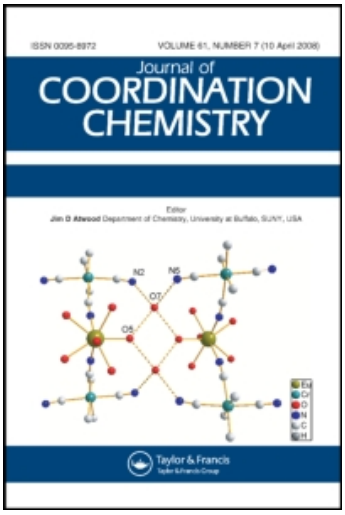

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Synthesis, characterization and acceptor behavior of *n*-butyltin(IV)-2,4-dimethylphenoxides

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Synthesis, characterization and acceptor behavior of *n*-butyltin(IV)-2,4-dimethylphenoxides

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The *n*-butyltin(IV) complexes, *n*-$BuSnCl_{3-x}(OC_6H_3(CH_3)_2\text{-}2,4)_x$ (where $x = 1$–3), have been synthesized in quantitative yields by employing the reaction of *n*-$BuSnCl_3$ with 2,4-dimethylphenol and sodium acetate in methanol and benzene solvents at room temperature. The complexes have been characterized by elemental analysis, molar conductivity, and FT-IR, ^{1}H- and ^{13}C-NMR, and mass spectral studies. Thermal behavior has been studied by TG–DTA techniques. Lewis acid character of *n*-$BuSn(OC_6H_3(CH_3)_2\text{-}2,4)_3$ has been investigated by reacting it with bases such as 2,2′-bipyridine and 1,10-phenanthroline (B), Ph_3PO and Ph_3AsO (LO) and phosphorus and arsenic donors Ph_3P, Ph_3As, and $As(SPh)_3$ (L). The formation of 1 : 1 and 1 : 2 (metal : base) coordination compounds [*n*-$BuSn(OC_6H_3(CH_3)_2\text{-}2,4)_3\cdot$B] and *n*-[$BuSn(OC_6H_3(CH_3)_2\text{-}2,4)_3\cdot$2LO/2L] has been authenticated by physicochemical and IR spectral studies. In order to infer the biological relevance of newly synthesized complexes, the antibacterial activity has been assayed against six bacterial strains *Klebsiella pneumoniae*, *Staphylococcus epidermidis*, *Staphylococcus aureus*, *Salmonella typhi*, *Salmonella paratyphi*, and *Escherichia coli*. In this study, *n*-$BuSnCl_2(OC_6H_3(CH_3)_2\text{-}2,4)$ and *n*-$BuSnCl(OC_6H_3(CH_3)_2\text{-}2,4)_2$ showed better activity than precursor and ligand, while *n*-$BuSn(OC_6H_3(CH_3)_2\text{-}2,4)_3$ did not exhibit improved activity.

Keywords: *n*-Butyltin(IV) complexes; 2,4-Dimethylphenol; Coordination compounds; Spectroscopic studies; Antibacterial activity

1. Introduction

The organometallic chemistry of main group elements has been widely studied due to their broad spectrum of applications [1] and their favorable environmental and toxicological properties [2–7]. The biological [8, 9] and medicinal applications of organotin compounds [10–12] are well-known. A literature survey on organotin chemistry in general [13–19] and organotin complexes derived from alcohols [20, 21] and phenols [22–24] in particular, reveals that, compared to voluminous documentation on di- and triorganotin(IV) complexes, monoorganotin analogs are less studied [25]. Despite the fact that monoorganotin complexes possess applications as homogeneous

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catalysts in transesterification reactions as synergists for PVC stabilization and in glass coatings [26], there are only scattered reports concerning monoorganotin complexes. Monoorganotin derivatives of non-steroidal anti-inflammatory drugs have been reported [25]. The hydrolysis of monoorganotin compounds to afford organostannic acids $[RSn(OH)O]_n$ of industrial importance in organic synthesis [27] and in catalytic reactions [28] has been a subject of research interest. Although monoorganotin compounds do not exhibit biological activity and their toxicity to mammals is very low, the low toxicity and good leach resistance of certain monoorganotin compounds are being used for food contact applications in the packaging industry. The use of a mixture of dimethyltin and monomethyltin isooctyl thioglycolates, di-*n*-octyltin and mono-*n*-octyltin isooctyl thioglycolates, and of poly (di-*n*-octyltin) maleate as primary heat stabilizers for PVC has been recommended. In continuation of our work on organotin(IV) phenoxides [29–31] and in view of the fact that compared to di- and triorganotin(IV) phenoxides, the monoorganotin analogs are rather scarcely studied, *n*-butyltintrichloride has been chosen as precursor and 2,4-dimethylphenol as the ligand for synthesis of monoorganotin(IV)-2,4-dimethylphenoxides. Interest in 2,4-dimethylphenol stems from the fact that of various alkylphenols, 2,4-dimethylphenol has drawn no attention. The reactivity of newly synthesized complex, $n\text{-BuSn}[OC_6H_3(CH_3)_2\text{-}2,4]_3$ with nitrogen, oxygen, phosphorus, and arsenic donors has also been studied.

2. Experimental

2.1. *Materials and methods*

n-$BuSnCl_3$ (Merck b.p. 93°C) and 2,4-dimethylphenol (Merck, b.p. 211°C) were used without purification. Solvents were dried before use by standard methods. The tin content was estimated as SnO_2 after decomposition of the complexes with a mixture of concentrated H_2SO_4 and HNO_3, followed by heating at 700–800°C. Chlorine was determined by Volhard's method. Microanalyses for carbon and hydrogen were performed on a Carlo-Erba 1108 elemental analyser. Molar conductances of complexes (10^{-3} mol L^{-1} solutions) in nitrobenzene were obtained at 25 ± 0.1°C on an Elico conductivity bridge (type CM-82T). Molecular weights of solid complexes were determined by Rast's camphor method. IR spectra were recorded (KBr pellets) on a Nicolet-5700 FTIR spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a BRUKER AVANCE II 400 spectrometer using $CDCl_3$ as solvent. Thermograms were recorded on the simultaneous DT-TG Shimadzu DT-60 thermal analyzer. Thermocouple used was Pt/Pt–Rh (10%).

2.2. *Synthesis*

2.2.1. Preparation of *n*-butyltin(IV)-2,4-dimethylphenoxides, $n\text{-BuSnCl}_{3-x}[OC_6H_3(CH_3)_2\text{-}2,4]_x$ ($x = 1$–3). In a typical reaction for the preparation of $n\text{-BuSnCl}_2[OC_6H_3(CH_3)_2\text{-}2,4]$, to a warm (35°C) methanolic solution (20 mL) of sodium acetate (0.98 g, 0.012 mol), an equimolar amount of 2,4-dimethylphenol

(1.41 mL, 1.44 g, 0.012 mol) in benzene (15 mL) was added and heated on a water bath for 5–10 min at 35°C. To this, a benzene solution of *n*-butyltintrichloride (1.97 mL, 3.33 g, 0.012 mol) was added slowly. The mixing of the reactants resulted in the separation of white solid. The reaction mixture was stirred on a magnetic stirrer for 10 h and then filtered to remove the white solid formed and the filtrate was then distilled under reduced pressure, whereupon a yellowish brown liquid was obtained.

Similar procedure was adopted for the preparation of *n*-BuSnCl[$OC_6H_3(CH_3)_2$-2,4]$_2$ and *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$, wherein two and three equivalents of 2,4-dimethylphenol and sodium acetate were added in separate experiments. The products were obtained as off-white solids. Anal. Calcd for *n*-$BuSnCl_{3-x}[OC_6H_3(CH_3)_2$-2,4]$_x$; for $x=1$, $C_{12}H_{18}Cl_2OSn$/368 (%): Sn, 32.60; Cl, 19.02; C, 39.13; H, 4.89. Found: Sn, 32.00; Cl, 19.38; C, 39.34; H, 4.81; b.p.; 110°C; Λ_m ($PhNO_2$): 0.30 $Scm^2\,mol^{-1}$. For $x=2$, i.e., $C_{20}H_{27}ClO_2Sn$/454 (%) Anal. Calcd Sn, 26.43; Cl, 7.71; C, 52.86; H, 5.95: Found Sn, 26.00; Cl, 8.14; C, 53.17; H, 6.15; m.p., 100°C; mol wt = 1372. Λ_m ($PhNO_2$): 0.30 $Scm^2\,mol^{-1}$; For $x=3$, i.e., $C_{28}H_{36}O_3Sn$/540, Anal. Calcd Sn, 22.22; C, 62.22; H, 6.66. Found: Sn, 22.02; C, 63.38; m.p., 138°C; Λ_m ($PhNO_2$): 0.30 $Scm^2\,mol^{-1}$; mol wt = 1642 (table 1).

2.2.2. Reactions of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ with 2,2′-bipyridine and 1,10-phenanthroline. To benzene solution of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$, equimolar amounts of 2,2′-bipyridine and 1,10-phenanthroline were added in separate experiments. The reaction mixture was stirred for 8 h at room temperature during which separation of pink solids was observed. The solid compounds so obtained were treated with petroleum ether and finally dried under vacuum. Anal. Calcd for $C_{38}H_{44}O_3SnN_2$/696 (%): Sn, 17.24; C, 65.52; H, 6.32. Found: Sn, 17.20; C, 65.67; H, 6.23; Λ_m ($PhNO_2$): 0.56 $Scm^2\,mol^{-1}$; decomposition temperature 210°C for $C_{39}H_{44}O_3SnN_2$/722 (%): Sn, 16.62; C, 64.82; and H, 6.10. Found: Sn, 16.54; C, 64.38; and H, 6.05; Λ_m ($PhNO_2$): 0.59 $Scm^2\,mol^{-1}$, decomposition temperature 224°C (table 2).

2.2.3. Reactions of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ with Ph_3PO, Ph_3AsO, Ph_3P, Ph_3As and $As(SPh)_3$. In a typical reaction, *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ dissolved in minimum benzene was treated with two molar equivalents of Ph_3PO, Ph_3AsO, Ph_3P, Ph_3As, and $As(SPh)_3$ in benzene in separate experiments. The contents were initially stirred for 5 h and then refluxed for 18 h. The addition of petroleum ether to the reaction mixture gave white, fine solids which were dried in vacuum. Anal. Calcd for $C_{64}H_{66}O_5SnP_2$/1095.58 (%): Sn, 10.95; C, 70.10; H, 6.02. Found: Sn, 10.98; C, 72.08; H, 6.09; Λ_m ($PhNO_2$): 0.66 $Scm^2\,mol^{-1}$. Anal. Calcd for $C_{64}H_{66}O_5SnAs_2$/1184.48 (%): Sn, 10.13; C, 64.84; and H, 5.57. Found: Sn, 10.08; C, 64.78; H, 5.51; Λ_m ($PhNO_2$): 0.48 $Scm^2\,mol^{-1}$. Anal. Calcd for $C_{64}H_{66}O_3SnP_2$/1064.58 (%): Sn, 11.27; C, 72.14; H, 6.20. Found: Sn, 11.20; C, 72.06; H, 6.25; Λ_m ($PhNO_2$): 0.61 $Scm^2\,mol^{-1}$. Anal. Calcd for $C_{64}H_{66}O_3SnAs_2$/1152 (%): Sn, 10.42; C, 66.67; H, 5.73. Found: Sn, 9.31; C, 59.94; H, 5.09; Λ_m ($PhNO_2$): 0.44 $Scm^2\,mol^{-1}$. Anal. Calcd for $C_{64}H_{66}O_3SnAs_2S_6$/1248 (%): Sn, 9.61; C, 61.54; H, 5.29. Found: Sn, 9.02; C, 57.10; H, 4.86; Λ_m ($PhNO_2$): 0.52 $Scm^2\,mol^{-1}$ (table 2).

Table 1. Analytical data of *n*-butyltin(IV)-2,4-dimethylphenoxides.

Complex (empirical formula)	Color	m.p./*b.p. temperature (°C)	Elemental analyses Found (calculated) (%)				Molar conductance (Λ_m Scm^2 mol^{-1})
			Sn	Cl	C	H	
n-BuSnCl$_2$[OC$_6$H$_3$(CH$_3$)$_2$-2,4][C$_{12}$H$_{18}$Cl$_2$OSn](368)	Yellowish brown liquid	*110	32.00 (32.60)	19.38 (19.02)	39.34 (39.13)	4.81 (4.89)	0.30
n-BuSnCl[OC$_6$H$_3$(CH$_3$)$_2$-2,4]$_2$[C$_{20}$H$_{27}$ClO$_2$Sn] (454)	Dirty white solid	100	26.00 (26.43)	8.14 (7.71)	53.17 (52.86)	6.15 (5.95)	0.33
n-BuSn[OC$_6$H$_3$(CH$_3$)$_2$-2,4]$_3$[C$_{28}$H$_{36}$O$_3$Sn] (540)	Dirty white solid	138	22.02 (22.22)	–	62.38 (62.22)	6.71 (6.66)	0.67

Table 2. Analytical data of coordination compounds of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ with N, O, P, and As donors.

Complex [molecular formula] (molecular weight)	Color	m.p./*decomposition temperature (°C)	Elemental analyses			Molar conductance Λ_m Scm^2 mol^{-1}
			Sn	C	H	
n-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·$C_{10}H_8N_2$ [$C_{38}H_{44}O_3SnN_2$] (696)	Pink	*210	17.20 (17.24)	65.67 (65.52)	6.23 (6.32)	0.56
n-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·$C_{12}H_8N_2$ [$C_{39}H_{44}O_3SnN_3$] (722)	Pink	*224	16.54 (16.62)	64.38 (64.82)	6.05 (6.10)	0.59
n-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·2($C_6H_5S)_3$As [$C_{64}H_{66}O_3SnAs_2S_6$] (1248)	White	72	9.02 (9.61)	57.10 (61.54)	4.86 (5.29)	0.52
n-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·2($C_6H_5)_3$As [$C_{64}H_{66}O_3SnAs_2$] (1152)	White	60	9.31 (10.42)	59.94 (66.67)	5.09 (5.73)	0.44
n-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·2($C_6H_5)_3$AsO [$C_{64}H_{66}O_5SnAs_2$] (1184.48)	White	165	10.08 (10.13)	64.78 (64.84)	5.51 (5.57)	0.48
n-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·2($C_6H_5)_3$PO [$C_{64}H_{66}O_5SnP_2$] (1095.58)	White	140	10.98 (10.95)	72.08 (70.10)	6.09 (6.02)	0.66
n-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·2($C_6H_5)_3$P [$C_{64}H_{66}O_3SnP_2$] (1064.58)	White	64	11.20 (11.27)	72.06 (72.14)	6.25 (6.20)	0.61

2.3. In vitro *antimicrobial assay*

n-$BuSnCl_3$, 2,4-dimethylphenol and *n*-butyltin(IV)-2,4-dimethylphenoxides were screened *in vitro* for their antibacterial activities on selected Gram (+ve) and Gram (−ve) bacterial strains using minimum inhibitory concentration (MIC) method [32]. The MIC values of tested compounds against Gram (−ve) *Escherichia coli*, *Salmonella typhi*, and *Salmonella paratyphi* and Gram (+ve) *Klebsiella pneumoniae*, *Staphylococcus epidermidis*, and *Staphylococcus aureus* were determined. All test cultures were streaked on soya bean casein digest agar and incubated overnight at 37°C. A stock solution of 5 μg mL^{-1} of each compound was prepared in DMSO and appropriately diluted to give final concentrations of 500, 250, 125, 62.5, 31.25, 15.6, 7.9, 3.9, 1.9, and 0.9 μg mL^{-1}. All samples were tested in triplicate.

2.4. *MIC determination by twofold serial dilution*

The MIC assay [33] was performed in a 96-well micro-titer plate. For MIC assay of each test drug, a row of 12 wells was used with the last 2 wells taken as control (no drug added). Each of the 10 wells received 100 μL of the Mueller–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 of broth was withdrawn with a sterile tip and added to the 100 μL of broth in the second well; the contents were mixed four times. Then, 100 μL was withdrawn from the second well and added to the third well. In this way, a range of twofold serial dilution was prepared (500–0.98 μg mL^{-1}). The broth in each of the wells was inoculated with 2 μL of the bacterial culture (*S. aureus*, *E. coli*, *S. typhi*, *S. paratyphi*, *K. pneumoniae*, and *S. epidermidis*) and the contents were mixed by 10 clockwise and 10 anticlockwise rotations on a flat surface. The plate was incubated at 35°C. The observations for the growth of bacteria were recorded after 24 h.

3. Results and discussion

The reaction of *n*-$BuSnCl_3$ with 2,4-dimethylphenol in the presence of sodium acetate in appropriate molar ratio afforded complexes according to scheme 1:

$$n\text{-BuSnCl}_3 + x\text{NaOOCCH}_3 + x\text{HOArMe}_2\text{-2,4} \xrightarrow[\text{Room temp.}]{\text{C}_6\text{H}_6+\text{MeOH}} n\text{-BuSnCl}_{3-x}(\text{OArMe-2,4})_x + x\text{CH}_3\text{COOH} + x\text{NaCl}$$

(where $x = 1$–3)

Scheme 1. Reaction scheme for preparation of complexes.

The complexes are soluble in most common organic solvents. The molar conductances of millimolar (10^{-3} mol L^{-1}) solutions of the complexes in nitrobenzene (ranging from 0.30 to 0.67 Scm^2 mol^{-1}) are too low to be attributed to a 1 : 1 electrolyte, hence the complexes are non-electrolytes. The molecular weight determinations of the

Table 3. Selected IR data (cm^{-1}) of *n*-butyltin(IV)-2,4-dimethylphenoxides.

Complex	υ(–OH)	υ(C–O)	υ(Sn–O)	υ(Sn–O–Sn)	υ(Sn–C)	υ(Sn–Cl)
$HO[C_6H_3(CH_3)_2$-2,4]	3405	1263, 1204	–	–	–	–
n-$BuSnCl_2[OC_6H_3(CH_3)_2$-2,4]	–	1255	489	685	590, 520	360
n-$BuSnCl[OC_6H_3(CH_3)$-2,4]$_2$	–	1250	469	680, 661	596, 522	306
n-$BuSn[OC_6H_3(CH_3)_2$-2,4]$_3$	–	1210	467	622, 661	595, 524	–

complexes *n*-$BuSnCl[OC_6H_3(CH_3)_2$-2,4]$_2$ and *n*-$BuSn[OC_6H_3(CH_3)_2$-2,4]$_3$ by Rast's camphor method indicated that these complexes exist as trimers.

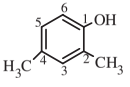
3.1. *IR spectra*

A comparison of IR spectra of *n*-butyltin(IV)-2,4-dimethylphenoxides with that of 2,4-dimethylphenol has shown changes in the vibrations of the coordinated phenol. The absence of bands due to phenolic –OH at 3405 cm^{-1} in free 2,4-dimethylphenol suggests deprotonation of the phenolic proton upon complexation, also supported by the fact that sodium chloride was formed during the reactions in the presence of sodium acetate. Bands due to υ(C–O) (1263–1204 cm^{-1} in free 2,4-dimethylphenol) appeared at 1255–1210 cm^{-1} in complexes indicating bonding through phenolic oxygen. The appearance of entirely new bands at 490–430 cm^{-1} in *n*-butyltin(IV)-2,4-dimethylphenoxides ascribed to υ(Sn–O) further supports their formation. Bands at 685–625 cm^{-1} in the complexes have been assigned to Sn–O–Sn stretches. Absorptions at 360 and 306 cm^{-1} in *n*-$BuSnCl_2(OC_6H_3(CH_3)_2$-2,4) and *n*-$BuSnCl(OC_6H_3(CH_3)_2$-2,4)$_2$ have been assigned to υ(Sn–Cl). Bands at ~590, 520 cm^{-1}; 596, 522 cm^{-1}, and 595, 524 cm^{-1} in *n*-$BuSnCl_2[OC_6H_3(CH_3)_2$-2,4], *n*-$BuSnCl[OC_6H_3(CH_3)_2$-2,4]$_2$, and *n*-$BuSn[OC_6H_3(CH_3)_2$-2,4]$_3$, respectively, have been assigned to υ(Sn–C) relative to that reported to occur at 596 and 518 cm^{-1} in *n*-$BuSnCl_3$ [34] (table 3).

3.2. *^{1}H-NMR spectra*

The formation of *n*-butyltin(IV)-2,4-dimethylphenoxides is confirmed from comparison of ^{1}H-NMR spectra of complexes with those of free 2,4-dimethylphenol recorded in $CDCl_3$. Free 2,4-dimethylphenol displays signals at δ 5.88 attributed to phenolic –OH and at δ 2.03 and δ 2.10 due to methyl substituents at 2- and 4- of phenolic ring. Signals due to 3-H, 5-H, and 6-H aromatic protons appear at δ 6.89, 6.78, and 6.48, respectively [35]. ^{1}H-NMR spectra of complexes showed that aromatic phenolic ring protons undergo moderate-to-significant upfield shifts upon complexation relative to 2,4-dimethylphenol. Weak bond formation between tin and oxygen may be presumed to shield the aromatic protons. The trend of upfield shift has been found as $BuSnCl_2[OC_6H_3(CH_3)_2$-2,4] > *n*-$BuSnCl[OC_6H_3(CH_3)_2$-2,4]$_2$ > *n*-$BuSn[OC_6H_3(CH_3)_2$-2,4]$_3$ attributed to the role of Cl attached to tin and the steric effect of methyl substituents of 2,4-dimethylphenol. The resonances due to methyl substituents remained unaltered. Resonances due to butyl group attached to tin appeared in δ 0.86–1.81 range (table 4).

Table 4. ^{1}H-NMR spectral data of *n*-butyltin(IV)-2,4-dimethylphenoxides.

Complex	OH^-	Aromatic protons			Substituents		Sn–R
		3-H	5-H	6-H	2-Me	4-Me	
	5.88	6.95	6.88	6.67	2.03	2.10	–
$[O^-C_6H_3(CH_3)_2$-2,4] *n*-$BuSnCl_2[OC_6H_3(CH_3)_2$-2,4]		6.89 6.46 (s, 1H)	6.78 6.32–6.4 (d, 1H) $^3J = 8$ Hz	6.48 6.11–6.14 (d, 1H) $^3J = 8$ Hz	2.01 1.92 (s, 3H)	2.09 1.96 (s, 3H)	– 0.86–1.00(δ, t, 3H) 1.37–1.59(α, t, 3H) 0.86–1.00(γ, m, 2H) 1.71–1.78(β, m, 2H)
n-$BuSnCl[OC_6H_3(CH_3)$-2,4$]_2$		6.82 (s, 2H)	6.74–6.76 (d, 2H) $^3J = 8$ Hz	6.58–6.60 (d, 2H) $^3J = 8$ Hz	2.12 (s, 3H)	2.23 (s, 3H)	0.88–0.93(δ, t, 3H) 1.17–1.27(α, t, 3H) 1.17–1.27(γ, t, 2H) 1.32–1.65(β, m, 2H)
n-$BuSn[OC_6H_3(CH_3)_2$-2,4$]_3$		6.93 (s, 3H)	6.86-6.88 (d, 3H) $^3J = 8$ Hz	6.65-6.67 (d, 3H) $^3J = 8$ Hz	2.11 (s, 3H)	2.18 (s, 3H)	0.89–0.95(δ, t, 3H) 1.15–1.57(α, t, 3H) 1.15–1.57(γ, m, 2H) 1.58–1.81(β, m, 2H)

3.3. *^{13}C-NMR spectra*

A comparison of ^{13}C-NMR spectra of the complexes with that of free 2,4-dimethylphenol further substantiates their formation. ^{13}C-NMR spectra of 2,4-dimethylphenol display the well-resolved carbon resonances of phenolic ring (δ 115.92–151.63) and that of 2- and 4-methyl substituents at δ 15.56 and δ 20.37, respectively. ^{13}C-NMR spectra of *n*-butyltin(IV)-2,4-dimethylphenoxides show that resonances due to (C-1) of phenolic ring as well as remaining ring carbons shifted slightly upfield. These observations support bonding through phenolic oxygen to tin. The carbon resonances of methyl substituents shift upfield. Resonances due to butyl bonded to tin (*n*-Bu–Sn) appear at δ 13.60–28.02 (table 5). The magnitude of coupling constant for monoorganotin(IV) complexes shows four-coordinate tin in solution.

3.4. *Mass spectra*

ES mass spectra of *n*-BuSnCl[$OC_6H_3(CH_3)_2$-2,4]$_2$ and BuSn[$C_6H_3(CH_3)_2$-2,4]$_3$ have been studied. The fragment ions containing tin have been identified by the presence of the characteristic clusters of isotopic peaks due to the presence of numerous tin isotopes. The mass spectrum of *n*-BuSnCl($OC_6H_3(CH_3)_2$-2,4)$_2$; [M] did not display molecular ion peak at *m*/*z* 454, but fragments at *m*/*z* 440 and 426 corresponding to $[M-Me]^+$ and $[M-2Me]^+$ substantiated its formation. The base peak at 859 assigned to $[Sn_3(OC_6H_3(CH_3)_2)_4+Me]^+$ and peaks observed at *m*/*z* 908, 1362 corresponding to $[2M]^+$ and $[3M]^+$ suggest the complex exists as a trimer. Fragment ions at *m*/*z* 844, 759, 440, and 426 are assigned to the formation of $[Sn_3((OC_6H_3(CH_3)_2)_4]^+$, $[\{n\text{-BuSnClOC}_6H_3(CH_3)_2\}_2OC_6H_5]^+$, $[M-Me]^+$, and $[M-2Me]^+$ fragments (tables 6 and 7).

The mass spectrum of *n*-BuSn($OC_6H_3(CH_3)_2$)$_3$ [M] showed the base peak at 1492, assigned to the formation of $[\{n\text{-BuSn}(OC_6H_3(CH_3)_2)_3\}_3\text{-2Bu-Me}]^+$ resulting from elimination of two butyl groups linked to tin and a methyl substituent from phenol. However, the fragment ion beyond *m*/*z*, i.e., 1635 assigned to the formation of $[3M+Me]^+$ suggests the polymeric nature of the complex. Other fragments appearing at 1052, 526, 483, 270, and 177 corresponded to $[2M-2Me]^+$, $[M-Me]^+$, $[M-Bu]^+$, $[n\text{-BuSn}(OC_6H_5)]^+$, and $[n\text{-BuSn}]^+$, respectively (table 8).

On the basis of analytical, IR, and mass spectral studies, a distorted five-coordinate geometry around tin has been proposed (figures 1 and 2).

3.5. *Thermal studies*

The results obtained from TG–DTA curves are presented in table 8. Complexes *n*-BuSnCl$_2$[$OC_6H_3(CH_3)_2$-2,4], *n*-BuSnCl[$OC_6H_3(CH_3)_2$-2,4]$_2$, and *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ thermally stable up to 75.70°C, 125.50°C, and 142.24°C, respectively, suggest the order of thermal stability as *n*-BuSnCl$_2$[$OC_6H_3(CH_3)_2$-2,4] < *n*-BuSnCl[$OC_6H_3(CH_3)_2$-2,4]$_2$ < *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ (Supplementary material). Strikingly, *n*-BuSnCl$_2$[$OC_6H_3(CH_3)_2$-2,4] has shown 100% weight loss in the 75.70–790.73°C range without leaving residue, suggesting thereby the volatile nature of the complex. Thermal decomposition has been accompanied by an endothermic peak at 200.61°C. In the case of *n*-BuSnCl[$OC_6H_3(CH_3)_2$-2,4]$_2$, the weight loss amounting to

Table 5. ^{13}C-NMR spectral data of *n*-butyltin(IV)-2,4-dimethylphenoxides.

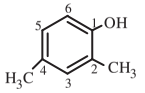
Complex	Aromatic carbons						Substituent carbons		Sn–R
	C-1	C-2	C-3	C-4	C-5	C-6	2-Me	4-Me	
	148.82	126.15	129.21	121.54	124.64	112.17	17.52	20.60	–
n-BuSnCl$_2$[OC$_6$H$_3$(CH$_3$)$_2$-2,4]	149.22	127.50	129.43	121.23	125.18	112.63	17.54	20.64	13.60($^{\alpha}$ CH$_2$) 18.31($^{\beta}$ CH$_2$) 23.45($^{\gamma}$ CH$_2$) 24.75($^{\delta}$ CH$_3$)
n-BuSnCl[OC$_6$H$_3$(CH$_3$)$_2$-2,4]$_2$	149.45	126.50	129.33	121.27	124.94	112.58	17.61	20.52	13.80 ($^{\alpha}$ CH$_2$) 18.36($^{\beta}$ CH$_2$) 23.20($^{\gamma}$ CH$_2$) 24.37($^{\delta}$ CH$_3$)
n-BuSn[OC$_6$H$_3$(CH$_3$)$_2$-2,4]$_3$	149.91	126.76	129.36	121.38	126.02	112.56	17.56	20.57	18.36($^{\alpha}$ CH$_2$) 28.0($^{\beta}$ CH$_2$) 27.2($^{\gamma}$ CH$_2$) 13.73($^{\delta}$ CH$_3$)

Table 6. Mass fragments of *n*-BuSnCl($OC_6H_3(CH_3)_2$-2,4)$_2$ [M] and relative isotopic abundance.

n-BuSnCl($OC_6H_3(CH_3)_2$-2,4)$_2$ [M]	*m/e* (%)	M − 8* (%)	M − 6* (%)	M − 5* (%)	M − 4* (%)	M − 3* (%)	M − 2* (%)	M − 1* (%)	M* (%)	M + 1* (%)	M + 2* (%)
$[3M]^+$	1362(22)	8.8	25.5	42.5	57.7	72.4	91.5	92.1	100	89.7	84.1
$[2M + 2Me]^+$	938(45)	7.2	15.5	54.9	29.7	93.2	46.1	85.1	100	51.7	43.0
$[2M]^+$	908(49)	4.0	16.4	18.2	41.7	42.8	73.1	65.6	100	65.8	97.7
$[Sn_3(OC_6H_3(CH_3)_2)_4]^+$	844(77)	6.6	83.97	22.3	44.4	48.4	77.7	72.3	100	76.1	90.7
$[Sn_3(OC_6H_3(CH_3)_2)_4 + Me]^+$	859(100)	6.4	19.3	21.5	47.2	49.1	77.0	71.7	100	76.4	76.4
$[\{n\text{-BuSnCl}(OC_6H_3(CH_3)_2\}_2 + OC_6H_5]^+$	759(97)	3.4	15.1	16.6	40.2	47.7	84.8	75.9	100	91.3	88.6
$[M + Me]^+$	469(17)	2.7	3.6	1.8	40.6	31.10	12.9	43.5	100	27.7	18.1
$[M - Me]^+$	440(18)	2.2	2.9	1.4	34.4	25.3	71.2	39.8	100	26.6	36.8
$[M - 2Me]^+$	426(5)	2.4	2.0	1.5	36.1	26.3	74.3	29.3	100	10.5	38.3

Table 7. Mass fragments of *n*-BuSn($OC_6H_3(CH_3)_2$)$_3$ [M] and relative isotopic abundance.

n-BuSn($OC_6H_3(CH_3)_2$-2,4)$_3$ [M]	*m/e* (%)	M − 8* (%)	M − 6* (%)	M − 5* (%)	M − 4* (%)	M − 3* (%)	M − 2* (%)	M − 1* (%)	M* (%)	M + 1* (%)	M + 2* (%)
$[3M + Me]^+$	1635(2)	8.9	16.7	24.7	44.2	53.6	79.7	84.4	100	94.7	98.6
$[3M - 2Bu - Me]^+$	1492(100)	5.3	17.0	24.4	44.3	52.8	79.5	82.7	100	92.1	96.9
$[2M - 2Me]^+$	1052(12)	3.3	13.6	17.2	26.2	45.0	61.7	77.2	100	72.2	81.8
$[2M - Bu]^+$	1023(22)	3.2	13.6	17.3	39.7	45.3	84.2	77.4	100	71.4	81.6
$[Sn_2(OC_6H_3(CH_3)_2)_5OC_6H_5]^+$	938(15)	7.2	15.5	54.9	29.7	93.2	46.1	85.1	100	51.7	43.0
$[2M - Bu\text{-}2OC_6H_3(CH_3)_2\text{-}2Me]^+$	753(23)	1.6	4.4	5.6	23.6	16.0	60.9	94.1	100	96.9	87.1
$[M - Me]^+$	526(4)	3.0	2.9	1.1	44.6	23.6	74.3	26.3	100	32.5	14.2
$[M - 2Me]^+$	512(41)	2.7	2.6	1.8	40.5	33.0	74.9	44.4	100	26.8	17.0
$[M - Bu]^+$	483(11)	47.5	2.6	1.5	40.8	32.4	74.9	42.4	100	24.9	16.6
$[n\text{-BuSn}(OC_6H_5)]^+$	270(90)	2.9	2.8	1.5	43.02	27.7	74.7	33.8	100	11.2	14.5
$[n\text{-BuSn} + 2Me]^+$	207(3)	2.9	2.9	1.3	43.8	26.1	74.6	30.9	100	6.8	14.1
$[n\text{-BuSn}]^+$	177(7)	3.0	2.9	1.1	44.6	23.6	74.3	26.3	100	4.6	14.2

Table 8. Thermal decomposition data of *n*-butyltin(IV)-2,4-dimethylphenoxides.

Complex	Initial decomposition temperature (°C)	Stages of decomposition	TGA data			DTA data	
			Decomposition range (°C)	Weight loss (%)	Decomposition products	Peak temperature (°C)	Peak nature
n-BuSnCl$_2$[OC$_6$H$_3$(CH$_3$)$_2$-2,4]	75.70	Single	75.70–790.73	100		200.61	Endothermic (sharp)
n-BuSnCl[OC$_6$H$_3$(CH$_3$)-2,4]$_2$	125.50	Single	125.50–845.59	68.02	SnO	314.43	Exothermic (feeble)
n-BuSn[OC$_6$H$_3$(CH$_3$)$_2$-2,4]$_3$	142.24	Single	142.24–733.38	75.69	SnO	283.47 433.16	Exothermic (sharp) Exothermic (feeble)

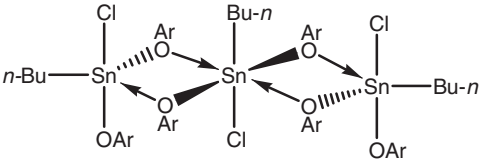


Figure 1. Proposed structure of *n*-BuSnCl[$OC_6H_3(CH_3)_2$-2,4]$_2$.

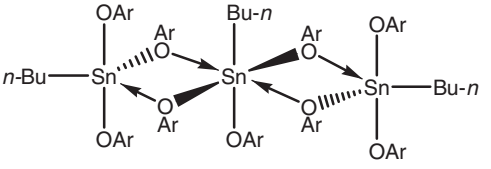


Figure 2. Proposed structure of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$.

68.021% in a single step accounted for the formation of SnO as the final decomposition product. A small exothermic peak at 314.43°C in the DTA curve indicated single-stage decomposition. For *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$, a weight loss of 75.69% corresponded to SnO as the final residue. The DTA curve of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ showed one sharp and one small exothermic peak at 283.47°C and 433.16°C, respectively.

3.6. *Reactions of n-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ with 2,2′-bipyridine, 1,10-phenanthroline, Ph_3PO, Ph_3AsO, Ph_3P, Ph_3As, and $As(SPh)_3$*

Literature contains numerous reports concerning the formation of coordination compounds of organotin(IV) halides with 2,2′-bipyridine [36], 1,10-phenanthroline [37], Ph_3AsO, and Ph_3PO [38, 39]. Lewis acid character of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ has therefore been established by reacting it with bases (2,2′-bipyridine, 1,10-phenanthroline, triphenylphosphine oxide, triphenylarsine oxide, triphenylphosphine, triphenylarsine, and arsenic trithiophenoxide). The 1 : 1 and 1 : 2 (metal : base) coordination compounds of composition *n*-BuSn[$OAr(Me)_2$-2,4]$_3$·B (B = 2,2′-bipy;1,10-phen), *n*-BuSn[$OAr(Me)_2$-2,4]$_3$·2LO (LO = Ph_3PO, Ph_3AsO), and *n*-BuSn[$OAr(Me]_2$-2,4)$_3$·2L [L = Ph_3P, Ph_3As, $(PhS)_3As$] have been isolated from reaction of parent complex with various bases in benzene, confirmed by elemental analyses. The molar conductances of millimolar solutions of the coordination compounds are low, suggesting they are non-electrolytes.

Formation of coordination compounds has been authenticated from the comparison of their IR spectra with that of free bases/donors. IR spectra of compounds with 2,2′-bipyridine and 1,10-phenanthroline show that bands due to υ(C=C) and υ(C=N) and C–H out of plane deformation modes of free bases at 1600–1400 cm^{-1} and 759, 837,

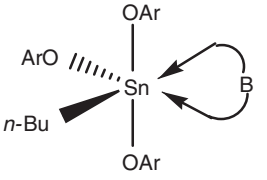


Figure 3. Proposed Structure of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·B.

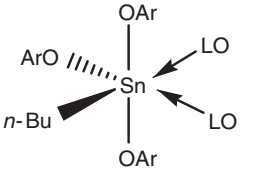


Figure 4. Proposed structure of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·LO.

and 852 cm^{-1} in respective free bases moved to higher wavenumbers by 15–20 cm^{-1}. Positive shifts in these modes suggest coordination through both nitrogens. Coordination of these bases to tin is also substantiated by the appearance of bands at 369 and 362 cm^{-1} ascribed to υ(Sn–N) (Supplementary material).

In *n*-BuSn[OAr$(Me)_2$-2,4]$_3$ with Ph_3PO and Ph_3AsO, the υ(P=O) and υ(As=O) are at 1185 and 881 cm^{-1} relative to those at 1192 and 879 cm^{-1} in free Ph_3PO and Ph_3AsO, respectively [40, 41]. Bands due to υ(P–C) and υ(As–C) at 455 and 479 cm^{-1} move to higher spectral region, at 465 and 485 cm^{-1}, in agreement with earlier reports [40, 42].

Bands at 1475, 1152, 1119, 1087, 745, 536, and 492 cm^{-1} in *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·2Ph_3P and at 1435, 1179, 749, 616, and 471 cm^{-1} in *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·2Ph_3As due to υ(C–C), υ(C–H), δ(P–C) and δ(As–C) coupled to aromatic ring vibrations support their formation.

Spectra of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·2As$(SPh)_3$ showed bands at 484 and 371 cm^{-1} due to υ(As–S) and at 744 and 688 cm^{-1} due to υ(As–S–C) relative to those at 492, 400, and 372 cm^{-1} due to υ(As–S) and at 744 and 684 cm^{-1} due to υ(As–S–C) in uncoordinated As$(SPh)_3$ (figure 3).

An interesting feature of the spectra of coordination compounds with these bases/donors has been the absence of bands due to Sn–O–Sn stretching modes, which is indicative of the breakdown of bridging in the parent complex upon coordination. Based upon physicochemical and IR spectral studies, distorted six-coordinate geometry around tin in compounds may tentatively be proposed (figures 4 and 5).

3.7. *Antibacterial activity*

To explore the antibacterial activity of *n*-butyltin(IV)-2,4-dimethylphenoxides, the precursor, ligand, and complexes were tested *in vitro* for their antibacterial

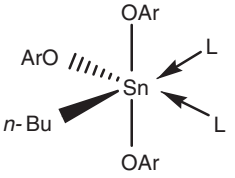


Figure 5. Proposed structure of n-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$·L.

Table 9. *In vitro* antibacterial activities of monoorganotin(IV) complexes (MIC in $\mu g\,mL^{-1}$).

	Bacteria					
Ligand/complex	*S. aureus*	*S. epidermidis*	*K. pneumoniae*	*S. typhi*	*E. coli*	*S. paratyphi*
2,4-Dimethylphenol	125	125	125	125	125	125
n-$BuSnCl_3$	125	125	125	125	125	125
n-$BuSnCl_2(OC_6H_3(CH_3)_2$-2,4)	62.5	31.25	31.25	62.5	62.5	31.25
n-$BuSnCl(OC_6H_3(CH_3)_2)_2$-2,4)$_2$	125	62.5	62.5	125	125	62.5
n-$BuSn(OC_6H_3(CH_3)_2$-2,4)$_3$	125	125	125	125	125	125

activities (table 9) against *E. coli*, *S. aureus*, *S. typhi*, *S. paratyphi*, *K. pneumoniae*, and *S. epidermidis*.

The n-$BuSnCl_3$ and 2,4-dimethylphenol show similar antibacterial activity with MIC $125\,\mu g\,mL^{-1}$ for all the bacterial species. Of the three complexes studied, n-$BuSnCl_2[OC_6H_3(CH_3)_2$-2,4] has been found to exhibit enhanced activity toward all bacteria at MIC of 31.25–62.5 $\mu g\,mL^{-1}$ range. Enhanced activity has also been shown by $BuSnCl[OC_6H_3(CH_3)_2$-2,4]$_2$ against *K. pneumoniae*, *S. epidermidis*, *S. typhi*, and *S. paratyphi* at $62.5\,\mu g\,mL^{-1}$ while it inhibits the bacterial growth at MIC $125\,\mu g\,mL^{-1}$ for *E. coli* and *S. aureus*, not different from that of n-$BuSnCl_3$ and $HOC_6H_3(CH_3)_2$-2,4, suggesting thereby that the latter bacterial strains are not affected by the complex. $BuSn[OC_6H_3(CH_3)_2$-2,4]$_3$ inhibits bacterial growth at MIC $125\,\mu g\,mL^{-1}$ for all the bacterial strains, similar to that shown by precursor and phenolic ligand.

The order of antibacterial activity is n-$BuSnCl_3 \approx HOC_6H_3(CH_3)_2$-2,4 $\approx n$-$BuSn[OC_6H_3(CH_3)_2$-2,4]$_3 < n$-$BuSnCl[OC_6H_3(CH_3)_2$-2,4]$_2 < n$-$BuSnCl_2[OC_6H_3(CH_3)_2$-2,4]. The present observations are contrary to previous reports, wherein enhancement of activity has been described due to coordination of ligand to metal and efficient diffusion of the metal complexes into bacterial cell takes place [43,44]. The simultaneous presence of chlorine and phenolic ligands in n-$BuSnCl[OC_6H_3(CH_3)_2$-2,4]$_2$ and n-$BuSnCl_2[OC_6H_3(CH_3)_2$-2,4] seems to facilitate enhanced intracellular uptake of these compounds leading to higher activity. The results were compared with standard drug tetracycline hydrochloride.

4. Conclusion

A facile method for quantitative synthesis of n-butyltin(IV)-2,4-dimethylphenoxides is described. A five-coordinate tin for complexes has been proposed from physicochemical

and spectral characterization. Reactions of *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ with nitrogen, oxygen, phosphorus, and arsenic donors afford coordination compounds, establishing its Lewis acid character. Antibacterial activities of complexes has shown the order *n*-BuSn[$OC_6H_3(CH_3)_2$-2,4]$_3$ < *n*-BuSnCl[$OC_6H_3(CH_3)_2$-2,4]$_2$ < *n*-$BuSnCl_2$ [$OC_6H_3(CH_3)_2$-2,4]. Previous reports [45] show that the biochemical activity of organotin(IV) complexes is not only influenced by the number and nature of the groups attached to tin but also the structure and coordination number of tin. The trialkyl and triaryltin(IV) complexes have been reported to exhibit pronounced bacteriostatic properties [2], while monoorganotin compounds do not display antibacterial activity [25]. Two newly synthesized monoorganotin(IV) complexes show promising antibacterial activity, presumably from the presence of –Cl.

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