Coordination chemistry of organotin(IV) complexes with substitute thiosemicarbazone ligands

Adibah Amirah Binti Abdul Nasir (23033)

This Project is submitted in Partial Fulfillment of the requirement for the Degree of Bachelor of Science with Honours (Resource Chemistry)

Resource Chemistry

Department of Chemistry

Faculty of Resource Science and Technology

University Malaysia Sarawak

July 2012
DECLARATION

I declare that this is my own research paper except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature for any other degree.

_______________________________
Adibah Amirah Binti Abdul Nasir (23033)
Chemistry Department
Faculty of Resources Science and Technology
University Malaysia Sarawak
Acknowledgement

First of all, I would like to give my special thanks to those who have supported and helped me during the Final Year Project (FYP) research.

Firstly, I would like to thank my supervisor, Assoc. Prof. Dr. Md. Abu Affan for his help and supervised me until I complete doing this project. Unforgettable, I would like to thanks and appreciate Mr. Abdus Salam and Ms Norrihan Sam for their helps and contribution and willing to share their experience and knowledge with me from start until the end of this project.

I would like to say greatest appreciation to Faculty of Resource Science and Technology for preparing all instrumental analysis for the sample analyses. Laboratory assistants of Inorganic Chemistry laboratory also have contributed their help in order to handle this project.

Thanks to my beloved family that support and give me strength to finish this project successfully. To my fellow friends especially those who work together with me, I would like to thank all of them for all their helps and support to finish this research.
**Table of Contents**

Acknowledgement........................................................................................................... i

Table of Contents............................................................................................................ ii

List of Abbreviations..................................................................................................... iv

List of Scheme................................................................................................................ v

List of Figure..................................................................................................................... vi

List of Table ...................................................................................................................... vii

Summary........................................................................................................................... 1

1.0 Introduction................................................................................................................... 2

1.1 Objective..................................................................................................................... 3

2.0 Literature Review....................................................................................................... 4

3.0 Experimental............................................................................................................... 9

3.1 Materials and methods.............................................................................................. 9

3.2 Synthesis of thiosemicarbazone ligands (1-2)......................................................... 10

3.2.1 Synthesis of Pyruvic acid-4-ethyl-3-thiosemicarbazone ligand [H₂L₁] (1).............. 10

3.2.2 Synthesis of 2-acetylpyridine-4-ethyl-3-thiosemicarbazone ligand [H₂L₁] (2)......... 12

3.3 Synthesis of organotin(IV) complexes (3-9)......................................................... 13
3.3.1 Synthesis of [Me₂Sn(L₁)] (3)…………………………………………………………… 13

3.3.2 Synthesis of [Bu₂Sn(L₁)] (4)…………………………………………………………… 15

3.3.3 Synthesis of [Ph₂Sn(L₁)] (5)…………………………………………………………… 15

3.3.4 Synthesis of [MeSnCl(L₁)] (6)…………………………………………………………… 15

3.3.5 Synthesis of [PhSnCl(L₁)] (7)…………………………………………………………… 15

3.3.6 Synthesis of [Me₂SnCl(L)] (8)…………………………………………………………… 16

3.3.7 Synthesis of [Ph₂SnCl(L)] (9)…………………………………………………………… 18

4.0 Results and discussion…………………………………………………………………… 19

4.1 Spectroscopy studies of ligand (1-2) and organotin(IV) complexes (3-9)……… 22

   4.1.1 UV-visible spectra of (H₂L₁) (1) and its organotin(IV) complexes (3-7)….. 22

   4.1.2 UV-visible spectra of (HL) (2) and its organotin(IV) complexes (8-9)…… 23

   4.1.3 IR spectra of ligand (H₂L₁) (1) and its organotin(IV) complexes (3-7)…… 26

   4.1.4 IR spectra of ligand (HL) (2) and its organotin(IV) complexes (8-9)…… 28

   4.1.5 ¹H NMR spectra of (H₂L₁) (1) and its methyltin(IV) complex (6)……… 35

5.0 Conclusion………………………………………………………………………………… 38

6.0 Suggestion For Further Research……………………………………………………… 39

7.0 References………………………………………………………………………………… 40

iii
## List of Abbreviations

<table>
<thead>
<tr>
<th>Sn(IV) atom</th>
<th>Tin(IV) atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H₂L₁)</td>
<td>Pyruvic acid-4-ethyl-3-thiosemicarbazone</td>
</tr>
<tr>
<td>(HL)</td>
<td>2-acetylpuridine-4-ethyl-3-thiosemicarbazone</td>
</tr>
<tr>
<td>[Me₂Sn(L₁)]</td>
<td>Dimethyltin(IV) complex</td>
</tr>
<tr>
<td>[Bu₂Sn(L₁)]</td>
<td>Dibutyltin(IV) complex</td>
</tr>
<tr>
<td>[Ph₂Sn(L₁)]</td>
<td>Diphenyltin(IV) complex</td>
</tr>
<tr>
<td>[MeSnCl(L₁)]</td>
<td>Methyltin(IV) chloride complex</td>
</tr>
<tr>
<td>[PhSnCl(L₁)]</td>
<td>Phenyltin(IV) chloride complex</td>
</tr>
<tr>
<td>[Me₂SnCl(L)]</td>
<td>Dimethyltin(IV) chloride complex</td>
</tr>
<tr>
<td>[Ph₂SnCl(L)]</td>
<td>Diphenyltin(IV) chloride complex</td>
</tr>
</tbody>
</table>
List of Schemes

**Scheme 1:** Synthesis of pyruvic acid-4-ethyl-3-thiosemicarbazone ligand [H$_2$L$_1$] (1)

**Scheme 2:** Synthesis of 2-acetylpyridine-4-ethyl-3-thiosemicarbazone ligand [HL] (2)

**Scheme 3:** Synthesis of organotin(IV) complexes (3-7) with (H$_2$L$_1$) (1)

**Scheme 4:** Synthesis of organotin(IV) complexes (8-9) of ligand [HL] (2)
List of Figures

Figure 1: Synthesis of 4-chlorobenzaldehyde thiosemicarbazone

Figure 2: Tautomerization of thiosemicarbazone ligand derived from pyruvic acid

Figure 3: Structure of organotin(IV) complexes with Pyruvic acid thiosemicarbazone ligand

Figure 4: Molecular structure of [SnPh₂(L)(DMSO)]

Figure 5: Synthesis of triorganotin(IV) complexes

Figure 6: UV-Visible spectra of ligand (1) and its methyltin(IV) complex (6) in DMF (10⁻⁴ M)

Figure 7: UV-Visible spectra of ligand (2) and its phenyltin(IV) complex (9) in CHCl₃ (10⁻⁴ M)

Figure 8: IR spectrum of (H₂L₁) (1) (As KBr disc)

Figure 9: IR spectrum of [MeSnCl(L₁)] (6) (As KBr disc)

Figure 10: IR spectrum of (HL) (2) (As KBr disc)

Figure 11: IR spectrum of [Ph₂SnCl(C₁₀H₁₃N₄S)] (9) (As KBr disc)

Figure 12: ¹H NMR spectrum of ligand [H₂L₁, (1)] (in MeOH-d₄)

Figure 13: ¹H NMR spectrum of methyltin(IV) complex (6) (in MeOH-d₄)
List of Tables

Table 1: Physical properties and elemental analysis data for the ligands (1-2) and their organotin(IV) complexes (3-9)

Table 2: Molar conductivities for organotin(IV) complexes (3-9)

Table 3: The $\lambda_{\text{max}}$ (nm) of ligand (1) and its complexes (3-7)

Table 4: The $\lambda_{\text{max}}$ (nm) of (HL) (2) and its complexes (8-9)

Table 5: Main IR data of ligand (1) and its organotin(IV) complexes (3-7) (cm$^{-1}$)$^a$

Table 6: Main IR data of ligand (2) and its organotin(IV) complexes (8-9) (cm$^{-1}$)$^a$
Coordination chemistry of organotin(IV) complexes with substitute thiosemicarbazone ligands

Adibah Amirah binti Abdul Nasir

Resource Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak

Summary

Seven new organotin(IV) complexes (3-9) of pyruvic acid-4-ethyl-3-thiosemicarbazone (H₂L₁) (1) and 2-acetylpyridine-4-ethyl-3-thiosemicarbazone (HL) (2) have been synthesized and characterized by elemental analysis, molar conductivity, UV-Vis, FT-IR and ¹H NMR spectral studies. The spectroscopic data indicate that all the organotin(IV) complexes (3-7) of the ligand [(H₂L₁) (1)], the ligand moiety COO⁻ act as monodentate group, and coordinated to tin(IV) atom through carboxylato-O, azomethine-N, and thiolato-S atoms. Another organotin(IV) complexes (8-9) of the ligand [(HL) (2)], coordinated to tin (IV) atom through pyridine-N, azomethine-N, and thiolato-S atoms.

Key words: Thiosemicarbazones, organotin(IV) complexes, spectral analysis.

Summary

Tujuh kompleks baru organotin(IV) (3-9) telah terhasil daripada ligan asid piruvik-4-ethyl-3-thiosemikarbazon (H₂L₁) (1) dan ligan 2-asetilpiridin-4-ethyl-3-thiosemikarbazon (HL) (2) dan telah dicirikan melalui analisa mikrounsur, molar kondaktiviti, ultra-ungu cahaya nampak, inframerah dan spektroskopi Resonan Magnetik Nuklear ¹H. Data spektroskopi menunjukkan bahawa kompleks-kompleks organotin(IV) (3-7) daripada ligan asid piruvik-4-ethyl-3-thiosemikarbazon (H₂L₁) (1) telah terikat kepada atom tin(IV) melalui atom carboxylato-O, azomethine-N, dan thiolato-S. Manakala, kompleks-kompleks organotin(IV) (8-9) daripada ligan 2-asetilpiridin-4-ethyl-3-thiosemikarbazon (HL) (2) pula terikat kepada atom tin(IV) melalui atom piridin-N, azomethine-N, dan thiolato-S. Kumpulan berfungsi COO⁻ dalam ligan [(H₂L₁) (1)] bertindak sebagai kumpulan monodentat.

Kata kunci: thiosemikarbazon, kompleks-kompleks organotin(IV), analisa spectral.
1.0 Introduction

Thiosemicarbazone and metal complexes are chemical compounds that have a structural formula of NH$_2$C(S)-NH-N= and [RnSnCl$_n$](L)], respectively (Affan et al., 2011). Thiosemicarbazones usually act as chelating ligands with transition metals ions by bonding through the sulfur and hydrazinic nitrogen atom. Thiosemicarbazones of $\alpha$-$N$(4)-heterocyclic aldehydes and ketones possess a broad spectrum of potentially useful chemotherapeutic activities such as antimalarial, antibacterial, antiviral and antileishmanial activities (Klayman et al., 1984). Sampath et al., (2010) have synthesized 4-chlorobenzaldehyde thiosemicarbazone derivatives that have wide range of biological activities such as antitumour properties. Organotin(IV) complexes of thiosemicarbazone ligands containing NNS/ONS-donor atoms cosiderably important and responsible for the pharmacological activity. Salam et al., (2012) have reported the synthesis and spectral characterization of organotin(IV) complexes with 2-benzoilpyridine-$N$(4)-cyclohexylthiosemicarbazone ligand. According to Sen et al. (2008), thiosemicarbazones and transition metals have been developed in the areas of biology and chemistry due to biological activities such as antiviral, antitumor, fungicidal and bactericidal. Recently, pharmacological studies of 2-formyl, 2-acetyl and 2-benzoilpyridine thiosemicarbazone have been investigated because of their various biological properties. Therefore, the production of new thiosemicarbazone and their complexes will develop the application in medical especially.

Herein, organotin(IV) complexes with substitute thiosemicarbazone ligands having ONS/NNS donor atoms appeared interesting to me and here I report some new organotin(IV) complexes of pyruvic acid-4-ethyl-3-thiosemicarbazone and 2-acetylpyridine-4-ethyl-3-thiosemicarbazone ligands (1-2).
1.1 Objective

The general aim for the described in this project was the synthesis and characterization of organotin(IV) complexes with pyruvic acid-4-ethyl-3-thiosemicarbazone ligand as well as 2-acetylpyridine-4-ethyl-3-thiosemicarbazone ligand.

1) to synthesize pyruvic acid-4-ethyl-3-thiosemicarbazone ligand (1) and 2-acetylpyridine-4-ethyl-3-thiosemicarbazone ligand (2).

2) to synthesize organotin(IV) complexes with pyruvic acid-4-ethyl-3-thiosemicarbazone ligand and 2-acetylpyridine-4-ethyl-3-thiosemicarbazone ligand.

3) to characterize the above ligands and their organotin(IV) complexes by elemental analysis, FT-IR, UV-Visible, and $^1$H NMR spectroscopy.

4) to determine the molar conductance values of the synthesized organotin(IV) complexes.
2.0 Literature review

Sampath et al., (2010) have reported the synthesis of 4-chlorobenzaldehyde thiosemicarbazone (p-CBT). The (p-CBT) was formed from the condensation reaction of respective benzaldehydes with thiosemicarbazide in presence of conc. HCl in absolute ethanol (Figure 1).

![Figure 1: Synthesis of 4-chlorobenzaldehyde thiosemicarbazone](image)

Thiosemicarbazones are very resourceful tridentate ligands having the ability to bind transition metal ions by bonding trough sulfur and hydrazinic nitrogen atoms and capable to form metal chelates. Generally, thiosemicarbazide is a tridentate ligand, which combines with an aldehydes or a ketones (Sampath et al., 2010). Salicylaldehyde thiosemicarbazone was first used to study its reactivity to the metal ions (Indrani et al., 2002). They found that salicylaldehyde thiosemicarbazone ligand was coordinated to the metal as bidentate N,S-donors forming an unusual four-membered chelate ring (Indrani et al., 2002). Sen et al. (2008) have synthesized tridentate thiosemicarbazone ligand by mixing 2-hydroxy-3-methoxybenzaldehyde with thiosemicarbazide in methanolic solution.
Affan et al. (2010) have reported the synthesis of organotin(IV) complexes of 2-benzoylpyridine-\(N(4)\)-cyclohexylthiosemicarbazone, they found that the geometry about tin(IV) atom is distorted octahedral. In their other studies, organotin(IV) complexes with 2-hydroxyacetophenone-\(N(4)\)-cyclohexylthiosemicarbazone has been synthesized and characterized. These compounds have shown their cytotoxic and antibacterial activity against brine shrimps (\textit{A. salina}) (Affan et al., 2012).

Affan et al. (2009) have synthesized substitute thiosemicarbazone ligand derived from pyruvic acid. The ligand is particularly interested because of its structural diversity. Pyruvic acid - \(N(4)\) – cyclohexylthiosemicarbazone ligand acted as dinegative tridentate nature, some cases is acting as a mononegative monodentate system.

![Thione tautomer and Thiol tautomer](image)

\textbf{Figure 2: Tautomerization of thiosemicarbazone ligand derived from pyruvic acid}
Affan et al. (2009) have also synthesized dimethyltin(IV) complex of pyruvic acid thiosemicarbazone ligand. The X-ray studies suggested that this ligand is bound with organotin(IV) core in dinegative tridentate pattern; which involved thiol sulfur, hydrazinic nitrogen, and carboxyl oxygen (Figure 3). The coordination number of tin(IV) moiety is five. This complex is concluded to has trigonal bipyramidal geometry (Affan et al., 2009).

![Structure of organotin(IV) complexes with Pyruvic acid thiosemicarbazone ligand](image)

**Figure 3**: Structure of organotin(IV) complexes with Pyruvic acid thiosemicarbazone ligand

Wieck et al. (2010) have synthesized and studied spectral characterization of novel diorganotin complexes with 3-hydroxypyridine-2-carbaldehyde thiosemicarbazone. Single crystal X-ray structure of complex [SnPh₂(L)(DMSO)] (Figure 4) shows that the ligand is doubly deprotonated and coordinated as dinegative tridentate ligand. The six coordination number is completed by two carbon atoms of phenyl groups and DMSO.
Recently, Affan *et al.*, (2012) have synthesized new triorganotin(IV) complex with pyruvic acid-N(4)-cyclohexylthiosemicarbazone (HPACT) ligand. The X-ray studies of tributyltin(IV) complex suggested that the ligand acts as a mononegative monodentate ligand while the thiolate-S, azomethine-N atoms remain uncoordinated because due to the presence of bulky Ph$_3$ groups. Only Sn-atom is preferred to coordinate to carboxylate oxygen because oxygen is considered hard donor according to Hard acid-base theory (Figure 5).
Figure 5: Synthesis of triorganotin(IV) complexes

To the best of my knowledge, so far no organotin(IV) compounds with 2-acetylpyridine-4-ethyl-3-thiosemicarbazone and pyruvic acid-4-ethyl-3-thiosemicarbazone have ever been synthesized. Therefore, seven organotin(IV) derivatives were prepared by direct reaction of 2-acetylpyridine with 4-ethyl-3-thiosemicarbazide and pyruvic acid with 4-ethyl-3-thiosemicarbazide at 1:1 molar ratio and coordination chemistry of the synthesized organotin(IV) complexes studied by UV, IR, and $^1$H NMR spectroscopy.
3.0 Experimental

3.1 Materials and methods

This research was conducted in Inorganic Research Laboratory at UNIMAS. All reagents were purchased from Fluka, Aldrich and J.T. Baker. All the solvents were purified according to standard procedures (Armarego & Perrin, 1996). CHN analyses, UV-Visible, FT-IR and $^1$H NMR were used for characterization of thiosemicarbazone ligands and organotin(IV) complexes. The CHN analysis was recorded with Flash EA 1112 Series CHN elemental analyzer. UV-Vis spectra were recorded with DMF and CHCl$_3$ on a Perkin Elmer Lambda 25 UV-Visible spectrophotometer. FT-IR spectra were recorded on KBr discs using a Perkin Elmer Spectrum GX Fourier-Transform spectrometer in the range 4000-370 cm$^{-1}$. $^1$H NMR was recorded in MeOH-d$_4$ solution on a JEOL 500 MHz-NMR spectrophotometer. The melting point was measured by open capillary in Stuart MP3. The molar conductance values were measured with DMF solvent at room temperature using Jenway 4510 conductivity meter.
3.2 Synthesis of thiosemicarbazone ligands (1-2)

3.2.1 Synthesis of Pyruvic acid-4-ethyl-3-thiosemicarbazone ligand [H$_2$L$_1$] (1)

The 4-ethyl-3-thiosemicarbazide (0.596 g, 5 mmol) was dissolved in 10 mL dry methanol before mixing it with 10 mL of dry methanolic solution of pyruvic acid (0.440 g, 5 mmol). The mixture was refluxed for 4 hours (Scheme 1) and cooled at room temperature. Yellow microcrystals were formed and filtered off. The microcrystals were washed with small amounts of cold methanol followed by hexane. The microcrystals were recrystallized from methanol and dried in vacuo over anhydrous silica gel. Yield: 1.81 g, 87%. M.p: 170-172 °C; UV-Vis (DMF) $\lambda_{\text{max}}$/nm: 300; FT-IR (KBr disc, cm$^{-1}$) $\nu_{\text{max}}$: 3320 (b, OH), 3191 (m, NH), 1736 (m, C=O), 1605 (m, C=N), 1358, 845 (s, C=S), 942 (m, N-N); $^1$H NMR (MeOH-d$_4$) $\delta$: 9.99 (s, 1H, OH), 9.03 (s, 1H, CSNH), 3.31 (s, 3H, N=C−CH$_3$), 2.13 (q, 2H, CH$_2$), 1.24 (t, 3H, CH$_3$).
Scheme 1: Synthesis of pyruvic acid-4-ethyl-3-thiosemicarbazone ligand $\left[H_2L_1\right]$ (1)
3.2.2 Synthesis of 2-acetylpyridine-4-ethyl-3-thiosemicarbazone ligand [HL] (2)

The 4-ethyl-3-thiosemicarbazide (0.60 g, 5 mmol) was dissolved in 10 mL dry methanol before mixing it with 10 mL of dry methanolic solution of 2-acetylpyridine (0.61 g, 5 mmol). The mixture was refluxed for 4 hours (Scheme 2) and cooled at room temperature. Yellow microcrystals were formed and filtered off. The microcrystals were washed with small amounts of cold methanol followed by hexane. The microcrystals were recrystallized from methanol and dried in vacuo over anhydrous silica gel. Yield: 0.75 g, 62%; M.p: 130-132 °C; UV-Vis (CHCl₃) λ_max/nm: 314; FT-IR (KBr disc, cm⁻¹) ν_max : 3206 (b, NH), 1580 (m, C=N), 1305, 822 (m, C=S), 935 (m, N−N), 619 (w, pyridine).

Scheme 2: Synthesis of 2-acetylpyridine-4-ethyl-3-thiosemicarbazone ligand [HL] (2)
3.3 Synthesis of organotin(IV) complexes (3-9)

3.3.1 Synthesis of [Me₂Sn(L₁)] (3)

The (H₂L₁) (1) ligand (0.57 g, 3 mmol) was dissolved in absolute methanol (10 mL) in Schlenk round bottom flask under nitrogen atmosphere. Then, a methanolic solution of dimethylditin(IV) dichloride (0.66 g, 3 mmol) was added dropwise. The resulting reaction mixture was refluxed for 4 hours (Scheme 3) and cooled to room temperature. The yellow microcrystals were obtained from slow evaporation of the resulting solution at room temperature. The microcrystals were filtered off, washed with a small amount of cold methanol and dried in vacuo over anhydrous silica gel. Yield: 0.90 g, 73%; m.p: 179-181°C; molar conductance (DMF) Ω cm² mol⁻¹: 9.54; UV-Vis (DMF) λmax nm: 301,341; FT-IR (KBr disc, cm⁻¹) νmax : 3308 (b, NH), 1716 [s, νas(C=O)], 1437 [m, νs(C=O)], 1550 (b, C=N), 1060 (m, N−N), 1220, 806 (m, C=S), 529 (w, Sn−O), 498 (m, Sn−N).

The complexes [Bu₂Sn(L₁)] (4), [Ph₂Sn(L₁)] (5), [MeSnCl(L₁)] (6) and [PhSnCl(L₁)] (7) were synthesized using similar procedure to organotin(IV) complex (3) by using appropriate organotin(IV) chloride(s).
Scheme 3: Synthesis of organotin(IV) complexes (3-7) with (H$_2$L$_1$) (1)