SYNTHESIS AND CHARACTERIZATION OF ORGANOTIN (IV) COMPLEXES OF SCHIFF BASE LIGAND CONTAINING -ON DONOR ATOMS

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Synthesis and characterization of organotin(IV) complexes of Schiff base ligand containing –ON donor atoms

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This project is submitted partial fulfillment of the requirements for the Degree of Bachelor of Science with Honours (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 of qualification of this other university or institution of higher learning.

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Synthesis and characterization of organotin(IV) complexes of Schiff base ligand containing -ON donor atoms

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ABSTRACT

Six organotin(IV) complexes of benzaldehyde-isonicotinic hydrazone ligand (1) with R\textsubscript{n}SnCl\textsubscript{4-n} (n = 1,2) have been synthesized in the presence of base and refluxing methanol in 1:1:1 mole ratio (ligand:base:metal). All organotin(IV) complexes (2-7) have been analyzed using FTIR, UV-Visible, CHN analyzer and \textsuperscript{1}H NMR spectral studies. All organotin(IV) complexes (2-7) are non-electrolytic in nature. Spectral suggested that ligand (1) act as mononegative bidentate nature in its organotin(IV) complexes. Therefore, a five coordinated molecular structure has been proposed for all the mentioned organotin(IV) complexes.

Keywords: Organotin(IV) complexes; benzaldehyde-isonicotinic hydrazone; spectral studies

ABSTRAK

Enam kompleks organotimah(IV) dengan ligan (1) iaitu benzaldehid-isonikolinik hidrazon dengan R\textsubscript{n}SnCl\textsubscript{4-n} (n = 1,2) telah disintesis dengan kehadiran bes dan direfluks dengan metanol dalam kadar nisbah molar 1:1:1 (ligan:bes:logam). Semua kompleks organotimah(IV) (2-7) dianalisis menggunakan kajian spekttra FTIR, UV-Visible, CHN dan \textsuperscript{1}H NMR. Kesemua kompleks organotimah(IV) (2-7) bersifat bukan elektrolit secara semulajadi. Kajian spekttra membuktikan ligan (1) bertindak sebagai bidentat mononegatif secara semulajadi dalam kompleks organotimah(IV). Oleh itu, struktur molekul kompleks organotimah(IV) dicadangkan sebagai lima koordinatan.

Kata kunci: Kompleks organotimah(IV); benzaldehid-isonikotininik hidrazon; kajian spekttra
1. Introduction

1.1 Schiff base ligands and their organotin(IV) complexes

Any class of derivatives of aldehydes or ketones with primary amines will give stable and well-characterized imines through the condensation reaction. When one or both of the reactants is aromatic, the imine is known as Schiff base (Parker, 1993).

Schiff bases are important class of ligands in metal coordination chemistry even after almost a century since their discovery (Pettinari et al., 2001). They may coordinate with the central metal ion or atom either in keto or anionic (enol) forms via the loss of ‘amide’ hydrogen (Affan et al., 2003). Organotin(IV) compounds have numerous applications, for example antifungal and antibacterial (Ghosh et al., 2005). More recently diorganotin(IV) compounds are being synthesized in view of their potential applications in medicinal chemistry and biotechnology (Pettinari et al., 2001; Singh, 1998; Belwal et al., 1997).

On the other hand, organotin(IV) compounds are compounds that have at least one tin-carbon with +4 oxidation state. Organotin(IV) compounds usually have the general formula R₄Sn, R₃SnX, R₂SnX₂ and RSnX₃ where R is an alky1 or phenyl and X is an inorganic substituent, commonly chloride, fluoride, oxide, hydroxide, carboxylate or thiolate (Parker, 1993).
Organotin(IV) complexes have been demonstrated to exhibit relatively high antitumor activity, as emphasized in recent survey (Szorcsik et al., 2004). Organotin(IV) compounds have gained an edge over other organometallics owing to their bioavailability in the ecosystem and entrance into the food chain, the fact they are less hazardous to the environment and their pharmaceutical implications (Shahzadi et al., 2005).

In view of this, the present project will be focused mainly on the synthesis and characterization of organotin(IV) complexes with tridentate Schiff base ligand containing ON-donor atoms.

2 Objectives

The purposes of this research are:

i. to synthesize Schiff base ligand containing ON-donor atoms.

ii. to synthesize organotin(IV) complexes with Schiff base ligands containing ON-donor ligand.

iii. to characterize Schiff base ligand and their organotin(IV) complexes by CHN analyses, UV-Visible, FTIR and 1H NMR spectra analyses.

iv. to determine the molar conductance values of the synthesized organotin(IV) complexes.
2. Literature Review

2.1 Schiff base ligands containing ON-donor atoms

A bifunctional ligands hydroxypyridine, hydroxypyrimidine and hydroxyquinoline contain both neutral coordinating {N} atom and a negative charged {O\textsuperscript{-}} coordination site, which can simultaneously be attached to two different metal ions. Such ligands therefore are suitable agents for the synthesis of mixed metal complexes. Maity \textit{et al.} (2002) reported a novel type of mixed dinuclear cyclopalladated complexes of azobenzenes with 2-hydroxypyridine and 2-mercaptopyridine. In these complexes, the phenolic hydroxy moiety is deprotonated and generally abbreviated as {N, O} (Sorcsik \textit{et al.}, 2005).

Pyridine-2,6-dicarboxylic acid (or dipicolinic acid) form stable chelates with simple metal ions and oxo-metal cations can display widely varying coordination behaviour, functioning as multidentate ligand. Like picolinic acid, dipicolinic acid can stabilize unusual oxidation states. The other isomeric pyridine-dicarboxylic acids, for example pyridine-2,3-, 2,4- and 2,5-dicarboxylic acids, behave like picolinic acid and act as bidentate (chelating) N, O donors (Sorcsik \textit{et al.}, 2004).
The Schiff base has been prepared with 3-hydroxy-2-naphthoic acid hydrazide with pyruvic acid in ethanol according to the literature as shown in Figure 1 (Yin and Chen, 2006).

![Figure 1: Pyruvic acid-3-hydroxy-2-naphthoyl hydrazone.](image)

Due to labile binding of copper ions by exclusively O-donor ligands, the study has performed the possible binding of the copper(I) complex fragment \([(PPh_3)_2Cu]^+\) by three N,O-donor containing ligands, viz, the deprotonated forms of 2-(benzylideneimino)phenol (BimOH), 4-(benzylideneimino)resorcinol (Bim(OH)_2) and \(N\)-(2,4-dihydroxy-5-isopropylphenyl)acetamide (DipaH_3) as shown in Figure 2 (Sixt and Kaim, 2000).

![Figure 2: 2-(benzylideneimino)phenol (BimOH), 4-(benzylideneimino)resorcinol (Bim(OH)_2) and \(N\)-(2,4-dihydroxy-5-isopropylphenyl)acetamide (DipaH_3).](image)

\[R = H; \text{BimOH}\]
\[R = OH; \text{Bim(OH)}_2\]
Yin and his co-workers (2007) have synthesized Schiff base ligand of Pyruvic acid thiophene-2-carboxylic hydrazone from pyruvic acid and thiophene-2-carboxylic hydrazide in ethanol solution as shown in Figure 3.

![Pyruvic acid thiophene-2-carboxylic hydrazone.](image)

A tridentate dibasic Schiff base ligand with an ONO donor set reacts with (n-C4H9)4NVO3 in the presence of small amount of acetic acid to form a monomeric and five-coordinated oxovanadium(V) complexes of the type \([\text{VO(L)}\text{OCH}_2\text{CH}_3])\)(H2L = \(N\)-benzoylaceton-m-Bromobenzoylhydrazone) (Wang et al., 1996).

Another type of ONO- tridentate ligand has been reported by Hassan (1997). A few metal complexes of isatin-isonicotinoylhydrazone has been synthesized and characterized. The isatin-isonicotinoylhydrazone is derived from isatin and isonicotinic acid hydrazide, as shown in Figure 4.

![Isatin-isonicotinoylhydrazone.](image)
Two isomeric ONO Schiff base donor ligands (I and II) derived from salicylaldehyde, 2-hydroxy-1-naphthaldehyde and o-hydroxybenzylamine or o-aminobenzylalcohol have been prepared and characterized (Maurya et al., 1997) (Figure 5).

![Figure 5: Ligand I and II.](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Ligand</th>
<th>X</th>
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<tr>
<td>1.</td>
<td>I</td>
<td>H</td>
</tr>
<tr>
<td>2.</td>
<td>II</td>
<td>H</td>
</tr>
<tr>
<td>3.</td>
<td>I</td>
<td>5,6-C₄H₄</td>
</tr>
<tr>
<td>4.</td>
<td>II</td>
<td>5,6-C₄H₄</td>
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Dey and his co-workers (1999) have synthesized a Schiff base (Figure 6) by using 1:1 mole ratio of anthranilic acid and salicylaldehyde in methanol.

![Figure 6: N-(2-carboxylphenyl)salicylideneimine.](image)
Another type of novel ONO-donor Schiff bases, \(N\)-salicylidene-\(n\)-alkanoylhydrazines derived from \(n\)-alkanoylhydrazines and salicylaldehyde in methanol by Iskander and his co-workers (2003) (Figure 7).

\[
\begin{align*}
\text{ON} & \quad \text{OH} \\
\text{N} & \quad \text{N-H} \\
\text{O} & \quad \text{(CH}_2\text{nCH}_3
\end{align*}
\]

\[n = 0,4,5,6\]

Figure 7: \(N\)-salicylidene-\(n\)-alkanoylhydrazines.

A novel tridentates Schiff base [ONO] donor ligand has been synthesized by Chen and his co-workers (2005) (Figure 8).

\[
\begin{align*}
\text{MeO} & \quad \text{OH} \\
\text{N} & \quad \text{N} \\
\end{align*}
\]

Figure 8: ONO-Schiff base ligand.
A new tridentate ONO-ligand derived from salicylaldehyde and 2-aminophenol containing the ONO donor atoms which is shown in Figure 9 (Barba et al., 2005).

Figure 9: Tridentate ONO- Schiff base ligand.

The complexation behaviour of N-(2-hydroxymethylphenyl)salicylideneimine, which contain benzyl alcoholic oxygen has been studied (Koikawa et al., 2005). This ligand was derived from salicylaldehyde and 2-aminobenzyl alcohol (Figure 10).

Figure 10: N-(2-hydroxymethylphenyl)salicylideneimine.
2.2 Organotin(IV) complexes with Schiff base ligands containing ON donor atoms

The hydroxypyridine-carboxylic acids were found to bind with different organotin(IV) cations in a variety ways which were via monodentate, bridging and \( \{N, O\} \) chelating coordination modes. They therefore tend to form four-, five- and six-membered chelate rings and to undergo keto-enolic tautomerization as in Figure 11 (Szorcsik et al., 2005).

![Keto-enol tautomerism of ligand HL and H2L.](image)

Figure 11: Keto-enol tautomerism of ligand HL and H2L.

A report on the synthesis and characterization of some mono- and dimethyltin(IV) complexes with potentially tridentate \( N \)-salicylidene- and \( N \)-pyridoidene acylhydrazines have been reported by Labib and his co-workers (1996). The reported structure for the organotin(IV) complexes are monochloromethyl[(\( N \)-salicylidene acylhydrazinato)ONO(-2)]tin(IV), dimethyl[(\( N \)-salicylidene acylhydrazine)ONO(-2)]tin(IV) and dimethyl[(\( N \)-pyridoxylidene acylhydrazine)ONO(-2)]tin(IV) which are shown in Figure 12-15.
Figure 12: Monochloromonomethyl\([\text{N-salicylidene acylhydrazinato} \text{ONO}(-2)]\text{tin(IV)}.\)

Figure 13: Dimethyl\([\text{N-salicylidene acylhydrazine} \text{ONO}(-2)]\text{tin(IV)}.\)

Figure 14: Monomethylmonochloro\([\text{N-pyridoxylidene acylhydrazine} \text{ONO}(-2)]\text{tin(IV)}.\)
From the interaction of 2-\{(2-hydroxyphenyl)iminomethyl\}phenol (salopH_2) with tin(IV) and organotin(IV) acceptors, the derivatives [SnR_3(salopH)] (R = Me or Bu\textsuperscript{n}), [SnR_2(salop)] (R = Me, Bu\textsuperscript{n}, Bu\textsuperscript{'}, Vi or Ph), [SnRX(salop)(solvent)] (R = Me, Bu\textsuperscript{n}, Ph or X; X = Cl, Br or I; solvent = CH_3OH or H_2O, [Sn(salop)_2], [R_2SnCl_2(salopH_2)] (R = Me or Bu\textsuperscript{n}) have been obtained and characterized, as shown in Figure 16 (Pettinari et al., 2001).
Another research reported that two diorganotin(IV) complexes of the general formula $\text{R}_2\text{Sn[Ph(O)C=CH-C(Me)=N-N=C(O)Ph]}$ ($\text{R} = \text{Ph, } 1; \text{R} = \text{Me, } 2$) are shown in Figure 17. Both complexes have been synthesized from the corresponding diorganotin(IV) dichloride and the ligand $[4$-phenyl-2,4-butanedionebenzoylhydrazone(2-)], derived from benzoyl acetone and benzoyl hydrazide in methanol at room temperature in presence of triethylamine (Dey et al., 2003).

![Proposed structure of compound (1) and (2).](image)

Figure 17: Proposed structure of compound (1) and (2).
From the reaction of salicylaldehyde thiophene-2-carboxylic hydrazone. Organotin(IV) acceptors have been prepared with dibutyltin(IV) dichloride, dimethyltin(IV) dichloride and diphenyltin(IV) dichloride with triethylamine in ethanol. The structures are shown in Figure 18 (Yin et al., 2007).

![Proposed structure of compound (1), (2) and (3).](image)

Figure 18: Proposed structure of compound (1), (2) and (3).
3. Materials and Methods

3.1 Experimental

All chemicals were purchased from Fluka, Aldrich and J.T. Baker. All solvents were distilled according to published methods by Armarego before used (Armarego et al., 1996). All the reactions were carried out under dry nitrogen atmosphere using Schlenk Vacuum Line techniques.

3.2 Measurement

Schiff base ligand and their organotin(IV) complexes were characterized by elemental analyzer, UV-Visible and FTIR spectral studies. Most of the organotin(IV) halide(s) and their organotin(IV)-Schiff base complexes were preserved in freezer for long-term storage and stability.

Infrared spectra were recorded as KBr disc using Perkin Elmer Spectrum GX Fourier-Transform Spectrometer (4000-400 cm\(^{-1}\)) at UNIMAS. Electronic absorption spectra were recorded with methanol on a Perkin Eimer Lambda 25 UV-Visible spectrometer at UNIMAS. Molar conductances were measured at room temperature using Jenway 4510 conductivity meter at UNIMAS. Elemental analyses were recorded by using elemental analysers UNIMAS (Flashea 1112 series). \(^1\)H NMR spectra were recorded in DMSO-\(d_6\) on a JOEL 500 MHz spectrophotometer at UNIMAS.
3.3 Synthesis of Schiff base ligand (1)

3.3.1 Synthesis of Benzaldehyde-isonicotinic hydrazone ligand \([C_{13}H_{11}N_3O]\) (1) containing ON donor atoms

A mixture of isonicotinic hydrazide (1.37 g, 0.01 mole) and benzaldehyde (1.06 g, 0.01 mole) in absolute ethanol (15 mL) were stirred and heated under reflux for 4 hours. The reaction mixture was allowed to cool to room temperature for 30 minutes. The white precipitate formed was filtered and washed several times using absolute ethanol. The white crystalline solid was purified by recrystallization with ethanol and dried in vacuo over silica gel. Yield = 88%, 2.143 g, m.p. 196-198 °C.

![Synthesis reaction](image)

Benzaldehyde + Isonicotinic hydrazide

Abs. ethanol
\(-H_2O,\) stirred, refluxed 4 hours

Keto form

Figure 19: Structure of benzaldehyde-isonicotinic hydrazone ligand (1)