SYNTHESIS, SPECTRAL STUDIES AND CYTOTOXICITY OF ORGANOTIN(IV) COMPLEXES WITH HYDRAZONE LIGANDS

NUR HAFIZAH BT RAMLI (24577)

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NUR HAFIZAH BT RAMLI

This Final Year Project is submitted in partial fulfillment of the degree of Bachelor of Science with Honours (Resource Chemistry)

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DECLARATION

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

______________________________
NUR HAFIZAH BT RAMLI

Chemistry Department
Faculty of Resource Science and Technology
University Malaysia Sarawak
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Synthesis, Spectral Studies and Cytotoxicity of Organotin(IV) Complexes with Hydrazine Ligands

Nur Hafizah Bt Ramli

Resource Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak

ABSTRACT
Eight new organotin(IV) complexes of 2-hydroxy-3-methoxybenzaldehyde isonicotinylhydrazone \([L_1(1)]\) with general formula \([R_nSnCl_{3-n}(L_1)]\) \([R = Me, n = 2 (3); R = Bu, n = 2 (4); R = Ph, n = 2 (5); R = Me, n = 1 (6); R = Bu, n = 1 (7); R = Ph, n = 1 (8)\] were synthesized by direct reaction of the ligand (1), base and organotin(IV) chloride(s) in absolute methanol under \(N_2\) atmosphere. Another four organotin(IV) complexes of \(p\)-aminoacetophenone isonicotinylhydrazone \([L_2(2)]\) with general formula \([R_nSnCl_{3-n}]\) \([R = Me, n = 2 (9); R = Bu, n = 2 (10); R = Me, n = 1 (11); R = Ph, n = 1 (12)\] were also synthesized by direct reaction of the ligand (2), base and organotin(IV) chloride(s). The ligands (1-2) and their organotin(IV) complexes (3-12) have been characterized by elemental analyses, UV-Visible, FT-IR and \(^1\)H NMR spectral studies. Spectroscopic data suggested that ligand (1) acted as a dinegative tridentate and ligand (2) acted as uninegative bidentate chelating agent. The toxicity of the hydrazine ligands (1-2) and their selected organotin(IV) complexes were evaluated against \textit{Artemia salina}. The results shown that the selected organotin(IV) complexes have better cytotoxicity than the free ligands (1-2). Furthermore, it has been shown that diphenyltin(IV) complex exhibit significantly better activity than the other organotin derivatives.

Key words: Hydrazine ligands, organotin(IV) complexes, toxicity

ABSTRAK
Lapan kompleks organostanum(IV) bagi ligan 2-hidroksida-3-metoksibenzaldehyde isonikotinilhidrazon \([L_1(1)]\) dengan formula am \([R_nSnCl_{3-n}(L_1)]\) \([R = Me, n = 2 (3); R = Bu, n = 2 (4); R = Ph, n = 2 (5); R = Me, n = 1 (6); R = Bu, n = 1 (7); R = Ph, n = 1 (8)\] telah disentesis dengan tindak balas terus antara ligand (1), bes dan organostanum(IV) klorida dalam methanol kering di bawah persekitaran \(N_2\) tulen. Empat kompleks organostanum(IV) bagi ligan \(p\)-aminoasetofenon isonikotinilhidrazon \([L_2(2)]\) dengan formula am \([R_nSnCl_{3-n}]\) \([R = Me, n = 2 (9); R = Bu, n = 2 (10); R = Me, n = 1 (11); R = Ph, n = 1 (12)\] telah disentesis dengan tindak balas terus antara ligand (2), bes dan organostanum(IV) klorida dalam methanol kering di bawah persekitaran \(N_2\) tulen Kompleks-kompleks organostanum(IV) tersebut telah dicirikan dengan menggunakan analisis elemen, ultralungu cahaya nampak, inframerah dan Resonan Magnetik Nuklear \(^1\)H. Hasil daripada analisa tersebut menunjukkan ligan (1) bertindak sebagai dinegatif tridentat dan ligan (2) bertindak sebagai uninegatif bidentat terhadap ion stamin(IV). Ketoksian ligan hidrazon (1-2) dan kompleks organostanum(IV) yang terpilih telah dikaji dengan \textit{Artemia salina}. Hasil daripada keputusan menunjukkan kompleks organostanum(IV) lebih toksik berbanding dengan ligan (1-2). Di-fenilstanum(IV) menunjukkan ketoksian yang paling tinggi berbanding kompleks yang lain.

Kata kunci: Ligan hidrazon, kompleks organostanum(IV), ketoksian.
1.0 Introduction

Hydrazones are important class of ligands that containing an azomethine group which synthesized by heating the appropriate substituted hydrazines/hydrazides with an aldehyde and a ketone in solvents like ethanol, methanol, tetrahydrofuran, butanol, glacial acetic acid, ethanol-glacial acetic acid (Angel et al., 2010). The development in the synthesis of new hydrazone ligand played an important role in order to make progress in the synthesis of metal complexes, which exhibited unique properties and novel reactivity (Ahmed et al., 2009). The chemistry of hydrazone ligands plays an important role in coordination chemistry owing to their coordination capabilities (Affan et al., 2009). Hydrazones are versatile class of compounds which present a wide range of biological applications as antimicrobial, antitubecular, anticonvulsant, anti-inflammatory, cytotoxic and vasolidator agents (Ragavendran et al., 2007; Bezerra- Avaji et al., 2009; Kümmerle et al., 2009; Angel et al., 2010).

\[
\begin{align*}
R-NH &+ R^1-CO \rightarrow R-N=N-R^1
\end{align*}
\]

Scheme 1: General synthesis of hydrazone ligand

According to Lau et al., (1999) isocyanides react with 2-pyridylhydrazine to form hydrazone ligand. This hydrazone derivative has been studied because of its potential for self-association via hydrogen bonding. Several novel molecular structures of organotin(IV) complexes with hydrazone ligands have been reported by Affan et al., (2007).
Tin(IV) compounds used as PVC stabilizers, for chemical vapor decomposition (CVD), in non-linear optics and in catalyses (Angel et al., 2010). Organotin(IV) complexes have attracted more and more attention in recent years, owing to their potentially pharmaceutical value (Torres et al., 2011). Recently, several studies have been reported on the synthesis and spectroscopic characterization of organotin(IV) complexes due to their various industrial and agricultural application as well as their potential biocidal properties and cytotoxicity (Affan et al., 2011). Besides that, this organotin(IV) complex becomes major attention in organometallic research field due to capabilities to form a stable bond with carbon and other hetero atoms. There were also some observations about organotin(IV) complexes that act as antifouling, antimicrobial and antiviral agent (Angel et al., 2010).

In view of the surprising applications of organotin(IV) complexes, the author has taken this project for the synthesis, spectral studies and cytotoxicity of organotin(IV) complexes with the proposed hydrazone ligands (1-2).
1.1 Objectives

1) To synthesize hydrazone ligands.

2) To synthesize the organotin(IV) complexes with the proposed hydrazone ligands.

3) To characterize the hydrazone ligands and their organotin(IV) complexes by FT-IR, UV-Visible, \(^1\)H NMR spectroscopic and elemental analyses.

4) To determine the molar conductance values of the synthesized organotin(IV) complexes.

5) To study the biological activity (toxicity) of hydrazone ligands and their organotin(IV) complexes.
2.0 Literature Review

2.1 Synthesis of hydrazone ligands and their organotin(IV) complexes

A new hydrazone ligand has been synthesized by the condensation reaction of isonicotinic hydrazide with pyruvic acid \([\text{H}_2\text{PAI}]\) (Affan \textit{et al.}, 2009). The ligand and its organotin(IV) complexes were characterized by elemental analyses, molar conductivity, UV-Visible, IR, and \(^1\)H NMR spectral studies. They have also determined the crystal structure of dibutyltin(IV) complex \([\text{n-Bu}_2\text{Sn(H}_2\text{PAI)}\cdot\text{H}_2\text{O}].\)

![Scheme 2: Pyruvic acid isonicotinoylhydrazone ligand](image)

X-ray structural investigation of \([\text{n-Bu}_2\text{Sn(H}_2\text{PAI)}\cdot\text{H}_2\text{O}].\) revealed that the pyruvic acid isonicotinoyl hydrazone ligand is coordinated to tin(IV) \textit{via} O, N, O-donor atoms. The tin(IV) atom is six coordinated in a distorted octahedral arrangement. The molar conductance values showed that the organotin(IV) complexes are non-electrolyte in nature. They found that these organotin(IV) complexes were shown good antibacterial activity against tested bacteria (Affan \textit{et al.}, 2009).
Affan et al., (2009) were synthesized the pyruvic acid 2-pyridylhydrazone by condensation reaction of pyruvic acid and 2-pyridylhydrazine in the presence of absolute ethanol. Mono-\textit{n}-butyltin (IV) complex was synthesized by direct reaction of tin(IV) salts with the ligand in presence of KOH in 1:1:1 mole ratio under nitrogen atmosphere. The reaction is shown below (Scheme 3).

![Scheme 3: Synthesis of mono-\textit{n}-butyltin(IV) dichloride complex](image)

In this research, they have studied the characterization and X-ray single crystal of mono-\textit{n}-butyltin(IV) dichloride complex of pyruvic acid-2-pyridylhydrazone. The molecular structure of [\textit{n}-BuSnCl$_2$(PAP)] was determined by X-ray crystallography. The molecular geometry of this compound is distorted octahedral (Affan et al., 2009).

Recently, Li et al., (2011) have synthesized a new hydrazone ligand by condensation reaction of benzoyleformic acid and 4-hydroxybenzoic hydrazide in absolute ethanol.

Dibutyltin(IV) complex was synthesized by direct reaction of ligand and dibutyltin(IV) dichloride in absolute ethanol under nitrogen atmosphere. The synthesis is shown in Scheme 4.
They found that the tin atom was seven-coordinated and it was confirmed by X-ray crystal studies.
Affan et al., (2009) were synthesized thiophene-2-carboxaldehyde benzhydrazone ligand (HTCB) by condensation reaction between benzhydrazide and thiophene-2-carboxaldehyde in absolute methanol with ratio of 1:1. The reaction is shown below (Scheme 5).

Scheme 5: Synthesis of thiophene-2-carboxaldehyde benzhydrazone ligand

Four organotin(IV) complexes have been synthesized by direct reaction of thiophene-2-carboxaldehyde benzhydrazone ligand, base and tin(IV) salts in absolute methanol under nitrogen atmosphere. Scheme 5 shows the synthesis of organotin(IV) complexes.
In this research, they have also studied the toxicity test of ligand and complexes against *Artemia salina*. Based on their results, HTCB ligand has higher LC$_{50}$ value compared to all its complexes. Diphenyltin(IV) and monophenyltin(IV) complexes showed highest cytotoxicity against *Artemia salina* than others organotin(IV) derivatives.
Sam et al., 2012 were synthesized the \textit{o}-vanillin-2-hydrazinopyridine (VHP) by condensation reaction between 2-hydrazinopyridine and \textit{o}-vanillin in absolute ethanol with 2-3 drops of glacial acetic acid. The reaction is shown below (Scheme 7).

\begin{center}
\begin{tabular}{c c c}
<table>
<thead>
<tr>
<th>Ortho vanillin</th>
<th>2-hydrazinopyridine</th>
<th>VHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>\includegraphics[width=0.3\textwidth]{ortho_vanillin}</td>
<td>\includegraphics[width=0.3\textwidth]{2-hydrazinopyridine}</td>
<td>\includegraphics[width=0.3\textwidth]{VHP}</td>
</tr>
</tbody>
</table>
\end{tabular}
\end{center}

\textbf{Scheme 7: Synthesis of ortho-vanillin-2-hydrazinopyridine (VHP)}

They were synthesized five organotin(IV) complexes by direct reaction of \textit{o}-vanillin-2-hydrazinopyridine (VHP), potassium hydroxide and organotin(IV) dichloride(s) in absolute methanol (Scheme 8). In the complexes (2-4), the ligand (1) acted as a neutral bidentate ligand and is coordinated to the tin(IV) atom \textit{via} the azomethine nitrogen and pyridyl nitrogen atoms, the ligand (1) acted as a uninegative tridentate ligand and coordinated to the tin(IV) atom through phenolic-O, azomethine-N and pyridyl-N atoms in complexes (5-6).
Scheme 8: Synthesis of organotin(IV) complexes for VHP ligand

Based on the application of hydrazone ligands and their organotin(IV) complexes, the author is interested to synthesize, characterize and also to study the biological activities of proposed hydrazone ligands and their organotin(IV) complexes against *Artemia salina.*
3.0 Experimental

3.1 Materials and method

All reagents were purchased from Fluka and Merck without purification. All solvents were purified according to standard procedures (Armarego & Perrin., 1996). The melting point was measured using open capillary in Stuart MP3. UV-Visible spectra studies were measured using Perkin Elmer Lambda 25 spectrophotometer. The FT-IR spectra were obtained with a Perkin Elmer Spectrum GX Fourier-Transform spectrometer in the range of 4000-370 cm$^{-1}$ using KBr disc at room temperature.$^1$H NMR spectra were recorded in DMSO-$d_6$ solution on a Jeol 500 MHz-NMR spectrophotometer. CHN analyses were obtained with Flash EA 1112 series CHN elemental analyzer. The molar conductance values of all the synthesized organotin(IV) compounds were measured using Jenway 4510 conductivity meter.
3.2 Synthesis of hydrazone ligands and their organotin(IV) complexes

The procedures for the synthesis of hydrazone ligands and their organotin(IV) complexes are based on the standard procedure reported previously (Affan et al., 2009).

3.2.1 Synthesis of 2-hydroxy-3-methoxybenzaldehyde isonicotinylhydrazone ligand (C_{14}H_{13}N_{3}O_{3}) (1)

Isonicotinic hydrazide (1.37 g, 0.01 mol) and 2-hydroxy-3-methoxybenzaldehyde (1.52 g, 0.01 mol), each dissolved in absolute methanol (20 mL) were mixed with constant stirring and heated under reflux condition for 3 hours (Scheme 9). On cooling the solution at room temperature, the light yellow powder formed, filtered off and washed several times with methanol and dried in vacuo over anhydrous silica gel. The light yellow powder was recrystallized from methanol and dried in vacuo anhydrous silica gel. Yield: 2.34 g, 80%; m.p.: 233-235 °C

![Scheme 9: Synthesis of 2-hydroxy-3-methoxybenzaldehyde isonicotinylhydrazone (1)](image-url)
3.2.2 Synthesis of \( p \)-aminoacetophenone isonicotinylhydrazone \( (C_{14}H_{14}N_4O) \) (2)

Isonicotinic hydrazide (2.74 g, 0.02 mol) was dissolved in 30 mL of absolute ethanol before mix with 20 mL of ethanolic solution of \( p \)-aminoacetophenone (2.70 g, 0.02 mol). The mixture was stirred with constant and refluxed for 5 hours. A light yellow precipitates were formed and allowed to cool at room temperature. The precipitates were filtered off and dried \textit{in vacuo} over anhydrous silica gel. The \( p \)-aminoacetophenone isonicotinylhydrazone (2) was recrystallized from methanol. Yield: 2.08 g, 76%; m.p: 228-230 °C.

Scheme 10: Synthesis of \( p \)-aminoacetophenone isonicotinylhydrazone (2)
3.2.3 Synthesis of organotin(IV) complexes (3-8) with ligand (1)

3.2.3.1 Synthesis of [Me₂Sn(C₁₄H₁₁N₃O₃)] (3)

2-hydroxy-3-methoxybenzaldehyde isonicotinylhydrazone ligand (1) (0.81 g, 0.003 mol) was dissolved in absolute methanol (15 mL) under nitrogen atmosphere. The mixture was stirred with constant stirring and refluxed for 30 minute. Then, 10 mL of methanolic solution of potassium hydroxide (0.34 g, 0.006 mol) was added in dropwise and the colour was changed from light yellow to light orange colour. The mixture was stirred with constant stirring and refluxed for 1 hour. Then, 10 mL methanolic solution of di-methyltin(IV) dichloride (0.66 g, 0.003 mol) was added drop wise to a solution of ligand and the colour was changed to orange colour with precipitate occurred. The resulting reaction mixture was refluxed for 5 hours (Scheme 5) and cooled to room temperature. There was solid formed after cooled at room temperature for overnight. The solution was filtered off and dried in vacuo over anhydrous silica gel. The precipitate of di-methyltin(IV) complex (3) was recrystallized with methanol in order to purify it. Yield: 0.99 g, 67%; m.p 239-241 °C.

3.2.3.2 Synthesis of organotin(IV) complexes (4-8)

Organotin(IV) complexes (4-8) were synthesized using a similar procedure to [Me₂Sn(C₁₄H₁₁N₃O₃)] (3) using the appropriate organotin(IV) chloride(s).

3.2.3.3 Synthesis of [Bu₂Sn(C₁₄H₁₁N₃O₃)] (4)

The colour of the Bu₂Sn(C₁₄H₁₁N₃O₃) (4) was bright orange. Yield: 1.19 g, 64%; m.p: 225-227 °C.