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Synthesis, spectral and biological studies of organotin(IV) complexes of heteroscorpionate

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A heteroscorpionate ligand, potassium hydrobis(benzoato)(salicylaldehyde)borate (KL), has been synthesized. This was converted into organotin complexes R_2SnL_2 and R_3SnL complexes by mixing and stirring with a methanolic solution/suspension of organotin chloride. The ligand and its complexes were characterized by elemental analyses and spectral studies (IR, ^1H NMR, ^{13}C NMR, ESI mass spectra and Thermo gravimetric analysis (TGA)). Antibacterial and antifungal studies of these compounds were evaluated by the disc diffusion method at variable concentration against three species of bacteria (*Staphylococcus aureus, Klebsiella pneumonia* and *Bacillius subtillis*) and two species of fungi (*Asperjillius fiavus* and *Candida albicans*). It was found that triorganotin derivatives (R_3SnL) of the ligand were more effective as compared with diorganotin derivatives (R_2SnL_2). The organotin complexes of borates were tested for their algicidal activity on the cyanobacterial strains *Aulosira fertilissma, Anabaena species, Anabaena variabilis* and *Nostoc muscorum* and showed high to moderate toxicity towards the above species. The ligand and its complexes were also tested for its pH effect on soil *in vitro* for a duration of more than one month and it was found that they are able to kill pests without damaging the soil quality. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: borates; organotin(IV); heteroscopionate ligand; antimicrobial activity; algicidal activity

INTRODUCTION

Borates have found widespread use in a variety of applications as biocides[1] on account of their moderate to high level of biological activity. They display broad-spectrum activity against bacteria, fungi and insects when coupled with some toxic organic and organometallic compounds.[2,3] Borates along with organometal are commonly used in wood preservation.[4,5] Despite their favorable attributes, high relative activity and low toxicity, low corrosiveness and non-combustionability, the borate can be used in non-exposed applications.[4,6] There is substantial interest in the development of leach-resistant borates. This study aimed to develop biosates, less toxic, hydrolytical and oxidative stable borates, and study their synthetic and systematic physicochemistry and biological activity. This approach was adopted to take advantage of the intrinsic ability of borates ion to form boroesters with acids, aldehydes and phenols.[7] This ester formation provides a mean of production of hydrostatic boron compounds.[8] Such monocarboxylic acid complexes of metals are widely used as antimicrobials and as catalysts.[9–12] The bioassay results have shown that some of the compounds are good acaricidals.[13] The organotin complexes of carboxylates attract considerable attention in structural studies, because there are many possible binding modes.[14] The tin carboxylates adopt a structure that depends on the nature of the alkyl substituent bonded with the tin atom, and the type of carboxylate ligand.[15,16] The compounds of organotin along with boron and carboxylate are very scarce.[17] These esters offer an improvement in performance of an exposed surface over conventional water-soluble borates[18] to prevent biological attack. This system is of particular interest because borates have relatively low mammalian toxicity.[19,20] However information on the antifungal and antibacterial properties of these esters is scanty.[2,3] To achieve broad spectrum and low mammalian toxic organotin complexes,

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we have reported the synthesis and characterization of the scorpionate ligand of boron and its organotin complexes with additional hetero-organic moieties residing on the boron. Their encouraging results on antifungal, antibacterial and algicidal properties have also been reported here.

RESULTS AND DISCUSSION

The complexes were obtained as white solids in fair-to-good yield, by reacting the ligand with the appropriate organotin halides in methanol solution/suspension. All the compounds are air stable and their molar conductances indicate the non-electrolytic nature of the compounds in water and methanol solution.

Spectroscopic characterization

IR spectra support the proposed structure of the ligand and its organotin complexes; Fig. 1–3. The ligand (KL) showed B–H stretching vibration[21] at 2300–2400 cm^{-1} and B–O stretching vibration[22] at 1380–1410 cm^{-1}, showing boron–carboxylate linkage. The B–O stretching frequency in complexes showed insignificant shifting, due to non-involvement of ester oxygen in coordination with organotin. The presence of stretching vibration of Sn–O at 647–670 cm^{-1} in all the compounds suggests the linkage between tin and oxygen of the ligand.[23] The shifted stretching vibration of C═O obtained at 1551–1595 cm^{-1} suggests the formation of coordinate bond through ketonic oxygen with organotin moiety.

The Sn–C signal of complex **1** was observed at 600 cm^{-1}, whereas in complex **2**, 615 cm^{-1} showed the non-planar nature[24–26] of C–Sn–C. In complex **3**, the Sn–C signal was observed at 549 cm^{-1} as a weak peak, showing symmetric linear[24–26] C–Sn–C moiety. A weak doublet signal appeared at 570 cm^{-1}, suggesting the bent structure C–Sn–C moiety[27] in complex **4**.

In proton NMR spectra, a broad singlet at δ 3.4–4.7 showed the presence of B–H in all the compounds.[28] A sharp doublet at δ 7.85–7.96 and 7.4–7.48 showed protons at different locations of the phenyl ring (benzoic acid), whereas a broad multiplet centered at δ 7.2–7.5 was due to ring protons of salicyaldehyde. The appearance of R–Sn group protons with appropriate shifting towards the upfield regions confirmed the desired complexation. The methyl protons of organotin appeared as a singlet at δ 0.929 and the broad multiplet centered at δ 0.75–2.15 was due to butyl protons. The peaks observed in the region δ 7.2–7.9 were assigned to phenyl protons (Sn–C_6H_5) of complex **4** and all other protons gave signals at their usual position.

In ^{13}C NMR spectra, the aromatic carbon signals were obtained as sharp multiplets at 118–135 ppm, undergoing only a slight displacement during the complex formation. A weak singlet observed in the range 168–172 ppm was due to carbonyl carbon of the carboxylic group. The downfield shifting of the signals suggested the coordination of carbonyl group with organotin atom. Alkyl carbon signals (R–Sn) for butyl observed at 13.5, 25.5, 26.8 and 30.4 ppm, methyl at 16.8 ppm and phenyl (C_6H_5–Sn) were intermixed with aromatic carbon signals.

The electron spray mass ionization spectra of the compound shows simple fragmentation pattern. A significant fragment at m/z 402 was attributed to negative-ion spectra for the ligand ($C_{21}H_{16}O_6BK$). The peaks in complex **1** occurred at m/z 1089, 842 and 595 whereas in complex **2** they were at m/z 682 and 561 and in complex **3** at m/z 838, 674 and 599. More fragmentations were observed in diorganotin derivatives due to their inferior stability. In some cases the molecular ion was also associated with the solvent, water molecules and some adduct ions from the mobile phase solution.[29,30]

Thermal studies

Table 1 summarizes some results of thermal analysis of the ligand and its metal complexes. It shows that they are thermally stable to a varying temperature. The complexes showed a gradual loss in weight up to 100–110 °C, indicating the presence of water molecule. The proposed decomposition of the complexes occurred by fragmentation and the thermal degradation of the organic part in the metal complexes, resulting in the corresponding oxyborates and tin oxides as a residue. The ligand and complexes **1**–**3** show higher stability over 150 °C and they lose the organic moiety first followed by CO_2 and H_2O. In complexes **1** and **3**, SnO_2 was also lost up to 700 °C, however in complexes **2** and **4** the residue was left in the form of the oxyborates and tin oxide. Complex **1** was comparatively less stable and it lost all organic moiety as well as SnO_2 due to its bulkier nature, which causes instability of the complex. Complex **4** was very stable up to 800 °C, leaving more than 40% residue.

Algicidal activity

The results of test strains varied from the ligand to the diorganotin and triorganotin derivatives of borates.[31] In the ligand 100 ppm concentration showed little effect, i.e. the cell count was less. This means there was no further cell growth. Complex **1** gave a lethal effect above 10 ppm, whereas complex **2** was very potent among these compounds, showing inhibition even below 10 ppm. However, complex **3** showed inhibition starting from 16 ppm. A different inhibition pattern was observed in complex **4**. It released its toxicity gradually, hence its effect appeared after 15 days and became comparable to complex **2**. The final lethal gradation of these complexes was $2 \geq 4 > 1 > 3 >$ KL as shown in Fig. 4.

Antimicrobial activity

It is well documented that organotin complexes with borate possess biological activity.[1] The antibacterial and antifungal activity of the synthesized ligand and its organotin complexes were studied against three bacteria (*Staphylococcus aureus, Klebsiella pneumonia* and *Bacillius subtillis*) and two fungi (*Asperjillius fiavus* and *Candida albicans*). The results from

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Table 1. The TGA data of heteroscorpionate ligand and its organotin complexes

Compound	Temperature range (°C)	Weight lost (%)		Group/Moiety lost	Metal oxide residue (%)	
		Calculated	Found		Calculated (group)	Found
Ligand (KL)	32–115	9.4	8.81	K		
	115–225	25.99	26.53	C_7H_5O		
	225–575	27.99	27.65	$C_7H_5O_2$		
	575–700	35.99	36	$C_7H_5O_4B$		
Bu_2SnL_2	80–154	4.47	4.21	CO_2	7.12	7.19
	154–230	27.36	27.75	$C_{18}H_{21}O_2$	(B_2O_3)	
	230–342	60.1	60.99	$C_{31}H_{31}O_5$		
Bu_3SnL	60–306	54.88	53.89	$C_{26}H_{37}O_2$	29.17	29
	036–594	11.57	12.54	C_7H_5	($SnO_2 + BO_2$)	
	594–850	4.51	4.58	H_2O		
Me_2SnL_2	85–425	68.15	68.99	$C_{44}H_{36}O_4$	13.80	14.99
	425–825	16.81	16.52	SnO_2	(H_3BO_3)	
Ph_3SnL	85–245	21.22	22.70	$C_{12}H_{10}$	39.92	40.37
	245–425	36.52	36.93	$C_{18}H_{15}O$	($SnO_2 + H_3BO_3 + C_6H_5$)	

KL = heteroscorpionate ligand; Me = methyl; Bu = butyl; Ph = phenyl.

Table 2 reflect that the ligand exhibited weak biological activity against microorganisms. During the experiment, complex **2** was found to be the most inhibitory compound at the lowest concentration. In the case of antifungal activity it showed the highest inhibitory zone against *A. flavus*, i.e. 18 mm (100 ppm) and 24 mm (300 ppm). Complexes **1** and **3** show its highest activity against *C. albicans* but lowest activity against *A. flavus*. The antibacterial activity of complex **2** shows inhibition of 16 mm at 100 ppm and 19 mm at 300 ppm as the highest inhibitory against *S. aureus.* However, it gave its lowest inhibitory zone of 13 mm against *B. subtilis* when employed with 100 ppm concentration. Complex **1** revealed its highest inhibitory results at 14 mm (1500 ppm) and 17 mm (2000 ppm) against *B. subtilis*. Similarly, complex **3** showed its highest inhibitory zone against *K. pneumonia*, i.e. 12 mm (1500 ppm) and 14 mm (2000 ppm). Conclusively, it may be assumed from the resulting data that antifungal activity as well as antibacterial activity of the ligand is significantly enhanced on complexation and also found that the inhibitory effect increased with the concentrations increment. Chelation reduced the polarity of the metal ion in the complex[32] considerably because of the partial sharing of its positive charge with the donor groups and possible π electron delocalization with the whole chelating ligand, which increased the lyphophilic nature of the central atom and favored its permeation through the lipid layer of the membrane.

Chemical impact on soil

As noted, soil pH and organic matter strongly affect soil functions and plant nutrient availability.[33] Our test results in Fig. 5 show that soil quality is not damaged by the organotin-based complexes; the experiment showed that an insignificant effect was observed on the quality of soil. Up to 15 days the alkanity of the soil decreased; however, after 15 days the alkanity increased with the addition of organotin complexes. It may be due to the evaporation of water, which increased the concentration of salt. The tin metal remained associated with organic moiety, which did not cause considerable infertility or production problems in the soil. Therefore we conclude that our compounds do not affect or degrade the quality of soil; however it potentially affects microorganisms, which utilize more nutrients from the soil. Thereby the soil will become less productive.

CONCLUSION

Our synthetic organotin borates and their derivatives are useful to control pests and microorganisms and maintain the quality of soil because they did not release any toxic metal ions; after very long exposure of the organotin it dissociates to inorganic tin, which does not harm the fertility of soil.[34,35] Therefore, these organotin borates and derivatives are superior to other marketed pesticides, whose persistence and survival are many days to years, and circulate in food chain and cause harm.

EXPERIMENTAL SECTION

Material and methods

Potassium borohydrides and all organotin chloride were purchased from Acros Organics and Fluka, respectively, and were used as received. All the solvents were purchased from Merck. The reactions were carried out under atmospheric

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conditions and samples for microanalysis were dried out *in vacuo* to constant weight. Melting point was recorded on a Metrix melting point apparatus. IR spectra were recorded on a Perkin-Elmer model 1620 FT-IR spectrometer using KBr discs. TGA Data were obtained using a TA-2000 Dupont (USA) instrument. Proton NMR spectra were carried out on a Bruker-DPX, 300 MHz. spectrometer, using tetramethyl silane (TMS) as an internal standard. ^{13}C NMR spectra were carried out on an Instrum-DPX, 300 MHz. spectrometer. Positive and negative ESI mass spectra were measured on a TOF analyzer (LC/MS, Water India Ltd, model LCP). The samples were dissolved in DMSO and methanol and analyzed by direct infusion using acetonitrile–water (1 : 1 mixture) as mobile phase

Synthesis

Synthesis of potassium hydrobis(benzoato) (salicylaldehyde)borate (KL)

The heteroscorpionate ligand (KL) was formed in the following two steps.

(A) *Potassium dihydrobis(benzoato)borate* [$KH_2B(Bz)_2$]—benzoic acid (6.10 g, 50 mmol) was dissolved in ethanol (100 ml) and stirred for a while in a 250 ml Schlenk flask. Then finely divided potassium borohydride (1.35 g, 25 mmol) was added to the flask and heated at 50 °C. The flask was attached with a gas collecting device through an air condenser. The reaction was stopped when 1082 ml (50 mmol) of hydrogen gas had evolved. A white crystalline solid compound appeared on cooling at room temperature; the solid was filtered and washed with acetone and diethyl ether. It was then air-dried, and the compound was recrystallized in methanol, yielding 55%; the m.p. was >300 °C and the compound was characterized by means of IR and ^1H NMR spectra.

(B) *Potassium hydrobis(benzoato)(salicylaldehyde)borate*—$KH_2B(Bz)_2$ (2.94 g, 10 mmol) was stirred in methanol (70 ml) in a 250 ml Schlenk flask. Then salicylaldehyde (1.81 ml, 10 mmol) was added and the contents of the flask were heated at 50–70 °C until 216 ml (10 mmol) of hydrogen gas had evolved. The solution was filtered hot and was left for crystallization for 48 h. A whitish yellow flat type of crystals was obtained. The crystals were washed with diethyl ether and acetone. This process was repeated three times and the obtained crystals were vacuum dried, yielding 67%; the m.p. was >300 °C. IR (KBr, cm^{-1}): 1398s (B–O), 1595s (C═O), 2360w (B–H), 1200–1400s (Ar. C–H). ^1H NMR (D_2O, 298 K): δ 4.7–4.9 (sbr, 1H, B–H), 7.42–7.52 [s. multiplet, 4H, (phenyl ring)], 7.94 [s. multiplet, 2H, (phenyl ring)], 7.41[s. multiplet, 1H, 5-C–H (salicylaldehydic ring)], 7.52 [s. multiplet, 2H, 4,6-C–H (salicylaldehydic ring)], 7.58 [s. multiplet, 1H, 3-CH (salicyaldehydic ring)]. ^{13}C NMR (DMSO, 300 K): δ 127.8–135.5 (aromatic carbons), 168.53 (>C═O). Anal. found: C, 61.02; H, 3.86; O, 23.26; calcd for $C_{21}H_{16}O_6BK$: C, 61.83; H, 3.86; O, 23.18%.

Complex formation

Hydrobis(benzoato)(salicylaldehyde)borate dibutyltin(IV)

Methanolic solution (50 ml) of dibutyl tindichloride (0.6077 g, 2 mmol) was added to 50 ml of a solution of the ligand (KL) (1.656 g, 4 mmol) at room temperature. The mixture was stirred for 6 h at 40 °C. The suspension of KCl was separated by filtration and then filtrate was concentrated under reduced pressure to give the colorless precipitate, which was again filtered. The precipitate obtained was washed with diethyl ether. The microcrystalline compound was recovered in solid state with 67% yield and m.p. >300 °C. IR (KBr, cm^{-1}): 1385s (B–O), 1552s (C═O), 2340w (B–H), 669w (Sn–O), 600m (Sn–C). ^1H NMR (DMSO, 298 K): δ 3.93 (sbr, 1H, B–H), 7.86–7.89 [s, multiplet, 5H (phenyl ring)], 7.29–7.39 [s, multiplet, 4H, (salicylaldehydic ring)], 0.75, 1.5, 2.5 [m, 9H (butyl-Sn)]. ^{13}C NMR (DMSO, 300 K): δ 128.4–132.5 (aromatic carbons), 171.7 (>C═O), 13.5, 25.5, 26.8 and 30.4 (Sn–C_4H_9). Anal. found: C, 61.91; H, 5.20; O, 19.94; calcd for $C_{50}H_{50}O_{12}B_2Sn$: C, 61.03; H, 5.08; O, 19.53%.

Hydrobis(Benzoato)(salicyalldehyde)borate tributyltin(IV)

Complex **2** was prepared similarly to complex **1**, using tributytin chloride (0.65198 g, 2 mmol) and the ligand (0.828 g, 2 mmol) in methanol (50 ml) at 40 °C. A white solid in 38% yield was obtained which did not melt up to 300 °C. IR (KBr, cm^{-1}): 1383s (B–O), 1583s (C═O), 2310w (B–H), 661w (Sn–O), 615w (Sn–C). ^1H NMR (DMSO, 298 K): δ 4.23 (sbr, 1H, B–H), 7.86–7.89 [s, multiplet, 5H (phenyl ring)], 7.29–7.39 [s, multiplet, 4H (salicylaldehydic ring)], 0.85, 1.6, 2.7 [m, 9H (butyl-Sn)]. ^{13}C NMR (DMSO, 300 K): δ 125.4–137.8 (aromatic carbons), 173.7 (>C═O), 13.1, 25.7, 27.8 and 39.2 (Sn–C_4H_9). Anal. found: C, 59.44; H, 6.51, O, 14.62; calcd for $C_{33}H_{43}O_6BSn$: C, 59.54; H, 6.46; O, 14.43%.

Hydrobis(Benzoato)(salicylaldehyde)borate dimethyltin(IV)

Complex **3** was prepared similarly to complex **1** using dimethyltin dichloride (0.4393 g, 2 mmol) and ligand (1.656 g, 4 mmol) in methanol (50 ml) at 50 °C, a solid off-white precipitate was formed and it was recrystalized in methanol to yield 57% with an uncorrected melting point. IR (KBr, cm^{-1}): 1410s (B–O), 1542s (C═O), 2325w (B–H), 647s (Sn–O), 525–549w (Sn–C). ^1H NMR (CD_3OD, 298 K): δ 4.76 (sbr, 1H, B–H), 7.41 [s, multiplet, 2H (phenyl ring)], 7.74–7.96 [s, multiplet, 3H (phenyl ring)], 7.36, 7.38, 7.48, 7.50 [s, multiplet, 4H (salicylaldehydic ring)], 0.29 [w, 3H, (CH_3–Sn)]. ^{13}C NMR (DMSO, 300 K): δ 118.69–133.54 (aromatic carbons), 169.34 (>C═O), 16.88 (Sn–CH_3). Anal. found: C, 58.83; H, 4.14; O, 21.41; calcd for $C_{44}H_{38}O_{12}B_2Sn$: C, 58.73; H, 4.22; O, 21.35%.

Hydrobis(Benzoato)(salicylaldehyde)borate triphenyltin(IV)

Complex **4** was prepared similar to complex 1 by using dimethyltin dichloride (0.0828 g, 2 mmol) and ligand

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(0.7717g, 2 mmol) in methanol (50 ml) at 50 °C. A solid white precipitate was obtained; yield 60%, m.p. >300 °C IR (KBr, cm^{-1}): 1390s (B–O), 1551s (C═O), 2335w (B–H), 668w (Sn–O), 570m (Sn–C), 1200–1400s (Ar, C–H). ^{1}H NMR (DMSO, 298 K): δ 3.47 (sbr, 1H, B–H), 7.86–7.89 [s, multiplet, 5H (phenyl ring)], 7.64–7.68 [s, multiplet, 4H (salicyaldehydic ring)], 7.01, 7.26, 7.27 [s, multiplet, 5H (C_6H_5–-Sn)]. ^{13}C NMR (DMSO, 300 K): δ 127.50–134.70 (aromatic carbons), 168.5 (>C═O), 127.50–134.70 (Sn–C_6H_5). Anal. found: C, 64.11; H, 4.15; O, 13.39; calcd for $C_{39}H_{31}O_6BSn$: C, 64.55; H, 4.27; O, 13.24%.

Biological activity

The cyanobacterial strains *Aulosira fertilissma*, *Anabaena species*, *Anabaena variabilis* and *Nostoc muscorum* were procured from NCCU-BGA, IARI, New Delhi. The test strains were raised in BG–11 medium.[36] The stock and test cultures were maintained at 30 ± 1 °C in a BOD cabinet illuminated with 20 W fluorescent tube providing a light intensity of 2000 ± 200 LUX around the cultured vessels, following a light/dark cycle of 12 : 12 h. In order to examine the effect of ligand and its organotin complexes on these strains, they were added separately to the (fresh) growth medium in calculated amounts to obtain the final concentrations of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90 and 100 ppm.

The paper (cellulose) disk diffusion method[37] was employed to study the antimicrobial effects against the pathogens. Two different concentrations of the ligand and its organotin complexes were prepared in DMSO in a hot water bath to examine the variable concentration effects. The activity was assessed by measuring the inhibition zone diameter around the cellulose disk. The resulting activity data of the ligand and organotin complexes **1, 2** and **3** with kanamicine and miconazole as standard drugs for bacteria and fungi, respectively, are tabulated in Table 2. The sterilized Wattman filter paper disks of 6 mm diameter were dipped in the solutions of different concentrations of organotin complexes

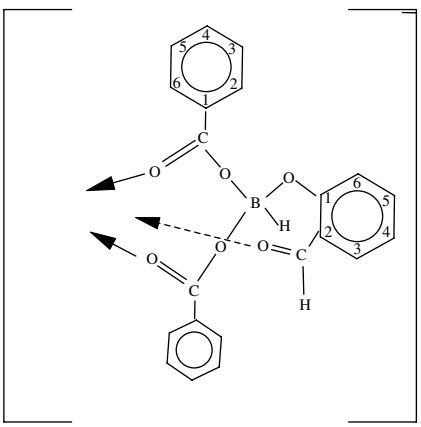

Figure 1. Structure of the tridentate heteroscorpionate ligand showing the possible coordination sites.

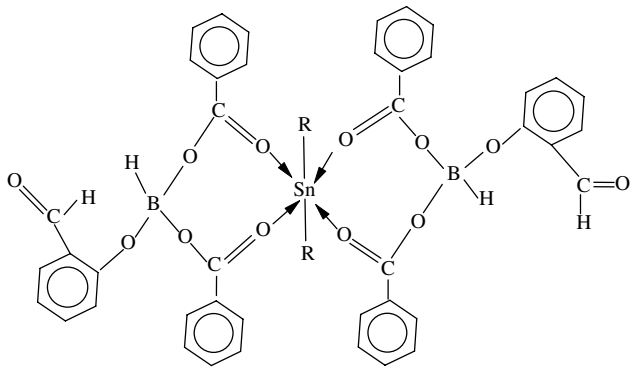

Figure 2. Proposed structure of the diorganotinborates complex (R = methyl and butyl).

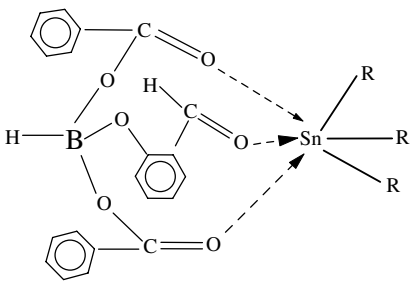

Figure 3. Proposed structure of the triorganotinborates complex (R = phenyl and butyl).

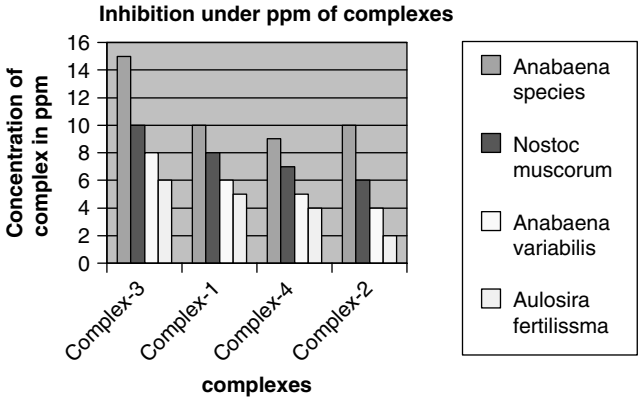

Figure 4. Inhibition under ppm of highest concentration of organotin(IV) complexes.

and were then placed on the surface of the agar. The plates were incubated at 37 °C for 24 h for bacteria and 72 h for fungi.

Soil testing

Ten fresh soil samples (garden soil, rich nutrients) were taken each for the ligand and its organotin complexes **1**–**4**, to check the effect of these compounds on the soil pH. All the compounds were mixed with the soil samples in different

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Table 2. Antimicrobial eveluation of heteroscorpionate ligand and its organotin(IV) complexes

Compound	Concentration (ppm)	*S Aureus*	*K. Pneumonia*	*B. subtilis*	*A. fiavus*	*C. albicans*
KL	1500	07	07	09	09	07
	2000	08	09	10	11	08
Bu_2SnL_2	1500	13	11	14	12	15
	2000	15	16	17	15	20
Bu_3SnL	100	16	15	13	18	16
	300	19	18	18	24	24
Me_2SnL_2	1500	10	12	09	11	13
	2000	13	14	15	15	16
Kanamicine (standard)		32	29	31	—	—
Micronazole (standard)		—	—	—	34	29

KL = heteroscorpionate ligand; Me = methyl; Bu = butyl; Ph = phenyl.

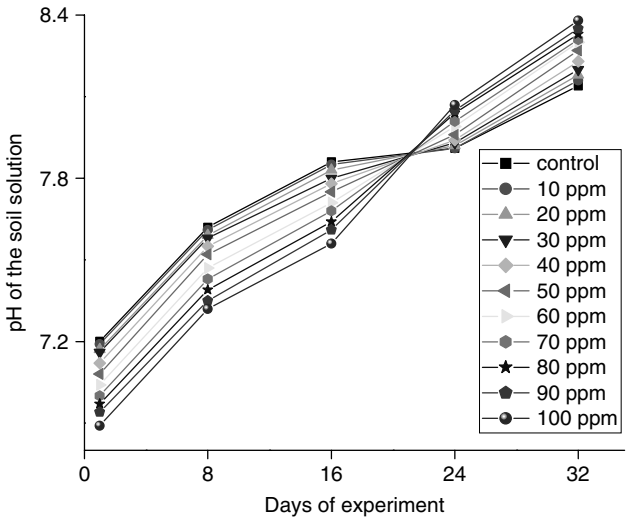

Figure 5. Effect of complexes on the soil pH.

concentrations varying from 10 to 100 ppm in a 500 ml beaker. The pH of all the soil sample solutions was checked with a pH meter in a fixed interval of time. The same setup of the fresh soil was also considered without the ligand or its complexes as a standard sample. The pH of this solution was also checked. All the beakers containing the soil samples were kept at room temperature and covered with aluminum foil during the experiment.

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