SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES WITH HYDRAZONE SCHIFF BASE LIGANDS

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Bachelor of Science with Honours
(Resource Chemistry)
2013
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This report is submitted in partial fulfillment of the requirement for the degree of Bachelor of Science with Honours

Resource Chemistry
Faculty of Resource Science and Technology
University Malaysia SARAWAK

2013
Declaration

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

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Acknowledgment

My first and foremost gratitude goes to my project supervisor, Dr Tiong Pei Jen, who introduced me to the field of hydrazone Schiff base ligands and their metal complexes. I sincerely thank her for innovative ideas, encouragement, guidance, unreserved assistance and scientific knowledge with which she has inspired me profoundly during this work. Her friendly approach during my laboratory work and open discussion are unforgettable. Special thanks to Dr Tay Meng Guan for his guidance and knowledge. I would like to convey my deep regards to Dr Tay Meng Guan who has provided me with some chemicals and apparatus and has enlightened me with useful and guiding comments during my proposal writing.

I would like to express my appreciation and thanks to all the lab assistants and technical staffs for their help and providing the necessary facilities for the analysis. Not forgetting my fellow course mates for their support and help which enable me to complete this project successfully.

Finally, I would like to express my gratitude towards my family who was always there to give me undivided moral support and positive encouragements for me to pursue this project.

Thank you.
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Synthesis and Characterization of Transition Metal Complexes with Hydrazone Schiff Base Ligands

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ABSTRACT

The synthesis and spectroscopic characterization of two hydrazone Schiff base ligands (1-2) and their metal complexes Zn(C$_{30}$H$_{30}$N$_6$O$_2$), Co(C$_{30}$H$_{30}$N$_6$O$_2$), Fe(C$_{30}$H$_{30}$N$_6$O$_2$), Ni(C$_{30}$H$_{26}$N$_4$O$_6$), Zn(C$_{30}$H$_{26}$N$_4$O$_6$) & Fe(C$_{30}$H$_{26}$N$_4$O$_6$) (3-8) are reported in this thesis. Hydrazone Schiff base ligands 1 and 2 were obtained through the condensation reactions of 4-aminoacetophenone with benzhydrazide and 2'-hydroxyacetophenone with 4-hydroxybenzhydrazide respectively. The metal:ligand ratio is 1:2 for all complexes 3-8. The ligands experienced keto and enol tautomerization. The hydrazone Schiff base ligands (1-2) and their metal complexes (3-8) were characterized using FTIR, UV-Vis and $^1$H NMR spectroscopic studies. All hydrazone Schiff base ligands (1-2) and their metal complexes (3-8) are non-electrolyte in nature. Spectral studies suggested that hydrazone Schiff base ligand 1 acts as neutral bidentate ligand (N,O) whereas ligand 2 acts as a monoanionic bidentate ligand (N,O) towards central transition metal ions, and their metal complexes (3-8) were suggested to demonstrate a square planar geometry.

Key words: hydrazone Schiff base ligands, transition metal complexes, spectroscopic studies

ABSTRAK

Sintesis dan pencirian spektroskopi bagi dua ligan hydrazon bes Schiff (1-2) dan kompleks unsur peralihan Zn(C$_{30}$H$_{30}$N$_6$O$_2$), Co(C$_{30}$H$_{30}$N$_6$O$_2$), Fe(C$_{30}$H$_{30}$N$_6$O$_2$), Ni(C$_{30}$H$_{26}$N$_4$O$_6$), Zn(C$_{30}$H$_{26}$N$_4$O$_6$) & Fe(C$_{30}$H$_{26}$N$_4$O$_6$) (3-8) dilaporkan dalam tesis ini. Ligan hydrazon bes Schiff 1 dan 2 diperolehi melalui tindak balas kondensasi antara 4-aminoacetophenone dengan benzhydrazida dan 2'-hidroxyacetophenone dengan 4-hydroxybenzhydrazida masing-masing. Nisbah logam:ligan ialah 1:2 bagi semua kompleks 3-8. Ligan tersebut mengalami pentautomeran antara keto dan enol. Semua ligan hydrazon bes Schiff (1-2) dan kompleks (3-8) telah dicirikan dengan menggunakan infra merah, cahaya ulta lembayung-tampak dan resonans magnet nuklear proton. Semua ligan hydrazon bes Schiff (1-2) dan kompleksnya (3-8) adalah bukan bersifat elektrolit. Kajian spectroskopik mencadangkan ligan hydrazon bes Schiff 1 dan 2 masing-masing bertindak sebagai ligan neutral dan monoanionic bidentat (N,O) yang terikat ke ion logam pertengahan, manakala kompleks yang terbentuk (3-8) dicadangkan menunjukkan geometri segi empat planar.

Kata kunci: Ligan hydrazon bes Schiff, kompleks logam peralihan, kajian spectroskopik
1.0 Introduction

Hydrazones are a class of organic compounds in the Schiff bases family with the structure of azomethine (\(>\text{C} = \text{N}-\text{N}=\text{C}<\)) functional group (Cornelissen et al., 1992). Hydrazone Schiff base compounds are formed usually through the condensation reaction of hydrazine/hydrzone with carbonyl compounds such as aldehydes and ketones in alcoholic solvents like ethanol (Rollas et al., 2007) to yield a product with general formula, R-CO-NH-N=CR’R”’. In general, hydrazone Schiff bases can undergo tautomerization between keto and enol forms (Figure 1) (Fita et al., 2005). Coupling of aryldiazonium salts with active hydrogen compounds is another synthetic route for the synthesis of hydrazone Schiff base ligands (Rollas et al., 2007).

![Keto and Enol Forms](image)

Figure 1: Tautomerization

Hydrazone Schiff bases of acyl, aroyl, and heteroaroyl compounds contain C=O group which can act as an additional donor site (Shelke et al., 2011). This additional donor site resulted in a wider range of properties for hydrazone Schiff base compounds which include the role as good polydentate chelating agents. This polydentate chelating agents can form a variety of stable complexes with various transition and inner transition metals (Cornelissen et al., 1992) because of the complexing ability of ligand through keto-enol tautomerization and availability of other donor sites in the ligand (Kelode et al., 2013). Moreover, with this additional donor site, hydrazone Schiff base compounds are able to demonstrate versatility incoordination, a tendency to yield
stereochemistry (Shelke et al., 2011) of higher coordination number, an ability to behave as neutral or deprotonated ligands, and flexibility in assuming different conformations.

Hydrazone ligands and their complexes have been the subject of studies for many years due to their wide applications in different fields, such as liquid crystal and in catalytic processes (Hamon et al., 2009), extraction of some metal ions, micro determination of metal ions (Nawar et al., 1999), determination of titanium in bauxite, Portland cement, amphibolites granites (Gui et al., 1998), and different biological activities, such as antimicrobial (Chohan et al., 1996) which used iron chelators in the treatment of anemias and as antiviral drugs (Aguelles et al., 2004, Rollas & Kucukguzel, 2007), antifungal (Deepa et al., 2001), antitumor (Iskander et al., 2004), and insecticides (Pokhariyal et al., 1997). In addition they have been studied also as a group of useful spectrophotometric reagents (Singh et al., 1982, Kumar et al., 2004, Vallinath et al., 2010).

Recently, several metal complexes with O-N and O-S donor hydrazone ligands have been widely synthesized and studied because of their potential biological and pharmacological applications of these donor ligands and the complexes obtained from them (Shelke et al., 2011). A lot of attention has been paid on the studies of hydrazone compounds obtained through the reaction of aromatic and heterocyclic hydrazides with aldehydes and ketones. In addition, these hydrazone compounds have been extensively investigated and a versatile behavior in metal coordination have been revealed which depend on the nature of the ligands and the metal ions, the anions of the metal salt, the pH of the reaction medium and the solvent used (Hueso-Urena et al., 2000, Maurya et
From the literature reviews, there has been growing interest in the study of the transition metal complexes with hydrazone Schiff base ligands. Thus, based on the previous reported work, it is possible to further the study on the synthesis of metal complexes with new hydrazone Schiff base ligands. In order to continue to expand the studies in this field, the research project focused on the synthesis, characterization and biological activity of two O-N donor hydrazone Schiff base ligands and their corresponding cobalt, nickel, iron and zinc complexes. It was thought that the metal complexes formed with this potent hydrazone Schiff base ligand should be more biologically active than the metal salts or the ligand individually.
1.1 Objectives

I. To synthesize the hydrazone Schiff base ligands, 4’-aminoacetophenone benzohydrazone (1) and 2’-hydroxyacetophenone-4-hydroxybenzohydrazone (2).

II. To synthesize cobalt(II), nickel(II), zinc(II) and iron(II) complexes of the above mentioned ligands 3-8.

III. To characterize the hydrazone Schiff base ligands (1-2) and their transition metal complexes 3-8 by elemental analysis, UV-Vis, FTIR, GC-MS and 1H and 13C-NMR spectroscopy.

IV. To determine the molar conductivity of ligands (1-2) and their transition metal complexes 3-8.

V. To study the biological activity of ligands 1-2 and their transition metal complexes 3-8.
2.0 Literature Review

2.1 Hydrazone Schiff Bases

In 2009, Affan et al., reported the successful synthesis of a dinegative tridentate hydrazone Schiff base, namely benzoylacetonelisonicotinylhydrazone \((C_{16}H_{15}N_3O_2)\) (Figure 2). This compound was synthesized through the condensation reaction of benzoylacetonel and lisonicotinichydrazide in absolute ethanol, giving a 92% yield. They reported that \((C_{16}H_{15}N_3O_2)\) is biologically less active compared with its organotin(IV) complexes.

![Figure 2: Synthesis of benzoylacetonelisonicotinylhydrazone \((C_{16}H_{15}N_3O_2)\)](image)

Diao and co-workers (2008) reported on the synthesis of \((E)-4\)-Bromo-N’-\(2\)-hydroxy-1-naphthylmethylene)benzohydrazide \((C_{18}H_{13}BrN_2O_2)\) via the reaction of 2-hydroxy-1-naphthaldehyde with 4-bromobenzohydrazide in absolute methanol as shown in Figure 3. This Schiff base molecule was reported to have an E configuration about the C-N bond and is almost planar.
In a separate study, N’-(3,4,5-trimethoxybenzylidene)-2-phenylacetohydrazide, (C\textsubscript{13}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2}) was prepared by reacting 3,4,5-trimethoxybenzaldehyde with 2-phenyl acetohydrazide in methanol (Figure 4). HCl was added as catalyst in this reaction (Jadon et al., 2011). This Schiff base molecule was reported to possess varied biological activities.

In 2007, Pouralimardan et al., reported the synthesis of five dissymmetric tridentate hydrazone Schiff base ligands containing a mixed donor set of ONN and ONO through the reaction of benzhydrazide with the appropriate salicylaldehyde and pyridine-2-carbaldehyde. The results suggested that four of the synthesized ligands (HL1, HL2, HL3, and HL4) coordinate as univalent anions with their tridentate O,N,O donors derived from the carbonyl and phenolic oxygen and azomethine nitrogen while one of them (L5) is a neutral tridentate Schiff base with N,N,O donors as shown in
Figure 5. They reported that HL1 has a trans-C=N-N-C conformation and hydrogen bonding from the phenolic OH to the azomethine nitrogen atom.

\[
\begin{align*}
\text{HL1: } Y &= \text{OCH}_3, X = \text{H} \\
\text{HL2: } Y &= \text{OH}, X = \text{H} \\
\text{HL3: } Y &= \text{H}, X = \text{H} \\
\text{HL4: } Y &= \text{H}, X = \text{Br}
\end{align*}
\]

Figure 5: Synthesis of five dissymmetric tridentate hydrazone Schiff base ligands, containing a mixed donor set of ONN and ONO

In 2010, Zoubi et al., reported the synthesis of macrocyclic hydrazone Schiff bases through the reaction of succinicdihydrazide, adipicdihydrazide with acetylacetone, adipicdihydrazide with terephtaldialdehyde and sebacidihydrazide with terephtaldialdehyde (Figure 6). They reported that these hydrazone Schiff bases act as hexadentate ligands. They also suggested that the prepared Schiff bases could be used to extract cations of the transition elements from their aqueous phases to another organic phase, which they are not dissolved.
Figure 6: Synthesis of macrocyclic hydrazone Schiff bases
2.2 Metal Complexes with Hydrazone Schiff Base Ligands

Ray et al., (2007) reported the synthesis of two new coordination complexes of Zn(II) using two different tridentate (N,N,O) donor hydrazone ligands, Hpbh and Hacpbh respectively. The complexes [Zn(pbh)₂] and [Zn(acpbh)₂] have been synthesized by reacting ZnSO₄·7H₂O with Hpbh and Hacpbh hydrazone ligands, respectively. The ligands Hpbh and Hacpbh were prepared by condensing pyridine-2-carboxaldehyde and 2-acetylpyridine with benzhydrazide, respectively. Both complexes demonstrate octahedral structure as shown in Figure 7 below.

In 2012, Alhadi et al., synthesized Ni(II), Cu(II), Zn(II) and Cd(II) complexes of a new hydrazone Schiff base derived from 5-bromo-2-hydroxybenzylidene-3,4,5-trihydroxybenzohydrazide (GHL1). In these complexes, the ligand GHL1 acts as a
mononegatively charged tridentate ligand and coordinated with the metal ions through O, N, O atoms, except for Ni(II) and Cd(II) complexes where the ligand behaves as a neutral bidentate ligand and coordinated with the metal ions through O, N atoms. Thermogravimetric Analysis (TGA) spectral observation suggested a tetrahedral geometry around the Ni(II) complex (Figure 8) but octahedral geometry for the Cu(II), Zn(II) (Figure 9) and Cd(II) complexes. The magnetic moment value for Ni(II) complex is 3.4 Bohr Magneton (B.M.), which demonstrates that the Ni(II) complex is paramagnetic and has a high spin tetrahedral configuration whereas the Zn(II) and Cd(II) complexes are both diamagnetic. Furthermore, the molar conductivity of $10^{-3}$ M in DMSO at room temperature is 73 ohm$^{-1}$cm$^2$mol$^{-1}$ indicating that the Ni(II) complex is electrolyte.

Figure 8: Ni(II) complex with hydrazone Schiff base ligand
Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with hydrazone Schiff base (LH2) derived from 2-hydroxy-5-chloro-3-nitroacetophenone and isonicotinoyl hydrazide have been synthesized by Kelode et al., in 2012 (Figure 10). The hydrazone Schiff base was reported to act as a monobasic bidentate ligand, commonly coordinates through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of the azomethine group. The molar conductance values in DMF (10⁻³ M) solution at room temperature showed that all the complexes are non electrolytes. The compounds are found to show low bactericidal behavior against most of the bacterial culture and resistance towards the other. In general, the results reveal that complexation with metals was found to enhance the antibacterial activity of the ligand.
Figure 10: Synthesis of Co(II), Ni(II), Cu(II) and Zn(II) complexes with hydrazone Schiff base (LH2)

In 1999, Jayaramudu et al., reported the synthesis of Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) complexes of diacetylmonoxime isonicotinoylhydrazone (DMH) (Figure 11). Characterizations were carried out using magnetic moment data, electronic and IR spectral measurements. The molar conductivity measurements show that the complexes are electrolytes. The IR spectra suggest that the ligands are tetradeinate in all cases whilst the electronic spectra together with the magnetic moment data suggest an octahedral geometry for all the complexes except for copper complex. In all these complexes, the oxime (=N-O) group acts as a bridging function to give dimeric structures.
Nigussie (2010) reported the synthesis of a Fe(III) complex with hydrazone Schiff base ligand, namely Bis-(N-Salicylaldehyde)-1,3-dihydrazone-inden-2-one, (BNSDHIO) as shown in (Figure 12). The ligand behaves as a pentadentate ONONO donor. They reported that the Fe(III) complex has an octahedral geometry and it was found to be a neutral complex.

Figure 11: Ni(II), Co(II), Fe(II) and Mn(II) complexes of diacetylmonoximeisonicotinoylhydrazone (DMH)

Figure 12: Synthesis of Fe(III) complex with Bis-(N-Salicylaldehyde)-1,3-dihydrazone-inden-2-one, (BNSDHIO)