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# Antimicrobial studies of newly synthesized organotin(IV) complexes of dihydrobis(2-mercaptothiazolinyl)borate

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Four organotin(IV) complexes of dihydrobis(2-mercaptothiazolinyl)borate were synthesized and characterized by elemental analysis and spectroscopic techniques (IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>11</sup>B-NMR, and <sup>119</sup>Sn-NMR). All the compounds were screened against bacterial, fungal, and cyanobacterial strains. Among the complexes, triorganotin(IV) complexes show better inhibition growth as compared to diorganotin(IV) complexes.

Keywords: Organotin(IV); Borate; 2-Mercaptothiazolyl; Biological activity

#### 1. Introduction

Borates, in general and polyorganyl borates in particular, constitute a family of stable and flexible polydentate ligands discovered by Trofimenko [1]. Nitrogen, sulfur, and oxygen containing boron ligands exhibit antimicrobial activity [2, 3]. The structural aspects of 2-mercaptothiazolyl borates of rhenium(I) tricarbonyl extended to the preparation of radiopharmaceuticals by Santos *et al.* [4]. Antibiotic properties are greatly enhanced when similar ligands are coordinated to organotin compounds [5]. Being a subject of growing interest in biological assay for bactericide [6] and fungicide activities [7], antitumor activity of  $R_2Sn^{2+}$  adducts of oxygen, nitrogen, and halogen have been established [8, 9]. Organotin complexes are used in the treatment of trypanosomal and bilharzia diseases [10]. Various triorganotin derivatives have been reported to be effective against mosquito larvae and adult mosquito responsible for malaria and yellow fever [11], and cardiovascular activity [12]. Pharmacological importance of organotin(IV) mercaptazole derivatives have also been reported [13, 14].

The combination of boron, sulfur, and nitrogen containing ligands led us to work on the coordination chemistry of borate ligands and their organotin derivatives. In this article, we report the synthesis, spectroscopic characterization, and antimicrobial

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assay of dihydrobis(2-mercaptothiazolinyl)borate (scheme 1), and its organotin(IV) complexes.

#### 2. Experimental

Potassium borohydride and organotin chloride were purchased from Acros Organics and Fluka Chemicals, respectively. 2-Mercaptothiazoline was purchased from Aldrich Chemical and used as received. The solvents were purchased from E. Merck (India Ltd.). All the syntheses were carried out under nitrogen. Elemental analysis was performed on a PerkinElmer 2400 CHN elemental analyzer; IR spectra as KBr disks were recorded on a PerkinElmer model 1620 FT-IR spectrophotometer. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>11</sup>B-NMR, and <sup>119</sup>Sn-NMR were recorded using Bruker Avance II 400 NMR and INSTRUM DPX-300 MHz NMR spectrometers, respectively. Tetramethylsilane (<sup>1</sup>H- and <sup>13</sup>C-NMR), tetramethylstannane (<sup>119</sup>Sn-NMR), and borontrifluoride (<sup>11</sup>B-NMR) were used as internal standards, whereas CDCl<sub>3</sub> was used as a solvent. The chemical shift ( $\delta$ ) was reported in ppm. Electrospray ionization (ESI) mass spectra were recorded on a MICROMASS QUATTRO II triple quadruple mass spectrometer. The sample (dissolved in methanol) was introduced into the ESI source through a syringe pump at the rate of  $5\,\mu$ L per min. The ESI capillary was set at 3.5 kV and voltage 40 V. The spectrum was obtained in 6s scans and the printouts were averaged spectra of 6-8 scans.

#### 2.1. Synthesis of potassium dihydrobis(2-mercaptothiazolinyl)borate

Fine powder of potassium borohydride (30 mM) and 2-mercaptothiazoline (90 mM) were placed in a 250-mL Schlenk flask connected with gas collecting device. The mixture was then heated to 100°C to start the solid state reaction with the evolution of hydrogen. The temperature was raised to 140°C until 60 mM (1344 mL) of hydrogen gas evolved. The mixture was allowed to cool to room temperature and 20 mL of dichloromethane was added and stirred for 15 min. The solid was separated and this process was repeated for three times to remove excess 2-mercaptothiazoline. The remaining white  $K(BH_2L_2)$  was dried under vacuum and washed with three 20 mL portions of THF, giving an off-white solid.



Scheme 1. Proposed tetrahedral geometry of the ligand.

Yield (%): 74; m.p. 166–170°C; IR (cm<sup>-1</sup>): 2910s  $\nu$ (C–H), 2362m  $\nu$ (B–H), 1478s  $\nu$ (B–N), and 1009s  $\nu$ (C=S); <sup>1</sup>H-NMR ( $\delta$ ): 3.37 (t, 2H,  $J_{AB}$ =7.1, N–CH<sub>2</sub>), 3.68 (t, 2H,  $J_{AB}$ =7.4, S–CH<sub>2</sub>), 4.70 (sbr, 1H, B–H); <sup>13</sup>C-NMR ( $\delta$ ): 57.16 (NCH<sub>2</sub>), 35.27 (SCH<sub>2</sub>), 197.2 (C=S); <sup>11</sup>B-NMR ( $\delta$ ): -4.41; MS (ESI+): 495, 443.7, 423.7, 195.8; MS (ESI–): 481.5, 421.8, 365, 305; Elemental Anal. (%) found (Calcd for KBC<sub>6</sub>H<sub>10</sub>N<sub>2</sub>S<sub>4</sub>): C 24.86 (24.99), H 3.29 (3.50), N 9.43 (9.72).

#### 2.2. Synthesis of triphenyltin(IV) dihydrobis(2-mercaptothiazolinyl) borate (1)

The solution (25 mL) of triphenyltin chloride (1 mM) in dichloromethane was added 25 mL dichloromethane solution/suspension of potassium dihydrobis to (2-mercaptothiazolinyl)borate (KL) (1 mM). The resulting solution was stirred for 12 h, filtered, and the precipitate of potassium chloride removed. The filtrate was concentrated at low temperature and allowed to crystallize. Obtained crystals were recrystallized from chloroform and n-hexane (1:3) to get a bone white compound in 62% yield; m.p. 145–148°C; IR (cm<sup>-1</sup>); 3051s v(C–H), 2362m v(B–H), 1427s v(B–N), and 1073s  $\nu$ (C=S), 585m  $\nu$ (Sn-C); <sup>1</sup>H-NMR ( $\delta$ ): 3.27 (t, 2H,  $J_{AB}$ =7.1, N-CH<sub>2</sub>), 3.46 (t, 2H,  $J_{AB} = 7.3$ , S–CH<sub>2</sub>), 4.59 (sbr, 1H, B–H), 7.45–7.75 (m, 5H, Sn–C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C-NMR ( $\delta$ ): 56.02 (N-CH<sub>2</sub>), 31.2 (S-CH<sub>2</sub>), 199 (C=S), 128, 137, 138 [<sup>1</sup>J(<sup>13</sup>C-<sup>119</sup>Sn): 629 Hz]; <sup>11</sup>B-NMR ( $\delta$ ): -5.45; <sup>119</sup>Sn-NMR ( $\delta$ ): -45; MS (ESI+): 743 [C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>S<sub>4</sub>BSn.H<sub>2</sub>O], 725 [C<sub>24</sub>H<sub>21</sub>N<sub>2</sub>S<sub>4</sub>BSn], 350 [C<sub>18</sub>H<sub>15</sub>Sn]; MS (ESI-) 421 [C<sub>18</sub>H<sub>15</sub>S<sub>2</sub>BSn]; Elemental Anal. (%) found (Calcd for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>S<sub>4</sub>SnB): C 48.08 (48.10), H 4.07 (4.21), N 4.76 (4.67).

#### 2.3. Synthesis of tributyltin(IV) dihydrobis(2-mercaptothiazolinyl)borate (2)

This complex was prepared by stirring tributyltin chloride (2 mM) and potassium dihydrobis(2-mercaptothiazolinyl) borate (2 mM) in dichloromethane (50 mL) for 15 h at 30°C following the same procedure as for **1**. White solid yield (%): 65; m.p. 132–136°C; IR (cm<sup>-1</sup>); 2958s  $\nu$ (C–H), 2362m  $\nu$ (B–H), 1452s  $\nu$ (B–N), and 1050s  $\nu$ (C=S), 590w  $\nu$ (Sn–C); <sup>1</sup>H-NMR ( $\delta$ ): 3.38 (t, 2H,  $J_{AB}$ =7.1, N–CH<sub>2</sub>), 3.58 (t, 2H,  $J_{AB}$ =7.3, S–CH<sub>2</sub>), 5.13 (sbr, 1H, B–H), 0.89, 1.36, 1.69, 1.71 (m, 9H, J=101, Sn–C<sub>4</sub>H<sub>9</sub>); <sup>13</sup>C-NMR ( $\delta$ ): 55.27 (N–CH<sub>2</sub>), 34.17 (S–CH<sub>2</sub>), 201 (C=S), 15, 27, 28, 30 [C<sub>4</sub>H<sub>9</sub>) (<sup>1</sup>J(<sup>13</sup>C–<sup>119</sup>Sn): 609 Hz)]; <sup>11</sup>B-NMR ( $\delta$ ): –2.10; <sup>119</sup>Sn-NMR ( $\delta$ ): 84; MS (ESI+): 701 [C<sub>18</sub>H<sub>37</sub>N<sub>2</sub>S<sub>4</sub>BSn], 629 [C<sub>18</sub>H<sub>37</sub>N<sub>2</sub>S<sub>4</sub>BSn]; MS (ESI–): 410 [C<sub>14</sub>H<sub>34</sub>NS<sub>2</sub>BSn], 364 [C<sub>12</sub>H<sub>26</sub>S<sub>2</sub>BSn]; Elemental Anal. (%) found (Calcd for C<sub>18</sub>H<sub>37</sub>N<sub>2</sub>S<sub>4</sub>SnB): C 40.31 (40.10), H 6.73 (6.92), N 5.23 (5.19).

#### 2.4. Synthesis of dibutyltin(IV) dihydrobis(2-mercaptothiazolinyl)borate (3)

This complex was synthesized according to the synthesis method of 1 and 2. Here, dibutyltin dichloride (1 mM) and KL (2 mM) were taken in dichloromethane (50 mL) and stirred 14 h at 30°C, which yielded a white precipitate.

Yield: 76 (%); m.p. 152–157°C; IR (cm<sup>-1</sup>); 3003s  $\nu$ (C–H), 2360m  $\nu$ (B–H), 1452s  $\nu$ (B–N), and 1053s  $\nu$ (C=S), 520m  $\nu$ (Sn–C); <sup>1</sup>H-NMR ( $\delta$ ): 3.39 (t, 2H,  $J_{AB}$ =7.1, N–CH<sub>2</sub>), 3.47 (t, 2H,  $J_{AB}$ =7.3, S–CH<sub>2</sub>), 5.27 (sbr, 1H, B–H), 0.90, 1.31, 1.58, 1.74 (m, 9H, J=104, Sn–C<sub>4</sub>H<sub>9</sub>); <sup>13</sup>C-NMR ( $\delta$ ): 53.14 (N–CH<sub>2</sub>), 33.92 (S–CH<sub>2</sub>), 199 (C=S),

8, 15, 27, 28  $[C_4H_9 ({}^{1}J({}^{13}C_{-}^{119}Sn): 804 Hz)]; {}^{11}B-NMR (\delta): -4.49; {}^{119}Sn-NMR (\delta): -210; MS (ESI+): 767 [C_{20}H_{38}N_4S_8B_2Sn\cdot 2H_2O], 613 [C_{17}H_{34}N_3S_6B_2Sn], 412 [C_9H_{18}N_2S_4BSn]; MS (ESI-): 605 [C_{13}H_{28}N_4S_7B_2Sn], 323 [C_6H_{18}N_2S_2B_2Sn], 307 [C_8H_{18}S_2BSn]; Elemental Anal. (%) found (Calcd for C_{20}H_{38}N_4S_8SnB_2): C 32.23 (32.84), H 5.29 (5.24), N 7.41 (7.66).$ 

#### 2.5. Synthesis of dimethyltin(IV) dihydrobis(2-mercaptothiazolinyl)borate (4)

Similar procedure for above complexes, dimethyltindichloride (1 mM), and KL (2 mM) in dichloromethane (50 mL) yielded white complex in 59% yield and 148–157C m.p.; IR (cm<sup>-1</sup>); 2957s  $\nu$ (C–H), 2362w  $\nu$ (B–H), 1458s  $\nu$ (B–N), and 1051s  $\nu$ (C=S), 530w  $\nu$ (Sn–C); <sup>1</sup>H-NMR ( $\delta$ ): 3.31 (t, 2H,  $J_{AB}$  = 7.1, N–CH<sub>2</sub>), 3.57 (t, 2H,  $J_{AB}$  = 7.3, S–CH<sub>2</sub>), 5.08 (sbr, 1H, B–H), 0.96 (s, 3H, J = 89 Hz, Sn–CH<sub>3</sub>); <sup>13</sup>C-NMR ( $\delta$ ): 54.19 (N–CH<sub>2</sub>), 33.50 (S–CH<sub>2</sub>), 201 (C=S), 12.8 [CH<sub>3</sub> (<sup>1</sup>J(<sup>13</sup>C–<sup>119</sup>Sn): 930 Hz]; <sup>119</sup>Sn-NMR ( $\delta$ ): –243; MS (ESI+): 647 [C<sub>14</sub>H<sub>26</sub>N<sub>4</sub>S<sub>8</sub>B<sub>2</sub>Sn], 392 [C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>S<sub>4</sub>BSn], 350 [C<sub>7</sub>H<sub>12</sub>S<sub>3</sub>NBSn]; MS (ESI–): 338 [C<sub>8</sub>H<sub>16</sub>NS<sub>2</sub>BSn · H<sub>2</sub>O], 483 [C<sub>8</sub>H<sub>12</sub>N<sub>3</sub>S<sub>6</sub>BSn], 265 [C<sub>4</sub>H<sub>9</sub>NS<sub>2</sub>BSn]; Elemental Anal. (%) found (Calcd for C<sub>14</sub>H<sub>26</sub>N<sub>4</sub>S<sub>8</sub>SnB<sub>2</sub>): C 25.58 (25.98), H 4.24 (4.05), N 8.69 (8.66).

#### 2.6. Antimicrobial activity

The agar diffusion method [15] was adopted for measuring the effectiveness of the compounds. Mueller Hinton agar was used as nutrient standard medium that allowed growth of test microbes. Using this method, one species of bacteria was uniformly swabbed onto the nutrient agar in a Petri plate. The paper disc containing the compound to be tested was then placed on the surface of the agar. Petri plates were incubated. Effective agents inhibited microbial growth and measurements quantified the size of the zones of inhibition around the disc.

#### 3. Results and discussion

The KL, prepared by solid state reaction of potassium borohydride and 2-mercaptothiazoline, was treated with organotin chloride  $(R_nSnCl_{4-n})$  to obtain organotin(IV) derivatives. The obtained complexes were colorless solids stable in air and water when the mixture of KBH<sub>4</sub> and mercaptothiazoline was heated, and temperature reached the melting point of mercaptothiazoline, converting to another tautomeric form *via* transfer of proton from sulfur to nitrogen.

The conductivity of the ligand and its complexes were measured in dichloromethane and methanol. The results showed that the conductivity of the ligand decreases upon complexation and that all complexes are nonelectrolytes. The purity of compounds was confirmed through the elemental analysis.

#### 3.1. IR spectra

IR spectra support the formation of all the compounds and their proposed structures (schemes 2 and 3). B–H bond vibrations were obtained at 2360–2362 cm<sup>-1</sup> [16], suggesting the presence of BH<sub>2</sub>. Strong stretching vibrations at 1478 cm<sup>-1</sup>, due to B–N bond [17], favored the formation of ligand. The aromatic ring C–H stretching vibration was observed at 2910 cm<sup>-1</sup>. The C=S stretching vibration in ligand at 1009 cm<sup>-1</sup> shifted to higher wavenumber 1050–1073 cm<sup>-1</sup> [18] after coordination with organotin. The  $v_{sym}$  (Sn–C) at < 580 cm<sup>-1</sup> indicates nonplanar bent structure, whereas > 580 cm<sup>-1</sup> suggests the linear *trans*-structure of the C–Sn–C. For 1 the Sn–C vibration was observed at 585 cm<sup>-1</sup> whereas for 2 it was observed at 590 cm<sup>-1</sup>, suggesting bent C–Sn–C moiety [19]. In 3 the Sn–C vibration is at 520 cm<sup>-1</sup> and in 4 at 530 cm<sup>-1</sup>, suggesting linear *trans*-configuration of C–Sn–C [20].

#### 3.2. <sup>1</sup>*H*-*NMR*

<sup>1</sup>H-NMR spectra show two different <sup>1</sup>H-NMR signals for 2-mercaptothiazoline ring protons, suggesting two nonequivalent sets of protons. The signals of thiazolyl ring protons (NCH<sub>2</sub>) and (SCH<sub>2</sub>) for ligand are triplets at  $\delta = 3.37$  ppm and 3.68 ppm, respectively [4], shifting upfield to 3.27–3.39 and 3.46–3.58 ppm, due to complex formation. A broad singlet of BH protons at 4.70–5.27 ppm [16] confirmed the formation of ligand. The <sup>1</sup>H-NMR spectrum of **4** showed the expected integration and



Scheme 2. Proposed octahedral geometry of diorganotin(IV) dihydrobis(2-mercaptothiazolinyl)borate complexes (R = methyl and butyl).



Scheme 3. Proposed distorted pentagonal bipyramidal geometry of triorganotin(IV) dihydrobis (2-mercaptothiazolinyl)borate complexes (R = butyl and phenyl).

peak multiplicities of methyl attached to tin as a singlet at 0.96–1.21 ppm. The  ${}^{2}J$  (<sup>119</sup>Sn–<sup>1</sup>H) at 89 Hz indicates six-coordinate octahedral geometry [21]. The Sn–C angle was calculated by the Lockhart –Manders equations [22] as 143.4°, favoring the proposed geometry. The butyl protons of **2** are at 0.89, 1.36, 1.69, and 1.71 ppm with  ${}^{2}J$  (<sup>119/117</sup>Sn–H) of 101 Hz. This coupling constant agrees with literature values [23] for five coordinated N-, O-, and S-donor ligands [24]. In **3** the Sn–C<sub>4</sub>H<sub>9</sub> protons are at 0.90, 1.31, 1.58, and 1.74 ppm as multiplets. The  ${}^{2}J$  (<sup>119</sup>Sn–<sup>1</sup>H) for this complex of 104 Hz showed the six-coordinate octahedral tin [25]. In **1** the C<sub>6</sub>H<sub>5</sub>–Sn protons appeared at 7.45–7.75 ppm as multiplets and  ${}^{2}J$  (<sup>119</sup>Sn–H) was not observed; chemical behavior of this complex was similar to other five-coordinate triorganotin complexes with trigonal bipyramidal geometry.

#### 3.3. <sup>13</sup>C-NMR

<sup>13</sup>C-NMR peaks at  $\delta = 57.16$  and 35.27 ppm are attributed to NCH<sub>2</sub> (C-1) and SCH<sub>2</sub> (C-2), respectively, whereas  $\delta = 197.2$  ppm is due to C=S (C-3) [26] of the ligand. The formation of organotin(IV) complexes shifts the peaks upfield, C-1, C-2, and C-3 of **1** are at  $\delta = 55.18$ , 31.2, and 199 ppm, respectively, whereas phenyl carbons (Sn–C<sub>6</sub>H<sub>5</sub>) are at  $\delta = 128-138$  ppm. C-1, C-2, and C-3 of **2** are at  $\delta = 55.27$ , 34.17, and 201 ppm, while Sn–C<sub>4</sub>H<sub>9</sub> are at  $\delta = 15$ , 27, 28, and 30 ppm. In **3** the C-1, C-2, and C-3 are at  $\delta = 53.14$ , 33.92, and 199 ppm, respectively, while Sn–C<sub>4</sub>H<sub>9</sub> are at  $\delta = 8$ , 15, 27, and 28 ppm. The CH<sub>3</sub>–Sn of **4** is at  $\delta = 12$  ppm, whereas C-1, C-2, and C-3 were recorded at 54, 33, and 201 ppm, respectively.

KL is bonded to organotin through the sulfur of C=S group. The spectroscopic data and the C-Sn-C bond angle explain that triorganotin(IV) complexes are trigonal bipyramidal, whereas diorganotin(IV) complexes are octahedral.

#### 3.4. <sup>119</sup>Sn-NMR spectra

The presence of a sharp singlet <sup>119</sup>Sn peak in each complex suggests that the compounds are not fluxional and only one isomer is present. <sup>119</sup>Sn peaks of **3** and **4** are at  $\delta = -210$  and -243 ppm, respectively, in accordance with those of six-coordinate diorganotin(IV) complexes, involving S-, O-, and N-donor groups [27]. The chemical shifts of **1** and **2** were at  $\delta = -45$  and 84 ppm, respectively, indicating five-coordinate organotin(IV) complexes [28].

#### 3.5. Electron spray ionization mass spectra

The simple fragmentation of ligand and its organotin complexes dissolved in methanol were detected at 40 V in positive and negative ion ESI mass spectrometry with various isotopic ranges of tin, i.e. <sup>113</sup>Sn, <sup>115</sup>Sn, <sup>117</sup>Sn, <sup>119</sup>Sn, and <sup>123</sup>Sn. In some cases, the obtained fragmentation peak of molecular ion was associated with solvents, water, and other adducts from the mobile phase solution [29].

In positive ion ESI-mass spectrum of the ligand, a fragment associated with solvent was obtained at m/z 495 [K{H<sub>2</sub>B(C<sub>3</sub>H<sub>4</sub>S<sub>2</sub>N)<sub>2</sub>}]. This fragment further fragmented into three small fragments and lost organic adducts. The molecular ion peak of ligand at m/z

195 is KBC<sub>5</sub>H<sub>8</sub>S<sub>2</sub>N. In negative ion spectra, the molecular ion peak of ligand was at m/z421 as adduct of acetylacetonitrile. The positive ion ESI-mass spectrum of 1 showed molecular ion peaks at m/z 347, 349 and 351 [C<sub>18</sub>H<sub>15</sub>Sn] and other fragments at m/z743, 747, 745, 747 [SnC $_{24}H_{25}N_2S_4B \cdot H_2O$ ], 715, 717, 721, 725 [SnC $_{24}H_{21}N_2S_4B$ ] as adducts with solvent or water. These fragments also indicate less stability of organotin in solution [30]. The negative ion ESI-mass spectra of this complex has less fragments and molecular ion peaks were obtained at m/z 419, 421, 423 [C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>S<sub>2</sub>BSn]. In 2, the molecular ion fragments are at m/z 696, 698, 700, 702, 704 [C<sub>18</sub>H<sub>37</sub>N<sub>2</sub>S<sub>4</sub>BSn] and 625, 627, 629  $[C_{18}H_{37}N_2S_4BSn \cdot 5H_2O]$  as adducts with solvent or water. The negative ESI mass spectrum shows the molecular ion peaks at m/z 357, 359, 361, 363 [C<sub>12</sub>H<sub>26</sub>S<sub>2</sub>BSn] and other fragments at m/z 403, 405, 407, 411 [C<sub>14</sub>H<sub>34</sub>S<sub>2</sub>NBSn]. Dibutyltin(IV) derivative (3) contains more fragments in both the positive and negative ion ESI-mass spectra, due to inferior stability [31], like the positive ion isotopic mass fragments at m/z 406, 408, 412, 414, 416 [C<sub>9</sub>H<sub>18</sub>N<sub>2</sub>S<sub>4</sub>BSn], 610, 612, 614, 616, 618, 620, 622  $[C_{17}H_{34}N_3S_6B_2Sn]$ , 759, 765, 767  $[C_{20}H_{38}N_4S_8B_2Sn \cdot 2H_2O]$ , and the negative ion fragments 297, 299, 301, 303, 305, 307 [C<sub>8</sub>H<sub>18</sub>S<sub>2</sub>SnB], 320, 322, 324 [C<sub>6</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>B<sub>2</sub>Sn], and 599, 601, 605 [ $C_{13}H_{28}S_7N_4B_2Sn$ ]. Dimethyltin derivative (4) fragmented similar to 2 with main fragments recorded at m/z 641, 643, 645, 647, 652 [C<sub>14</sub>H<sub>26</sub>N<sub>4</sub>S<sub>8</sub>B<sub>2</sub>Sn]. A fragment at m/z 400 [C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>S<sub>4</sub>BSn] probably contains <sup>113</sup>Sn isotopic form of tin. Other fragments were recorded at m/z 348, 350, 352, 354 [C<sub>7</sub>H<sub>12</sub>S<sub>3</sub>NBSn] in positive ion spectra. The fragments at m/z 336, 338, 340 [C<sub>8</sub>H<sub>16</sub>S<sub>2</sub>NBSn · H<sub>2</sub>O], 479, 481, 483, 485  $[C_8H_{12}N_3S_6BSn]$ , and 263, 265, 267  $[SnBC_4H_9S_2N]$  in negative ion mass spectra were noticed.

#### 3.6. Antimicrobial activity

Antibacterial activities of the ligand and its complexes were studied against three bacterial strains. As shown in tables 1 and 2, the ligand shows the least activity for both bacterial and fungal species, with activity drastically increased for complexes. Triphenyltin complex showed the highest inhibition to growth of organisms, i.e., 23, 21, and 20 mm inhibition zones against *Escherichia coli*, *Staphylococcus epidermidis*, and *Staphylococcus dysentral*, respectively. Tributyltin complex was second in toxicity to all bacterial strains with inhibition zones of 21, 19, 18 mm against *E. coli*, *S. epidermidis*, and *S. dysentral*, respectively. Both dimethyl and dibutyltin complexes showed approximately equal toxicity toward bacterial strains with inhibition zones in the range of 15–19 mm.

For antifungal activity the highest inhibition zones, i.e., 22, 20, 20 mm were for tributyltin complex, against *Aspergillus niger*, *Candida albicans*, and *Aspergillus flavus*, respectively. Triphenyltin complex showed the second highest inhibition zones, i.e., 22, 19, 18, against *A. niger*, *C. albicans*, and *A. flavus*, respectively. Dibutyltin complex had third highest inhibition activities, i.e., 19, 18, and 18 mm, against *A. niger*, *A. flavus*, and *C. albicans*, respectively. Dimethyltin complex was least toxic among these complexes with 18, 17, and 16 mm against *A. niger*, *C. albicans*, and *A. flavus*, and *A. flavus*, respectively. The ligand was weakly active toward the organisms but dramatically increased after chelation with organotin [32].

Compounds	Concentration (ppm)	Bacterial strains			
		E. coli	S. epidermidis	S. dysentral	
KL	500	09	10	09	
	1000	10	11	11	
Ph <sub>3</sub> SnL	500	18	16	15	
	1000	23	21	20	
$Bu_2SnL_2$	500	17	16	15	
	1000	19	17	18	
$Me_2SnL_2$	500	15	14	15	
	1000	18	18	18	
$Bu_3SnL$	500	18	15	15	
	1000	21	19	18	
Kanamycine	500	23	23	21	
	1000	29	28	25	

Table 1. Bactericidal screening data of the ligand and its organotin(IV) complexes (growth inhibition in mm, after 24 h at  $36 \pm 1^{\circ}$ C).

18-30 significantly active; 10-17 moderately active; <10 weakly active.

KL, potassium dihydrobis(2-mercaptothiazolinyl)borate; L, dihydrobis(2-mercaptothiazolinyl)borate; Me, methyl; Bu, butyl; Ph, phenyl.

Compounds	Concentration (ppm)	Fungal strains		
		A. niger	C. albicans	A. flavus
KL	500	09	10	09
	1000	11	11	10
Ph <sub>3</sub> SnL	500	17	15	14
	1000	22	19	18
$Bu_2SnL_2$	500	17	15	14
	1000	19	18	18
$Me_2SnL_2$	500	15	14	15
	1000	18	17	16
$Bu_3SnL$	500	18	15	15
	1000	22	20	20
Miconazole	500	22	21	19
	1000	30	28	25

Table 2. Fungicidal screening data of the ligand and its organotin(IV) complexes (growth inhibition in mm, after 48 h at  $36 \pm 1^{\circ}$ C).

Triorganotin(IV) complexes (tributyl and triphenyl) have more toxicity than diorganotin(IV) complexes (dibutyltin and dimethyl), with toxicity of organotin decreases with decreasing with the number of alkyl groups [33].

#### 4. Conclusion

Stable organotin mercapto borate complexes are characterized by spectroscopy and show good coordination through sulfur atom outside the ring. The coordination of

ligand with organotin enhanced toxicity toward bacteria and fungi. Several reports of organotin adducts with organic moieties are reported [34], with five- or six-coordinate structures of these complexes, but our synthesized complexes have much better biological activities due to the presence of a boron atom, which shows good biocidal properties.

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