Coordination Chemistry of Organotin(IV) Complexes with
ONO- donor ligands

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This project is submitted in partial fulfillment of
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(Resource Chemistry)

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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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Coordination Chemistry of Organotin(IV) Complexes with ONO-donor ligands

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ABSTRACT

Three organotin(IV) complexes of salicylaldehyde furoic acid hydrazone ligand (1) with \( R_nSnCl_{4-n} \) (n = 2, 3) have been synthesized in the presence of base in absolute methanol in 1:2:1 mole ratio (metal:base:ligand). Two organotin(IV) complexes of ligand (1) have also been synthesized in the presence of base in absolute methanol in 1:1:1 mole ratio (metal:base:ligand). Another three organotin(IV) complexes of 2-hydroxyacetophenone furoic acid hydrazone ligand (2) in 1:2:1 mole ratio (metal:base:ligand) have been synthesized using the same method. All organotin(IV) complexes (3-10) have been characterized by CHN analyses, UV-Visible and FTIR spectral analyses. Among them, ligand (2) and its organotin(IV) complex have also been studied by \(^1H\) NMR spectra. Spectral studies suggested that both the ligands (1-2) act as dinegative tridentate chelating agents in all the organotin(IV) complexes (3-10). Organotin(IV) complexes (3-5, 8-10) are non electrolytic in nature and are proposed to have five coordinated molecular geometry around the central tin(IV) atom whereas for the organotin(IV) complexes (6-7), they are electrolytic in nature and are proposed to have six coordinated molecular geometry around the central tin(IV) atom, respectively.

Key words: Organotin(IV) complexes; salicylaldehyde furoic acid hydrazone; 2-hydroxyacetophenone furoic acid hydrazone; spectral studies.

ABSTRAK

Tiga kompleks organotin(IV) dari ligan (1) iaitu salisilaldehid asid furoik hidrazon dengan formula \( R_nSnCl_{4-n} \) (n = 2, 3) telah disintesis dalam kehadiran bes serta direfluks bersama-sama dengan methanol pada nisbah molar 1:2:1 (logam:bes:ligan). Dua kompleks organotin(IV) daripada ligan (1) juga telah disintesis dalam kehadiran bes serta direfluks bersama-sama dengan methanol pada nisbah molar 1:1:1 (logam:bes:ligan). Tiga kompleks organotin(IV) dari ligan (2) iaitu 2-hidroksiasetofenon asid furoik hidrazon telah disintesis pada nisubah molar 1:2:1 (logam:bes:ligan) dengan menggunakan kaedah yang sama. Semua kompleks organotin(IV) (3-10) telah dicirikan melalui analisis CHN, UV-Visible dan kajian spectra FTIR. Ligan (2) dan kompleks organotin(IV)nya turut dikaji dengan menggunakan spektra \(^1H\) NMR. Kajian spektra menunjukkan bahawa kedua-dua ligan (1-2) bertindak sebagai dinegatif tridentat secara semulajadi dalam kompleks organotin(IV). Kompleks organotin(IV) (3-5, 8-10) bersifat bukan elektrolitik secara semulajadi dan dicadang mempunyai struktur molekul dengan kekoordinatan lima yang mengelilingi pusat atom tin(IV) manakala bagi kompleks organotin(IV) (6-7) pula, kompleks organotin(IV) berkenaan bersifat elektrolitik secara semulajadi dan masing-masing dicadang mempunyai struktur molekul dengan kekoordinatan enam yang mengelilingi pusat atom tin(IV).

Kata kunci: Kompleks organotin(IV); salisilaldehid asid furoik hidrazon; 2-hidroksiasetofenon asid furoik hidrazon; kajian spectra.
1.0 Introduction

1.1 Hydrazine ligands and their organotin(IV) complexes

Hydrazine is a compound that contains –NH-N=C- functional group. It is formed from any class of derivatives of an aldehyde or a ketone with hydrazine through condensation reaction.

On the other hand, organotin(IV) complexes are compounds consisting of a minimum of one tin-carbon bond with +4 oxidation state.

Studies regarding to the coordination chemistry of ONO- donor ligands have nowadays received great attention, as they are pharmacologically active. Furthermore, organotin(IV) complexes have shown antitumor activity. Besides being the active components in a series of biocidal formulations, they are also widely been tested for the purpose of cancer chemotherapy. Moreover, the importance of diorganotin(IV) complexes is in part due to their toxicological activities, as well as their applications as initiators for lactide polymerization (Barba et al., 2007; Shahzadi et al., 2005).

Thus, studies on the coordination chemistry of organotin(IV) complexes with hydrazine ligands containing ONO-donor atoms deserves further and deeper research. Thus, additional efforts have been undertaken for the synthesis and characterization of the organotin(IV) complexes with hydrazine ligands containing ONO-donor atoms in view of the various possible interactions of the hydrazine ligands containing ONO-donor atoms with organotin(IV) chloride(s).
1.2 Objectives

The objectives of this research are:

i) to synthesize hydrazone ligands containing ONO- donor atoms.

ii) to synthesize organotin(IV) complexes with hydrazone (ONO) ligands.

iii) to characterize hydrazone (ONO) ligands and their organotin(IV) complexes by CHN analyses, UV-Visible, FTIR and $^1$H NMR spectra analyses.

iv) to determine the molar conductivity of the synthesized organotin(IV) complexes.
2.0 Literature Review

2.1 Hydrazone ligands containing ONO- donor atoms

A hydrazone, consists of ONO- donor atoms (2-hydroxy-4-methoxyacetophenone nicotinic acid hydrazone), has been synthesized by refluxing an equimolar of nicotinic acid hydrazide with 2-hydroxy-4-methoxyacetophenone in ethanol or methanol (alcoholic medium) for 4 hours. The synthesis route is as shown in Scheme 1 (Seena et al., 2008).

![Diagram of 2-hydroxy-4-methoxyacetophenone nicotinic acid hydrazone](image1)

Sch. 1: 2-hydroxy-4-methoxyacetophenone nicotinic acid hydrazone.

Another tridentate ONO- donor hydrazone ligand has been synthesized by Ghosh et al. (2007). The 2-hydroxyacetophenone benzoyl hydrazone has been derived from the condensation of benzoyl hydrazine with 2-hydroxyacetophenone, as shown in Figure 1.

![Diagram of 2-hydroxyacetophenone benzoyl hydrazone](image2)

Fig. 1: 2-hydroxyacetophenone benzoyl hydrazone.
Three hydrazone ligands containing ONO- donor atoms have been synthesized by refluxing an ethanolic solution of 2-methyl pyrazole-4-carboxyhydrazide with salicyaldehyde, o-hydroxyacetophenone and 5-bromosalicylaldehyde to yield salicylaldehyde-2-methyl pyrazole-4-carboxyhydrazone, o-hydroxyacetophenone-2-methyl pyrazole-4-carboxyhydrazone and 2-bromosalicylaldehyde-4-methyl pyrazole-3-carboxyhydrazone, respectively (Gupta et al., 2007) (Figure 2-4).

Fig. 2: Salicylaldehyde-2-methyl pyrazole-4-carboxyhydrazone.

Fig. 3: o-hydroxyacetophenone-2-methyl pyrazole-4-carboxyhydrazone.

Fig. 4: 5-bromosalicylaldehyde-2-methyl pyrazole-4-carboxyhydrazone.
2.2 Organotin(IV) complexes with hydrazone ligands containing ONO- donor atoms

Recently, the first 1D tetranuclear organotin(IV) complex has been successfully synthesized in high yield and characterized by X-ray crystallography analysis. The structure of organotin(IV) complex with \(N^\prime\)-acylsalicylhydrazone ligand 4-[2-(2-hydroxybenzoyl) hydrazinyl]-4-oxobut-2-enoic acid is shown as in Figure 5 (Yin et al., 2008).

![Organotin(IV) complex](image)

Fig. 5: Organotin(IV) complex with \(N^\prime\)-acylsalicylhydrazone ligand 4-[2-(2-hydroxybenzoyl) hydrazinyl]-4-oxobut-2-enoic acid.

The reaction of dimethyltin(IV) dichloride with 4-nitrobenzanilide thiosemicarbazone and 4-chlorobenzanilide semicarbazone have been carried out in 1:2 mole ratio in MeOH. The tin(IV) complexes were obtained in good yield and their molecular structures were determined by X-ray diffraction as octahedral (Figure 6-7) (Singh et al., 2007).
Fig. 6: Molecular structure of tin(IV) complex with 4-nitrobenzanilide thiosemicarbazone ligand.

Fig. 7: Molecular structure of tin(IV) complex with 4-chlorobenzanilide semicarbazone ligand.
3.0 Materials and Methods

3.1 Experimental

All chemicals were purchased from Fluka, Aldrich or J. T. Baker. Besides, all the solvents were purified before used as follows: ethanol and methanol form magnesium turnings and iodine, then stored in molecular sieves (Amergo et al., 1996). All the reactions were carried out using Schlenk Vacuum line techniques under dry nitrogen atmosphere.

3.2 Measurement

The hydrazone ligand and its organotin(IV) complexes were characterized by CHN analyses, UV-Visible, FTIR and $^1$H NMR spectral analyses. Electron absorption spectra were recorded with a suitable solvent on a Perkin Elmer Lambda 25 UV-Visible spectrophotometer at UNIMAS. Infrared spectra were recorded as KBr disc using Perkin Elmer Spectrum GX Fourier-Transform Spectrometer (4000-370 cm$^{-1}$) at UNIMAS. $^1$H NMR spectra were recorded in DMSO-$d_6$ solution on a Jeol 500 MHz FT-NMR spectrophotometer at UNIMAS. Molar conductances were measured at room temperature using Jenway 4510 molar conductivity meter at UNIMAS. The synthesized organotin(IV)-hydrazones complexes were kept in the freezer to enhance stability for long term storage.
3.3 Synthesis of hydrazone ligand (1) and its organotin(IV) complexes (3-7)

3.3.1 Synthesis of salicylaldehyde furoic acid hydrazone ligand, \([\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_3]\) (1) containing ONO- donor atoms

A mixture of salicylaldehyde (0.120 g, 0.001 mole) and furoic acid hydrazide (0.130 g, 0.001 mole) in absolute ethanol (10 ml) were heated under reflux for 4-5 hours. The reaction mixture was allowed to cool to room temperature for 30 minutes. The light yellow precipitate formed was filtered off and washed several times using absolute ethanol. The crystalline light yellow solid obtained was purified by recrystallization from hot ethanol and dried in vacuo over silica gel. Yield: 1.00 g, 87 %, m.p. 176-178 °C

![Sch. 2: Proposed structure of salicylaldehyde furoic acid hydrazone (1).](image-url)
3.3.2 Synthesis of [Bu₂Sn(C₁₂H₈N₂O₃)] (3)

Potassium hydroxide solution (0.110 g, 0.002 mole) was added by stirring to a ligand (1) (0.230 g, 0.001 mole) in absolute methanol (10 mL) under nitrogen atmosphere. The colour of the solution changed from light yellow to yellow. The resulting solution was refluxed with constant stirring for one hour. Then, a solution of Bu₂SnCl₂ (0.304 g, 0.001 mole) in absolute methanol (10 mL) was added dropwise and the solution was refluxed for 5-6 hours. It was allowed to cool to the room temperature. The potassium chloride was removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The solid formed was washed by hexane and dried in vacuo over silica gel. The organotin(IV) complex (3) was obtained as yellowish orange solid by recrystallization from absolute methanol. Yield: 0.38 g, 82 %, m.p.: 104-107 °C.

Sch. 3: Proposed structure of organotin(IV) complexes (3-5).
3.3.3 Synthesis of [Me₂Sn(C₁₂H₈N₂O₃)] (4)

The procedure described above for complex (3) was followed to prepare the complex (4), with dimethyltin(IV) dichloride (0.220 g, 0.001 mole) used instead of dibutyltin(IV) dichloride. The organotin(IV) complex (4) was obtained as yellow solid by recrystallization from absolute methanol. Yield: 0.30 g, 80 %, m.p.: 182-184 °C.

3.3.4 Synthesis of [Ph₂Sn(C₁₂H₈N₂O₃)] (5)

Complex (5) was prepared similarly to complex (3), diphenyltin(IV) dichloride (0.688 g, 0.001 mole) was used instead of dibutyltin(IV) dichloride. The organotin(IV) complex (5) was obtained as yellow solid by recrystallization from absolute methanol. Yield: 0.41 g, 81 %, m.p.: 194-196 °C.
3.3.5 Synthesis of $[\text{Ph}_3\text{Sn(C} \text{C}_{12} \text{H}_8 \text{N}_2 \text{O}_3)] \ (6)$

The procedure described earlier for (3) was followed for the preparation of (6). Triphenyltin(IV) chloride (0.390 g, 0.001 mole) was used instead of dibutyltin(IV) dichloride. The organotin(IV) complex (6) was obtained as yellow solid by recrystallization from absolute methanol. Yield: 0.48 g, 83 %, m.p.: 194-196 °C.

![Sch. 4: Proposed structure of organotin(IV) complexes (6-7).](image)

3.3.6 Synthesis of $[\text{Bu}_3\text{Sn(C} \text{C}_{12} \text{H}_8 \text{N}_2 \text{O}_3)] \ (7)$

Complex (7) was synthesized in a similar way as in complex (3). Tributyltin(IV) chloride (0.330 g, 0.001 mole) was used instead of dibutyltin(IV) dichloride. The organotin(IV) complex (7) was obtained as yellow solid by recrystallization from absolute methanol. Yield: 0.40 g, 78 %, m.p.: 155-157 °C.
3.4 Synthesis of hydrazone ligand (2) and its organotin(IV) complexes (8-10)

3.4.1 Synthesis of 2-hydroxyacetophenone furoic acid hydrazone, [C_{12}H_{10}N_{2}O_{3}] (2) containing ONO- donor atoms

A mixture of 2-hydroxyacetophenone (0.140 g, 0.001 mole) and furoic acid hydrazide (0.130 g, 0.001 mole) in absolute ethanol (10 ml) were heated under reflux for 4-5 hours. The reaction mixture was allowed to cool to room temperature for 30 minutes. The light yellow precipitate was obtained after slow evaporation of solvent at room temperature and washed several times using absolute ethanol. The compound was purified by recrystallization from hot ethanol. Finally, it was dried in vacuo over silica gel. Yield: 1.02 g, 85 %, m.p. 145-147 °C.

![Sch. 5: Proposed structure of 2-hydroxyacetophenone furoic acid hydrazone (2).](image-url)
3.4.2 Synthesis of [Bu$_2$Sn(C$_{13}$H$_{10}$N$_2$O$_3$)] (8)

Potassium hydroxide solution (0.110 g, 0.002 mole) was added by stirring to a ligand (2) (0.240 g, 0.001 mole) in absolute methanol (10 mL) under nitrogen atmosphere. The resulting solution was refluxed with constant stirring for one hour. Then, a solution of dibutyltin(IV) dichloride (0.300 g, 0.001 mole) in absolute methanol (10 mL) was added dropwise and the solution was refluxed for 5-6 hours. It was allowed to cool to the room temperature. The potassium chloride was removed by filtration and the clear solution of filtrate was evaporated to dryness under reduced pressure to leave a yellowish brown solid. The solid formed was washed by hexane and dried in vacuo over silica gel. The organotin(IV) complex (8) was obtained as yellowish brown solid by recrystallization from absolute methanol. Yield: 0.38 g, 81 %, m.p.: 111-113 °C.

Sch. 6: Proposed structure of organotin(IV) complexes (8-10).
3.4.3 Synthesis of [Me\textsubscript{2}Sn(C\textsubscript{13}H\textsubscript{10}N\textsubscript{2}O\textsubscript{3})] (9)

The procedure described earlier for complex (8) was followed to prepare the complex (9) using dimethyltin(IV) dichloride (0.220 g, 0.001 mole), instead of dibutyltin(IV) dichloride. The organotin(IV) complex (10) was obtained as yellowish orange solid by recrystallization from absolute methanol. Yield: 0.29 g, 75 %, m.p.: 115-117 °C.

3.4.4 Synthesis of [Ph\textsubscript{2}Sn(C\textsubscript{13}H\textsubscript{10}N\textsubscript{2}O\textsubscript{3})] (10)

Complex (10) was synthesized in a similar way as in complex (8). Diphenyltin(IV) dichloride (0.360 g, 0.001 mole) was used instead of dibutyltin(IV) dichloride. The organotin(IV) complex (10) was obtained as yellow solid by recrystallization from absolute methanol. Yield: 0.42 g, 82 %, m.p.: 173-175 °C.
4.0 Results and Discussion

In the present study, two hydrazone ligands (1-2) were synthesized by direct condensation reactions of furoic acid hydrazide with salicylaldehyde and 2-hydroxyacetophenone in 1:1 mole ratio in absolute ethanol, respectively. Five organotin(IV) complexes (3-7) have been synthesized by direct reaction of appropriate organotin(IV) chloride(s) and salicylaldehyde furoic acid hydrazone ligand (1) in the presence of base [Equation 1-2]. Another three organotin(IV) complexes (8-10) of ligand (2) have also been synthesized with the similar path [Equation 3].

\[
\text{Ligand (1) + 2KOH + R}_n\text{SnCl}_4 \rightarrow \text{Organotin(IV) complexes (3-5) + KCl + H}_2\text{O} \quad (1)
\]

\[R_n\text{SnCl}_4 = \text{Bu}_2\text{SnCl}_2 (3), \text{Me}_2\text{SnCl}_2 (4), \text{Ph}_2\text{SnCl}_2 (5).\]

\[
\text{Ligand (1) + KOH + R}_n\text{SnCl}_4 \rightarrow \text{Organotin(IV) complexes (6-7) + KCl + H}_2\text{O} \quad (2)
\]

\[R_n\text{SnCl}_4 = \text{Ph}_3\text{SnCl} (6), \text{Bu}_3\text{SnCl} (7).\]

\[
\text{Ligand (2) + 2KOH + R}_n\text{SnCl}_4 \rightarrow \text{Organotin(IV) complexes (8-10) + KCl + H}_2\text{O} \quad (3)
\]

\[R_n\text{SnCl}_4 = \text{Bu}_2\text{SnCl}_2 (8), \text{Me}_2\text{SnCl}_2 (9), \text{Ph}_2\text{SnCl}_2 (10).\]

Two hydrazone ligands (1-2) and their organotin(IV) complexes (3-10) have been characterized by element analyses (Table 1), molar conductances (Table 2) and other spectroscopic studies such as UV-Visible (Table 3 and 6) and IR (Table 4 and 7) spectral analyses.