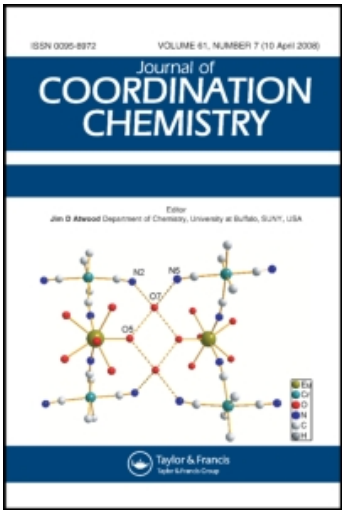

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Organotin(IV) *oxo*-homoscorpionate: preparation, spectroscopic characterization and antimicrobial properties

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An *oxo*-homoscorpionate ligand [potassium *bis*(phthalato)borate] (KL) was prepared by solid state reaction of potassium borohydride and phthalic acid (1 : 3 molar ratio). The ligand is uninegative and can be a *bi*, *tri* and *tetra*-dentate chelating agent. The *di*- and *tri*-organotin(IV) complexes of this ligand are formed by replacement of chloride in R_2SnCl_2 and R'_3SnCl (R = methyl, butyl and R′ = phenyl and butyl). The ligand and all its complexes were characterized by elemental analyses and spectral studies (IR, ^1H, ^{13}C, ^{119}Sn NMR and ESI mass spectra). Spectroscopic data reveal that all the complexes are hexacoordinate; the diorganotin complexes have *trans* octahedral geometry while the triorganotin complexes are distorted octahedral geometry. The toxicity of these organotin(IV) derivatives on selected microbes was considered. The compounds exhibit antibacterial (*Bacillus anthracius* and *Escherichia coli*) and antifungal (*Candida albicans* and *Penicillium italicum*) activities *in vitro*. The ligand shows less toxicity towards the microorganisms and its toxicity significantly increased after complexation with organotin(IV). Triorganotin derivatives (R_3SnL) of the ligand are more effective compared to diorganotin derivatives (R_2SnL_2).

Keywords: Organotin(IV); *oxo*-Homoscorpionate; Borate; Phthalic acid; Antimicrobial activity

1. Introduction

The coordination chemistry of organotin acceptors has been extensively studied due to their important biological and catalytic properties [1]. For exploration of relationships between biological activity and structure, a number of investigations of such molecule have been reported [2].

The aromatic carboxylic acid complexes provide interesting coordination compounds because the phenoxy carboxylate ions adopt various coordination modes [3, 4]. Interest in symmetric and asymmetric aromatic carboxylic acid derivatives of metals arise from the influence of the substituent organic group on biocides, fungicides, anticancer and antitumor agents [5]. Some organotin carboxylates have cytotoxic activity [6]; they are also used as agrochemical and antifouling paints due to their low photo-toxicity and favorable environmental degradation [7–9]. Organotin(IV) compounds as biocides are

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harmless for living beings because of the detoxification of organotin compounds through biodegradation to other alkyl tin species with fewer organic groups or to inorganic tin [10].

Here the synthesized ligand is a boroester which also have wide use in a variety of applications as biocides [11]. The biocidal activity of these boroesters is tremendously enhanced when coupled with metal atoms [12]. Boron and its compounds are essential for healthy plant growth, carbohydrate hormone action and membrane formation [13]. This approach was adopted to take advantage of intrinsic ability of borate ions to form boroesters with acids, aldehydes and phenols [14]; ester formation provides for production of hydrostatic boron compounds [15]. The bioassay results show that such compounds are good acaricide [16] with low mammalian toxicity [17].

Oxohomoscorpionate ligands and organotin derivatives can be considered as a model system for metal ligand interaction in biological systems. Here we report the synthesis, spectroscopic characterization and antimicrobial activity of the potassium *bis*(phthalato)borate and four organotin(IV) derivatives.

2. Experimental

2.1. *General*

Potassium borohydride (Acros Organics) and all organotin chlorides (Fluka Chemicals) were purchased and used as received. The solvents were purchased from E. Merck (India Ltd.). Hydrocarbon solvents were dried by distillation from sodium-potassium. All solvents were degassed with dry nitrogen prior to use. Samples for microanalysis were dried *in vacuum* to constant weight. All syntheses were carried out under a nitrogen atmosphere. Elemental analysis was performed by a Perkin Elmer 2400 CHN elemental analyzer. IR spectra were recorded from 4000–400 cm^{-1} with a Perkin-Elmer system 1620 FT-IR instrument. ^{1}H and ^{13}C NMR spectra were recorded using a Brucker DPX-300 MHz spectrometer operating at room temperature with $CDCl_3$ as solvent. The ^{119}Sn NMR spectra were recorded using a Brucker Avance II 400 NMR spectrometer. The chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (for ^{1}H and ^{13}C) and tetramethylstannane (for ^{119}Sn). ESI mass spectra of the ligand and organotin complexes were obtained on a LC/MS (Water India Ltd., Model LCP) mass spectrometer.

2.2. *Syntheses*

2.2.1. Synthesis of potassium *bis*(phthalato)borate (KL). Potassium borohydride 5.4 g (100 mmol) and phthalic acid 49.8 g (300 mmol) in 1 : 3 molar ratio in a Schlenk flask attached to a gas-collecting device through an air condenser, were carefully heated on a controlled temperature oil bath until 9260 mL (400 mmol) of hydrogen gas was evolved. The melt was cooled until it became viscous, poured into 500 mL of hot toluene and stirred for one hour. The mixture was filtered and a white solid obtained, which was washed with successive portions of hot toluene, benzene and diethyl ether. The white

solid was dried in a vacuum desiccator to constant weight under reduced pressure. Yield: 76%. Mp. 175–180°C. IR (KBr pellets, υcm^{-1}): 1693s (>C=0), 1350s (B–O), 3084w (aromatic ring CH). ^{1}H NMR (300 MHz, ppm, from TMS in CD_3OD at 300K): 7.49–7.77 (m, 4H, Ar-protons). ^{13}C NMR (300 MHz, δ ppm, from TMS in CD_3OD at 300 K): 129 (3 -or 6-CH), 130.5 (4- or 5-CH), 132.8 (1- or 2-C), 168 (>C=O). Elem. Anal. (%) Calcd: C (50.79), H (2.11) and O (33.86). Found: C (50.62), H (2.07) and O (33.98).

2.2.2. *Bis*(phthalato)borate dibutyltin(IV). A 25 mL methanol solution of dibutyltin dichloride 0.608 g (2 mmol) was added to a 25 mL methanolic solution/suspension of potassium *bis*(phthalato)borate 1.512 g (4 mmol) and stirred for 8 h at 30°C. The white suspension of potassium chloride was separated by filtration. The filtrate was concentrated under reduced pressure to give colorless precipitate, which was filtered. The precipitate was washed with 50 mL of diethyl ether and 50 mL hexane and dried in a vacuum desiccator to constant weight under reduced pressure. Yield: 57%. M.p. 165–168°C. IR (KBr pellets, υcm^{-1}): 1598s (>C=0), 1354s (B–O), 2926w (Ar-ring CH), 658m (Sn–O), 492w (υ_s Sn–C), 589m (υ_a Sn–C). ^{1}H NMR (300 MHz, δ ppm from TMS in $CDCl_3$, 300 K): 7.46–7.61 (m, 4H, Ar-ring, protons), 0.71–0.75, 1.16, 1.23, 1.47 (m, 9H, Sn–C_4H_9). ^{13}C NMR (300 MHz, δ ppm from TMS in $CDCl_3$, 300 K): 13.95, 26.11, 27.15, 34.2 (Sn–C_4H_9), 129.10 (3- or 6-CH), 130.96 (4- or 5-CH), 132.64 (1- or 2-C), 170.16 (>C=O). ^{119}Sn NMR (600 MHz, δ ppm from Me_4Sn in $CDCl_3$, 300 K): 250 ($(C_4H_9)_2Sn$). Elem. Anal. (%) Calcd: C (52.68), H (3.73) and O (28.10). Found: C (52.47), H (3.79) and O (28.34).

2.2.3. *Bis*(phthalato)borate dimethyltin(IV). Complex **2** was formed by the procedure of **1** by using dimethyltin dichloride 0.440 g (2 mmol) and potassium *bis*(phthalato)-borate 1.512 g (4 mmol) in methanol (70 mL) and stirred for 10 h at 30°C. A bone white precipitate was obtained. Yield: 64%. M.p. 171–176°C. IR (KBr pellets, υcm^{-1}): 1638s (>C=0), 1361m (B–O), 3016w (Ar-ring, CH), 647m (Sn–O), 486s (υ_s Sn–C), 556m (υ_a Sn–C). ^{1}H NMR (300 MHz, δ ppm from TMS in $CDCl_3$, 300 K): 7.49–7.69 (m, 4H, Ar-ring), δ 0.87 (s, 3H, Sn–CH_3). ^{13}C NMR (300 MHz, δ ppm from TMS in $CDCl_3$, 300 K): 11.2 (Sn–CH_3), 128.46 (3- or 6-CH), 130.59 (4- or 5-CH), 132.55 (1- or 2-C), 169.91 (>C=O). ^{119}Sn NMR (600 MHz, δ ppm from Me_4Sn in $CDCl_3$, 300 K): −267.27 ($(CH_3)_2Sn$). Elem. Anal. (%) Calcd: C (49.33), H (2.66) and O (30.95). Found: C (49.14), H (2.81), and O (31.05).

2.2.4. *Bis*(phthalato)borate triphenyltin(IV). Complex **3** was formed according to the synthetic method for **1** by using triphenyltin chloride 1.155 g (3 mmol) and potassium *bis*(phthalato)borate 1.134 g (3 mmol) in methanol (50 mL) and stirred for 7 h at 40°C. A microcrystalline precipitate was obtained. Yield: 55%. M.p. 148–150°C. IR (KBr pellets, υcm^{-1}): 1654s (>C=0), 1348s (B–O), 3066w (Ar-ring, CH), 616m (Sn–O), 478s (υ_s Sn–C). ^{1}H NMR (300 MHz, δ ppm from TMS in $CDCl_3$, 300 K): 7.65–7.78 (m, 4H, Ar-ring), 7.26–7.78 (m, 5H, Sn–C_6H_5). ^{13}C NMR (300 MHz, δ ppm from TMS in $CDCl_3$, 300 K): 127–136 (Sn–C_6H_5), 135 (3- or 6-CH), 135 (4- or 5-CH), 136 (1- or 2-C), 170 (>C=O). ^{119}Sn NMR (600 MHz, δ ppm from Me_4Sn in

$CDCl_3$, 300 K): −227 ($(C_6H_5)_3Sn$). Elem. Anal (%) Calcd: C (59.21), H (3.33) and O (18.57). Found: C (59.37), H (3.19) and O (18.12).

2.2.5. *Bis*(phthalato)borate tributyltin(IV). Complex **4** was prepared by the procedure for **1** using tributyltin chloride 0.978 g (3 mmol) and potassium *bis*(phthalato)borate 1.134 g (3 mmol) in methanol (50 mL) and stirred 6 h at 30°C. A white precipitate was obtained. Yield: 40%. M.p. 192–195°C. IR (KBr pellets, $\upsilon\,cm^{-1}$): 1585s (>C=0), 1357s, (B–O), 2961w (Ar-ring, CH), 660w (Sn–O), 480s (υ_s Sn–C), 582w (υ_a Sn–C). ^1H NMR (300 MHz, δ ppm from TMS in $CDCl_3$, 300 K): 7.45–7.66 (m, 4H, Ar-ring), 0.73–0.78, 1.16, 1.23, 1.45 (m, 9H, Sn–C_4H_9). ^{13}C NMR (300 MHz, δ ppm from TMS in $CDCl_3$, 300 K): 12.3, 26.1, 30.6 and 35.8 (Sn–C_4H_9), 129 (3- or 6-CH), 131 (4- or 5-CH), 133.4 (1- or 2-CH), 169 (>C=O). ^{119}Sn NMR (600 MHz, δ ppm from Me_4Sn in $CDCl_3$, 300 K): −289 ($(C_4H_9)_3Sn$). Elem. Anal. (%) Calcd: C (53.41), H (5.56) and O (20.34). Found: C (53.47), H (5.62) and O (20.41).

2.3. *Bacterial and fungicidal activity*

The disc diffusion method [18, 19] was used to measure the antimicrobial activity of the ligand and its complexes. Paper discs (Whatman number 3 filter paper) impregnated with known amounts of target compounds were placed on agar medium seeded with known species of bacteria (*B. anthracius* and *E. coli*) and fungi (*C. albicanes* and *P. italicum*). The ligand and its metal complexes were dissolved in DMSO to prepare the test solution. As the compound diffused into the medium, it produced a gradient of compound concentration. After suitable incubation (24 h for bacteria and 48 hours for fungi at 35 ± 2°C) the activities were determined by the width of inhibition zone (mm) around the disc. Antibacterial activities of the compounds were compared to that of the standard Kanamycine, whereas antifungal activity was compared with Miconazole.

3. Results and discussion

The ligand and its organotin(IV) complexes were formed according to equations (1) and (2) from interaction of potassium *bis*(phthalato)borate with the appropriate organotin chloride in methanol solution/suspension. The compounds were obtained as white solids in fair-to-good yield (table 1), are air stable, and their molar conductances indicate the non-electrolytic nature in water and methanol solution.

$$KBH_4 + 3C_6H_4(COOH)_2 \xrightarrow{\text{solid state}} K[B(C_6H_4(COO)_2)_2] + C_6H_4(COOH)_2 \qquad (1)$$

$$mK[B(C_6H_4(COO)_2)_2] + R_nSnCl_{4-n} \xrightarrow{\text{MeOH/r.t.}} [mB(C_6H_4(COO)_2)_2R_nSn]Cl_{4-n-m} + mKCl \qquad (2)$$

(R = methyl, butyl and phenyl, $n = 2$ and 3, $m = 1$ and 2)

Table 1. Physical properties and elemental analysis of the ligand and its organotin(IV) complexes.

Compounds	M.p.	Molecular formula	Elemental analysis (%)		
			C	H	O
KL	175–180°C	$KC_{16}H_8O_8B$	50.62 (50.79)	2.07 (2.11)	33.98 (33.86)
Bu_2SnL_2	165–168°C	$C_{40}H_{34}O_{16}B_2Sn$	52.47 (52.68)	3.79 (3.73)	28.34 (28.10)
Me_2SnL_2	171–176°C	$C_{34}H_{22}O_{16}B_2Sn$	49.14 (49.33)	2.81 (2.66)	31.05 (30.95)
Ph_3SnL	148–150°C	$C_{34}H_{23}O_8BSn$	59.37 (59.21)	3.19 (3.33)	18.12 (18.57)
Bu_3SnL	192–195°C	$C_{28}H_{35}O_8BSn$	53.47 (53.41)	5.62 (5.56)	20.41 (20.34)

The found, (calculated) values, KL = Potassium *bis*(phthalato)borate, L = *bis*(phthalato)borate ion, Bu = butyl, Me = methyl, Ph = phenyl. NO = not observed.

3.1. *Infrared spectra*

IR spectral bands of ligand and its organotin(IV) complexes, listed in table 2, suggest formation of desired complexes and their structures. The spectrum of ligand showed the absence of O–H adsorption band at 2500–3100 cm^{-1}, indicating deprotonation of phthalic acid. Similarly, absence of B–H absorption in the 2200–2400 cm^{-1} region indicates formation of the desired ligand. The weak absorption at 3084 cm^{-1} is due to C–H stretching vibrations of aromatic ring. The characteristic >C=O stretching band is at 1693 cm^{-1}. The absorption band at 1350 cm^{-1} may be assigned to ν_{sym} (B–O) bond [20], again confirming formation of ligand shown in figure 1. After complexation, the B–O stretching vibrations appear at 1348–1361 cm^{-1} with negligible shift, discounting coordination through esteric oxygen (B–O). The CH stretching vibrations of the aromatic ring for the complexes is at 2926–3066 cm^{-1}. The >C=O stretching vibrations in the complexes at 1638–1585 cm^{-1} have significant shifts from the ligand and clearly indicate formation of a bond through this group. The Sn–O stretch at 616–660 cm^{-1} in all the organotin complexes confirmed the linkage between tin and oxygen. The Sn–C stretching modes of **1** are at 492 cm^{-1} (υ_s Sn–C) and 589 cm^{-1} (υ_a Sn–C), however in **2** were at 486 cm^{-1} (υ_s Sn–C) and 556 cm^{-1} (υ_a Sn–C), indicating linear *trans* configuration [21] of the C–Sn–C moiety (figure 2). Complex **3** shows symmetric Sn–C absorption at 478 cm^{-1} but its antisymmetric stretching vibration was not observed. The Sn–C symmetric and antisymmetric stretching vibration of **4** at 480 cm^{-1} and 582 cm^{-1}, respectively, suggest bent [22] C–Sn–C (figure 3).

3.2. *^{1}H NMR spectra*

^{1}H NMR support and provide additional information about the ligand and its organotin(IV) complexes. Chemical shifts are reported in table 3. In the spectra of the ligand, absence of signal at δ 9–12 indicates removal of protons of phthalic acid. Similarly, the absence of broad signal at 3.4–5.0 ppm due to B–H protons showed deprotonation in formation of ligand. The sharp multiplets at 7.49–7.77 ppm show the presence of aromatic ring protons of phthalic acid.

After complexation the ring protons of phthalic acid shift to 7.45–7.78 ppm in the organotin(IV) complexes. A singlet centered at 0.87 ppm was obtained due to methyl protons of CH_3–Sn in dimethyltin(IV) complexes **2**. The tin-proton coupling constant ^2J (^{119}Sn – ^{1}H) for this complex was 90.0 Hz, showing the hexacoordinate nature of tin [23]. Substituting the value of the coupling constant in the Lockhart Manders

Table 2. IR spectra of the *oxo*-homoscorpionate ligand and its organotin(IV) complexes.

Compounds	Assignments (cm^{-1})					
	ν(Ar–CH)	ν(B–O)	ν(C=O)	ν(Sn–O)	ν_s(Sn–C)	ν_a(Sn–C)
KL	3084	1350	1693			
Bu_2SnL_2	2926	1354	1598	658	492	589
Me_2SnL_2	3016	1361	1638	647	486	556
Ph_3SnL	3066	1348	1654	616	478	NO
Bu_3SnL	2961	1357	1585	660	480	582

ν_s, symmetric; ν_a, anti-symmetric, KL = potassium *bis*(phthalato)borate, L = *bis*(phthalato)borate ion, Bu = butyl, Me = methyl, Ph = phenyl.

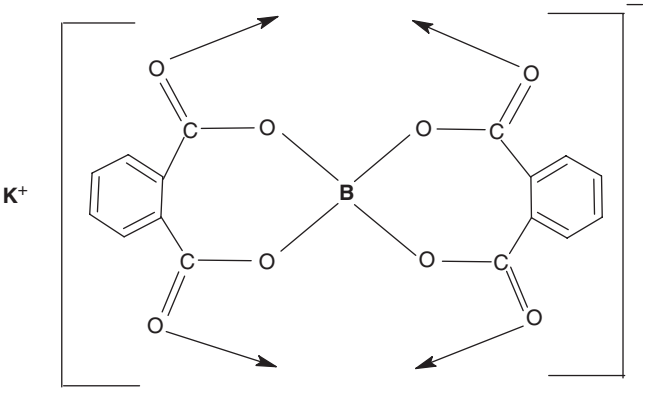

Figure 1. Proposed structure of the multidentate *oxo*-homoscorpionate ligand showing possible coordination sites.

equation [24], the C–Sn–C angle is calculated as 145°. Therefore, in solution, $-SnMe_2$ has a distorted *trans*-octahedral geometry. In dibutyltin(IV) complex **1**, the $Sn–C_4H_9$ signals are a 0.71–0.75 ppm triplet (due to $-CH_3$ group protons) and multiplets (due to $-CH_2-$ group protons) at 1.16, 1.23 and 1.47 ppm. The ^2J ($^{119}Sn-{}^1H$) values of this compound are higher (105 Hz) and the Bu–Sn–Bu angle is 172°, suggesting *trans* octahedral [25]. The ^1H NMR spectrum of tributyltin(IV) complex **4** are at 0.73–0.78, 1.16, 1.23, and 1.45 ppm, quite similar to **1**, but the ^2J ($^{119}Sn - {}^1H$) and Bu–Sn–Bu angles were 99 Hz and 160.5°, respectively. These results again suggest six-coordination and distorted *trans*-octahedral geometry [26]. In **3** the signals of phenyl ring (C_6H_5–Sn) and benzoic acid ring protons were intermixed and appeared as multiplet at 7.26–7.78; due to overlapping signals of protons, ^3J ($^{119}Sn-{}^1H$) cannot be determined, but we assume the same geometry as other triorganotin(IV) derivatives of the *oxo*-homoscorpionate ligand.

3.3. *^{13}C NMR spectra*

In the ^{13}C NMR spectrum of the ligand, the phenyl ring carbons of phthalic acid show three peaks of aromatic carbons at 129, 130.5 and 132.8 ppm and one peak of the carbonyl group appeared at 168 ppm. After coordination, the phenyl carbons show no

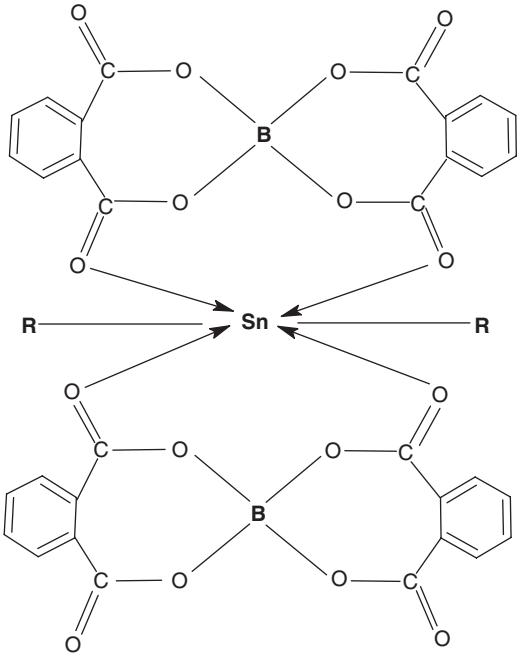

Figure 2. Proposed structure of the diorganotin(IV) *oxo*-homoscorpionate complex (R = methyl and butyl).

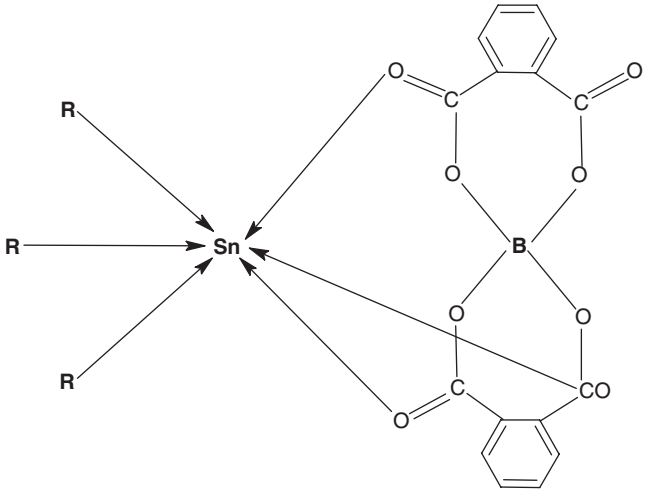

Figure 3. Proposed structure of the triorganotin(IV) *oxo*-homoscorpionate complex (R = phenyl and butyl).

significant shifts, remaining at 129–135 ppm in the organotin(IV) complexes. The signals due to >C=O shift significantly downfield indicating coordination of carbonyl oxygen with organotin. In dimethyltin(IV) complex, the carbonyl group is at 169.91 ppm and the methyl carbon at 11.2 ppm; in the dibutyltin(IV) complex the carbonyl group signal was at 170.16 ppm while the butyl carbons are at 13.95, 26.11,

Table 3. ^{1}H and ^{119}Sn NMR spectra of the *oxo*-homoscorpionate ligand and its organotin(IV) complexes.

Compounds	Ar-protons (δ ppm)	R_n–Sn (alkyl/aryl protons) (δ ppm)	^{119}Sn (δ ppm)	$^{2}J(^{119}Sn - {}^{1}H)$ Hz
KL	7.49–7.77	–	–	–
Bu_2SnL_2	7.46–7.61	0.71–0.75, 1.16, 1.23, 1.47	−250	105
Me_2SnL_2	7.49–7.69	0.87	−267	90
Ph_3SnL	7.65–7.78	7.26 – 7.50	−227	–
Bu_3SnL	7.45–7.66	0.73–0.78, 1.16, 1.23, 1.45	−289	99

KL = potassium *bis*(phthalato)borate, L = *bis*(phthalato)borate ion, Bu = butyl, Me = methyl, Ph = phenyl.

27.15 and 34.2 ppm. Complex **4** shows the carbonyl signal at 169 ppm and the butyl group at 12.3, 26.1, 30.6 and 35.8 ppm. Triphenyltin(IV) complex has a chemical shift at 170 ppm due to carbonyl group and the phenyl carbons (C_6H_5Sn) at 127–136 ppm. All the signals were similar to the literature [27, 28]. ^{13}C NMR spectra of the complexes show a weak satellite due to the interaction of alkyl carbon and ^{119}Sn. The C–Sn–C values observed are not different from the reported values [29], supporting octahedral geometry of all di and triorganotin(IV) complexes.

3.4. *^{119}Sn NMR spectra*

In the ^{119}Sn spectra a singlet is observed in each case; since the compounds are not fluxional, only one isomer is present. The ^{119}Sn chemical shift of the diorganotin(IV) **1** and **2** at $\delta = -250$ and -267 ppm are in agreement with six-coordinate diorganotin(IV) borates involving S–, O– and N–donors [30, 31]. The chemical shifts of **3** and **4** at $\delta = -227$ and -289 ppm indicate hexacoordinate organotin(IV) [32].

3.5. *Electron spray ionization mass spectra*

Simple fragmentations of the ligand and its organotin(IV) complexes dissolved in methanol were detected at 40 V in positive and negative electron spray ionization mass spectra. Positive ion mass spectra gave better data than negative ion mass spectra. The ESI-MS spectra of the compounds have differences of 1, 2 or 3 amu in their calculated and observed mass fragmentations due to the isotopic nature of tin (ten isotopes like ^{115}Sn, ^{117}Sn, ^{119}Sn, ^{120}Sn, etc.), boron (^{10}B and ^{11}B) and carbon (^{12}C and ^{13}C) species. Results show in some cases molecular ion associated with solvents, water and some adduct from the mobile phase solution [33, 34]. The positive ion spectrum of the ligand showed m/z 371 (100%) $[K(B(C_{16}H_8O_8))]$ as a molecular ion peak, showing a stable ligand. Another major fragment of the ligand associated with one molecule of water from the mobile phase solution appeared at 387 (45%) $[K(B(C_{15}H_8O_8))] + H_2O$. Here only two fragmentations of the ligand indicate its stability in liquid as well as solid state. The positive ion mass spectra of dimethyltin(IV) complex shows more fragmentations due to the labile nature of organotin in solution [35]. The important fragments are m/z 930 (42%) $[NaB_2(C_{34}H_{22}O_{16})Sn] + 2CH_3OH + H_2O$, which is associated with two molecules of solvent and one molecule of water from the mobile phase solution. The peak split into a simpler one with elimination of the adduct and the weakly bonded groups of m/z 727 (85%) $[B_2(C_{25}H_{12}O_{15})Sn] + CH_3OH$, m/z 689 (75%) $[B_2(C_{25}H_{12}O_{15})Sn]$, and the

molecular ion peak of this complex appeared at m/z 523 (100%) [B($C_{18}H_{14}O_{10}$)Sn]. Dibutyltin(IV) compound shows a larger number of peaks in both spectra due to lower stability and rigidity. It was dissociated into different fragments [36] including m/z 885 (52%) [B_2($C_{38}H_{30}O_{16}$)Sn] losing two butyl groups, m/z 760 (68%) [B_2($C_{30}H_{30}O_{14}$)Sn] with the elimination of one butyl group and a carbon dioxide. A fragment at m/z 662 shows the highest peak intensity (100%) and is a molecular ion peak ([B_2($C_{23}H_{21}O_{14}$)Sn]). The triphenyltin(IV) complex has high stability in solution and showed only a few fragments at high voltage. A fragment observed at m/z 717 (84%) [B($C_{34}H_{21}O_{10}$)Sn], without losing any groups with the second highest intensity, clearly indicates the stability. When higher voltage is applied, the above fragment lost all organotin moieties. The molecular ion fragmentation **4** in positive ion spectrum was obtained as an adduct of acetonitrile and methanol at m/z 835 (100%) [B($C_{28}H_{35}O_8$)Sn]. This fragmented by losing solvents as well as some weakly bonded organic moieties. Some important fragments were obtained at m/z 690 (42%) [NaB$C_{28}H_{35}O_8$)Sn] + $2H_2O$ and m/z 522 (50%) [NaB($C_{19}H_{08}O_8$)Sn].

3.6. *Bacterial and fungicidal activity*

Bacterial strains such as *B. anthracis* and *E. coli* and fungal strains like *C. albicanes* and *P. italicum* were chosen to examine antimicrobial activity. Chosen bacterial and fungal strains are pathogenic, causing several diseases, are universally distributed in the environment, can be easily cultured in the laboratory, and test results can be obtained very quickly. The antimicrobial activity (*in vitro*) of the ligand and its organotin complexes were determined at two different concentrations (1000 ppm and 2000 ppm) against the strains. The results, summarized in table 4, suggest that ligand is not active against the pathogens, but complexes show significant activity. The degree of inhibition varied with the nature of compound and the data obtained reflects the following findings: (a) the ligand has low activity in both concentrations, weak against *C. albicanes* and *P. italicum* and moderate activity against *E. coli* and *B. anthracius*, (b) the antimicrobial activity increased after metal chelation [37], and (c) the activity of the ligand and its complexes increases as the concentration increases [38].

Table 4. Bactericidal and fungicidal screening data of *oxo*-homoscorpionate ligand and its organotin(IV) complexes (growth inhibition after 24 h at 35 ± 2°C).

Compound	Concentration (ppm)	*B. anthracius*[a]	*E. coli*[a]	*C. albicanes*[b]	*P. italicum*[b]
KL	1000	08	07	6.5	6.5
	2000	11	09	09	10
Bu_2SnL_2	1000	14	13	16	11
	2000	19	21	22	19
Me_2SnL_2	1000	12	12	11	13
	2000	17	16	19	18
Ph_3SnL	1000	15	14	16	13
	2000	24	24	26	22
Bu_3SnL	1000	14	12	15	13
	2000	21	19	21	22

18–30 mm significant active, 10–17 mm moderate active, <10 mm weak active, [a] = bacteria, [b] = fungi, KL = potassium *bis*(phthalato)borate, Me = methyl, Bu = butyl, Ph = phenyl.

4. Conclusion

Organotin(IV) complexes of potassium *bis*(phthalate)borate formed by mixing 1 : 1 and 1 : 2 molar ratios in methanol. The structure of the complexes was proposed on the basis of elemental analysis and spectroscopic methods. The complexes show better antimicrobial activity than the ligand against all pathogenic strains.

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