

Synthesis, Characterization and Antibacterial Activity of Organotin (IV) Complexes with Benzoylacetone Benzhydrazone Ligand

Dayang Norafizan A. Chee and Monica Lulo Rodis

Abstract—Six new organotin(IV) complexes which are $[\text{MeSnCl}_2(\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2)]$ (2), $[\text{BuSnCl}_2(\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2)]$ (3), $[\text{PhSnCl}_2(\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2)]$ (4), $[\text{Me}_2\text{SnCl}(\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2)]$ (5), $[\text{Bu}_2\text{SnCl}(\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2)]$ (6) and $[\text{Ph}_2\text{SnCl}(\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2)]$ (7) were synthesized by direct reaction of RSnCl_3 ($\text{R} = \text{Me, Bu and Ph}$) or R_2SnCl_2 ($\text{R} = \text{Me, Bu and Ph}$) and benzoylacetone benzhydrazone ligand $[(\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2)]$ (1) in Schlenk round bottom flask under purified nitrogen atmosphere in the presence of base in 1:2:1 molar ratio (metal: base: ligand). All organotin(IV) complexes (2-7) have been characterized by molar conductivity, UV-Visible, IR ^{13}C and ^1H NMR spectral studies. All organotin(IV) complexes (2-7) are non-electrolytic in nature. The benzoylacetone benzhydrazone ligand (1) and its organotin(IV) complexes (2-7) have also been tested for their antibacterial activity towards *Escherichia coli* by using turbidimetric kinetic method.

Keywords—Antibacterial activity, Benzoylacetone benzhydrazone ligand, Organotin(IV) complexes.

I. INTRODUCTION

SCHIFF base metal complexes containing hydrazone group have been studied extensively due to the interesting ligand systems containing different donor sites in heterocyclic rings, for instance NNO or NNS. These hydrazone chelate derivatives act as good potential oral drugs to cure the genetic disorders for example thalassemia [7]. Besides, hydrazones have many pharmacological properties including anti-tubercular activities and iron scavenging [5], [15]. Hydrazones also have been utilized as an analytical reagent and as polymer-coating, pigment, ink and fluorescent materials [9].

Organotin(IV) is one of the non-transition metal which have the hydrolytic instability and large lability in solution, therefore only a few studies about it along time ago [1]. Organotin(IV) compounds are identified by the existence of at least covalent C-Sn bond and containing tetravalent Sn centers are classified as mono-, di-, tri- or tetraorganotin(IV) depending on the number of alkyl or aryl group that attached to the organotin(IV) complex structure [10].

The biochemical activity of organotin compounds commonly greatly depend on the structure of the molecule and

the coordination number of the tin atoms [11]. Organotin(IV) complexes are known to stimulate therapeutic effects on various tumor cells [18]. Trialkyl and triaryl tin compounds are suitable as wood preservatives and as efficient fungicides due to their degradation ability in soil yet it is non-toxic compound. Meanwhile, the highly active dialkyl and diaryl tin compounds show pronounced bacteriostatic properties either towards Gram positive bacteria or Gram negative bacteria [16].

However, there are not many studies available for the complexation of organotin(IV) with benzhydrazone ligand. Therefore, benzhydrazone ligand with organotin(IV) was chosen to be synthesized in this study. Fig. 1 shows the structure of ligand (1) in keto and enol form.

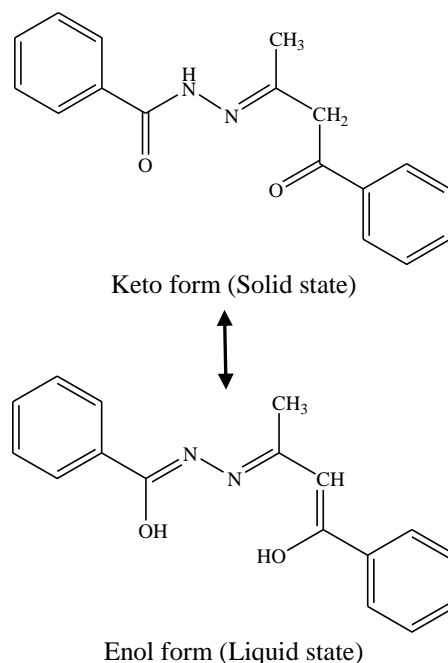


Fig. 1 Structure of benzoylacetone benzhydrazone ligand, $(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)$ (1)

II. MATERIALS AND METHODS

A. General and Instrumental

Chemicals were purchased from Aldrich, Fluka, Acros and J.T Baker. All solvents were distilled and purified by standard method [19]. The reactions were carried out under nitrogen atmosphere in Schlenk vacuum line apparatus. The melting point was measured using open capillary in Stuart MP3. The molar conductivities of the compound were recorded using

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digital Jenway 4510 conductivity meter. All the UV-Vis absorption spectra were recorded on a JASCO V-630 Spectrometer with a 1 cm quartz cuvette in the range 200-600 nm. The infrared spectra were analyzed on Thermo Scientific Nicolet iS10 Spectrometer using KBr disc. The ^1H and ^{13}C NMR spectra were recorded on a JEOL 500 MHz Spectrophotometer by dissolving samples in deuterated solvent (DMSO- d_6).

B. Preparation of Benzoylacetone benzhydrazone ($\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$) (1)

A solution of benzoylacetone (0.811 g, 0.005 mole) dissolved in 10 mL absolute ethanol was added to ethanolic solution of benzhydrazide (0.681 g, 0.005 mole). The reaction mixture was heated under reflux for 6 hours and constantly stirred. The reaction mixture was allowed to cool to room temperature for half an hour. The shiny white precipitate formed were filtered off and washed several times using absolute ethanol and dried under vacuum over silica gel overnight. Colourless crystals were obtained by slow evaporation of absolute ethanol solution at room temperature. Yield: 0.786 g, 56%. M.p: 140-141 °C. UV-Visible (MeOH) $\lambda_{\text{max}}(\text{nm})$: 335, 366. IR ($\nu_{\text{max}} \text{ cm}^{-1}$) (KBr): 3231 (NH), 1662 (C=O), 1603 (C=N), 924 (N-N). ^1H NMR (DMSO- d_6 , 500MHz), δ : 12.23 (s, 1H, CH=C(OH)), 10.92 (s, 1H, N=C(OH)), 7.34-7.89 (m, 10H, aromatic-H), 5.98 (s, 1H, CH=C), 2.07 (s, 3H, $\text{H}_3\text{C}-\text{C}=\text{N}$). ^{13}C NMR (DMSO- d_6 , 500MHz), δ : 187.40 (1C, HN-C-OH), 166.55 (1C, CH-C-OH), 155.68 (1C, C=N), 124.92-144.27 (12C, aromatic ring), 92.23 (1C, CH=C), 18.48 (1C, CH_3).

C. Preparation of Organotin(IV) Complexes

1. Synthesis of $[\text{MeSnCl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)]$ (2)

The ligand ($\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$) (1) (0.560 g, 0.002 mole) was dissolved in hot absolute methanol (10 mL) in a Schlenk round bottom flask. Potassium hydroxide (KOH) (0.224 g, 0.004 mole) dissolved in methanol was added dropwise to the ligand solution and the colour of the mixture changed from light yellow to golden yellow. The resulting mixture was refluxed under nitrogen atmosphere for one hour. A methanolic solution of methyltin(IV) chloride (0.439 g, 0.002 mole) was added dropwise into the resulting mixture causing the solution to change from golden yellow to bright yellow in colour. The solution was refluxed further for another 5-7 hours and allowed to cool to room temperature. The precipitate of potassium chloride (KCl) salt formed and removed by filtration. The filtrate was evaporated until precipitate/crystal formed and finally dried in vacuum over silica gel overnight. The methyltin(IV) complex was obtained as an intense yellow precipitate by recrystallization from hot methanol. Yield: 0.735 g, 86%. M.p: 219-220 °C. Molar conductivity (DMSO) $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$: 0.90. UV-Visible (MeOH) $\lambda_{\text{max}}(\text{nm})$: 239, 406. IR ($\nu_{\text{max}} \text{ cm}^{-1}$) (KBr): 3467 (OH), 1593 (C=N-N=C), 1523 (NCO $^-$), 1302 (C-O), 1031 (N-N), 557 (Sn-O), 453 (Sn-N). ^1H NMR (DMSO- d_6 , 500MHz), δ : 7.45-8.04 (m, 10H, aromatic-H), 6.04 (s, 1H, CH=C), 2.49 (s, 3H, $\text{H}_3\text{C}-\text{C}=\text{N}$), 1.00 (s, 3H, CH_3-Sn). ^{13}C NMR (DMSO- d_6 , 500MHz), δ : 171.80 (1C, N=C-O), 166.28 (1C, CH=C-O), 161.82 (1C, C=N), 126.64-138.36 (12C, aromatic ring), 95.51 (1C, CH=C), 22.03 (1C, CH_3), 9.52 (1C, Sn- CH_3).

The other complexes (3-7) were synthesized using the same procedure as $[\text{MeSnCl}_2(\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2)]$ (2) with appropriate organotin(IV) chloride(s).

2. Synthesis of $[\text{BuSnCl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)]$ (3)

Yield: 0.409 g, 82%. M.p: 146-148 °C. Molar conductivity (DMSO) $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$: 1.36. UV-Visible (MeOH) $\lambda_{\text{max}}(\text{nm})$: 238, 406. IR ($\nu_{\text{max}} \text{ cm}^{-1}$) (KBr): 3438 (OH), 1593 (C=N-N=C), 1519 (NCO $^-$), 1303 (C-O), 1030 (N-N), 541 (Sn-O), 450 (Sn-N). ^1H NMR (DMSO- d_6 , 500MHz), δ : 7.45-8.02 (m, 10H, aromatic-H), 6.04 (s, 1H, CH=C), 2.48 (s, 3H, $\text{H}_3\text{C}-\text{C}=\text{N}$), 0.94-1.86 (s, 9H, Bu-Sn). ^{13}C NMR (DMSO- d_6 , 500MHz), δ : 171.66 (1C, N=C-O), 165.05 (1C, CH=C-O), 162.51 (1C, C=N), 126.83-138.71 (12C, aromatic ring), 95.63 (1C, CH=C), 14.21 (1C, CH_3), 29.03, 27.62, 25.68, 22.31 (4C, Sn- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

3. Synthesis of $[\text{PhSnCl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)]$ (4)

Yield: 1.349 g, 97%. M.p: 285-286 °C. Molar conductivity (DMSO) $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$: 0.64. UV-Visible (MeOH) $\lambda_{\text{max}}(\text{nm})$: 238, 406. IR ($\nu_{\text{max}} \text{ cm}^{-1}$) (KBr): 3445 (OH), 1593 (C=N-N=C), 1517 (NCO $^-$), 1306 (C-O), 1027 (N-N), 540 (Sn-O), 452 (Sn-N). ^1H NMR (DMSO- d_6 , 500MHz), δ : 7.46-8.07 (m, 16H, aromatic-H/Sn- C_6H_5), 6.12 (s, 1H, CH=C), 2.54 (s, 3H, $\text{H}_3\text{C}-\text{C}=\text{N}$). ^{13}C NMR (DMSO- d_6 , 500MHz), δ : 171.92 (1C, N=C-O), 166.70 (1C, CH=C-O), 162.09 (1C, C=N), 126.83-146.31 (18C, aromatic ring/Sn- C_6H_5), 95.99 (1C, CH=C), 22.11 (1C, CH_3).

3. Synthesis of $[\text{Me}_2\text{SnCl}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)]$ (5)

Yield: 0.222 g, 76%. M.p: 144-146 °C. Molar conductivity (DMSO) $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$: 1.29. UV-Visible (MeOH) $\lambda_{\text{max}}(\text{nm})$: 243, 413. IR ($\nu_{\text{max}} \text{ cm}^{-1}$) (KBr): 3438 (OH), 1592 (C=N-N=C), 1530 (NCO $^-$), 1303 (C-O), 1026 (N-N), 528 (Sn-O), 448 (Sn-N). ^1H NMR (DMSO- d_6 , 500MHz), δ : 7.40-7.96 (m, 10H, aromatic-H), 5.83 (s, 1H, CH=C), 2.47 (s, 3H, $\text{H}_3\text{C}-\text{C}=\text{N}$), 0.69 (s, 3H, CH_3-Sn). ^{13}C NMR (DMSO- d_6 , 500MHz), δ : 172.75 (1C, N=C-O), 169.59 (1C, CH=C-O), 163.38 (1C, C=N), 126.64-138.39 (12C, aromatic ring), 94.21 (1C, CH=C), 23.13 (1C, CH_3), 3.00 (1C, Sn- CH_3).

4. Synthesis of $[\text{Bu}_2\text{SnCl}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)]$ (6)

Yield: 0.195 g, 51%. M.p: 148-149 °C. Molar conductivity (DMSO) $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$: 0.54. UV-Visible (MeOH) $\lambda_{\text{max}}(\text{nm})$: 245, 414. IR ($\nu_{\text{max}} \text{ cm}^{-1}$) (KBr): 3449 (OH), 1591 (C=N-N=C), 1529 (NCO $^-$), 1349 (C-O), 1028 (N-N), 526 (Sn-O), 449 (Sn-N). ^1H NMR (DMSO- d_6 , 500MHz), δ : 7.40-7.94 (m, 10H, aromatic-H), 5.83 (s, 1H, CH=C), 2.47 (s, 3H, $\text{H}_3\text{C}-\text{C}=\text{N}$), 0.75-1.57 (s, 18H, (Bu) $_2$ -Sn). ^{13}C NMR (DMSO- d_6 , 500MHz), δ : 173.16 (1C, N=C-O), 169.74 (1C, CH=C-O), 163.66 (1C, C=N), 126.57-138.40 (12C, aromatic ring), 94.10 (1C, CH=C), 13.77 (1C, CH_3), 26.73, 25.86, 23.34, 22.55 (4C, Sn- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

5. Synthesis of $[\text{Ph}_2\text{SnCl}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)]$ (7)

Yield: 0.032 g, 60%. M.p: 195-197 °C. Molar conductivity (DMSO) $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$: 1.23. UV-Visible (MeOH) $\lambda_{\text{max}}(\text{nm})$: 245, 413. IR ($\nu_{\text{max}} \text{ cm}^{-1}$) (KBr): 3064 (OH), 1592 (C=N-N=C), 1529 (NCO $^-$), 1302 (C-O), 1026 (N-N), 532 (Sn-O), 447 (Sn-N). ^1H NMR (DMSO- d_6 , 500MHz), δ : 7.39-8.13 (m, 22H, aromatic-H/ Sn-(C_6H_5) $_2$), 6.02 (s, 1H, CH=C), 2.49 (s, 3H, $\text{H}_3\text{C}-\text{C}=\text{N}$).

D. Antibacterial Test

The antibacterial activities of the synthesized compounds were studied against *E. coli* ATCC 8739 by using turbidimetric kinetic method [12]. The inoculums were allowed to grow on media which contain nutrient broth at 37°C with permanent shaking at 250 rpm for 18 hours. 7 mL of culture medium with increasing concentration of the compounds dissolved in DMSO were inoculated with 0.14 mL of inoculums and the mixture was shaken again at 250 rpm at 37°C. The solvent was used as negative control. Aliquots of each replicate were taken at every 1 h interval for 6 h and the transmittance (T) was registered in a Robert Scientific Metertech Plus SP-830 UV-Visible spectrophotometer. The antibacterial activity was determined by graph as $\ln N_t$ which related to the number cfu/mL (colony forming units/mL) for *E. coli* versus time.

III. RESULT AND DISCUSSION

A. Synthesis

The benzoylacetone benzhydrazone ligand [$C_{17}H_{16}N_2O_2$, (1)] was synthesized by condensation reaction of benzhydrazide and benzoylacetone in 1:1 mole ratio in alcoholic condition. The ligand ($C_{17}H_{16}N_2O_2$), (1) exists as keto form when it is in solid state and in the enol form when it is in solution. Six new organotin(IV) complexes (2-7) were synthesized by direct reaction of organotin(IV) chloride(s) with ligand (1) under nitrogen atmosphere in the presence of potassium hydroxide (KOH) as base. All newly synthesized organotin(IV) complexes are solids and soluble in range of organic solvents such as DMSO, MeOH and EtOH at room temperature. The molar conductivity of the organotin(IV) complexes in DMSO are in the range $0.54\text{--}1.36\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ showing that the complexes are non-electrolytic in nature [1]. The UV-Visible, IR, 1H and ^{13}C NMR spectral data are in the experimental section. The analytical data are in good agreement with the proposed molecular geometry of the synthesized organotin(IV) complexes.

B. UV-Vis Spectra

The absorption spectrum of ligand (1) was recorded in methanol in room temperature. Two absorption bands appeared at λ_{\max} of 335 and 366 nm which are suggested to be caused by $\pi\text{--}\pi^*$ transition of benzene ring and $n\text{--}\pi^*$ transition of imine group, respectively.

The electronic absorption spectra of complex (2-7) were also recorded in methanol at room temperature. The first peak at 238-248 nm region is attributed to $n\text{--}\pi^*$ transition which has hyperchromic (blue) shift suggested the free imine ($>C=N$) group of ligand (1) is coordinated to the tin(IV) atoms. Another new peak in the range 406-414 nm indicated the complexation occurred via ligand-to-metal transfer (LMCT) transition [1].

C. Infrared Spectra

In order to clarify the mode of the ligand coordination to the tin centre, IR spectra in the range of $4000\text{--}400\text{ cm}^{-1}$ were recorded. The IR spectrum of ligand (1) showed the peak appeared at 3231 cm^{-1} was assigned to NH stretching bond. A strong band in the ligands at 1662 cm^{-1} assigned to carbonyl ($C=O$) is indicative of their ketonic nature in the solid state. Another important stretching bands are at 1603 and 923 cm^{-1}

which are assigned to $\nu(C=N)$ and $\nu(N\text{--}N)$ respectively [1], [20].

The synthesized ligand (1) was reacted with methyltin(IV) trichloride, butyltin(IV) trichloride, phenyltin(IV) trichloride, dimethyltin(IV) dichloride, dibutyltin(IV) dichloride and diphenyltin(IV) dichloride, respectively. The structural analysis for all complexes was also done using IR spectroscopy. In the spectra of organotin(IV) complexes (2-7), the newly band formation $\nu(NCO^-)$ at $1517\text{--}1530\text{ cm}^{-1}$ indicated the coordination via deprotonation of enolic oxygen through tautomerisation process. In addition, the disappearance of $\nu(C=O)$ band at 1662 cm^{-1} in organotin(IV) complexes (2-7) indicated the coordination of both enolic oxygen atoms in ligand (1) to the central tin(IV) atom. However, the new band at $1302\text{--}1349\text{ cm}^{-1}$ in organotin(IV) complexes (2-7) is assigned to $\nu(C\text{--}O)$ which further supported the coordination of both of the enolic oxygen atoms to tin(IV) atom via deprotonation of OH group and also resulting to Sn–O bond in the range $526\text{--}557\text{ cm}^{-1}$ in organotin(IV) complexes (2-7) spectra. The presence of $\nu(C=N\text{--}N=C)$ band between $1591\text{--}1593\text{ cm}^{-1}$ has lower frequencies shift with respect to the ligand (1) at 1603 cm^{-1} confirming the azomethine nitrogen atom is coordinated to organotin(IV) moiety. This is also can be proved by the appearance of new band $\nu(Sn\text{--}N)$ at $447\text{--}453\text{ cm}^{-1}$ in the spectra of organotin(IV) complexes (2-7). A ligand hydrazinic $\nu(N\text{--}N)$ stretching band at 924 cm^{-1} went to higher wave number at $1026\text{--}1031\text{ cm}^{-1}$ further supporting the coordination of azomethine nitrogen to the central tin(IV) atom. The shift is because of the repulsion between the lone pairs of adjacent nitrogen atoms is reduced after complexation. The overlapped strong and typical broad bands which present at $3064\text{--}3467\text{ cm}^{-1}$ are due to either the $\nu(OH)$ or $\nu(NH)$ stretching vibration in the ligand (1) and lattice water (H_2O) in all organotin(IV) complexes (2-7), respectively, could not be notable properly [1].

D. 1H NMR Spectra

The formation of ligand (1) can be shown by the appearance of the $N=C(OH)$ resonance at δ_H 10.92 and the phenolic proton at δ_H 12.23. The others signals at δ_H 7.34-7.89, 6.81 and 2.07 are due to the aromatic-H, $CH=C$ and $H_3C\text{--}C=N$ protons, respectively.

The 1H NMR spectra of complexes (2-7) were successfully obtained. Upon complexation, the disappearance of $CH=C(OH)$ and $N=C(OH)$ singlet signals in the 1H NMR spectra of organotin(IV) complexes (2-6) are caused by the coordination of both enolic oxygen atoms to the central tin(IV) atom via deprotonation and further supported by the IR data. Generally, the aromatic-H multiplet signals range shifted down field from 7.34-7.89 ppm to 7.40-8.13 after complexation. This down field shift probably due to the deshielding of these protons which consequently lead to the reduction of electron density after coordination. The $CH=C$ resonance signal appeared at 5.98 ppm in free ligand showed down/up field shift for complex (2-7). The azomethine ($H_3C\text{--}C=N$) resonance signal is appeared at 2.47-2.54 ppm in complexes (2-7). This down field chemical shift showed the coordination of the azomethine nitrogen to the central tin(IV) atom [1].

E. ^{13}C NMR Spectra

The ^{13}C NMR for complex (2-6) was also obtained but spectra for complex 7 was not really successfully observed due to the low concentration.

After complexation, the carbon signals of the $\text{N}=\text{C}-\text{O}$ group shifted to up field at 173.16-171.66 ppm in the complexes (2-6) when comparing to the ligand (1), indicating participation of the $\text{N}=\text{C}-\text{O}$ group in coordination to the tin(IV) atom. Besides that, the coordination of ligand (1) to the tin(IV) atom can be observed through the chemical shifts shown by group $\text{CH}=\text{C}-\text{O}$ from 166.08-166.77 ppm to 165.05-169.74 ppm. The chemical shifts of carbon in $\text{C}=\text{N}$ and CH_3 in the free ligand (1) were observed at 155.68 and 18.48 ppm which were shifted to down field region at 161.82-163.66 ppm and 22.03-23.13 ppm, respectively, in the complexes (2), (4) and (5). While, the carbon signals of carbon in $\text{CH}=\text{C}$ of free ligand went to downfield at range 94.10-95.99 ppm upon complexation. Then, chemical shift of CH_3 for complex (3) and (6) went to the up field region (13.77-14.21 ppm) when comparing with free ligand (1). All of these observations indicated that the azomethine-N is coordinated to the tin(IV) moiety. The δ value of carbon atoms in aromatic ring slightly shift in the complexes (2-6) as compared to the free ligand. The butyl group attached to the organotin(IV) moiety in complex (3) and (6) gave four resonance signals at 29.03, 27.62, 25.68 and 22.31 ppm and 26.73, 25.86, 23.34 and 22.55 ppm, respectively. Meanwhile, the sharp signal attributed to the methyl group attached to the tin(IV) core appeared at 9.52 ppm and 3.00 ppm in complex (2) and complex (5), respectively. Apart from that, the phenyl group in complex (4) probably overlapped with aromatic ring from ligand (1) and result to the appearance of the resonance signals at 126.84-146.31 ppm [3], [14]. According to all of the analytical data, the proposed structure of the complexes is as in Fig. 2.

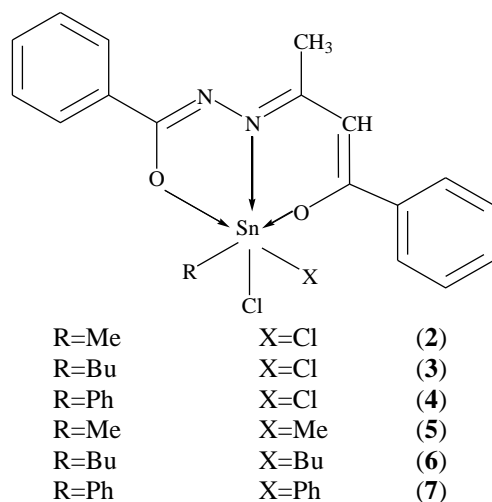


Fig. 2 Proposed structure of organotin(IV) complexes (2-7)

F. Antibacterial Activity

The antibacterial activities of ligand (1) and complexes (2-7) were assayed at the concentration 50, 80, 100 ppm against bacteria *E. coli* O157:H7 at 37°C. The antibacterial activities of ligand (1) and complexes (2-7) were compared with DMSO as a control.

All the synthesized compounds demonstrated a quite similar of bacteriostatic activities upon introduction at different concentrations. The equation of $\ln N_t = 27.1 - 8.56T$ was used to indicate the condition of the microbial specific growth and the amount of drug concentration used. The graph of control showed inactive for antibacterial activity, when tested against *E. coli*. The effect of the synthesized compounds, ligand (1) and complexes (2-7) was also further shown by their minimum inhibitory concentrations (MIC). The MIC of these compounds were determined by extrapolating the concentration at the zero growth rate of *E. coli* ($\mu=0$) [22]. Compound with the MIC value >200 ppm is not suitable to be used as antibacterial agent for clinical purpose [23], [24]. The MIC value for all synthesized compounds is as shown in Table I. The MIC values for ligand (1) and complex (2) were observed greater than 200 ppm, while complex (3-7) were below 200 ppm. Based on the results, ligand (1) and complex (2) showed poor activity against *E. coli*. Meanwhile, the antibacterial studies of the complexes (3-7) showed relatively better antibacterial activity than the free ligand (1). Among all organotin(IV) derivatives, the bactericidal activities of 3, 5, 6 and 7 are fairly good. Complex (4) was found to be active against *E. coli* strain in the assayed concentrations. Hence, the coordination of tin(IV) atom to the ligand enhanced the antibacterial activities. This is may be caused by a synergistic affect involving tin and the hydrazone ligand. Furthermore, in the structure organotin(IV) complexes consist more of chloride ion that potent to kill the microbes or inhibit their growth by blocking their active sites [2], [8]. Besides that, the increased antibacterial activity of organotin(IV) complexes (2-7) probably also based on the chelation theory. In organotin(IV) complexes, on chelation the polarity of the tin ion will be reduced to a greater extent due to the overlap of the substituted hydrazone ligand orbital and partial sharing of the positive charge of the tin ion with donor groups. The activity might be because of the increasing lipophilic nature of these complexes resulting from the metal chelation. Then, the lipophilic nature of the metals chelate is influenced by the electron delocalization in the chelate ring [1], [14].

TABLE I
MIC OF LIGAND (1) AND COMPLEXES (2-7)

Compound	MIC (ppm)
($\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$) (1)	766.7
[$\text{MeSnCl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)$] (2)	689.6
[$\text{BuSnCl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)$] (3)	116.4
[$\text{PhSnCl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)$] (4)	67.9
[$\text{Me}_2\text{SnCl}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)$] (5)	87.9
[$\text{Bu}_2\text{SnCl}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)$] (6)	93.3
[$\text{Ph}_2\text{SnCl}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)$] (7)	121.4

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