

**SYNTHESIS AND CHARACTERIZATION OF ORGANOTIN(IV) COMPLEXES
WITH TRIDENTATE SCHIFF BASE LIGANDS CONTAINING ONN/ONS-DONOR
ATOMS**

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

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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.

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Synthesis and characterization of organotin(IV) complexes with tridentate Schiff base ligands containing ONN/ONS-donor atoms

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ABSTRACT

Two tridentate Schiff base ligands, containing a donor set of ONN and ONS were prepared by the reaction of salicylaldehyde with 2-aminothiophenol and benzhydrazone with 2-benzoylpyridine. Four organotin(IV) complexes (**3-6**) of salicylaldehyde-2-aminothiophenol ligand (**1**) with R_nSnCl_{4-n} ($n = 1, 2, 3$) have been synthesized in the presence of base in absolute chloroform in 1:1 mole ratio under nitrogen atmosphere. Another three organotin(IV) complexes (**7-9**) of 2-benzoylpyridinebenzhydrazone ligand (**2**) with R_nSnCl_{4-n} ($n = 1, 2, 3$) have also been synthesized in the presence of base in absolute methanol in 1:1 mole ratio. Schiff base ligands (**1-2**) and their organotin(IV) complexes (**3-9**) have been characterized by CHN analyses, UV-visible, molar conductance and FTIR spectral analyses. Among them, ligand (**2**) and complex (**7**) have also been determined by 1H NMR spectral studies. All organotin(IV) complexes (**3-9**) are non-electrolytic in nature. Based on the FTIR and 1H NMR analyses, ligand (**1**) acts as dinegative tridentate ligand in the organotin(IV) complexes (**3-6**). Whereas the ligand (**2**) acts as uninegative tridentate nature in its organotin(IV) complexes (**6-9**). A five-coordinated molecular structure has been proposed for the organotin(IV) complexes (**3-6**) of ligand (**1**) while a six-coordinated molecular structure has been proposed for organotin(IV) complexes (**7-9**) of ligand (**2**).

Keywords: Salicylaldehyde-2-aminothiophenol; 2-benzoylpyridinebenzhydrazone; organotin(IV) complexes; spectroscopic studies.

ABSTRAK

*Empat organotin(IV) kompleks (**3-6**) dengan R_nSnCl_{4-n} ($n = 1, 2, 3$) bagi ligand salisilaldehid-2-aminotiofenol (**1**) telah disintesis dengan kehadiran bes dan pelarut klorofom dengan nisbah kemolaran 1:1. Tiga lagi organotin(IV) kompleks (**7-9**) dengan R_nSnCl_{4-n} ($n = 1, 2, 3$) bagi ligand 2-benzoilpiridinbenzihidrazon (**2**) juga telah disintesis dengan kehadiran bes di dalam pelarut metanol dengan nisbah kemolaran 1:1. Semua organotin(IV) kompleks telah dicirikan melalui kaedah analisis CHN, UV-visible, kemolaran konduktandan dan FTIR. Hanya ligand (**2**) dan kompleks (**7**) ditentukan dengan 1H NMR. Kesemua kompleks organotin(IV) adalah tidak berelektolitik. Berdasarkan analisis FTIR dan 1H NMR, ligand (**1**) bertindak sebagai ligand dinegatif tidentat dalam kompleks organotin(IV) (**3-6**). Manakala ligand (**2**) pula bertindak sebagai ligand uninegatif tridentat dalam kompleks organotin(IV) (**7-9**).*

Kata kunci: Salisilaldehid-2-aminotiofeno; 2-benzoilpiridinbenzihidrazon; organotin(IV) Kompleks; kajian spektroskopik.

1.0 Introduction

1.1 Schiff base ligands and their organotin(IV) complexes

Schiff base which is a compound that contains a carbon-nitrogen double bond. Schiff base is synthesized by condensation reaction of primary amine and aldehyde or ketone (Yazici and Akgun, 2005; Anora and Sharma, 2000).

Schiff base may form stable complexes with transition metals (Rabie *et al.*, 2007). Schiff bases and their metal complexes have diverse applications such as play an important role in the development of coordination chemistry and act as catalyst to many reactions (Chai *et al.*, 2001; El-Hendaway *et al.*, 1993; Battacharya, 1990; Henrici-Oleive and Olive, 1977).

Organotin(IV) complexes which have five- and six-coordinated geometry and +4 oxidation states (Singh and Varshney, 2005). They must at least contain a tin-carbon bond. They were also screened for antitumor activity (Dey *et al.*, 2002; Shahid *et al.*, 2002) and also shown effective antiviral and antineoplastic agents (Dey *et al.*, 2002). The dialkyltin(IV) derivatives showed a better antitumor activity than the mono-, tri- and tetraalkyl derivatives due to the activity of the diorganotin(IV), R_2SnX_2 which is controlled by the nature of the R_2Sn moiety (Abd-Alla, 2003). Organotin(IV) complexes also showed therapeutic effects on various tumor cells but the mode action is not known yet (Szorcisk *et al.*, 2002). Besides that, they may be used as catalysts, stabilizers, biocides, antifouling agents as well as for wood preservers (Rehman *et al.*, 2005). Schiff base ligands and organotin complexes also showed antibacterial and antifungal activities (Singh and Varshney, 2005).

In view of this, the present project discussed mainly on the synthesis and characterization of organotin(IV) complexes with tridentate Schiff base ligands containing ONN/ONS-donor atoms.

1.2 Objectives

The objectives of this research are:

- i. to synthesize tridentate Schiff base ligands containing ONN/ONS-donor atoms.
- ii. to synthesize organotin(IV) complexes with tridentate Schiff base ligands (ONN/ONS).
- iii. to characterize the Schiff base ligands (ONN/ONS) and their organotin(IV) complexes by CHN analyses, UV-Visible, FTIR and ^1H NMR spectra analyses.
- iv. to determine the molar conductivity of the synthesized organotin(IV) complexes containing ONN/ONS-donor atoms.

2.0 Literature Review

2.1 Schiff base ligands containing ONN/ONS-donor atoms

Two ligands, 2-acetylpyridine-N(4)-phenylthiosemicarbazone, HAP4P, and 2-hydroxyacetophenone-N(4)-phenylthiosemicarbazone, H₂DAP4P, with R_{4-m}SnX_m (m = 2, 3; R = Me, ⁿBu, Ph and X = Cl, Br) (Figure 1) have been synthesized by Sousa and his co-workers (2001). The reactions between these two ligands led to the formation of hexa- and penta-coordinated organotin(IV) complexes.

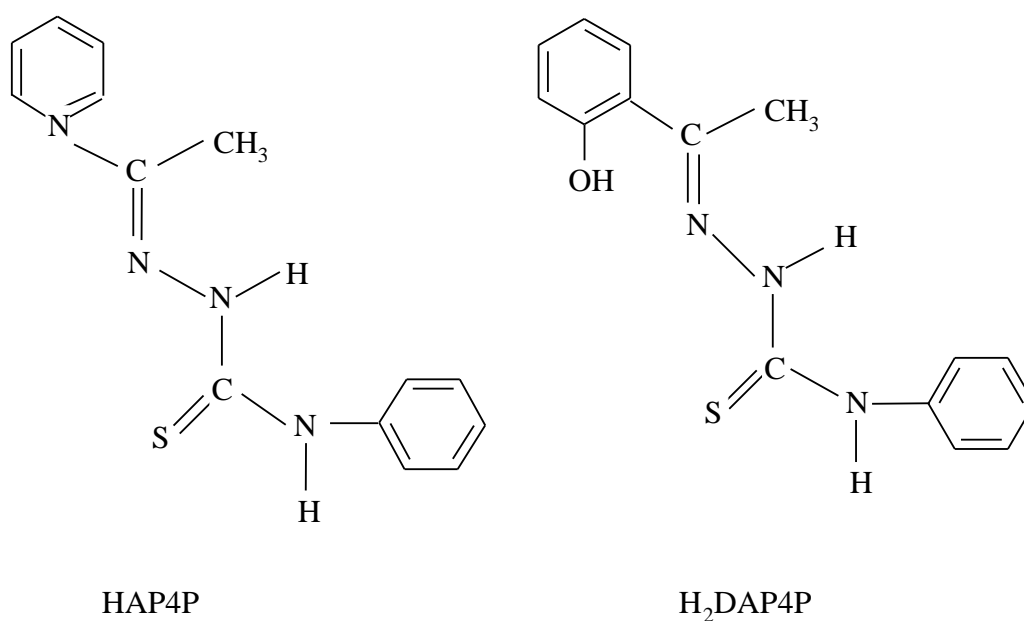


Figure 1: Structures of 2-acetylpyridine-N(4)-phenylthiosemicarbazone, HAP4P and 2-hydroxyacetophenone-N(4)-phenylthiosemicarbazone, H₂DAP4P.

Another tridentate ligand (Figure 2) has been reported by Yin and Chen (2006). This Schiff base has been prepared from 3-hydroxy-2-naphthoic acid hydrazide with pyruvic acid in ethanol with good yield.

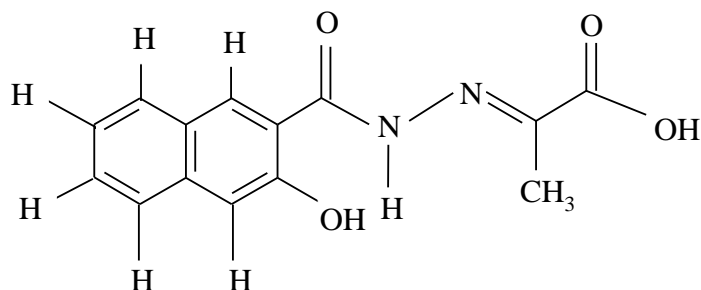


Figure 2: Formation of Schiff base ligand containing ONO-donor atoms.

Pramanik and his co-workers (2004) have synthesized the Schiff base ligands (Figure 3) by condensation reaction *S*-benzyl and *S*-methyl dithiocarbazates with salicylaldehyde in ethanol.

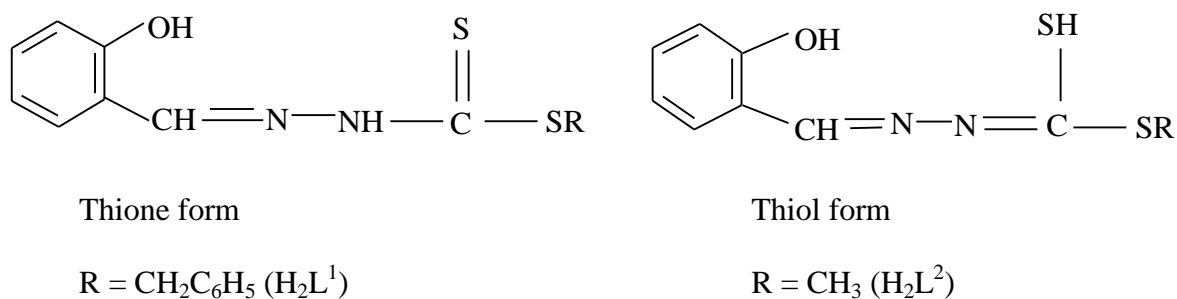


Figure 3: Schiff base ligand having ONS-donor atoms.

Another type of Schiff base ligand containing ONO-donor atoms has been reported (Figure 4). The Schiff base ligand has been synthesized condensation reaction of salicylaldehyde and 1-benzoylhydrazide in methanol in high yields (Dey *et al.*, 2003).

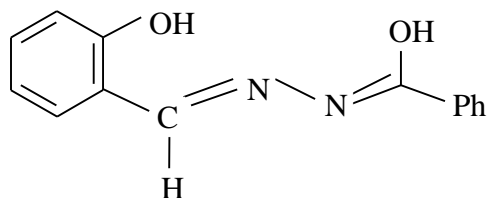


Figure 4: *N*-(2-salicylidene)-*N'*-benzoylhydrazone.

New type of Schiff base ligands has been synthesized and characterized (Figure 5) by condensing *S*-benzylthiocarbamate ($\text{NH}_2\text{NHCS}_2\text{CH}_2\text{C}_6\text{H}_5$) with heterocyclic aldehydes (Singh and Varshney, 2005).

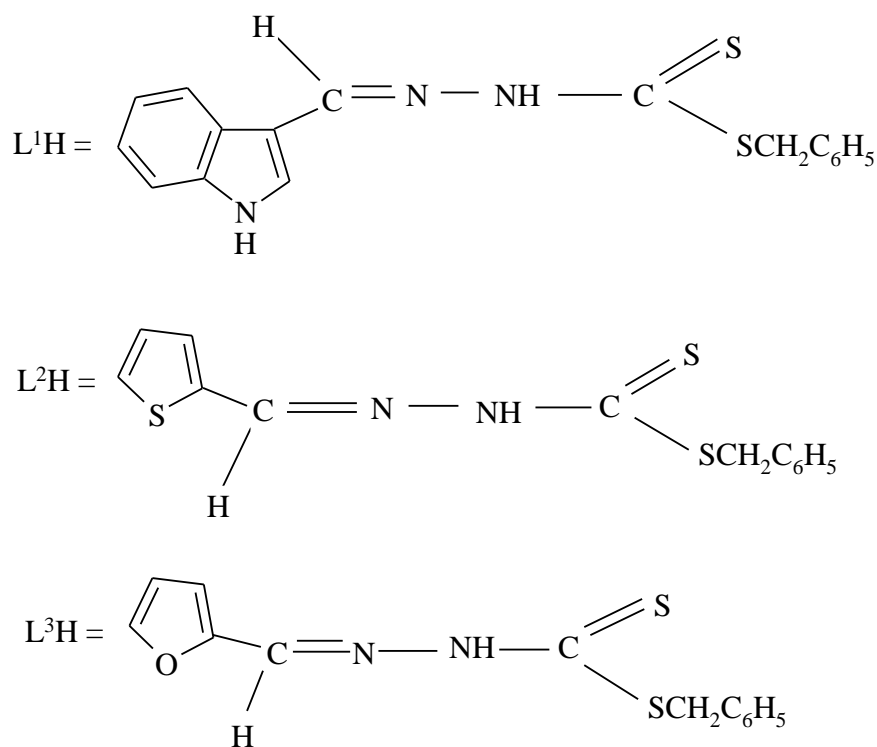
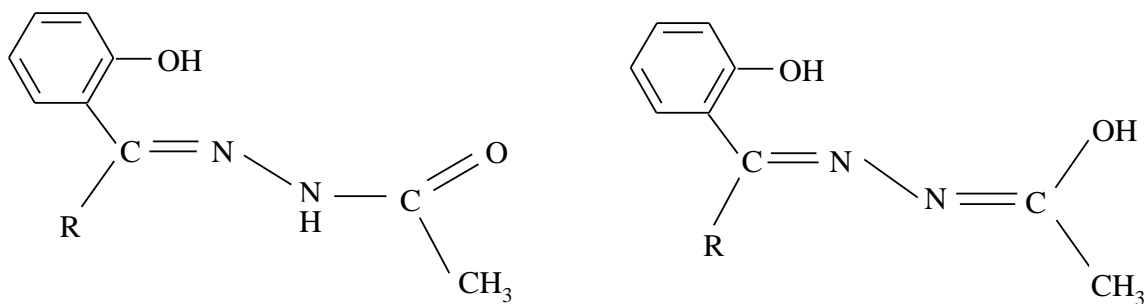


Figure 5: General scheme of Schiff base ligands.

Recently, a new Schiff base ligand (Figure 6) has been synthesized by condensing acetylaldehyde with 2-hydroxybenzaldehyde (H_2L^1) or 2-hydroxyacetophenone (H_2L^2) (Ghosh, 2006).



$\underline{\text{H}_2\text{L}}$	$\underline{\text{R}}$
H_2L^1	H
H_2L^2	CH_3

Figure 6: Structure of the tridentate Schiff base ligands containing ONO-donor atoms.

2.2 Organotin(IV) complexes with Schiff base ligands containing ONN/ONS-donor atoms

Rehman and his co-workers (2005) have synthesized a series of di- and tri- organotin(IV) complexes of monomethyl glutarate (Figure 7). These complexes have been synthesized from monomethyl glutarate in methanol.

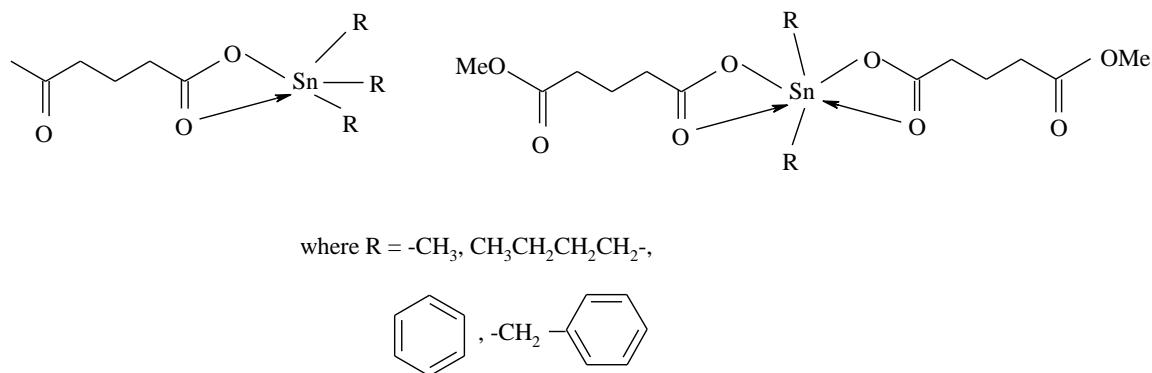


Figure 7: Proposed structures for the di- and tri-organotin(IV) complexes.

A report on the synthesis and characterization of two diorganotin(IV) complexes derived from the *N*-(2-Salicydene)-*N'*-benzoylhydrazone ligand have been reported (Figure 8). These two complexes have been characterized by X-ray crystallography (Dey *et al.*, 2003).

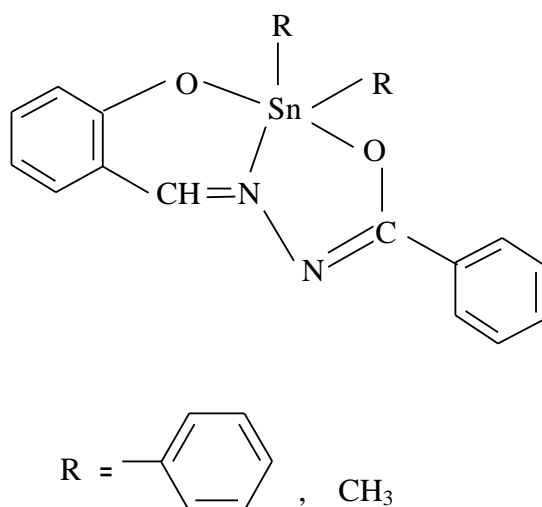


Figure 8: Structure of the diorganotin(IV) complexes.

Singh and Varshney (2005) have synthesized and characterized organotin(IV) complexes with three bidentate Schiff bases containing NS-donor atoms (Figure 9).

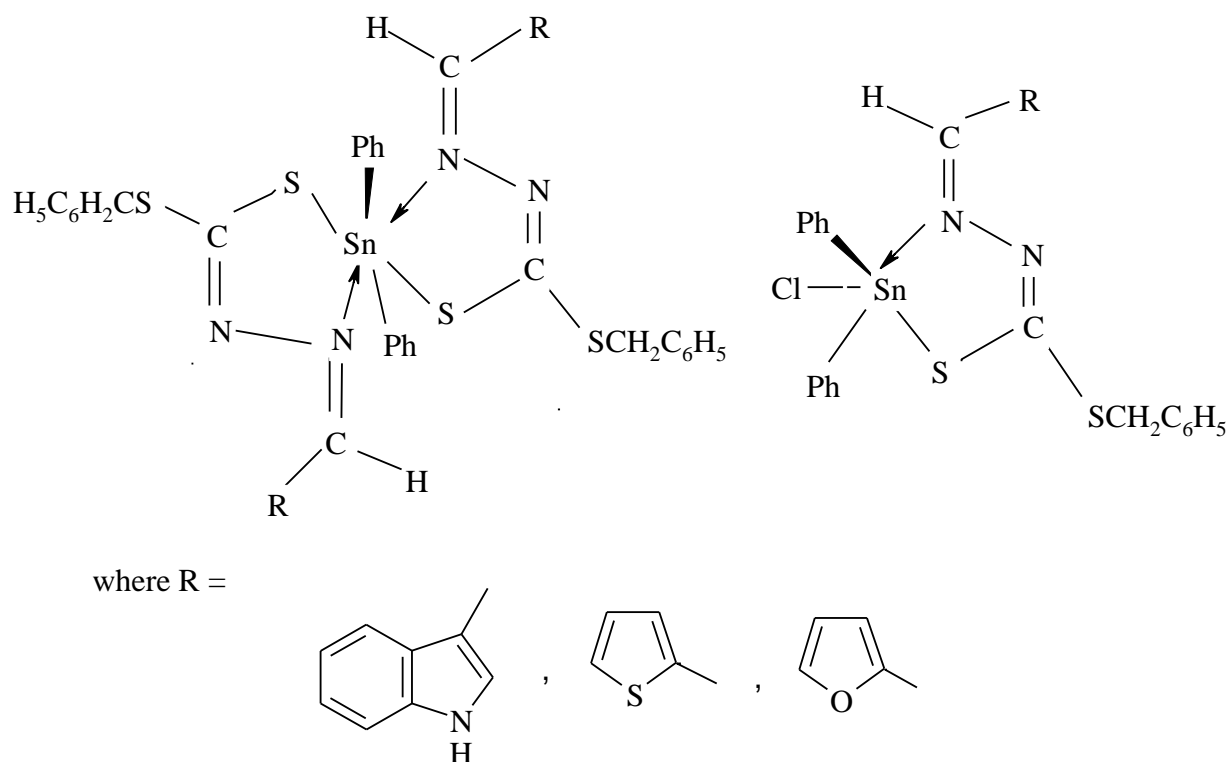


Figure 9: Formula structure of the organotin(IV) complexes with NS-donor atoms.

Yin and Chen (2006) have synthesized a series of organotin(IV) complexes with Schiff base ligand pyruvic acid 3-hydroxy-2-naphthoyl hydrazone $[R_2SnLY]_2$, $L = 3\text{-HO-C}_{10}\text{H}_6\text{-2-CONHN=C(CH}_3\text{)COOH}$, $R = n\text{-C}_4\text{H}_9$; $Y = \text{N}$ (2), $R = \text{PhCH}_2$ (3), $R = \text{Ph}$; $Y = \text{CH}_3\text{OH}$ (4), $R = \text{Me}$ (5) and $[R_3SnLY]$, $L = 3\text{-HO-C}_{10}\text{H}_6\text{-2-CONHNC(CH}_3\text{)COOH}$, $R = n\text{-C}_4\text{H}_9$, $Y = \text{H}_2\text{O}$ (6), $R = \text{Ph}$ (7), $R = \text{Me}$ (8) (Figure 10).

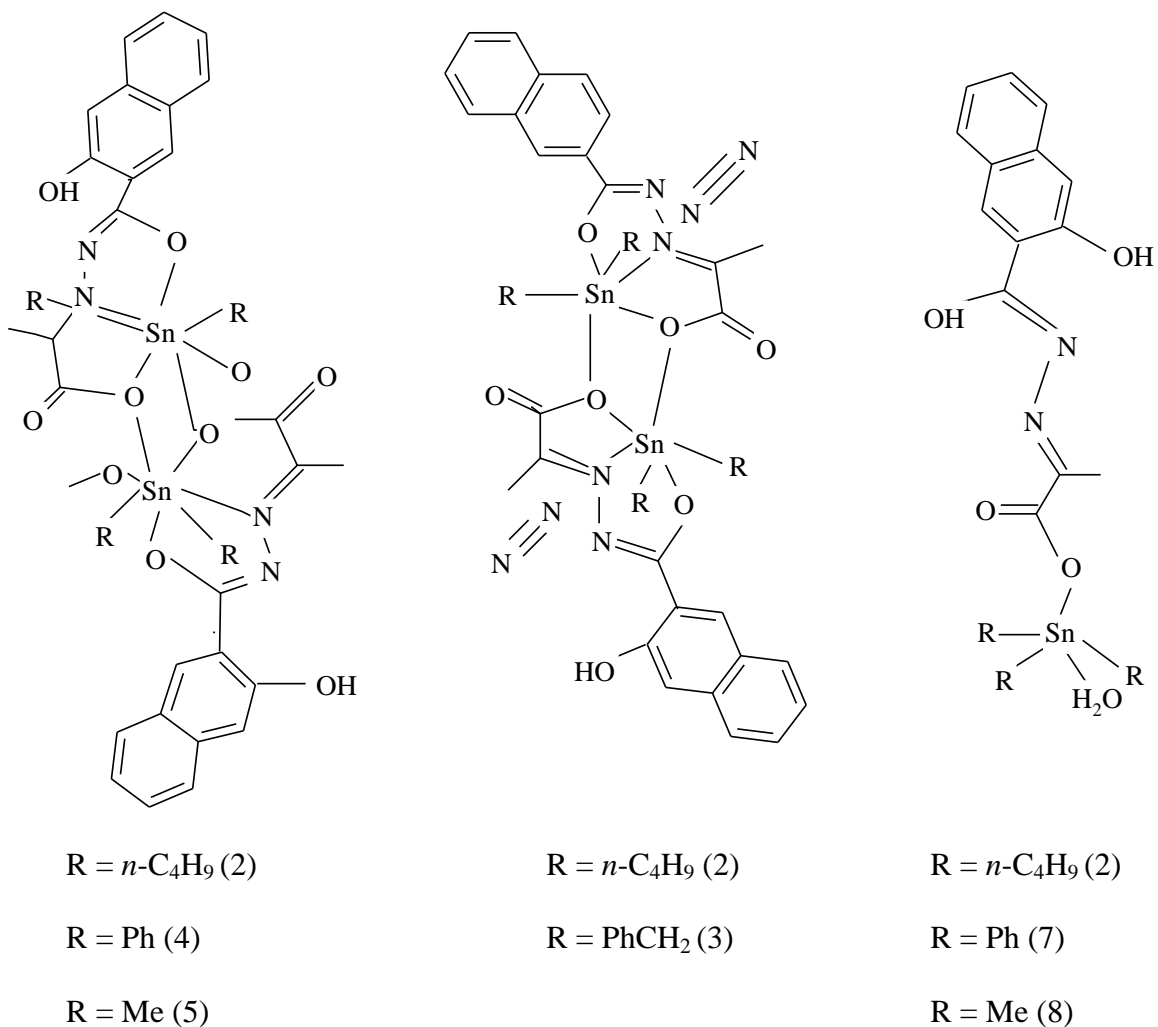
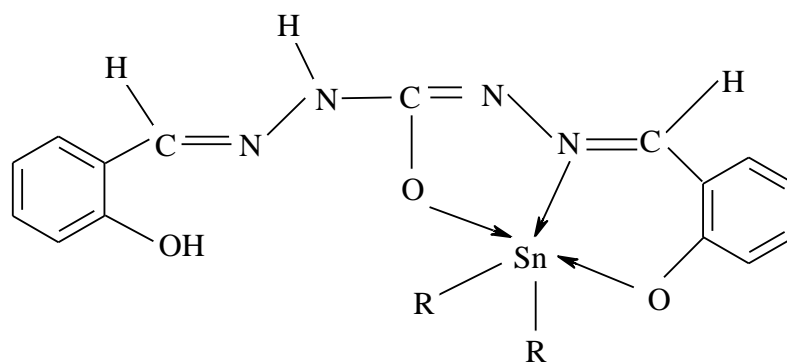


Figure 10: Proposed structures of organotin(IV) complexes containing Schiff base ligands.

Affan and co-workers (2007) have been synthesized and characterized three new diorganotin(IV) complexes by direct reaction of the diorganotin(IV) halide(s) with carbohydrazone-*bis*(salicylaldehyde) ligand (H_4CBS)[$\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_3$] (Figure 11) in good yields. These complexes have also been characterized by X-ray crystallography. All compounds were also showed moderate biological activity with various types of microorganisms.



R = Me, Bu and Ph

Figure 11: Structures of the diorganotin(IV) complexes.

From the literature review, studies on the synthesis and characterization of Schiff base ligands containing ONN/ONS-donor atoms and their organotin(IV) complexes have not sufficient and requires more and deeper researches. In view of the various interaction possibilities of the Schiff base ligands containing ONN/ONS-donor atoms with organotin(IV) chloride(s), the author has undertaken this project for the purpose of synthesizing and characterizing organotin(IV) complexes with the proposed Schiff base ligands containing ONN/ONS-donor atoms.

3.0 Materials and Methodologies

3.1 Physical measurements

The main research has been conducted in Inorganic Research Laboratory at UNIMAS. All chemicals have been purchased from Fluka, Aldrich or J. T. Baker. All solvents have been dried and purified by standard methods. All the reactions have been carried out under nitrogen atmosphere by using Schlenk Vacuum line techniques. Schiff base ligands and their organotin(IV) complexes have been characterized by elemental analysis namely CHN analyses, UV-Visible and FTIR. Among them, only ligand (2) and complex (7) have been determined by ^1H NMR spectra analysis. IR spectral analysis has been recorded as KBr disc using Perkin Elmer Spectrum GX Fourier-Transform Spectrometer ($4000\text{--}370\text{ cm}^{-1}$). ^1H NMR spectra have been recorded in CDCl_3 solution on a Jeol 500 NMR spectrophotometer at UNIMAS. Electronic spectra have been recorded with chloroform on a Perkin Elmer Lambda 25 UV-Visible Spectrophotometer. Molar conductances have been measured at room temperature using Jenway 4510 conductivity meter at UNIMAS. Elemental analyses have been recorded by using FlashEA 1112 series elemental analyzers at UNIMAS. Most of the organotin(IV) halide(s) and their organotin(IV) Schiff base complexes have been preserved in freezer for long-term storage and stability.

3.2 Synthesis of Schiff base ligand (1) and its organotin(IV) complexes (3-6)

3.2.1 Synthesis of salicylaldehyde-2-aminothiophenol (1) containing ONS-donor atoms

A mixture of salicylaldehyde (1.22 g, 0.01 mole) and 2-aminothiophenol (1.25 g, 0.01 mole) in absolute ethanol (30 mL) were stirred and heated under reflux for 5 hours. The reaction mixture was allowed to cool to room temperature for 30 minutes. The white precipitate formed was filtered off, and washed several times using absolute methanol. The crystalline white solid obtained was purified by recrystallization from hot ethanol and dried in vacuo over silica gel. Yield 1.75 g, 70.9 %, m.p. 122-123 °C.

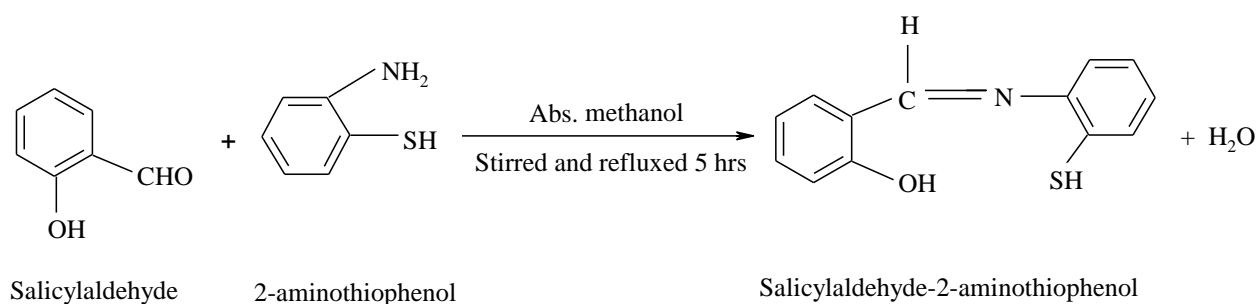


Figure 12: Structure of salicylaldehyde-2-aminothiophenol ligand (1).

3.2.2 Synthesis of [Me₂Sn(C₁₃H₉NOS)] (3)

The Schiff base ligand (1) (0.23 g, 0.001 mole) was dissolved in chloroform containing triethylamine solution (0.20 g, 0.002 mole) with constant stirring under nitrogen atmosphere. The colour of the solution changed from off-white to orange. The resulting mixture was stirred with constant stirring and refluxed for one hour. A solution of Me₂SnCl₂ (0.22 g, 0.001 mole) in chloroform (10 mL) was added dropwise. The resulting solution was gently refluxed for 4-5 hours and allowed it to cool to room temperature. The resulting solution was evaporated in fume cupboard. The solid dimethyltin(IV) complex (3) was filtered off, washed with absolute ethanol, recrystallized from absolute ethanol and dried in vacuo. Yield 1.46 g, 86.4 %, m.p. 101-103 °C.

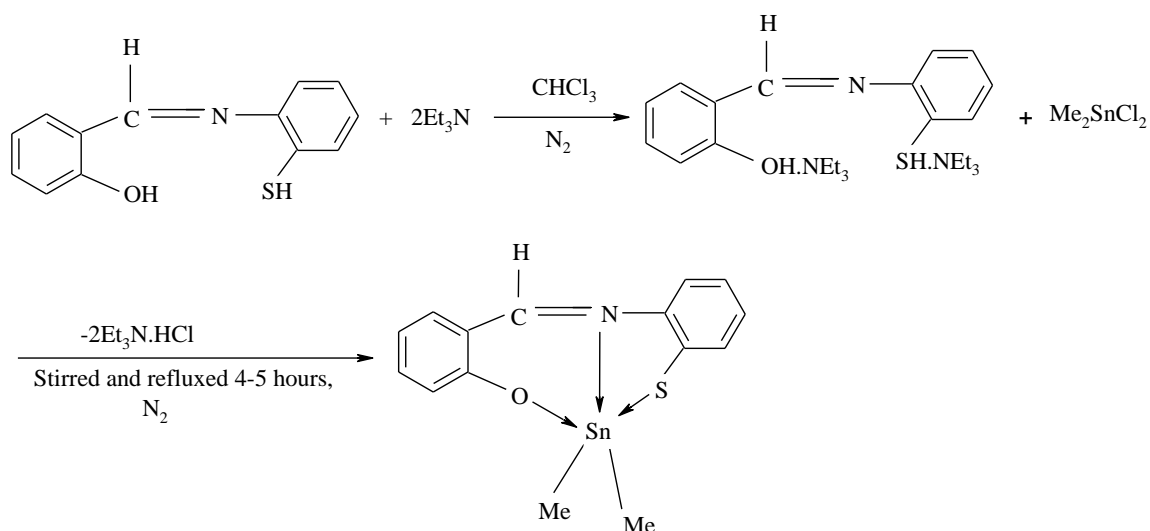


Figure 13: Proposed structure of dimethyltin(IV) complex (**3**).

3.2.3 Synthesis of $[\text{Bu}_2\text{Sn}(\text{C}_{13}\text{H}_9\text{NOS})]$ (**4**)

Complex (**4**) was prepared similarly to complex (**3**), dibutyltin(IV) dichloride (0.30 g, 0.001 mole) was used instead of dimethyltin(IV) dichloride. The dibutyltin(IV) complex (**4**) was obtained as light brown colour. Finally, it was recrystallized from ethanol and dried in vacuo. Yield 0.56 g, 76.4 %, m.p. 77-78 °C.

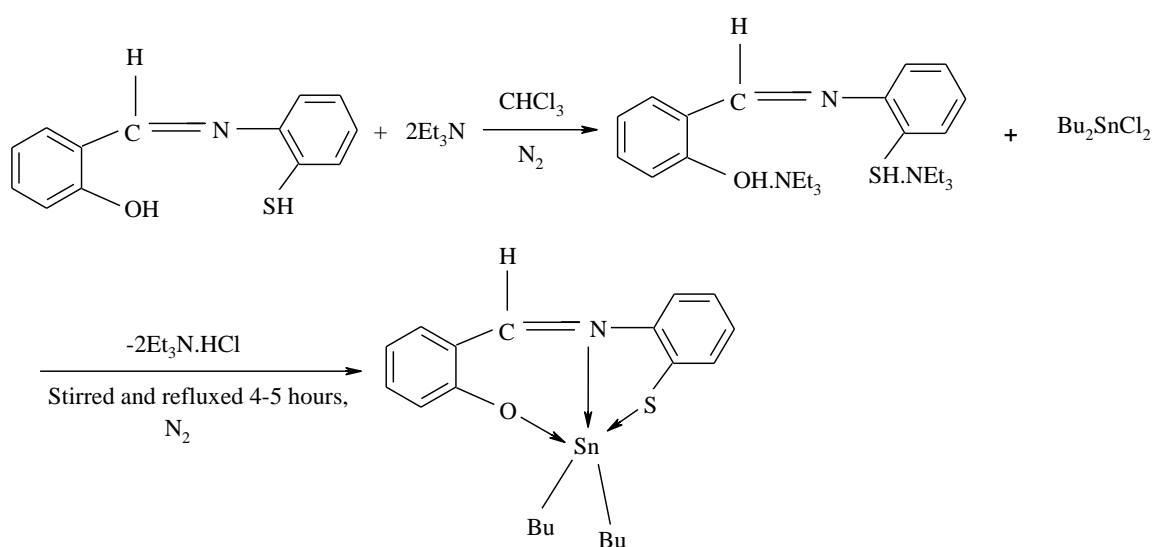


Figure 14: Proposed structure of dibutyltin(IV) complex (**4**).

3.2.4 Synthesis of $[\text{Ph}_2\text{Sn}(\text{C}_{13}\text{H}_9\text{NOS})]$ (**5**)

Complex (**5**) was prepared from diphenyltin(IV) dichloride (0.34 g, 0.001 mole). The diphenyltin(IV) complex (**5**) was washed with ethanol and recrystallized from ethanol. Yield 0.66 g, 80.0 %, m.p. 103-104 °C.

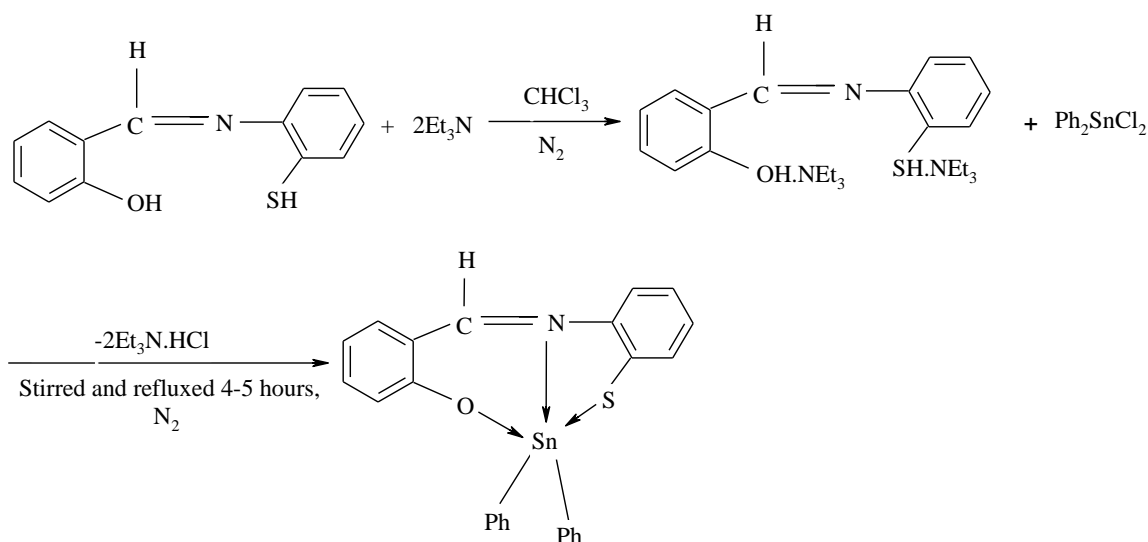


Figure 15: Proposed structure of diphenyltin(IV) complex (**5**).

3.2.5 Synthesis of $[\text{BuSnCl}(\text{C}_{13}\text{H}_9\text{NOS})]$ (**6**)

To a chloroform solution (10 mL) of the ligand (**1**) were added with triethylamine (0.20 g, 0.002 mole) and butyltin(IV) trichloride (0.28 g, 0.001 mole). The mixture was gently refluxed for 3-4 hours. After cooling, the resulting complex (**6**) was filtered off and recrystallized with ethanol. Yield 0.71 g, 80.0 %, m.p. 115-117 °C.

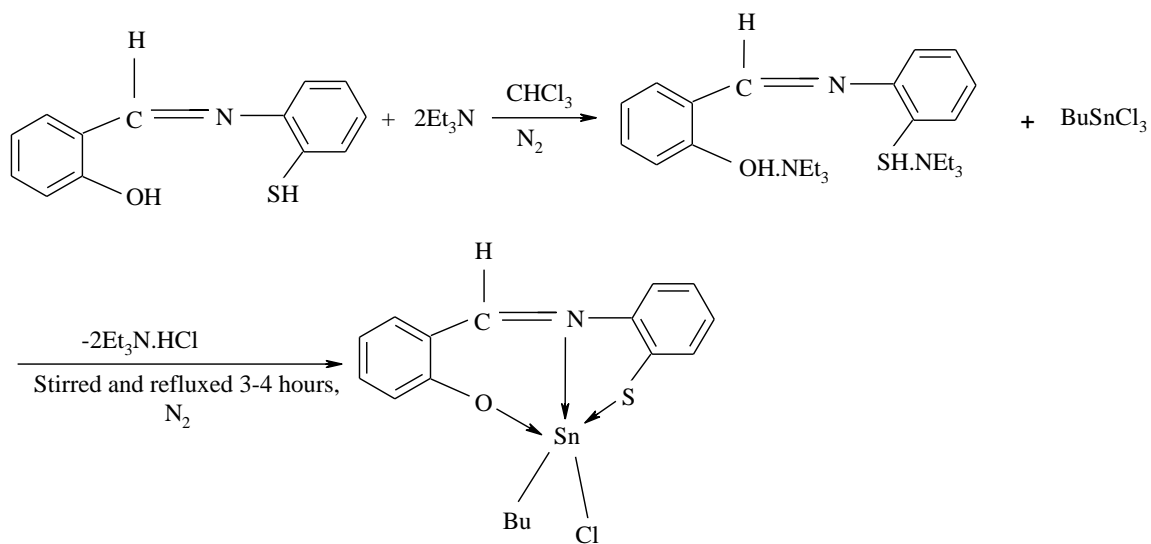


Figure 16: Proposed structure of butyltin(IV) complex (**6**).

3.3 Synthesis of Schiff base ligand (2) and its organotin(IV) complexes (7-9).

3.3.1 Synthesis of 2-benzoylpyridinebenzhydrazone ligand (2) containing ONN-donor atoms

A mixture of benzyhydrazide (0.36 g, 0.010 mole) and 2-benzoylpyridine (1.83 g, 0.010 mole) in absolute ethanol (10 mL) were stirred and heated under reflux for 6 hours. The reaction mixture was allowed to cool to room temperature for 30 minutes. The white color precipitate was obtained by filtration, washed several times with ethanol and dried in vacuo over silica gel. Yield 1.35 g, 84.0 %, m.p. 134-135 °C.

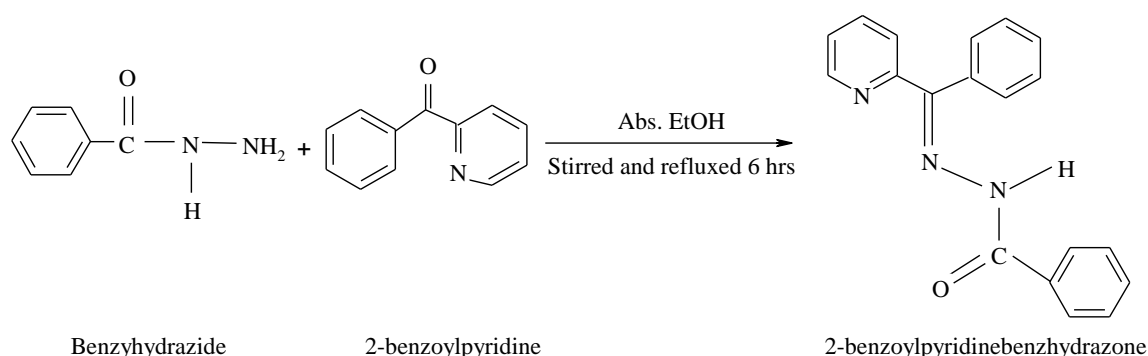


Figure 17: Structure of 2-benzoylpyridinebenzhydrazone ligand (2).

3.3.2 Synthesis of $[\text{Me}_2\text{SnCl}(\text{C}_{19}\text{H}_{14}\text{N}_3\text{O})]$ (7)

Ligand (2) (0.30 g, 0.001 mole) was dissolved in absolute methanol (10 mL) by stirring and added with a potassium hydroxide solution (0.056 g, 0.001 mole) under nitrogen atmosphere. The resulting mixture was stirred with constant stirring and refluxed for one hour. A methanolic solution (10 mL) of dimethyltin(IV) dichloride (0.22 g, 0.001 mole) was added dropwise with constant stirring to the potassium salt of the ligand (2). The resulting solution was refluxed for 4-5 hours and allowed to cool to room temperature. Potassium chloride (KCl) was removed by filtration. The clear filtrate removed using a rotavapor. The dimethyltin(IV)