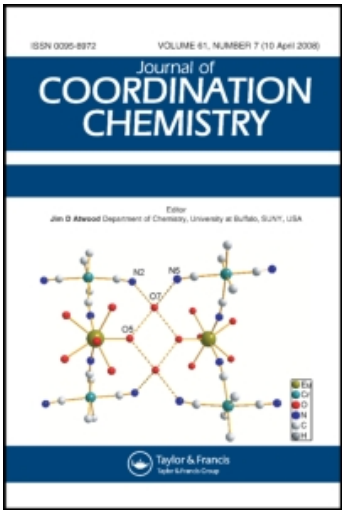

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Structural and antimicrobial studies of potassium hydrotris(2-mercaptobenzathiazolyl)borate and its organotin(IV) derivatives

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Potassium hydrotris(2-mercaptobenzathiazolyl)borate (KL) was formed by the solid state reaction of potassium borohydride and 2-mercaptobenzathiazoline. This ligand was reacted with R_nSnCl_{4-n} (R = methyl, butyl and phenyl, $n = 2$ and 3) in dichloromethane and four different neutral organotin(IV) complexes were obtained. All compounds were characterized by elemental analyses, FT-IR and multinuclear NMR (^1H, ^{13}C, ^{11}B and ^{119}Sn) spectroscopy. Spectroscopic data indicate the six-coordinated nature of tin in its di and triorganotin(IV) complexes.

To check the toxic potential of the ligand and its organotin(IV) complexes, selected bacterial (*E. coli*, *S. epidemidis* and *S. dysenteriae*) and fungal (*A. niger*, *C. albicanes* and *A. flaves*) species were screened. The results were compared with standard drugs kinamycine and miconazole for bacterial and fungal activity, respectively. The toxicity of the organotin(IV) complexes depends on the number and nature of organic groups attached to the tin atom; triorganotin(IV) complexes exhibit better inhibition than diorganotin(IV) complexes. All compounds were also screened on the cyanobacterial strains (*Aulosira fertillissma*, *Anabaena variabilis*, *Anabaena species* and *Nostoc muscorum*). Results show that the compounds inhibit the growth of organisms at very low concentration.

Keywords: Organotin(IV); 2-Mercaptobenzathiazoline; Borate; Antibacterial; Antifungal; Antialgal

1. Introduction

The hydrotris(pyrazolyl)borate (Tp) ligand was introduced into coordination chemistry by Trofimenko more than 30 years ago [1], and in various substituted forms has developed into one of the most versatile tripodal auxiliary ligands in bio-inorganic coordination chemistry [2–4]. Particular interest is devoted to special azolyl rings, such as triazolyl [5–8], tetraazolyl [9], 3,5-bis(bistrifluoromethyl) pyrazolyl [10], indazolyl [11, 12], poly(indazolyl) and poly(2-mercaptothiazolyl)borate [13] etc., which have

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excellent biological properties with transition metals, main group metals [14] and organotin(IV) compounds [15, 16].

The chemistry of organotin(IV) derivatives is of interest [17] not only because of the environmental consequences of the widespread use of their compounds [18], but also due to increasing importance for bactericides [19], fungicides [20], algaecides [16] and antitumor agents [21]. Various triorganotin compounds have been reported [22, 23] to be effective against mosquito larva and adduct mosquitoes responsible for malaria and yellow fever; various phenyltin derivatives show cardiovascular activity [24]. Structure activity relationships in such compounds are controversial.

In previous work [16], we synthesized and characterized organotin(IV) complexes containing oxo-borates having good biological activity. We describe in this paper the synthesis, structural study and antimicrobial activity (antibacterial, antifungal and antialgal) of a new 2-mercaptobenzathiazolylborate ligand and its organotin(IV) complexes. 2-Mercaptobenzathiazoline was chosen because of importance in biological systems and for pharmaceutical activity.

2. Experimental

2.1. *Materials and methods*

Potassium borohydride and all organotin chlorides were purchased from Acros Organics and Fluka Chemicals respectively and used as received. 2-Mercaptobenzathiazoline was purchased from Aldrich Chemicals and used as received. The solvents were purchased from E. Merck (India Ltd.). Solvents for microanalysis were dried *in vacuo* to constant weight. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. FT-IR spectra were recorded from 4000–400 cm^{-1} with a Perkin-Elmer system 1620 FT-IR instrument. ^{1}H, ^{13}C, ^{11}B and ^{119}Sn NMR spectra of the compounds dissolved in deuterated DMSO were recorded at 300 K using a Bruker Avance II 400 NMR, 400 MHz frequency spectrometer. The chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (^{1}H and ^{13}C), tetramethyltin (^{119}Sn) and borontrifluoride (^{11}B).

2.2. *Synthesis of compounds*

2.2.1. Potassium hydrotris(2-mercaptobenzathiazolyl)borate (KL). Fine powdered potassium borohydride (1.08 g, 20 mmol) and 2-mercaptobenzathiazoline (13.38 g, 80 mmol) were placed in a 250 mL round bottom flask connected with a gas collecting device through a condenser. This assembly was placed in an oil bath apparatus and heated to 150 °C with continuous stirring with evolution of hydrogen commencing and the temperature raised to 220°C until 60 mmol (1390 mL, room temp. 35 °C) of hydrogen gas evolved. After allowing the mixture to cool to room temperature, 20 mL of dichloromethane was added and the mixture was stirred for 15 min. Solid separated and this process was repeated three times. The solid was dried under vacuum dessicator at room temperature and 1 atm pressure. The solid compound was washed with 20 mL THF resulting in a light yellowish solid (92% yield) that decomposed over 172–175°C.

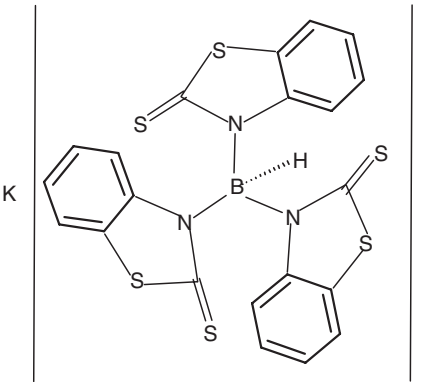

Figure 1. Proposed structure of potassium hydrotris(2-mercaptobenzathiazolyl)borate.

FTIR (KBr pellets, υ cm^{-1}): 1438 (B–N), 995 (C=S), 2358 (B–H) and 3010 (C–H). ^{1}H NMR (600 MHz, δ ppm from TMS in DMSO): 7.01–7.53 ppm (m, 4H, Ar–H), 5.3 ppm (s, 1H, BH). ^{13}C NMR (400 MHz, 300 K, δ ppm from TMS in DMSO): 112–140 ppm (Ar-carbons) and 192.25 ppm (>C=S). ^{11}B NMR (400 MHz, 300K, δ ppm from BF_3 in DMSO) – 8.77. Elem. Anal. (%), Calcd: C, 45.90; H, 2.36; N, 7.65. Found: C, 45.86; H, 2.29; N, 7.47.

2.2.2. Hydrotris(2-mercaptobenzathiazolyl)borate triphenyltin(IV) (1). A 25 mL solution of triphenyltin chloride (0.5775 g, 1.5 mmol) in dichloromethane was added to 25 mL solution of potassium hydrotris(2-mercaptobenzathiazolyl)borate (0.8235 g, 1.5 mmol). The resulting solution was stirred for one hour; a white precipitate of potassium chloride formed which was separated through filtration. The resulting filtrate was again stirred 20 h and then filtered. The filtrate was concentrated on a hot heating plate at ~40°C and a precipitate formed. This was crystallized with chloroform and n-hexane (1:3). A light yellow solid was obtained in 78% yield and melted at 185–189°C.

FTIR (KBr pellets, υ cm^{-1}): 1471 (B–N), 1070 (C=S), 2357 (B–H), 2986 (C–H) and 580 (Sn–C). ^{1}H NMR (400 MHz, 300 K, δ ppm from TMS in $CDCl_3$): 7.18–7.54 ppm (m, 4H, Ar–H), 4.4 ppm (s, 1H, BH), 7.81–7.99 (m, 5H, Ar–Sn). ^{13}C NMR (400 MHz, 300 K, δ ppm from TMS in $CDCl_3$): 112–141 ppm (Ar-carbons), 189.11 ppm (>C=S) and 112–143 ppm (C_6H_5–Sn). ^{11}B NMR (400 MHz, 300 K, δ ppm from BF_3 in $CDCl_3$): −3.37. ^{119}Sn NMR (600 MHz, δ ppm from $(CH_3)_4Sn$ in $CDCl_3$): −348. Elem. Anal. (%) Calcd: C, 54.41; H, 3.25; N, 4.88. Found: C, 53.89; H, 3.39; N, 5.02.

2.2.3. Hydrotris(2-mercaptobenzathiazolyl)borate tributyltin(IV) (2). This complex was synthesized according to the procedure of **1** using tributyltin chloride (0.40 mL, 1.5 mmol) and potassium hydrotris(2-mercaptobenzathiazolyl)borate (0.8235 g, 1.5 mmol) in 75 mL dichloromethane. The obtained solid was dissolved in (1 : 3) chloroform and n-hexane and left overnight to get crystals. A yellow solid was obtained in 62% yield and melting point 125–127°C.

FTIR (KBr pellets, υ cm^{-1}): 1453 (B–N), 1061 (C=S), 2354 (B–H), 2998 (C–H) and 588 (Sn–C). ^{1}H NMR (400 MHz, 300 K, δ ppm from TMS in $CDCl_3$): 7.23–8.39 ppm

(m, 4H, Ar–H), 4.6 ppm (s, 1H, BH), 1.1–1.72 (m, 9H, C_4H_9–Sn). ^{13}C NMR (400 MHz, 300 K, δ ppm from TMS in $CDCl_3$): 113–143 ppm (Ar-carbons), 187.25 ppm (>C=S) and 14–28 ppm (C_4H_9-Sn). ^{11}B NMR (400 MHz, 300 K, δ ppm from BF_3 in $CDCl_3$): −3.97. ^{119}Sn NMR (400 MHz, 300 K, δ ppm from $(CH_3)_4Sn$ in $CDCl_3$): −318. Elem. Anal. (%) Calcd: C, 49.59; H, 5.00; N, 5.25. Found: C, 49.32; H, 4.87; N, 5.49.

2.2.4. Hydrotris(2-mercaptobenzathiazolyl)borate dibutyltin(IV) (3). Complex **3** was synthesized according to the procedure of **1** by using dibutyltin dichloride (0.304 g, 1 mmol) and potassium hydrotris(2-mercaptobenzathiazolyl)borate (1.098 g, 2 mmol) in 70 mL of dichloromethane. Obtained solid was dissolved in (1 : 3) chloroform and n-hexane and left overnight to get crystals. A dark yellow solid was obtained in 57% yield and melting point 158–162°C.

FT-IR (KBr pellets, υ cm^{-1}): 1446 (B–N), 1068 (C=S), 2368 (B–H), 2995 (C–H) and 516 (Sn–C). ^{1}H NMR (400 MHz, 300 K, δ ppm from TMS in $CDCl_3$): 7.19–7.71 ppm (m, 4H, Ar–H), 4.2 ppm (s, 1H, BH), 0.63–1.21 (m, 9H, C_4H_9–Sn). ^{13}C NMR (400 MHz, 300 K, δ ppm from TMS in $CDCl_3$): 113–142 ppm (Ar-carbons), 189.60 ppm (>C=S) and 13–29 ppm (C_4H_9–Sn). ^{11}B NMR (400 MHz, 300 K, δ ppm from BF_3 in $CDCl_3$): −5.43. ^{119}Sn NMR (400 MHz, 300 K δ ppm from $(CH_3)_4Sn$ in $CDCl_3$): −378. Elem. Anal. (%) Calcd: C, 47.88; H, 3.51; N, 6.70. Found: C, 47.39; H, 3.39; N, 6.81.

2.2.5. Hydrotris(2-mercaptobenzathiazolyl)borate dimethyltin(IV) (4). This complex was synthesized according to the procedure of **1** using dimethyltin dichloride (0.304 g, 1 mmol) and potassium hydrotris(2-mercaptobenzathiazolyl)borate (1.098 g, 2 mmol) in 70 mL of dichloromethane. The resulting solid was dissolved in (1 : 3) chloroform and *n*-hexane and left overnight to get crystals. A light yellow solid was obtained in 71% yield having melting point 165–170°C.

FT-IR (KBr pellets, υ cm^{-1}): 1455 (B–N), 1064 (C=S), 2362 (B–H), 2967 (C–H) and 527 (Sn–C). ^{1}H NMR (400 MHz, 300 K, δ ppm from TMS in $CDCl_3$): 7.19–7.78 ppm (m, 4H, Ar–H), 4.1 ppm (s, 1H, BH), 0.63–1.21 (s, 3H, CH_3–Sn). ^{13}C NMR (400 MHz, 300 K, δ ppm from TMS in $CDCl_3$): 112–141 ppm (Ar-carbons), 189.69 ppm (>C=S) and 16 ppm (CH_3–Sn). ^{11}B NMR (400 MHz, 300 K, δ ppm from BF_3 in $CDCl_3$): −9.71. ^{119}Sn NMR (400 MHz, 300 K, δ ppm from $(CH_3)_4Sn$ in $CDCl_3$): −389. Elem. Anal. (%) Calcd: C, 45.16; H, 2.73; N, 7.18. Found: C, 44.98; H, 2.79; N, 7.52.

2.3. *Antimicrobial studies*

2.3.1. Antibacterial and antifungal activity. The disc diffusion method [25] was used to measure the antimicrobial activity of potassium hydrotris(2-mercaptobenzathiazolyl)-borate and its organotin(IV) complexes. The paper disc (Whatman number 3 filter paper), impregnated with known concentration of compounds, were placed on agar medium seeded with known species of fungi (*A. niger*, *C. albicanes* and *A. flaves*) and microbes (*E. coli*, *S. epidedemis* and *S. dysentry*). The ligand and its metal complexes were dissolved in DMSO to prepare the test solution. Different concentrations, *i.e.* 500 ppm and 1000 ppm, were considered. After suitable incubation (24 h for bacteria and 48 h for fungi at 36 ± 1°C) the activities were determined by the width of inhibition

zone in millimeters (mm) around the compound disc. Antibacterial activities of the compounds were compared to that of the standard kanamycine, whereas antifungal activity was compared with miconazole.

2.3.2. Algicidal activity. Four test strains, *Aulosira fertillissima*, *Anabaena variabilis*, *Nostoc muscorum* and *Anabaena species*, were procured from NCCU–BGA, IARI, New Delhi (India). The test strains were raised in BG–11 [26] medium without sodium nitrate, since it is a nitrogen fixation cyanobacteria. When culture/medium is supplemented with nitrile, nitrate or ammonium, heterocysts as well as nitrogenase disappear; this nitrogen fixation is self-controlled as soon as the production of ammonium exceeds bioconsumption [27]. The media was sterilized in an autoclave (Yorco, India) maintaining 15 lb/m^2 pressure for 15 min. For this, 50 mL inoculum was suspended in 500 mL sterile medium taken in 1000 mL EM flask (three sets) grown for 28 days, at $30 \pm 2^{\circ}$C under light intensity of 2000 lux (± 200) provided by 20 W fluorescent tubes following a 16 : 8 hours light/dark regime. Shaking was done at regular intervals. pH 7.5 was maintained for the appropriate growth of the test microorganisms.

Concentrations of 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 ppm of the ligand and its organotin(IV) complexes were used on these strains. Complexes **1**–**4** affect the growth of cyanobacteria under laboratory conditions differently. For "control" sets, the test microorganism was grown without adding any compound. For evaluating toxicity of these complexes, they were separately added to the fresh medium in calculated amounts to obtain final concentration of 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 ppm.

3. Results and discussion

The ligand and its organotin(IV) complexes were formed according to equations (1), (2) and (3) from interaction of potassium hydrotris(2-mercaptobenzathiazolyl)borate with organotin chlorides in dichloromethane. All the compounds were obtained as solids in fair-to-good yield, as reported in table 1. All compounds are air stable and their molar conductance indicates non-electrolytic nature in water and methanol. All

Table 1. Physical parameters and analytical analysis of hydrotris(2-mercaptobenzathiazolyl)borate and its organotin(IV) derivatives.

			Elemental Analysis, Found (Calcd) in %		
Compound	Color	m.p. (°C)	C	H	N
Ligand	Whitish yellow	172–175	45.86 (45.90)	2.29 (2.36)	7.47 (7.65)
Me_2SnL_2	Yellow	165–170	44.98 (45.16)	2.79 (2.73)	7.52 (7.18)
Bu_2SnL_2	Light brown	158–162	47.39 (47.88)	3.39 (3.51)	6.81 (6.70)
Bu_3SnL	Brown	125–127	49.32 (49.59)	4.87 (5.00)	5.49 (5.25)
Ph_3SnL	Whitish yellow	185–189	53.89 (54.41)	3.39 (3.25)	5.02 (4.88)

Ligand = Potassium hydrotris(2-mercaptobenzathiazolyl)borate. L = hydrotris(2-mercaptobenzathiazolyl)borate anion.

the compounds were characterized by the spectroscopic techniques; the ^{11}B NMR spectra were recorded only to check the presence of the ligand.

$$KBH_4 + 4\,C_7H_5NS_2 \xrightarrow{\text{Solid state}} K[HB(C_7H_4NS_2)_3] + 3\,H_2 + C_7H_5NS_2 \quad (1)$$

$$2\,K[HB(C_7H_4NS_2)_3] + R_2SnCl_2 \xrightarrow[\text{stirring}]{CH_2Cl_2} [(HB(C_7H_4NS_2)_3)_2SnR_2] + 2\,KCl \quad (2)$$

(R = Methyl and Butyl)

$$K[HB(C_7H_4NS_2)_3] + R_3SnCl \xrightarrow[\text{stirring}]{CH_2Cl_2} [HB(C_7H_4NS_2)_3SnR_3] + KCl \quad (3)$$

(R = Phenyl and Butyl)

3.1. *Infrared spectra*

All important IR spectral bands of ligand and organotin(IV) complexes were compared with the spectra of pure reagents. The ligand spectra showed a weak absorption at 2358 cm^{-1} due to the B–H [28]. A strong stretching vibration at 1438 cm^{-1}, due to the B–N [29], strongly favors formation of ligand. The C–H stretching vibration of benzene was at 3010 cm^{-1}. The medium strong vibration of C=S group at 995 cm^{-1} [30] confirmed attachment of 2-mercaptobenzathiazoline moiety with boron through nitrogen atom.

After coordination to organotin, all the above stretching bands were insignificantly shifted except the C=S absorption, which shifted 65–70 cm^{-1}, confirming formation of a coordinate bond between C=S and tin.

After complexation the Sn–C vibration significantly shifted lower due to change in C–Sn–C configuration. The Sn–C bond stretching vibration of **1** was at 580 cm^{-1}, while in **2** this was at 588 cm^{-1}. These Sn–C vibrations indicate the bent C–Sn–C in the complexes [31]. The same vibration of **3** and **4** were recorded at 516 cm^{-1} and 527 cm^{-1}, respectively, suggesting linear *trans* configuration of C–Sn–C in these complexes [32].

3.2. *^{1}H NMR spectra*

^{1}H NMR support the formation of the ligand and its organotin(IV) complexes. Important chemical shifts are reported in table 2. In ^{1}H NMR spectra of the ligand, the absence of signal at δ 8–12 indicates substitution of N–H or S–H proton of 2-mercaptobenzathiazoline. A broad singlet at 5.3 ppm indicates B–H of the ligand [33]. These confirm formation of the desired ligand. The sharp multiplets at 7.01–7.53 ppm show the presence of aromatic ring protons of 2-mercaptobenzathiazoline.

In organotin(IV) complexes, the aromatic ring signals of the ligand were obtained with negligible shift to 7.18–8.39 ppm. The B–H proton of the ligand significantly shifts to strong field 4.1–4.6 ppm. A singlet at 0.63–1.21 ppm was obtained due to

the methyl protons of CH_3–Sn in **4**. The tin-proton coupling constant ^2J (^{119}Sn–^{1}H) for this complex was 85.0 Hz, showing the six-coordinate nature of tin [33]. Substituting into the Lockhart Manders equation [34], the C–Sn–C angle was calculated as 130°C. Therefore, in solution –$SnMe_2$ moiety must have distorted *trans*-octahedral geometry. In dibutyltin(IV) complex **3**, the signals of Sn–C_4H_9 protons are at 0.64–2.63 ppm as triplet and multiplets. The ^2J (^{119}Sn–^{1}H) values are 97.41 Hz and Bu–Sn–Bu angle for this complex was estimated as 159.5°C. Since the Lockhart Manders equation is not as effective for butyl analogues of tin, we assume *trans* octahedral arrangement [35] of the alkyl group in this complex. The ^{1}H NMR spectra of **1** are obtained at 1.1–1.72 ppm and the ^2J (^{119}Sn–^{1}H) and Bu–Sn–Bu angle calculated at 102 Hz and 152.1°C, respectively. These results support six-coordinate environment with distorted *trans* octahedral geometry of the complex [36]. In **1** the phenyl ring (C_6H_5–Sn) and benzene ring signals of 2-mercaptobenzathiazolyl are an intermixed multiplet at 7.18–7.99 ppm. Due to overlapping signals, ^3J (^{119}Sn–^{1}H) cannot be determined but octahedral geometry is assumed, as for the other triorganotin(IV) derivatives.

3.3. *^{13}C NMR spectra*

The ^{13}C NMR spectra also favor formation of the compounds; spectra contain all the desired peaks of carbon skeleton of the compounds, as shown in table 3.

In the ^{13}C NMR spectra of ligand, the signals of benzene ring carbons of 2-mercaptobenzathiazoline are at 112–140 ppm. The chemical shift of >C–S–H and of >C–N–H group at 192.85 was lost and a new peak at 192.25 ppm was obtained, which strongly indicates the presence of >C=S group [31].

Table 2. ^{1}H and ^{119}Sn NMR data of hydrotris(2-mercaptobenzathiazolyl)borate and its organotin(IV) derivatives.

Compound	(Ar-ring protons)	δ(BH)	δ(Rn-Sn)	^{119}Sn	Group
Ligand	7.01–7.53	5.3	–	–	–
Bu_2SnL_2	7.19–7.71	4.2	0.64–2.63	−378	(C_4H_9Sn)
Me_2SnL_2	7.19–7.78	4.1	0.63–1.21	−389	(CH_3-Sn)
Bu_3SnL	7.23–8.39	4.6	1.1–1.72	−318	(C_4H_9Sn)
Ph_3SnL	7.18–7.54	4.4	7.81–7.99	−348	(C_6H_5Sn)

Ligand = Potassium hydrotris(2-mercaptobenzoxathiazolyl)borate ligand.L = Potassium hydrotris(2-mercaptobenzoxathiazolyl)borate anion.

Table 3. ^{13}C and ^{11}B NMR data of hydrotris(2-mercaptobenzathiazolyl)borate and its organotin(IV) derivatives.

Compound	δ(Ar-carbons)	δ(C=S)	δ(Sn-R_n)	δ(^{11}B)
Ligand	112,121,124,127,130,140	192.25	–	−8.77
Bu_2SnL_2	113,121,124,127,130,142	189.60	13,18,22,29	−5.43
Me_2SnL_2	112,121,124,127,130,141	189.69	16	−9.71
Ph_3SnL	112,121,124,128,130,141	189.11	121, 127,129, 135,136,143	−3.37
Bu_3SnL_2	113,121,124,127,131,143	187.25	14,19,27,28	−3.97

Ligand = Potassium hydrotris(2-mercaptobenzoxathiazolyl)borate ligand.L = Potassium hydrotris(2-mercaptobenzoxathiazolyl)borate anion.

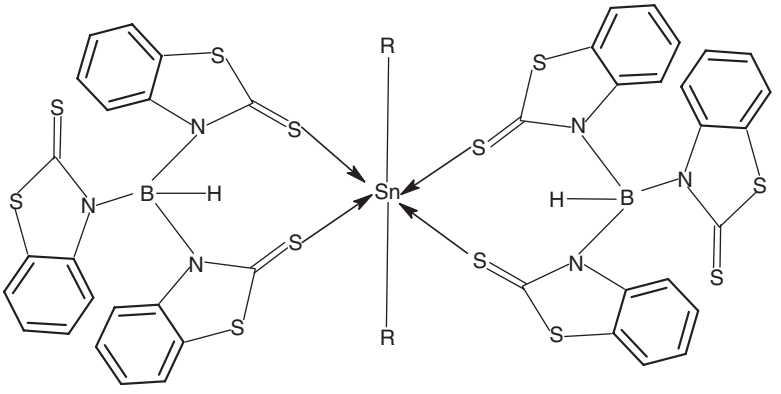

Figure 2. Proposed structure of the triorganotin(IV) complexes of potassium hydrotris(2-mercaptobenzathiazolyl)borate.

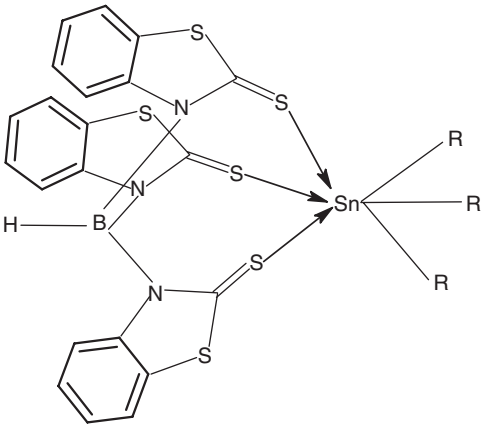

Figure 3. Proposed structure of the diorganotin(IV) complexes of potassium hydrotris(2-mercaptobenzathiazolyl)borate.

After coordination of this ligand to organotin(IV), the signals of benzene carbons of the ligand show insignificant shifts (112–143 ppm). The >C=S showed significant downfield shift in the various complexes, suggesting coordination of >C=S with organotin(IV). In the dimethyltin(IV) complex, the >C=S signals were at 189.69 ppm and the methyl carbon signal was at 16 ppm. However, in the dibutyltin(IV) complex the >C=S signal was at 189.60 ppm and the butyl carbon (C_4H_9–Sn) signals at 13, 18, 22 and 29 ppm. Complex **2** shows the carbonyl signal at 187.25 ppm and the butyl group at 14, 19, 21 and 28 ppm. The triphenyltin(IV) complex has a chemical shift at 189.11 ppm due to >C=S and the other phenyl carbons (C_6H_5Sn) at 121 ppm to 143 ppm. All the observed signals were similar to the literature [37, 38].

^{13}C NMR spectra of the complexes show a weak satellite due to the interaction of alkyl carbon and ^{119}Sn atom. The C–Sn–C values observed are not different from the reported values [39]. These values support the octahedral geometry of all di and triorganotin(IV) complexes.

3.4. *^{119}Sn NMR spectra*

In the ^{119}Sn spectra a singlet is observed since the compounds are not fluxional, only one isomer is present. The ^{119}Sn chemical shift of the dimethyltin(IV) complexes and dibutyltin(IV) complexes observed at $\delta = -389$ and -378 ppm are in accord with six-coordinate diorganotin(IV) complexes involving S-, O- and N-donor ligands [40]. The ^{119}Sn peak of tributyltin(IV) and triphenyltin(IV) complexes were at $\delta = -318$ and -348 ppm, respectively. This region of ^{119}Sn chemical shift suggests six-coordinate nature of tin [41].

3.5. *Antimicrobial studies*

3.5.1. Antibacterial and antifungal activity. The antimicrobial activities of the compounds listed in tables 4 and 5 show that all the compounds are highly active in inhibiting the growth of microorganisms.

Table 4. Antibacterial screening data (growth inhibition zone in mm) of hydrotris(2-mercaptobenzathiazolyl)borate and its organotin(IV) derivatives.

Compounds	Concentration (ppm)	Bacterial strains			
		E. coli	*S. epidedemis*	*S. dysentral*	*B.Anthracius*
KL	500	09	10	09	11
	1000	12	13	11	14
Ph_3SnL	500	21	19	18	16
	1000	30	27	29	25
Bu_3SnL	500	20.5	16	15	16
	1000	32	25	24	27
Me_2SnL_2	500	13	16	15	13
	1000	20	18	18	17
Bu_2SnL	500	15	17	14	13
	1000	21	23	17	20
DMSO[a]	–	–	–	–	

18–30 significantly active, 10–17 moderately active, <10 weakly active. [a]negative control.

Table 5. Antifungal screening data (growth inhibition zone in mm) of hydrotris(2-mercaptobenzathiazolyl)borate and its organotin(IV) derivatives.

Compounds (ppm)	Concentration	Fungal strains		
		A. niger	*A. flaves*	*P. Italicum*
Ligand	500	11	10	08
	1000	15	16	13
Ph_3SnL	500	19	17	16
	1000	31	30	28
Bu_3SnL	500	17	16	17
	1000	28	31	29
Me_2SnL_2	500	15	16	13
	1000	20	23	21
Bu_2SnL_2	500	18	15	15
	1000	25	26	22
DMSO[a]	–	–	–	–

18–30 significantly active, 10–17 moderately active, <10 weakly active. [a]negative control.

In antibacterial activity, KL is weakly active at 500 ppm. The inhibition zones of the strains were measured 9–11 mm and this zone of inhibition increased slightly, *i.e.* 11–14 mm upon increasing concentration to 1000 ppm. The ligand has no toxic metal but inhibits growth of bacterial strains, which by forming a bond from sulphur and nitrogen with the genetic material and restricting multiplication. The tributyltin(IV) complexes exhibit the highest toxicity towards all bacterial strains, significantly active for *E. coli* with inhibition 20.5 mm (500 ppm) and 32 mm (1000 ppm). The lowest inhibition growth of this complex was observed for *S. dysentral i.e.* 15 mm (500 ppm) and 24 mm (1000 ppm). Triphenyltin(IV) complexes have similar toxicity as tributyltin(IV) complexes, the highest inhibition zone recorded for *E. coli i.e.* 21 mm (500 ppm) and 30 mm (1000 ppm) and lowest growth inhibition for *B. anthracius i.e.* 16 mm (500 ppm) and 25 mm (1000 ppm). Diorganotin(IV) complexes (dibutyl and dimethyl) are less active than triorganotin(IV) complexes, moderately active *i.e.* 13–17 mm growth inhibition at 500 ppm for bacterial strains. At higher concentration *i.e.* 1000 ppm, they were significantly active *i.e.* 17–23 mm growth inhibition zone.

In antifungal activity, tributyltin(IV) shows highest inhibition 16 mm (500 ppm) and 31 mm (1000 ppm) for *A. flaves* and least inhibition *i.e.* 17 mm (500 ppm) and 28 mm (1000 ppm) for *A. niger*. Triphenyltin(IV) has the second highest toxicity towards fungal strains with growth inhibition of 19 mm (500 ppm) and 31 mm (1000 ppm) for *A. niger* and lowest inhibition growth *i.e.* 16 mm (500 ppm) and 28 mm (1000 ppm) for *P. italicum*. Dibutyltin(IV) was highly active *i.e.* 18 mm (500 ppm) and 25 mm (1000 ppm) for *A. niger*, and weakly active *i.e.* 15 mm (500 ppm) and 22 mm (1000 ppm) for *P. italicum*. Dimethyltin(IV) complex has least toxicity of the complexes with highest inhibition zone for *A. flaves i.e.* 16 mm and 23 mm for 500 ppm and 1000 ppm, respectively, and least inhibition zone for *P. italicum i.e.* 13 mm and 21 mm at 500 ppm and 1000 ppm, respectively. The ligand was weakly active towards the organisms, but its toxicity dramatically increased after chelation with organotin(IV) because chelation reduces the polarity of the central metal ion by partial sharing positive charge with the donor groups [42].

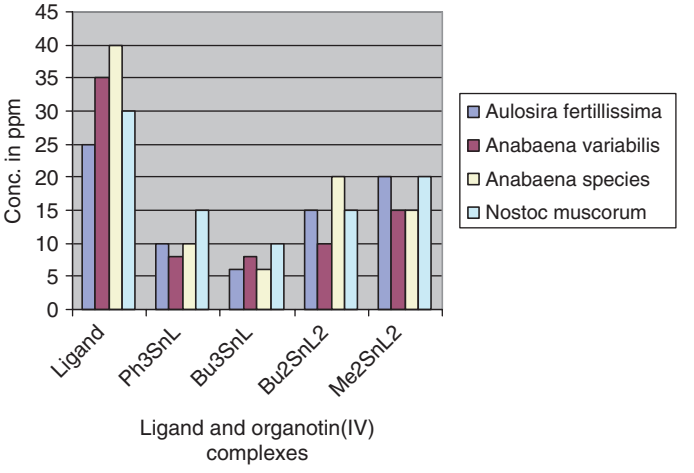

Figure 4. Growth inhibition effects of the ligand and its different organotin(IV) complexes on cyanobacterial strains.

This process increases the lipophilic nature of the central metal ion [43], which in turn favors permeation to the lipid layer of the membrane.

3.5.2. Algicidal studies. Growth behavior of exogenous addition with the different concentration (2, 5, 10, 20, 40, 50, 60, 70, 80 and 100 ppm) of ligand and its organotin(IV) complexes showed varying toxicity to the test cyanobacterial strains. The extent of the toxicity increased with increasing concentration of the complexes. Visually the adverse effects on the growth of the test strain was exhibited by (a) yellowing and fermentation of filaments and (b) reduction in the number of filaments. The order of toxicity among the complexes were $Bu_3SnL > Ph_3SnL > Bu_2SnL_2 > Me_2SnL_2 >$ ligand (KL). For the ligand the toxicity level was comparatively high at 40 ppm. The trialkylorganotin(IV) complexes show higher toxic effects than dialkyltin(IV) due to reduction of the alkyl group, toxicity of the compounds decreased [44, 45].

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