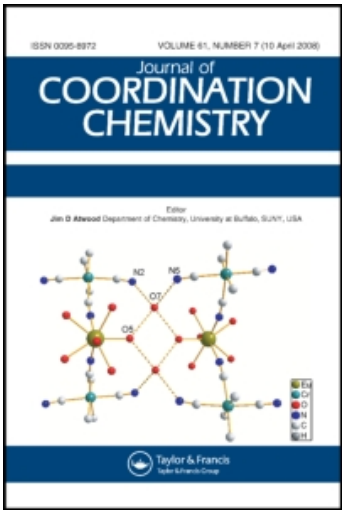

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Synthesis, characterization, and antibacterial activity of triorganotin(IV) complexes of 2-methylphenol

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The triorganotin(IV) complex Ph_3Sn(OPhMe-2) (**1**) has been synthesized by the reaction of Ph_3SnCl with NaOPhMe-2, while complexes of composition *n*-Bu_3Sn(OPhMe-2) (**2**) and Me_3Sn(OPhMe-2) (**3**) (where $-$OPhMe-2 $=-OC_6H_4CH_3$-2) have been obtained from the reaction of *n*-Bu_3SnCl and Me_3SnCl with 2-methylphenol in the presence of triethylamine in carbon tetrachloride. The complexes have been characterized by elemental analyses, molar conductance measurements, molecular weight determination, and IR, ^{1}H NMR, ^{13}C NMR, and mass spectral studies. Thermal behavior of the complexes has been studied by TG and DTA techniques. The organotin(IV) complexes have also been screened for antibacterial activity and exhibit appreciable activity. The reactions of the complexes with 3- and 4-cyanopyridines yielded 1 : 1 adducts authenticated by physicochemical and IR and ^{1}H NMR spectral data.

Keywords: Trialkyltin/triaryltinchlorides; 2-Methylphenol; Spectral studies; Antibacterial activity

1. Introduction

There has been sustained interest in the chemistry of organotin complexes [1–8] not only because of their potential industrial [9, 10], agricultural [11], and medicinal [12] applications but also due to their structural and stereochemical diversities [13–15]. In this context, systematic efforts have been made for the synthesis of new organotin complexes by choosing appropriate ligands. A variety of biologically potent ligands, amino acids [16], dipeptides [17, 18], Schiff bases [19], and dithiocarbamates [20], have been used for the synthesis of organotin complexes. Only a few scattered reports are available on the synthesis of organotin complexes of phenols [21, 22], despite the fact that phenolic ligands display great potential for tuning both steric and electronic influences. In order to distinguish electronic from steric influence, the substituents are incorporated at meta and para positions relative to metal. Phenolic ligand coordination to metal center is sometimes followed by carbon–hydrogen bond activation. Furthermore, the ortho position may undergo chelation to metal. Of the substituted

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phenols used for the synthesis of complexes, *o*-cresol remains unaddressed. Organotin phenoxides form a component of the Ziegler-Natta system [23] and also display antibacterial activity [24]. In continuation of our earlier work on the synthesis of organotin(IV) phenoxides, this article describes the synthesis and characterization of organotin(IV) complexes of 2-methylphenol. Since triorganotin compounds show high biocidal activity and find use as industrial biocides, the antibacterial activity of the newly synthesized complexes has been assayed. To explore the behavior of the isolated complexes as Lewis acids, reactions of triorganotin(IV) 2-methylphenoxides with 3- and 4-cyanopyridines have been undertaken and their coordination behavior has been studied.

2. Experimental

2.1. *Material and methods*

All solvents were of A.R. grade and dried by standard methods. 2-Methylphenol (Merck) was recrystallized from benzene and the purity was checked by its m.p. 29–31°C. Ph_3SnCl, *n*-Bu_3SnCl, Me_3SnCl, and 3- and 4-cyanopyridines were of Merck grade.

For determination of tin in organotin complexes, a known weight (~0.1 g) of the complex was treated with a mixture of conc. nitric acid (three volumes) and conc. sulfuric acid (two volumes). It was then ignited at 800°C to SnO_2 in an electric furnace. Chlorine was determined by Volhard's method. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Carlo-Erba 1108 Elemental Analyzer. The conductivity measurements in nitrobenzene were made on an Elico Conductivity Bridge type CM-82T. Molecular weights were determined by Rast's camphor method. IR spectra of the complexes were recorded as KBr pellets and CsI optics on a Nicolet-5700 FT-IR spectrophotometer. The pellets were prepared in a dry box to avoid moisture. ^1H NMR spectra were recorded on a Bruker Avance II 400 NMR using $CDCl_3$ as solvent. FAB-mass spectra were recorded on a Jeol SX 102/Da-6000 Mass Spectrometer/Data system using Argon/Xenon (6 kV, 10 mA0 as the FAB gas). The accelerating voltage was 10 kV and *m*-nitrobenzylalcohol (NBA) was used as the matrix. Thermograms of powdered samples were recorded with simultaneous TG-DTA SHIMADZU DT-60 thermal analyzer in air at a heating rate of 20°C min^{-1} using a platinum crucible.

2.2. *Synthesis*

2.2.1. NaOPhMe-2. To a solution of 2-methylphenol (5 g, 46 mmol) in CCl_4 was added an equimolar amount of sodium (1.06 g, 46 mmol). The reactants were stirred at room temperature for 10 h during which a dirty white solid separated. It was collected by filtration, washed with CCl_4, and dried under vacuum. (Yield: 4.8 g, 79%).

2.2.2. Preparation of 1. An equimolar amount of the Na-salt of 2-methylphenol (0.40 g, 3 mmol) dissolved in methanol was added to a solution of Ph_3SnCl (1.19 g, 3 mmol) in methanol. The reactants were then refluxed for 9 h, whereupon the

separation of NaCl formed by the metathesis reaction was observed. It was filtered and its formation was verified by solubility in water. The filtrate was concentrated by distilling off the solvent. The concentrate was dried under vacuum, whereupon a fine cream-colored crystalline solid separated. It was washed with petroleum ether and dried under vacuum. (Yield: 1.17 g, 81%). Anal. Calcd for $C_{25}H_{22}OSn$(457) (%): C, 65.69; H, 4.86; Sn, 25.97. Found (%): C, 65.85; H, 4.89; Sn, 26.15. Λ_m ($PhNO_2$): 2.2 S cm^2 mol^{-1}.

2.2.3. Preparation of 2 and 3. In a typical reaction, an equimolar amount of 2-methylphenol (2.47 g, 22 mmol) was added to a solution of *n*-Bu_3SnCl (7.44 g, 22 mmol) in dry CCl_4 in the same solvent followed by the dropwise addition of an equimolar amount of triethylamine (2.31 g, 22 mmol). Immediate formation of a white solid $Et_3N \cdot HCl$ was observed. The reactants were refluxed for 6 h to ensure completion of the reaction. The solid was removed by filtration. Formation of $Et_3N \cdot HCl$ was confirmed from its m.p. 261°C. The filtrate was concentrated by distilling off the solvent and drying under vacuum. The concentrate was then treated with petroleum ether and diethyl ether repeatedly and was kept for 2–3 days. Separation of solid was not observed. The extracting solvent was therefore removed by distillation and remainder was then distilled under vacuum to obtain a pale yellow liquid. (Yield: 8.07 g, 89%). Anal. Calcd for $C_{19}H_{34}OSn$(397.12) (%): C, 57.46; H, 8.63; Sn, 29.89. Found (%): C, 57.61; H, 8.62; Sn, 30.07. Λ_m ($PhNO_2$): 1.7 S cm^2 mol^{-1}.

Similar method was employed for the preparation of $Me_3SnOArMe$-2 by the reaction of Me_3SnCl (0.83 g, 4 mmol) with 2-methylphenol (0.45 g, 4 mmol) and triethylamine (0.45 g, 4 mmol). (Yield: 0.87 g, 78%). Anal. Calcd for $C_{10}H_{16}OSn$(270.89) (%): C, 44.33; H, 5.95; Sn, 43.81. Found (%): C, 44.35; H, 5.99; Sn, 44.00. Λ_m ($PhNO_2$): 1.2 S cm^2 mol^{-1}.

2.3. *Reactions with 3- and 4-cyanopyridines*

A solution of the parent complexes, **1** (0.5 g, 1.09 mmol) and **2** (0.5 g, 1.25 mmol), in ethanol (15 mL) was treated with ethanolic solution (15 mL) of 3- and 4-cyanopyridines (0.113 g, 1.09 mmol; 0.131 g, 1.25 mmol, respectively) in separate experiments. The contents were then refluxed for 7–8 h, when the appearance of a white or brown solid/liquid was observed. These were then dried under vacuum. **1**·CNpy-3. Anal. Calcd for $C_{31}H_{26}ON_2Sn$ (%): C, 66.34; H, 4.67; N, 4.99; Sn, 21.15. Found (%): C, 66.43; H, 4.74; N, 5.05; Sn, 21.24. Λ_m ($PhNO_2$): 1.4 S cm^2 mol^{-1}. **1**·CNpy-4. Anal. Calcd for $C_{31}H_{26}ON_2Sn$ (%): C, 66.34; H, 4.67; N, 4.99; Sn, 21.15. Found (%): C, 66.45; H, 4.77; N, 5.03; Sn, 21.25. Λ_m ($PhNO_2$): 1.5 S cm^2 mol^{-1}. **2**·CNpy-3. Anal. Calcd for $C_{25}H_{38}ON_2Sn$ (%): C, 59.90; H, 7.64; N, 5.59; Sn, 23.68. Found (%): C, 59.98; H, 7.70; N, 5.65 Sn, 23.71. Λ_m ($PhNO_2$): 0.9 S cm^2 mol^{-1}. **2**·CNpy-4. Anal. Calcd for $C_{25}H_{38}ON_2Sn$ (%): C, 59.90; H, 7.64; N, 5.59; Sn, 23.68. Found (%): C, 59.95; H, 7.68; N, 5.61; Sn, 23.773. Λ_m ($PhNO_2$): 1.3 S cm^2 mol^{-1}.

2.4. *Antibacterial activity*

2-Methylphenol and its organotin(IV) complexes were screened *in vitro* for their antibacterial activity on *Escherichia coli*, *Staphylococcus aureus*, *Proteus mirabilis*,

Pseudomonas aerogerosa, *Staphylococcus epidermidis*, and *Shigella flexneri* using the minimum inhibitory concentration (MIC) method [25]. All the samples were tested in triplicate.

2.5. *Preparation of nutrient medium*

In a typical experiment, 50 mL of nutrient agar media for growing bacteria consisting of peptone (0.5 g, 1%), yeast extract (0.5 g, 1%), and NaCl (0.25 g, 0.5%) were prepared in distilled water. The pH of the solution was maintained at 7.5 by the addition of NaOH solution. To this solution in a 250 mL conical flask was added agar-agar (1 g, 2%). The nutrient medium was then autoclaved for 2 h and equally distributed in four autoclaved test tubes in laminar flow. The medium was then allowed to solidify by keeping the test tubes in slant position. It was then kept in an incubator at 37°C for 24 h to check for contamination. The microorganism was then streaked into slants.

2.6. *Preparation of nutrient broth*

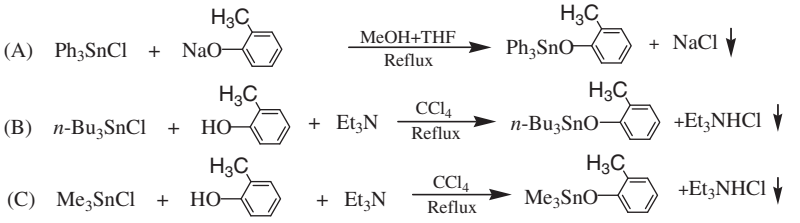
The nutrient broth (200 mL) was prepared by mixing peptone (2 g, 1%), yeast extract (2 g, 1%), and NaCl (1 g, 0.5%) in distilled water employing the procedure above without adding agar-agar. The medium was equally distributed in four 250 mL conical flasks and autoclaved. In laminar flow, the microorganism from slants was inoculated into two conical flasks and the other two were taken as control. These were then transferred to a shaker at 37°C and the contents were rotated at 160 rpm for 4–5 h till the optical density (O.D.) of the inoculums reached 0.8, which was used for screening antibacterial activity. The stock solutions of each compound were made in DMSO (1 mg mL^{-1}) and used by two-fold serial dilution.

2.7. *MIC determination by two-fold serial dilution*

MIC assay [26] was performed in a 96-well micro-titer plate. For MIC assay of each test drug, a row of 12 wells was used out of which two wells were taken as control (no drug added). Each of the 10 wells received 100 μL of the Muller–Hinton broth, except the first well that received 200 μL of broth containing 500 μg mL^{-1} concentration of the test drug. From the first well (containing test drug), 100 μL broth was withdrawn with a sterile tip, and same was added to the 100 μL of the broth in the second well; contents were mixed four times. Then 100 μL was withdrawn from second well and was added to the third well. In this way a range of two-fold serial dilution were prepared (500–0.98 μg mL^{-1}) by performing two-fold serial dilution. The broth in each well was inoculated with 2 μL of the bacterial culture and the contents were mixed by 10 clockwise and 10 anticlockwise rotations on a flat surface. The plate was incubated at 35°C thereafter. The observations for the growth of bacteria were recorded after 24 h.

3. Results and discussion

The formation of triorganotin(IV) 2-methylphenoxides in quantitative yields can be represented as



Elemental analyses confirmed their stoichiometric compositions. Compounds **1** and **3** are fine white crystalline and light yellow solids, respectively, exhibiting sharp melting points, while **2** is a pale yellow liquid. The complexes are stable in the absence of water. They are soluble in most common organic solvents. The molar conductance values of 10^{-3} mol L^{-1} solutions of the compounds in nitrobenzene suggest non-electrolytes. The molecular weight determination by Rast's camphor method suggests **1** as a monomer, while **2** and **3** have been indicated to be dimeric and polymeric, respectively. The molecular weights are an average of three molecular weight determinations.

3.1. *IR spectra*

A comparison of the IR spectra of triorganotin(IV) complexes with that of 2-methylphenol showed the absence of bands at 3400–3300 cm^{-1} due to hydrogen-bonded phenol (–OH), suggesting deprotonation of the phenolic proton as $Et_3N \cdot HCl$ formed during the reaction. Absorptions occurring at 1243–1174 cm^{-1} in free 2-methylphenol ascribed to ν(C–O) appeared at 1253–1183 cm^{-1} in **1**, 1258–1174 cm^{-1} in **2**, and 1258–1171 cm^{-1} in **3**, suggesting the involvement of phenolic oxygen in bonding. Bonding through phenolic oxygen to tin was further supported by bands at 540–470 cm^{-1} attributed to ν(Sn–O) [27, 28]. Bands at 788–612 cm^{-1} may be assigned to ν(Sn–O–Sn) [29–32], indicating dimeric or polymeric **2** and **3**. No such bands appeared in **1**, indicating that **1** is a monomer in agreement with its molecular weight determination. Bands at 332 and 271 cm^{-1} in far-IR may be assigned to ν(Sn–C) [33, 34] for triphenyl and methyltin(IV) phenoxides. Absorptions at 600 cm^{-1} in **2** may be ascribed to ν(Sn–C).

3.2. *^{1}H NMR spectra*

The ^{1}H NMR spectra of the complexes did not display a signal at δ 5.18 ppm due to phenolic (–OH) in free 2-methylphenol, confirming deprotonation and formation of complexes. The ^{1}H NMR spectra of 2-methylphenol has signals at δ 6.45–7.12 and at δ 2.17 ppm [35] attributed to aromatic ring and methyl protons, respectively (table 1). The aromatic phenolic ring protons were found to undergo significant downfield shift in **1** and **2** and moderate shift in **3**. The downfield shifts may be ascribed to deshielding of protons due to the donation of electron density from ring to tin. The resonances due to

Table 1. ^{1}H and ^{13}C NMR data.

			^{1}H NMR δ (ppm)								^{13}C NMR δ (ppm)		
Complexes	–OH	Aromatic protons	Substituent –Me	R–Sn	C_1	C_2	C_3	C_4	C_5	C_6	Substituent –Me	R–Sn	^{119}Sn δ (ppm)
2-Methylphenol	5.18	6.45–7.12	2.17 (s,3H)	–	153.5	124.0	131.1	121.4	127.7	115.9	17.70	–	
$Ph_3SnOPhMe$-2	–	6.76–7.13	2.25 (s,3H)	7.48(s,15H)	155.2	125.4	130.9	120.9	126.9	116.7	17.80	129.2 ($^{1}J(^{119}Sn–^{13}C) = 542.0$ Hz) ($^{2}J(^{119}Sn–^{13}C) = 48.6$ Hz) ($^{3}J(^{119}Sn–^{13}C) = 63.5$ Hz) ($^{4}J(^{119}Sn–^{13}C) = 14.5$ Hz)	−47.8
$Bu_3SnOPhMe$-2	–	6.72–7.07	2.20 (s,3H)	0.89–0.92(t,9H) $–CH_3(\delta)$ 1.22–1.41(m,6H) $–CH_2(\alpha)$ 1.60–1.68(m,6H) $–CH_2(\beta)$ 1.22–1.41(m,6H) $–CH_2(\gamma)$	155.8	124.8	131.5	121.7	126.1	116.2	17.70	C_α:18.50{$^{1}J(^{119}Sn–^{13}C) = 425.1$ Hz} C_β:27.89{$^{2}J(^{119}Sn–^{13}C) = 26.4$ Hz} C_γ:26.69{$^{3}J(^{119}Sn–^{13}C) = 75.4$ Hz} C_δ:12.8	+108.1
$Me_3SnOPhMe$-2	–	6.56–7.12	2.25 (s,3H)	0.54(s,9H)	154.5	125.2	130.5	122.1	127.9	116.4	17.50	8.83 ($^{1}J(^{119}Sn–^{13}C) = 427.0$ Hz)	+133.2

n-butyl, methyl, and phenyl groups attached to tin in the complexes remained unchanged relative to the respective triorganotin chlorides. Likewise, the signal due to methyl did not undergo a shift.

3.3. *^{13}C NMR spectra*

A comparison of ^{13}C NMR spectra of organotin(IV) 2-methylphenoxides with that of 2-methylphenol demonstrated the formation of complexes. The carbon resonances due to phenolic ring carbons at δ 115.9–155.8 ppm and methyl at 17.70 ppm in free 2-methylphenol suffered downfield shifts on complexation. The signal due to carbon resonances of methyl substituent did not undergo any change upon complexation. The carbon resonances due to organic groups attached to tin also remain unaltered relative to the chloride precursors (table 1).

The magnitude of the coupling constant $^{1}J(^{119}\text{Sn}–^{13}\text{C})$ for triorganotin(IV) complexes is consistent with four-coordinate geometry around tin. The coupling constant $^{n}J(^{119}\text{Sn}–^{13}\text{C})$ and the value of C–Sn–C bond angle are known to yield important structural information. The C–Sn–C angle determination using Howard's (i) (for **1**) and Lockhart's (ii) (for **2** and **3**) equations:

$$\theta(\text{C}-\text{Sn}-\text{C}) = 0.178J^{1}[\text{Sn}^{119}-\text{C}^{13}] + 14.7 \quad \text{(i)}$$

$$\theta(\text{C}-\text{Sn}-\text{C}) = \frac{J^{1}+875}{11.4} \quad \text{(ii)}$$

provided C–Sn–C angles of 111, 114, and 114 for triphenyl, tri-*n*-butyl, and trimethyl(IV) complexes, respectively. The observed magnitude of C–Sn–C angles correlate with four-coordinate tin.

3.4. *^{119}Sn NMR spectra*

^{119}Sn NMR spectroscopy plays a significant role for the determination of coordination around tin with ^{119}Sn chemical shifts depending on the nature and orientation of groups bonded to tin. ^{119}Sn NMR spectra of triphenyl, *n*-butyl, and methyltin(IV) 2-methylphenoxides exhibited a single resonance at δ −47.8, +108.1, and +133.2 ppm, respectively, relative to ^{119}Sn NMR values of δ −44.7, −141, and +164.2 ppm for triorganotin(IV) chloride precursors. The values are characteristic for tetrahedral Sn^{IV}. A tetrahedral geometry around tin in organotin(IV) methylphenoxides suggested from ^{13}C and ^{119}Sn NMR data, is in agreement with previous reports that dimeric/polymeric structures are lost in solution.

3.5. *Mass spectra*

The FAB-mass peaks observed for **1**, **2**, and **3** are given in tables 2–4. The complexes display molecular ion peaks at *m*/*z* 460 and 272 with 25% and 41.66% intensity for **1** and **3**, respectively, but **2** displayed no molecular ion peak. The most intense peaks at *m*/*z* 351, 291, and 179 corresponded to $[\text{Ph}_3\text{Sn}]^+$, $[n\text{-Bu}_3\text{Sn}]^+$, and $[\text{Me}_3\text{Sn} + \text{Me–H}]^+$ in respective complexes. The observance of fragment ions beyond molecular ion peaks for

Table 2. Mass spectral data and relative isotopic abundances.

		Calcd (Expt.)											
$Ph_3SnOPhMe$-2 (M)	m/z(%)	M − 8[a] (%)	M − 6[a] (%)	M − 5[a] (%)	M − 4[a] (%)	M − 3[a] (%)	M − 2[a] (%)	M − 1[a] (%)	M[a] (%)	M + 1[a] (%)	M + 2[a] (%)	M + 3[a] (%)	M + 4[a] (%)
$[Ph_3Sn]^+$	351.02(100)	2.8 (2.8)	2.8 (2.8)	1.6 (1.6)	42.6 (42.5)	30.9 (30.9)	75.1 (75.1)	39.1 (39.0)	100 (100)	19.0 (19.0)	13.5 (13.4)	2.7 (2.7)	16.9 (16.9)
$[Ph_2Sn]^+$	273.98(8.3)	2.9 (2.9)	2.8 (2.8)	1.4 (1.3)	43.2 (43.2)	28.5 (28.5)	74.8 (74.8)	35.0 (35.0)	100 (100)	12.9 (12.9)	13.7 (13.7)	1.9 (1.9)	17.2 (17.1)
$[SnOPhMe$-2$]^+$	226.96(5.5)	3.0 (3.0)	2.9 (2.8)	1.1 (1.1)	44.6 (44.6)	27.0 (27.0)	74.3 (74.2)	32.1 (32.1)	100 (100)	8.1 (8.1)	14.2 (14.2)	1.1 (1.1)	17.8 (17.8)
$[PhSn]^+$	196.94(33.33)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.6 (44.6)	26.5 (26.4)	74.3 (74.2)	31.3 (31.3)	100 (100)	6.7 (6.7)	14.2 (14.2)	–	17.4 (17.4)
$[Sn + 3Me]^+$	164.97(13.88)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.6 (44.6)	23.6 (23.6)	74.3 (74.3)	26.3 (26.2)	100 (100)	3.5 (3.4)	14.2 (14.2)	–	17.8 (17.8)
$[SnOH]^+$	136.90(13.88)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.6 (44.6)	23.6 (23.6)	74.3 (74.3)	26.4 (26.4)	100 (100)	–	14.4 (14.3)	–	17.8 (17.7)
$[Sn]^+$	119.90(8.33)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.6 (44.6)	23.6 (23.6)	74.3 (74.3)	26.3 (26.3)	100 (100)	–	14.2 (14.2)	–	17.8 (17.8)

[a]Relative isotopic abundances.

Table 3. Mass spectral data and relative isotopic abundances.

		Calcd (Expt.)											
n-$Bu_3SnOPhMe$-2 (M)	*m*/*z*(%)	M − 8[a] (%)	M − 6[a] (%)	M − 5[a] (%)	M − 4[a] (%)	M − 3[a] (%)	M − 2[a] (%)	M − 1[a] (%)	M[a] (%)	M + 1[a] (%)	M + 2[a] (%)	M + 3[a] (%)	M + 4[a] (%)
$[2M - 2Me + H]^+$	767(50.0)	4.4 (4.4)	15.3 (15.2)	15.0 (15.0)	48.1 (48.1)	37.6 (37.6)	97.7 (97.7)	53.5 (53.5)	100 (100)	36.8 (36.8)	75.1 (75.1)	49.1 (49.1)	17.6 (17.6)
$[n\text{-}Bu_3Sn(OPh)(OPh)SnBu_2\text{-}H]^+$	710(11.11)	3.6 (3.6)	15.3 (15.3)	16.9 (16.8)	42.5 (42.5)	43.3 (43.3)	88.2 (88.2)	70.4 (70.4)	100 (100)	60.5 (60.5)	80.5 (80.5)	33.0 (33.0)	32.5 (32.5)
$[M + 3Me]^+$	443(11.11)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.6 (44.5)	23.6 (23.6)	74.3 (74.3)	26.3 (26.30	100 (100)	26.2 (26.2)	14.2 (14.2)	3.8 (3.8)	18.2 (18.2)
$[n\text{-}Bu_3Sn]^+$	291(100)	3.0 (3.0)	2.9 (2.8)	1.1 (1.1)	44.6 (44.6)	23.6 (23.6)	74.3 (74.3)	26.3 (26.3)	100 (100)	14.0 (14.0)	14.2 (14.2)	2.0 (2.0)	17.9 (17.9)
$[n\text{-}Bu_2SnH]^+$	235(66.66)	3.0 (3.0)	2.9 (2.9)	1.4 (1.3)	44.6 (44.6)	27.5 (27.5)	76.4 (76.4)	32.9 (32.9)	100 (100)	8.9 (8.9)	14.2 (14.2)	1.3 (1.3)	17.8 (17.8)
$[n\text{-}BuSn]^+$	177(69.44)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.6 (44.6)	23.6 (23.5)	74.3 (74.3)	26.3 (26.3)	100 (100)	4.6 (4.6)	14.2 (14.2)	–	17.8 (17.8)
$[Sn]^+$	121(16.6)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.6 (44.6)	23.6 (23.6)	74.3 (74.2)	26.3 (26.3)	100 (100)	–	14.2 (14.2)	–	17.8 (17.8)

[a]Relative isotopic abundances.

Table 4. Mass spectral data and relative isotopic abundances.

		Calcd (Expt.)											
$Me_3SnOPhMe$-2 (M)	m/z(%)	M − 8[a] (%)	M − 6[a] (%)	M − 5[a] (%)	M − 4[a] (%)	M − 3[a] (%)	M − 2[a] (%)	M − 1[a] (%)	M[a] (%)	M + 1[a] (%)	M + 2[a] (%)	M + 3[a] (%)	M + 4[a] (%)
$[3M + Me - 4H]^+$	827(27.77)	6.3 (6.3)	18.2 (18.2)	22.2 (22.1)	44.5 (44.5)	46.9 (46.9)	77.6 (77.6)	70.3 (70.3)	100 (100)	74.0 (74.1)	88.0 (88.0)	54.0 (54.0)	59.2 (59.2)
$[2M + Me_3Sn + Na]^+$	732(38.88)	6.8 (6.8)	19.2 (19.2)	22.0 (22.0)	45.6 (45.6)	47.2 (47.2)	78.3 (78.3)	69.4 (69.3)	100 (100)	71.9 (71.9)	89.5 (89.5)	52.2 (52.2)	63.7 (63.7)
$[2M - 3H]^+$	541(8.3)	4.1 (4.1)	18.1 (18.0)	17.4 (17.4)	48.9 (48.9)	44.5 (44.5)	97.6 (97.6)	70.0 (70.0)	100 (100)	54.5 (54.5)	81.0 (81.0)	22.4 (22.4)	32.3 (32.3)
$[Sn(OPhMe\text{-}2)Sn + OH + Na - H]^+$	386(72.22)	4.0 (4.0)	17.5 (17.5)	15.1 (15.1)	45.9 (45.9)	37.9 (37.9)	92.7 (92.6)	56.2 (56.2)	100 (100)	41.5 (41.5)	80.7 (80.7)	15.2 (15.2)	31.6 (31.6)
$[Sn(OPhMe\text{-}2)Sn + Na - H]^+$	369(13.88)	4.0 (4.0)	17.5 (17.5)	15.1 (15.1)	8.4 (8.4)	37.9 (37.9)	61.4 (61.4)	56.2 (56.2)	100 (100)	41.6 (41.6)	80.6 (80.5)	15.3 (15.3)	32.0 (32.0)
$[Me_3Sn(OPhMe\text{-}2 + 2Me + (O)]^+$	318(11.11)	3.0 (3.0)	2.9 (2.8)	1.5 (1.5)	44.6 (44.6)	23.6 (23.6)	74.3 (74.3)	36.9 (36.9)	100 (100)	14.2 (14.2)	15.5 (15.5)	2.0 (2.0)	17.9 (17.9)
$[Me_3Sn(OPhMe\text{-}2) + OH]^+$	289(75.0)	2.9 (2.9)	2.8 (2.8)	1.4 (1.4)	43.0 (43.0)	27.6 (27.6)	71.6 (71.6)	33.8 (33.8)	100 (100)	11.3 (11.2)	14.7 (14.7)	1.6 (1.6)	17.3 (17.3)
$[Me_3Sn(OPhMe\text{-}2)]^+$	272(41.66)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.6 (44.6)	5.1 (5.0)	74.3 (74.3)	26.3 (26.3)	100 (100)	11.6 (11.6)	14.2 (14.2)	1.7 (1.7)	17.9 (17.9)
$[Sn(OC_6H_5) + Na - H]^+$	235(77.77)	2.9 (2.9)	2.9 (2.9)	1.3 (1.2)	43.8 (43.7)	26.1 (26.1)	74.5 (74.5)	30.8 (30.8)	100 (100)	6.7 (6.7)	14.3 (14.3)	–	17.4 (17.4)
$[Me_3Sn + Me - H]^+$	179(100)	2.9 (2.9)	2.9 (2.9)	1.2 (1.2)	44.1 (44.1)	25.1 (25.1)	74.3 (74.2)	29.4 (29.3)	100 (100)	4.6 (4.6)	14.2 (14.2)	–	17.8 (17.8)
$[SnO + H]^+$	137(33.33)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.6 (44.6)	23.6 (23.6)	74.3 (74.3)	26.4 (26.4)	100 (100)	–	14.4 (14.3)	–	17.8 (17.8)
$[MeSn]^+$	135(30.55)	3.0 (3.0)	2.9 (2.9)	1.1 (1.1)	44.5 (44.5)	24.0 (24.0)	74.4 (74.4)	27.1 (27.1)	100 (100)	1.2 (1.2)	14.2 (14.2)	–	17.7 (17.7)

[a]Relative isotopic abundances.

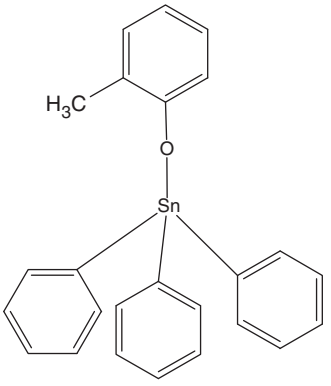


Figure 1. Proposed structure for $Ph_3SnOArMe$-2.

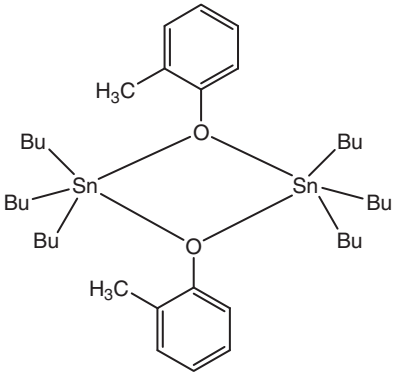


Figure 2. Proposed structure for $Bu_3SnOArMe$-2.

2 and **3** show marked tendency toward association and may be assumed to exhibit 1-D chain polymers, where planar or near planar $[n\text{-}Bu_3Sn]^+$ and $[Me_3Sn]^+$ units are bridged by 2-methylphenoxo groups.

Based upon the physicochemical and IR and mass spectral data, a distorted tetrahedral, dimeric and polymeric structure for **1**, **2**, and **3**, respectively, may tentatively be proposed (figures 1–3).

3.6. *Thermal studies*

Thermal behavior of the complexes was studied by TGA-DTA techniques in nitrogen. **1**, **2**, and **3** display initial decomposition temperatures at 176.72°C, 50.99°C, and 80.51°C, respectively, after which the complexes undergo decomposition in a single step with a continuous weight loss of nearly 100% leaving behind no residue in each case. An endothermic peak in DTA curve of the complexes substantiated the thermal decomposition.

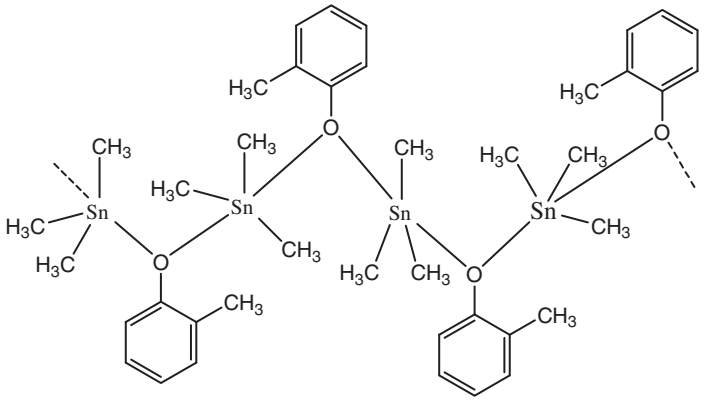


Figure 3. Proposed structure for $Me_3SnOArMe$-2.

3.7. *Reactions with 3- and 4-cyanopyridines*

The 3- and 4-cyanopyridines possess extensive coordination chemistry [36–41] owing to the presence of pyridine nitrogen and the nitrile nitrogen donor sites. Reports on coordination tendency of these bases with metal aryloxides are rather scarce [42]. Hence, the use of these bases forms the part of study in the present work.

Interaction of **1** and **2** with one equivalent of 3- and 4-cyanopyridines in absolute alcohol yielded 1 : 1 adducts in conformity with their analytical data. The molar conductance value of the millimolar solution of adducts in nitrobenzene suggested non-electrolytes.

3.8. *IR spectra of addition compounds*

Comparison of IR spectra of cyanopyridine adducts with those of free bases indicate coordination sites. The coordination-sensitive bands of 3- and 4-cyanopyridine are due to ν(C≡N), four principal bands due to symmetric and asymmetric in-plane ring deformation ν(C=C) and ν(C=N), and two low-frequency bands due to first and second ring breathing modes [43]. The bands at 2225 and 2240 cm^{-1} assigned to ν(C≡N) in 3- and 4-cyanopyridines, respectively, remained almost unaltered in the 4-cyanopyridine and 3-cyanopyridine adducts, suggesting non-participation of cyano in coordination. The frequencies of other two types of bands at 1600–1400 and 1080–965 cm^{-1} have, however, been found to move toward higher wave numbers suggesting coordination through pyridine nitrogen. This is further supported by the appearance of bands at 320–250 cm^{-1} in far-IR, assigned to ν(Sn–N) [44]. Since coordination of cyanopyridines takes place from ring nitrogen and not from nitrile nitrogen [45], monodentate coordination is suggested. Hence, a five-coordinate distorted trigonal–bipyramidal environment around tin may be proposed for the adducts.

3.9. *^{1}H NMR spectra of addition compounds*

A comparison of the room temperature ^{1}H NMR spectra of addition compounds with that of free 3- and 4-cyanopyridines substantiated the formation (table 5). The ^{1}H

Table 5. ^{1}H NMR spectral data of addition compounds.

^{1}H NMR δ(ppm)				
	Aromatic protons			
Complex	Pyridine ring	Phenolic ring	Substituent –Me	R–Sn
3-CNpy	7.39–8.87	–	–	–
($Ph_3SnOPhMe$-2)(CNpy-3)	7.40–8.89	6.79–7.16	2.23	7.47
($Bu_3SnOPhMe$-2)(CNpy-3)	7.41–8.88	6.77–7.09	2.22	0.89–0.92(t,9H)–$CH_3(\delta)$ 1.22–1.40(m,6H)–$CH_2(\alpha)$ 1.60–1.71(m,6H)–$CH_2(\beta)$ 1.22–1.40(m,6H)–$CH_2(\gamma)$
4-CNpy	7.49–8.79	–	–	–
($Ph_3SnOPhMe$-2)(CNpy-4)	7.52–8.81	6.78–7.15	2.18	7.45
($Bu_3SnOPhMe$-2)(CNpy-4)	7.50–8.83	6.76–7.10	2.15	0.88–0.92(t,9H)–$CH_3(\delta)$ 1.23–1.35(m,6H)–$CH_2(\alpha)$ 1.55–1.72(m,6H)–$CH_2(\beta)$ 1.23–1.35(m,6H)–$CH_2(\gamma)$

NMR spectra of 3- and 4-cyanopyridine exhibit signals at δ 7.39–8.87 and δ 7.49–8.79 ppm, respectively, due to pyridine ring protons. The triphenyl and tributyltin(IV) adducts derived from these bases showed pyridine ring proton resonances shift downfield, suggesting coordination. The resonances due to phenolic ring protons in parent complexes also suffered slight downfield shifts on adduct formation. The resonances due to methyl substituent and phenyl and butyl groups attached to tin remained unchanged.

3.10. *^{13}C NMR spectra*

^{13}C NMR spectra of 3- and 4-cyanopyridines exhibit six and four distinct carbon resonances due to pyridine ring and cyano group. The pyridine ring carbons are at δ 110.21–152.57 and δ 120.2–151.95 ppm (table 6) in 3- and 4-cyanopyridine, respectively. The carbon resonances due to cyano occurred at δ 116.10 and δ 116.80 ppm in respective bases. The adducts of triphenyl and tri-*n*-butyltin(IV) 2-methylphenoxides with these bases showed moderate to appreciable downfield shift in pyridine ring carbons, while carbon resonances due to cyano did not change. A slight downfield shift in carbon resonances of phenolic ring relative to that in parent complexes were also observed in adducts. The adducts of triorganotin(IV) 2-methylphenoxide exhibit $^{1}J(^{119}Sn–^{13}C)$ coupling constant in solution characteristics of five-coordinate geometry, 755–760 and 442–445 Hz in triphenyl and tri-*n*-butyltin(IV) derivatives, respectively.

3.11. *^{119}Sn NMR spectra*

The ^{119}Sn NMR spectra of adducts of triphenyltin(IV) 2-methylphenoxides with 3- and 4-cyanopyridines displayed signals at δ −185.7 and δ 193.4 ppm (table 6), respectively. The δ ^{119}Sn chemical shift appeared at δ −54.8 and −58.2 ppm in tri-*n*-butyltin(IV)

Table 6. ^{13}C NMR and ^{119}Sn spectral data of addition compounds.

	^{13}C NMR δ (ppm)														
	Aromatic carbon of pyridine						Aromatic carbon of phenol								
Complexes	C_2	C_3	C_4	C_5	C_6	CN	C_1	C_2	C_3	C_4	C_5	C_6	Substituent –Me	R–Sn	^{119}Sn δ (ppm)
3-Cyanopyridine	151.95	110.21	140.0	124.06	152.57	116.10									
Ph_3Sn(OPhMe-2). (CNpy-3)	152.0	110.32	140.11	124.14	152.78	116.28	155.4	126.0	131.0	121.2	127.3	117.1	17.90	129.9 ($^1J(^{119}Sn–^{13}C) = 755.0$ Hz) ($^2J(^{119}Sn–^{13}C) = 47.0$ Hz) ($^3J(^{119}Sn–^{13}C) = 62.0$ Hz)	−193.4
n-Bu_3Sn(OPhMe-2). (CNpy-3)	152.11	110.30	140.13	124.18	152.80	116.24	155.91	124.71	131.67	121.81	126.32	116.10	17.65	C_α:16.00{$^1J(^{119}Sn–^{13}C) = 442.0$ Hz} C_β:27.68{$^2J(^{119}Sn–^{13}C) = 18.0$ Hz} C_γ:26.76{$^3J(^{119}Sn–^{13}C) = 68.0$ Hz}	−58.2
4-Cyanopyridine	151.95	125.3	120.2	125.3	151.95	116.80									
Ph_3Sn(OPhMe-2). (CNpy-4)	151.98	125.38	120.22	125.36	151.99	116.92	155.0	125.51	131.21	120.95	126.99	116.82	17.89	129.34 ($^1J(^{119}Sn–^{13}C) = 760.0$ Hz) ($^2J(^{119}Sn–^{13}C) = 47.0$ Hz) ($^3J(^{119}Sn–^{13}C) = 63.0$ Hz)	−185.7
n-Bu_3Sn(OPhMe-2). (CNpy-4)	152.01	125.40	120.21	125.41	152.0	117.01	155.92	124.88	131.65	121.76	126.23	116.54	17.88	C_α:16.21{$^1J(^{119}Sn–^{13}C) = 445.0$ Hz C_β:27.82{$^2J(^{119}Sn–^{13}C) = 19.0$ Hz} C_γ:26.98{$^3J(^{119}Sn–^{13}C) = 67.0$ Hz}	−54.8

Table 7. Antibacterial activity of ligand and organotin(IV) complexes by MIC method in $\mu g\,mL^{-1}$.

Compound	*E. coli*	*S. aureus*	*S. epidermidis*	*S. flexneri*	*P. mirabilis*	*P. aerogerosa*
2-Methylphenol	125.0	250.0	125.0	125.0	125.0	250.0
$Ph_3SnOPhMe$-2	31.25	62.5	15.62	31.25	31.25	62.50
$Bu_3SnOPhMe$-2	7.82	15.62	7.82	15.62	15.62	7.82
$Me_3SnOPhMe$-2	15.62	31.25	15.62	15.62	15.62	31.25
Streptomycin	31.25	62.50	62.50	62.50	31.25	31.25

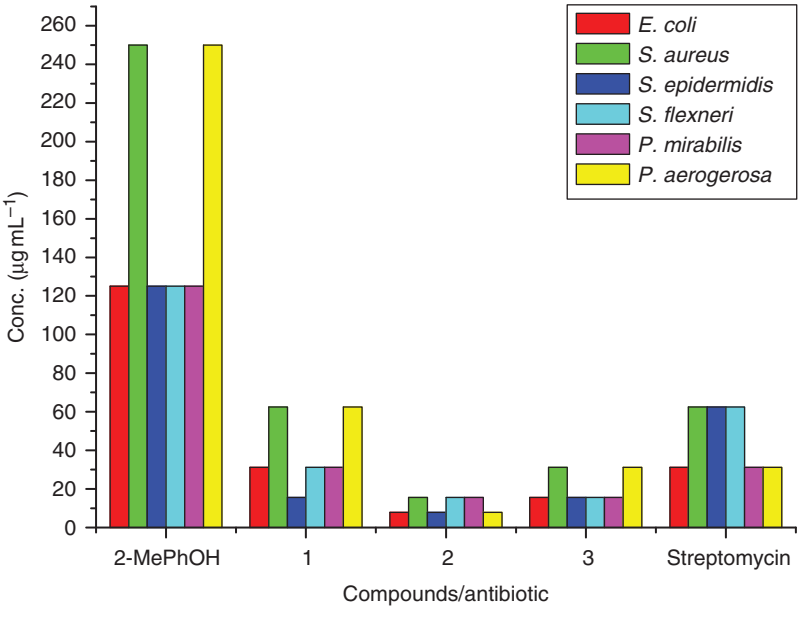


Figure 4. *In vitro* antibacterial activity of compounds and antibiotic.

adducts with 3- and 4-cyanopyridines, respectively. The observed ^{119}Sn chemical shifts are characteristic of five-coordination at tin.

Comparison of δ ^{119}Sn values of adducts with parent complexes show a shift of ^{119}Sn resonances to lower frequency in adducts. The effective charge and higher coordination number of tin may be ascribed to highly shielded tin in adducts.

3.12. *Antibacterial activity*

Literature contains numerous reports on the antimicrobial [46–54] and antitumor activity [55] of organotin(IV) complexes. The ligand and synthesized complexes were tested *in vitro* for their antibacterial activity against *E. coli*, *S. aureus*, *P. mirabilis*, *P. aerogerosa*, *S. epidermidis*, and *S. flexneri* (table 7, figure 4). The results were compared with positive control, containing both broth and bacteria, and control containing only broth. The results show that the ligands inhibit bacterial growth in conc. range 125–250 $\mu g\,mL^{-1}$.

All the complexes have been found to inhibit bacterial growth at 7.82–62.5 $\mu g\,mL^{-1}$. Complex **2** exhibits significantly enhanced activity toward all bacteria under study with MIC at 7.81–15.62 $\mu g\,mL^{-1}$. Complex **1** has most activity against *S. epidermidis* at 15.62 $\mu g\,mL^{-1}$ and is least effective against *S. aureus* and *P. aerogerosa* at 62.5 $\mu g\,mL^{-1}$. *Staphylococcus aureus* and *P. aerogerosa* are the least affected organisms by **3** at MIC 31.25 $\mu g\,mL^{-1}$; *E. coli*, *S. epidermidis*, *S. flexneri* and *P. mirabilis* are most affected at MIC 15.62 $\mu g\,mL^{-1}$. Enhancement in activity may be due to the coordination of phenol to metal ion and an efficient diffusion of the metal complexes into bacterial cell [56, 57]. The antibacterial activities of these compounds were compared with commercial antibiotic, streptomycin. It is quite difficult to compare these results of the antibacterial screening with those reported earlier because of the different methodology and strains assayed; yet, in view of the biological significance associated with both tin and phenoxides ligands, promising biological activity has been depicted by the complexes studied herein.

4. Conclusion

Synthetic strategy for the formation of triorganotin(IV) 2-methylphenoxides is deduced with monomeric (**1**), dimeric (**2**), and polymeric (**3**) structures. Dimeric/polymeric structures are lost in solution and four-coordinate tin has been proposed. Lewis acid character of the complexes has been established in the presence of nitrogen bases. The newly synthesized complexes have promising antibacterial activity.

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