P}_2\text{O}_5$ . Yield: 0.352 g, 57 %, melting point: 333-335 °C.

### 3.2.3.7 Synthesis of $[\text{Cu}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2)_2 \cdot \text{H}_2\text{O}]$ (9)

Synthesis of Cu(II) complex was same as described in (7).  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.17 g, 1mmol) was used instead of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . Green color precipitate formed and it was filtered and washed several times with ethanol. Ethanol was used to recrystallize the green precipitate. The precipitate was dried in *vacuo* over  $\text{P}_2\text{O}_5$ . Yield: 0.316 g, 61 %, melting point: 302-304 °C.

### 3.2.3.8 Synthesis of $[\text{Zn}(\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_6)_2 \cdot 2\text{H}_2\text{O}]$ (10)

Synthesis of Zn(II) complex was same as described in (7).  $\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O}$  (0.22 g, 1mmol) was used to synthesis this metal complex. The yellow precipitate was filtered and washed several times with ethanol. The precipitate was recrystallize from ethanol. The precipitate was dried in *vacuo* over  $\text{P}_2\text{O}_5$ . Yield: 0.355 g, 63%, melting point: 350-353 °C.