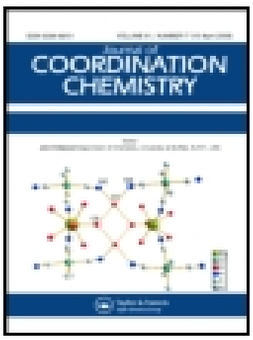

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Synthesis, spectroscopic characterization, crystal structure and anti-bacterial activity of diorganotin(IV) complexes with 5-bromo-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone

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Three new diorganotin(IV) complexes, [Me_2Sn(BDET] (**2**), [Bu_2Sn(BDET)] (**3**) and [Ph_2Sn(BDET)] (**4**), were synthesized by reacting R_2SnCl_2 (R = Me, Bu and Ph) with 5-bromo-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone [H_2BDET, (**1**)] in the presence of KOH in absolute methanol. The newly synthesized complexes were characterized by elemental analysis, molar conductivity, UV-Vis, FT-IR, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopies. The molecular structure of **4** was confirmed by X-ray crystallography. X-ray crystallography revealed that the doubly deprotonated O,N,S-tridentate thiosemicarbazone coordinates to tin(IV), resulting in a distorted trigonal bipyramidal geometry. Their ^{1}H, ^{13}C and ^{119}Sn NMR spectra support a five-coordinate tin(IV) in solution for all complexes, in accord with the solid state X-ray structure determined for **4**. Compounds **1**-**4** were evaluated for their antibacterial activities against *Staphylococcus aureus*, *Enterobacter aerogenes*, *Escherichia coli* and *Salmonella typhi*. The results exhibited that **2**-**4** were active with comparable potency compared to the standard drug. Antibacterial studies also indicated that the complexes have potential for biological evaluation.

Keywords: Synthesis; Organotin(IV) complexes; Spectral characterization; Crystal structure; Antibacterial activity

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1. Introduction

Thiosemicarbazone and its substituted derivatives have been investigated due to their flexible synthesis, chelating capability and various biological applications [1-4]. Thiosemicarbazones continue to hold an important position as chelating agents in metal coordination chemistry [5-8]. In particular, a number of transition metal complexes of thiosemicarbazone derivatives containing ONS donors have been studied during the past few years [9-12]. Thiosemicarbazone derivatives and their metal complexes are known for their range of biological as well as pharmacological applications [13, 14]. Most of the previous reports have been carried out for thiosemicarbazones with transition metal ions [15-17]. Tin complexes have various potential applications such as antibacterial, antifungal, biocides, cytotoxic agents and wood preservatives [18-20]. Organotin(IV) complexes with thiosemicarbazone derivatives have received attention due to their structural features, antimicrobial and antitumor activities [21, 22]. Recently, Li *et al.* reported the structural and biological activities of diorganotin(IV) complexes with *N*(4)-phenylthiosemicarbazones derived from 2-benzoylpyridine and 2-acetylpyrazine [23]. The results showed that thiosemicarbazones and their complexes exhibited remarkable biological activities. Important series of organotin(IV) complexes of thiosemicarbazone derivatives have prepared and investigated for their structural and biological applications [24-27]. Organotin(IV) complexes with ONS-donor thiosemicarbazone ligands have structural diversities and various applications depending on the coordination number and mode of the ligands about the tin(IV), with numerous studies on their structural interactions [28-30]. Khandani *et al.* reported the synthesis, crystal structures, and biological activities of diorganotin(IV) complexes with 3-methoxysalicylaldehyde thiosemicarbazone, which showed significant antibacterial and antitumor activities [31]. Synthesis, structural and biological properties of substituted thiosemicarbazones and their organotin(IV) complexes have become an important research field. From literature survey, diorganotin(IV) complexes of ONS-donor thiosemicarbazones are still scarce [32, 33]. This study reports the synthesis, spectroscopic characterization and antibacterial activity of three new diorganotin(IV) complexes with 5-bromo-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone. X-ray crystal structure of diphenyltin(IV) complex is also described.

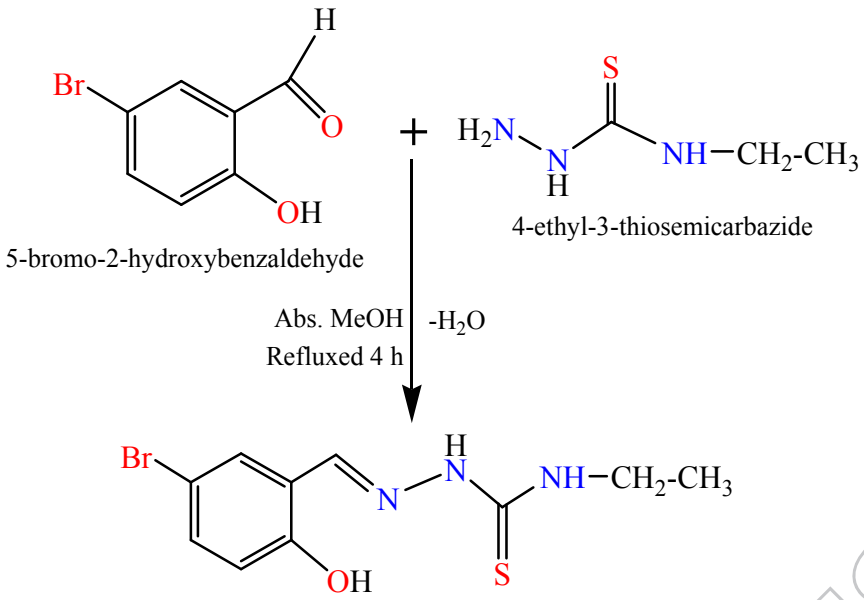
2. Experimental

2.1. *Materials and methods*

All reagents were purchased from Fluka, Aldrich, and Sigma. All solvents were received as reagent grade and used without purification. Melting points were measured by the Stuart Scientific SMP1 melting point apparatus. UV–Vis spectra were recorded in DMSO with a Perkin Elmer Lambda 25 UV–Vis spectrophotometer. Infrared (IR) spectra were recorded with a Perkin Elmer System 2000 spectrophotometer using KBr pellets from 4000–400 cm^{-1} at room temperature. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on Bruker 500 and 400 MHz NMR spectrophotometers relative to $SiMe_4$ and $SnMe_4$ in DMSO. Elemental analyses were conducted by the Perkin Elmer 2400 Series-11 CHN analyzer. Molar conductivity measurements were carried out with a Jenway 4510 conductivity meter using DMSO. X-ray crystallographic data were recorded on a Bruker SMART APEXII CCD area-detector diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 100 K. The data were collected and reduced using APEX2 and SAINT programs. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program [34]. All non-H atoms were anisotropically refined. The molecular graphics were created using SHELXTL-97.

2.2. *Synthesis of 5-bromo-2-hydroxybenzaldehyde-N(4)-ethylthiosemicarbazone [H_2BDET, (1)]*

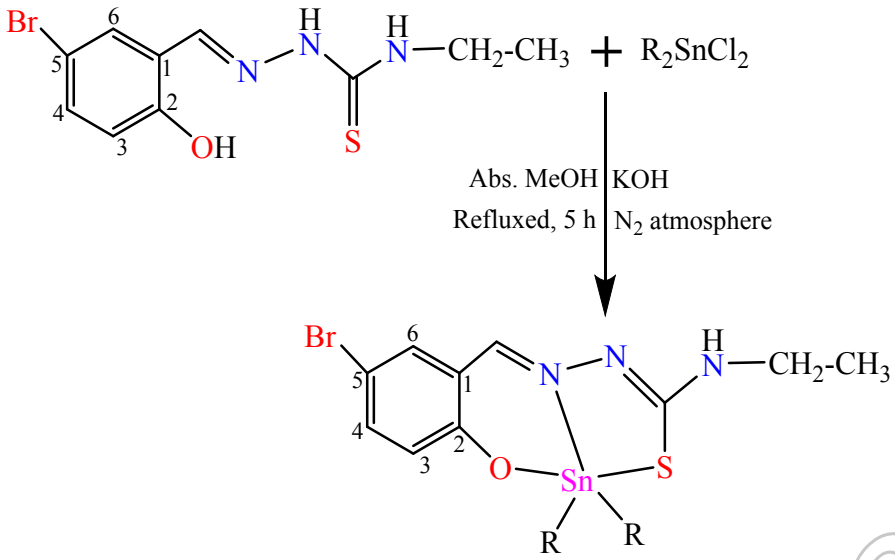
A solution of 4-ethyl-3-thiosemicarbazide (0.48 g, 4.0 mmol) in 10 mL methanol was treated with 10 mL methanolic solution of 5-bromo-2-hydroxybenzaldehyde (0.80 g, 4.0 mmol). The resulting reaction mixture was stirred and refluxed for 4 h (scheme 1) and then filtered. The solid was washed with methanol and dried in desiccators over anhydrous silica gel. Yield: 0.88 g, 68%: M.p: 178-180 °C: UV–Vis (DMSO)$\lambda_{max/nm}$: 256, 301, 347: FT-IR (KBr, cm^{-1}) ν_{max}: 3303 (s, OH), 3251, 3145 (s, NH), 1610 (m, C=N), 1551 (s, C_{aro}-O), 988 (m, N-N), 1351, 859 (w, C-S). ^{1}H NMR (DMSO-d_6, ppm): 11.30 (s, 1H, OH), 10.31 (s, 1H, N-NH), 8.58 (s, 1H, CS-NH), 8.27 (s, 1H, CH=N), 8.08 (d, 1H, J = 7.6, PhC3-H), 7.34 (d, 1H, J = 7.2, PhC4-H), 7.10 (s, 1H, PhC6-H), 3.56 (m, 2H, CH_2), 1.41 (t, 3H, CH_3). ^{13}C NMR (DMSO-d_6, ppm): 181.3 (C=S), 155.4 (C=N), 137.5, 132.4, 128.5, 124.3, 120.2, 112.0 (Ph-C), 30.5 (CH_2), 18.4 (CH_3). Anal. Calc. for $C_{10}H_{12}BrN_3OS$: C, 39.75; H, 4.00; N, 13.91. Found: C, 39.94; H, 4.16; N, 14.07%.



Scheme 1. Synthesis of 5-bromo-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone [H_2BDET, (**1**)].

2.3. *Synthesis of [Me_2Sn(BDET)] (2)*

A methanolic solution of Me_2SnCl_2 (0.219 g, 1.0 mmol) was added dropwise to a methanolic solution (10 mL) of 5-bromo-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone [H_2BDET, (**1**)] (0.302 g, 1.0 mmol) and KOH (0.11 g, 2.0 mmol). The resulting reaction mixture was stirred and refluxed for 5 h (scheme 2) and then filtered. The solid was washed with methanol and dried in desiccators over anhydrous silica gel. The yellow solids were purified by recrystallization from methanol and dried in *vacuo* over silica gel. Yield: 0.39 g, 74%: M.p: 222-224 °C: Molar conductivity (1×10^{-3} mol L^{-1}; DMSO) Ω^{-1} cm^2 mol^{-1}: 13.22: UV–Vis (DMSO)$\lambda_{max/nm}$: 250, 288, 342, 410: FT-IR (KBr, cm^{-1}) ν_{max}: 3171 (s, NH), 1590 (m, C=N), 1522 (s, C_{aro}-O), 1045 (m, N-N), 1328, 837 (w, C-S), 588 (w, Sn-C), 548 (w, Sn-O), 450 (w, Sn-N). ^{1}H NMR (DMSO-d_6, ppm): 8.55 (s, 1H, CS-NH), 8.24 (s, 1H, CH=N), 8.15 (d, 1H, J = 7.7, PhC3-H), 7.48 (d, 1H, J = 7.3, PhC4-H), 7.18 (s, 1H, PhC6-H), 3.54 (m, 2H, CH_2), 1.42 (t, 3H, CH_3) 1.05 (m, 6H, $^2J_{Sn-H}$ = 75.2 Hz, Sn-$(CH_3)_2$). ^{13}C NMR (DMSO-d_6, ppm): 169.3 (C=S), 162.4 (C=N), 142.2, 138.1, 132.3, 129.3, 125.4, 122.5 (Ph-C), 30.8 (CH_2), 18.5 (CH_3), 14.3 ($^1J_{Sn-C}$ = 541.0 Hz, Sn-$(CH_3)_2$). ^{119}Sn NMR (DMSO-d_6, ppm): –158.15. Anal. Calc. for $C_{12}H_{16}BrN_3OSSn$: C, 32.10; H, 3.59; N, 9.36%. Found: C, 32.26; H, 3.75; N, 9.49%.



Where, R = Me (**2**), R = n-Bu (**3**), R = Ph (**4**)

Scheme 2. Reaction scheme for the synthesis of diorganotin(IV) complexes (**2**-**4**).

The other diorganotin(IV) complexes (**3** and **4**) were synthesized following the same procedure by using the appropriate diorganotin(IV) chloride(s) (scheme 2).

2.4. *Synthesis of [Bu_2Sn(BDET)] (3)*

Yield: 0.52 g, 80%: M.p: 233-235 °C: Molar conductivity (1×10^{-3} mol L^{-1}; DMSO) Ω^{-1} cm^2 mol^{-1}: 10.81: UV–Vis (DMSO)$\lambda_{max/nm}$: 260, 274, 333, 409: FT-IR (KBr, cm^{-1}) ν_{max}: 3183 (s, NH), 1587 (m, C=N), 1531 (s, C_{aro}-O), 1030 (m, N-N), 1333, 840 (w, C-S), 582 (w, Sn-C), 544 (w, Sn-O), 448 (w, Sn-N). ^{1}H NMR (DMSO-d_6, ppm): 8.56 (s, 1H, CS-NH), 8.21 (s, 1H, CH=N), 8.14 (d, 1H, J = 7.5, PhC3-H), 7.50 (d, 1H, J = 7.4, PhC4-H), 7.22 (s, 1H, PhC6-H), 3.57 (m, 2H, CH_2), 1.43 (t, 3H, CH_3), 1.33-1.30 (t, 2H, J = 7.4 Hz, Sn-$\underline{CH_2}$-CH_2-CH_2-CH_3), 1.26-1.21 (m, 2H, Sn-CH_2-$\underline{CH_2}$-CH_2-CH_3), 1.13-1.10 (m, 2H, Sn-CH_2-CH_2-$\underline{CH_2}$-CH_3), 1.03-0.93 (t, 3H, J = 7.3 Hz, Sn-CH_2-CH_2-CH_2-$\underline{CH_3}$). ^{13}C NMR (DMSO-d_6, ppm): 170.8 (C=S), 165.2 (C=N), 144.4, 135.6, 130.1, 122.5, 118.8, 112.9 (Ph-C), 31.0 (CH_2), 28.4, 24.19, 22.7, 20.2 ($^1J_{Sn-C}$ = 535.1 Hz, Sn-Bu), 18.1 (CH_3). ^{119}Sn NMR (DMSO-d_6, ppm): –146.53. Anal. Calc. for $C_{18}H_{28}BrN_3OSSn$: C, 40.55; H, 5.29; N, 7.88%. Found: C, 40.43; H, 5.41; N, 7.96%.

2.5. *Synthesis of [$Ph_2Sn(BDET)$] (4)*

Yield: 0.56 g, 76%: M.p: 244-246 °C: Molar conductivity (1×10^{-3} mol L^{-1}; DMSO) Ω^{-1} cm^2 mol^{-1}: 8.95: UV–Vis (DMSO)$\lambda_{max/nm}$: 257, 292, 345, 418: FT-IR (KBr, cm^{-1}) ν_{max}: 3165 (s, NH), 1593 (m, C=N), 1537 (s, C_{aro}-O), 1038 (m, N-N), 1301, 819 (w, C-S), 589 (w, Sn-C), 546 (w, Sn-O), 459 (w, Sn-N). ^{1}H NMR (DMSO-d_6, ppm): 8.54 (s, 1H, CS-NH), 8.25 (s, 1H, CH=N), 8.10-7.20 (m, 13H, Ph-H), 3.55 (m, 2H, CH_2), 1.44 (t, 3H, CH_3). ^{13}C NMR (DMSO-d_6, ppm): 168.4 (C=S), 160.0 (C=N), 148.1-123.7 (Ph-C, $^1J_{Sn-C}$ = 524.8 Hz, Sn-Ph), 30.5 (CH_2), 18.8 (CH_3) ^{119}Sn NMR (DMSO-d_6, ppm): –162.38. Anal. Calc. for $C_{22}H_{20}BrN_3OSSn$: C, 46.11; H, 3.52; N, 7.33%. Found: C, 46.27; H, 3.68; N, 7.49%.

2.6. *Antibacterial test*

The synthesized compounds **1-4** were screened *in vitro* for their antibacterial activities against *Staphylococcus aureus* (ATCC 6538), *Enterobacter aerogenes* (ATCC 13048), *Escherichia coli* (ATCC 15224) and *Salmonella typhi* (ATCC 10749) using the agar well diffusion method [35]. Ciprofloxacin was used as the reference drug. The bacteria from stock culture were lightly inoculated into the Mueller Hinton Broth (MHB) and allowed to grow overnight at 37 °C in an ambient air incubator. The culture was diluted with new MHB in order to get an absorbance value of 2.0×10^6 colony forming units (CFU/mL) or 0.168 at wavelength of 550 nm in the spectrophotometer. Sterile cotton swab was dipped into the broth culture and inoculated on the Mueller Hinton Agar (MHA). Sterile paper discs with 6 mm diameter were placed on the agar in equal distance. The recommended concentration of the test sample (2 mg/mL in DMSO) was introduced individually to each of the discs. The agar plates were incubated immediately at 37 °C for 24 h. For each plate, DMSO mixture and reference antibacterial drug like doxycycline served as negative and positive controls, respectively. The activity was confirmed by measuring the diameter of zones showing complete inhibition (mm). Growth inhibition was calculated with reference to the positive control.

3. Results and discussion

3.1. *Synthesis*

5-Bromo-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone (**H_2BDET**) was synthesized by condensation of 5-bromo-2-hydroxybenzaldehyde and 4-ethyl-3-thiosemicarbazide (scheme 1).

The new complexes **2-4** were synthesized by reaction of R_2SnCl_2 (R = Me, Bu and Ph) with H_2BDET (**1**) in absolute methanol in the presence of KOH in 1:2:1 molar ratio (metal:base:ligand) (scheme 2). All these new diorganotin(IV) complexes were yellow solids, air stable and soluble in DMSO, DMF, $CHCl_3$, CH_2Cl_2, and THF at RT. The low molar conductivities of the complexes (8.5-13.5 $\Omega^{-1}cm^2mol^{-1}$) in DMSO show the non-electrolytic behavior of the complexes [36]. All the complexes were characterized by various physico-chemical techniques. The physical properties and analytical data of **1**-**4** are given in section 2. The molecular structure of **4** has been determined by X-ray diffraction studies. H_2BDET (**1**) coordinated to tin(IV) center in all complexes as dinegative ONS-tridentate chelating agent.

3.2. *UV–Vis spectra*

The electronic spectra of the H_2BDET (**1**) and its complexes (**2-4**) were carried out in DMSO at RT (figure 1). Electronic spectra of H_2BDET (**1**) showed three broad bands at 256, 301 and 347 nm. The absorption band at 256 nm may be due to π-π* (aromatic ring) transitions. Bands at 301 and 347 nm were assigned to n-π* transitions of the C=N chromophore and thiolate group, respectively. A little shift of these absorption bands in the complexes may be due to the intra-ligand transitions. Furthermore, a new sharp band was observed at 418-410 nm in the spectra of the complexes (**2-4**), which can be assigned as ligand to metal charge transfer (LMCT) transitions [37]. There is significant shifting in the chromophore due to coordination with tin [38]. The appearance of these peaks depends on the electron donor ability of the R groups attached to the Sn atom. Therefore, the shift in the bands indicates coordination between ligand and tin(IV).

3.3. *Infrared spectra*

The IR spectra of H_2BDET (**1**) show a strong band at 3303 cm^{-1} due to ν(OH) and a strong band at 3251 cm^{-1} due to ν(NH). These bands are not observed in **2-4**, indicating coordination with tin(IV) after deprotonation of H_2BDET. A medium band at 1610 cm^{-1} due to the ν(C=N) in free **1** is shifted 23-17 cm^{-1} to lower frequencies on complexation, indicating coordination of azomethine nitrogen to tin(IV) [38]. A medium intensity band at 1551 cm^{-1} may be due to the ν(C_{aro}–O) of free **1**. This band is slightly shifted to the lower frequencies in spectra of **2-4**, indicating coordination of phenolic oxygen to tin(IV). The band at 988 cm^{-1} in free **1** due to the

ν(N-N) shifted to higher frequencies after complexation, further indicating coordination through the azomethine nitrogen [39]. Absorption in the spectra of free **1** at 1351 and 859 cm^{-1} are due to ν(C=S). The lowering of these absorptions in spectra of **2-4** indicate that the thiolate sulphur bonded to tin(IV) [40]. The appearance of some new bands in spectra of **2-4** at 589-582, 548-544 and 459-448 cm^{-1} are possibly due to ν(Sn-C), ν(Sn-O) and ν(Sn-N), respectively, support for the bonding of oxygen and nitrogen to tin(IV) [41]. Therefore, IR spectra support the proposed coordination in the organotin(IV) complexes which is confirmed by the X-ray crystal studies.

3.4. *^{1}H, ^{13}C and ^{119}Sn NMR spectra*

NMR spectral studies of **1** and **2-4** were carried out in DMSO and interpreted according to the atom labelling in scheme 2. **1** exhibits sharp OH and NH-N proton signals at 11.30 and 10.31 ppm, respectively. The absence of both signals in the diorganotin(IV) complexes indicates deprotonation and coordination of phenolic oxygen and thiolate sulphur of the ligand. **1** shows a CH=N proton signal at 8.27 ppm, which shifts slightly downfield in **2-4** due to participation of the azomethine nitrogen in bonding with tin(IV). The signal due to aromatic protons of **1** is shifted slightly downfield in the complexes, indicating phenolic oxygen is coordinated to tin(IV). Complex **2** exhibits a sharp singlet at 1.05 ppm for $Sn(Me)_2$ protons. The ^{2}J [^{119}Sn-^{1}H] coupling satellite for this complex is 75.2 Hz, supporting five-coordinate tin(IV), comparable to published reports [41, 42]. Substituting the value of ^{2}J[^{119}Sn-^{1}H] in the Lockhart–Manders equations ($\theta = 0.0161\ [^{2}J]^{2} - 1.32[^{2}J] + 133.4$) affords 125.18° for Me-Sn-Me angle in **2**, which also supports the five-coordinate tin(IV) [43]. **1** shows a multiplet at 3.56 ppm for ($-CH_2$) and a triplet at 1.41 ppm for ($-CH_3$) protons and these are at almost the same chemical shifts in spectra of the diorganotin(IV) complexes. Complex **3** shows four resonances at 1.33-1.30 ppm (t, 2H, J = 7.4 Hz, $-CH_2$), 1.26-1.21 ppm (m, 2H, $–CH_2$), 1.13-1.10 ppm (m, 2H, $–CH_2$) and 1.03–0.93 ppm (t, 2H, J = 7.3 Hz, CH_3) due to the Sn-Bu protons.

The ^{13}C NMR spectra of **1** and **2-4** were recorded in DMSO and given in Section 2. Free **1** exhibited resonances at 181.37 and 155.40 ppm due to (C=S) and (C=N) groups, respectively. The carbon signals of the (C-S) group shifted upfield to 170.85-168.42 ppm whereas chemical shifts of (C=N) carbon shifted downfield to 165.27–160.08 ppm in all the complexes, clearly indicating coordination of thiolate sulphur and azomethine nitrogen to tin(IV). The δ value of aromatic ring carbon was observed to be slightly downfield in the

complexes compared to the free ligand, indicating involvement of phenolic oxygen in coordination. The chemical shifts of (-CH_2CH_3) carbons were observed at similar position in the complexes with free **1**. The carbons of butyl groups attached to the tin(IV) in **3** were observed at 28.48-20.25 ppm and comparable with other diorganotin(IV) complexes [44]. The $^1J(^{13}C\text{-}^{119}Sn)$ value is a key parameter to determine the possible coordination number of diorganotin(IV) complexes in solution. The calculated $^1J(^{13}C\text{-}^{119}Sn)$ values are 562.33, 548.45 and 552.34 Hz for [Me_2Sn(BDET] (**2**), [Bu_2Sn(BDET)] (**3**) and [Ph_2Sn(BDET)] (**4**), respectively, indicating five-coordinate tin(IV) in these complexes [45]. In diorganotin(IV) complexes, the C–Sn–C angle can be assessed using the Lockhart–Manders equation θ(C-Sn-C) = [$|^1J(^{13}C\text{-}^{119}Sn)|$ + 875]/11.4. The observed C–Sn–C angles for the diorganotin(IV) complexes (**2**-**4**) were 126.08-125.20°, consistent with five-coordinate geometry around tin(IV) [46]. The estimated C-Sn-C angles observed from NMR spectra of **2**-**4** show a little deviation from C_{ph}-Sn-C_{ph} angle found from X-ray crystal analysis of **4**.

The ^{119}Sn chemical shifts present key information to authenticate the coordination environment around the central tin atom. The occurrence of sharp signals from -162.38 to -146.53 ppm in the ^{119}Sn NMR spectra of **2**-**4** strongly indicates five-coordinate geometry around tin(IV) [47, 48].

3.5. *Crystallographic study of [Ph_2Sn(BDET)] (4)*

The molecular structure of diphenyltin(IV) complex of 5-bromo-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone (**4**) was determined by single crystal X-ray diffraction. The molecular structure of **4** along with the atomic numbering scheme is shown in figure 2. X-ray crystallographic data and structure refinement results of **4** are summarized in table 1. Selected bond lengths (Å) and angles (°) are given in table 2. Compound **4** crystallizes in a triclinic lattice with space group *P-1*. X-ray structure of **4** revealed that the doubly deprotonated ligand is coordinated to tin(IV) *via* phenolic oxygen, azomethine nitrogen and thiolate sulphur. The structure shows that tin(IV) is five coordinate in a trigonal bipyramidal geometry. In **4**, the ligand is coordinated to tin(IV) as a tridentate ONS-donor. In the coordination polyhedron one carbon of each of two phenyl groups (C11 and C17) and azomethine nitrogen (N1) occupy the equatorial plane whereas the coordinated O1 and S1 occupy the axial positions. The bond angles may be ascertained as a proof of distorted trigonal bipyramidal geometry, equatorial–equatorial

angles are C11–Sn1–C17 (112.07(6)°, N1–Sn1–C11 (112.77(6)° and N1–Sn1–C17 (135.11(6)°. The whole sum of equatorial angles is 359.95° showing tin(IV) lies in the plane of the thiosemicarbazone moiety. These geometric arrangements are in agreement with other organotin(IV) complexes [32, 49]. The thiolate sulphur (S1) and phenolic oxygen (O1) are apical. The axial S1-Sn1-O1 angle (160.13(4)°) is evidence of the distorted trigonal bipyramidal geometry of **4**, deviating from 180°. The sum of bond angles of N1-Sn1-O1 (83.59(5)°) and N1-Sn1-S1 (78.08(4)°) is 161.67°, evidence of distortion from 180°. The deviation from perfect trigonal bipyramidal geometry is most probably owing to the non flexibility of chelate rings and large covalent radius of Sn(IV). The tin(IV) atom makes the following non-planar six- and five-membered chelate rings upon complexation: Sn1-N1-C7-C6-C1-O1 and Sn1–N1-N2-C8-S1. The bond angles of N1-Sn1-C11 of 112.77°, N1-Sn1-C17 of 135.11° and C11-Sn1-C17 of 112.07° where N1, C11 and C17 are placed at the three corners of TBP plane. This is may be due to the repulsion of the two phenyl groups at tin(IV). Hence, the geometric results are strong evidence for distorted trigonal bipyramidal environment around Sn(IV) moiety. To describe the geometrical environment around tin we use τ value, the so called trigonal index. The τ value can be defined as $\tau = (\beta-\alpha)/60$, where β and α are two largest donor-metal-donor angles around tin(IV) center [50]. For ideal trigonal bipyramidal geometry τ value should be equal to unity. For the diphenyltin(IV) complex **4**, $\beta = 160.13$ and $\alpha = 112.07$; so $\tau = 0.80$ regarded as a distorted trigonal-bipyramidal geometry around tin [51]. The bond distance of Sn1–N1 bond (2.2068 Å) is a little longer than the Sn–N (2.15 Å) [52], indicating strong bonding between azomethine nitrogen (N1) and Sn1. The observed Sn1-O1 bond distance (2.0710 Å) is similar with Sn-O (2.10 Å) and comparable to reported organotin(IV) complexes [53, 54]. The Sn1-S1 bond distance (2.5163 Å) is comparable to reported organotin(IV) complexes and is near to the sum of the Sn-S covalent radii (2.42 Å) [55, 56]. The bond distances of Sn1-C11 (2.1333 Å) and Sn1-C17 (2.1426 Å) are comparable with values reported but slightly shorter than the Sn-C (2.17 Å) covalent radii [57, 58]. The packing diagram of [Ph_2Sn(BDET)] (**4**) is given in figure 3. In the crystal structure of **4** dimeric structures are formed by N-H···S hydrogen bonding interactions between two neighboring molecules. Furthermore, the crystal packing structure of **4** is stabilized by C-H...π and π...π interactions of the phenyl fragments in successive layers.

3.6. *Antibacterial activity*

The in *vitro* antibacterial properties of the ligand and diorganotin(IV) complexes were examined against the strains of the *Staphylococcus aureus*, *Enterobacter aerogenes*, *Escherichia coli* and *Salmonella typhi* and the results are reported in table 3. Test compounds are considered active against the bacteria if the inhibition zone diameter is over 7 mm [59]. The free ligand showed moderate activity, perhaps due to the presence of NH/OH groups in their structure which impart biological activity [60]. Metal compounds having halogen groups at different positions of the aromatic ring show more inhibitory effects [61]. Considering the N(4)-substituted ligand and its complexes examined, complexes **2**, **3** and **4** have more activities than the free ligand. **4** presented higher inhibition to growth of organisms 28.1 29.8, 27.5 and 26.5 mm against *S. Aureus*, *E. coli*, *E. aerogenes* and *S. typhi*, respectively, which represent the highest activity. Complex **2** exhibited second highest activity to four strains of bacteria. Perhaps the presence of bulky phenyl or methyl groups promote binding to biological molecules *via* π-π interactions causing improvement of their activities. This observation suggested that the activity of the studied compound is dependent on the group attached to tin(IV) in the order $Ph_2 > Me_2 > Bu_2$. The effect of various compounds may then vary among microorganisms due to difference in the structures of the cell. Metal chelation with a ligand, when compared with the free ligand improves biological activities, may favor their permeation through the lipid layer of the cell membrane [62, 63]. This antibacterial result is corroborated to those reported for other tin compounds, wherein enhancement of activity has been described due to coordination into bacterial cells [64-66]. These results also show that efficiency is enhanced by the bromine substituent on the aromatic ring of the complexes compared with previously published papers [67, 68]. Results were compared with those of Ciprofloxacin, which is commonly used as a reference in antibacterial studies because of its high activity against bacteria [68].

4. Conclusion

5-Bromo-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone (H_2BDET) is a tridentate ligand coordinating to tin(IV) through azomethine nitrogen, thionic sulphur, and phenolic oxygen. UV-Vis, IR, ^{1}H, ^{13}C and ^{119}Sn NMR indicated five-coordinate geometries for these organotin(IV) complexes. The X-ray crystallographic studies show distorted trigonal bipyramidal Sn(IV) in **4**. Coordination of N(4)-thiosemicarbazone ligand to Sn(IV) results in an enhancement

of their antibacterial activities. All complexes show antibacterial activities against four bacterial strains in the order **4** > **2** > **3** > **1**. The study showed all complexes were active but found to be less active compared to the standard drug. **4** may represent a new strategy to prepare antibacterial agents. Further investigations must be done to design new metal-based drugs in the future.

Supplementary data

CCDC reference number 1400811 contains the supplementary crystallographic data for $[Ph_2Sn(BDET)]$ (**4**). This data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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Graphical abstract

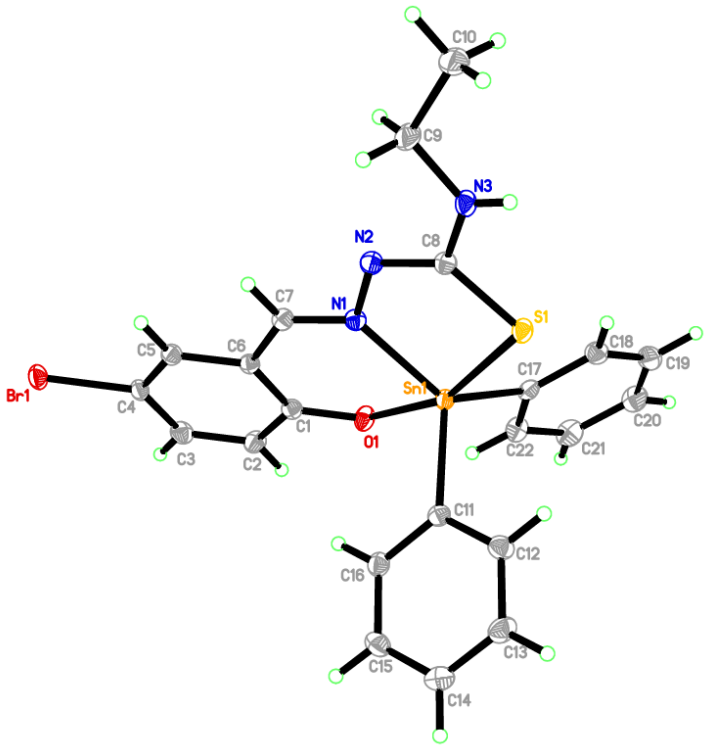

Table 1. Crystal data and structure refinement parameters for [Ph_2Sn(BDET)] (**4**).

Empirical formula	$C_{22}H_{20}BrN_3OSSn$
Formula weight	573.07
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a (Å)	8.5020(3)
b (Å)	11.2097(5)
c (Å)	12.3125(5)
α (°)	71.8201(10)
β (°)	78.5679(11)
γ (°)	72.1086(10)
V (Å^3)	1054.13(7)
Z	2
Calculated density (mg/m^3)	1.805
Radiation type λ (Å)	M_0K/α
F(000)	564
Crystal size (mm)	0.320 × 0.208 × 0.134
Crystal color	Yellow
Scan range θ (°)	2.26-30.26
Absorption coefficient (μ) (mm^{-1})	3.225
Max. and min. trans.	0.425 and 0.672
Goodness-of-fit (GOF) on F^2	1.034
Data / restraints / parameters	6251 / 0 / 267
Final R indices [I> 2σ(I)]	R_1 = 0.0210, wR_2 = 0.0466
R indices (all data)	R_1 = 0.0262, wR_2 = 0.0489

Table 2. Selected bond lengths (Å) and angles (°) of **4**.

Bond lengths (Å)			
Sn1-S1	2.5162(5)	O1-C1	1.323(2)
Sn1-O1	2.0710(14)	N1-N2	1.388(2)
Sn1-N1	2.2068(14)	N1-C7	1.304(2)
Sn1-C11	2.1333(18)	N2-C8	1.310(2)
Sn1-C17	2.1427(18)	N3-C8	1.345(2)
Br1-C4	1.8978(18)	N3-C9	1.451(2)
S1-C8	1.7467(17)	C1-C2	1.406(3)
Bond angles (°)			
S1-Sn1-O1	160.13(4)	C11-Sn1-C17	112.07(6)
N1-Sn1-C11	112.77(6)	Sn1-S1-C8	96.17(6)
S1-Sn1-C11	99.33(5)	Sn1-O1-C1	132.63(12)
S1-Sn1-C17	96.95(5)	Sn1-N1-N2	121.92(11)
O1-Sn1-N1	83.59(5)	Sn1-N1-C7	125.52(12)
O1-Sn1-C11	94.76(6)	N2-N1-C7	112.53(14)
O1-Sn1-C17	90.60(6)	N1-N2-C8	116.34(14)
S1-Sn1-N1	78.09(4)	C8-N3-C9	122.73(17)

Table 3. Antibacterial activities[a] of free **1** and **2**-**4** (inhibition zone in mm).

Samples	Bacterium			
	S. aureus	*E. coli*	*E. aerogenes*	*S. typhi*
1	13.2	11.4	10.1	9.2
2	26.4	24.7	26.7	25.4
3	20.6	22.8	25.6	24.3
4	28.1	29.8	27.5	26.5
R	33.9	34.5	31.8	33.8

[a]Concentration used: 2 mg/ml of DMSO, R = standard drug: ciprofloxacin

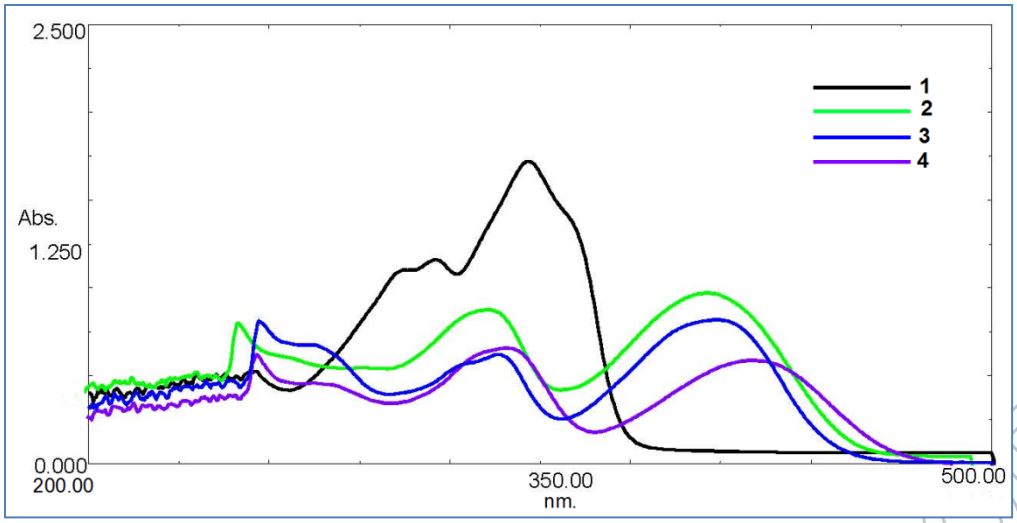

Figure 1. Electronic spectra of **1**-**4** in DMSO (1×10^{-4} M).

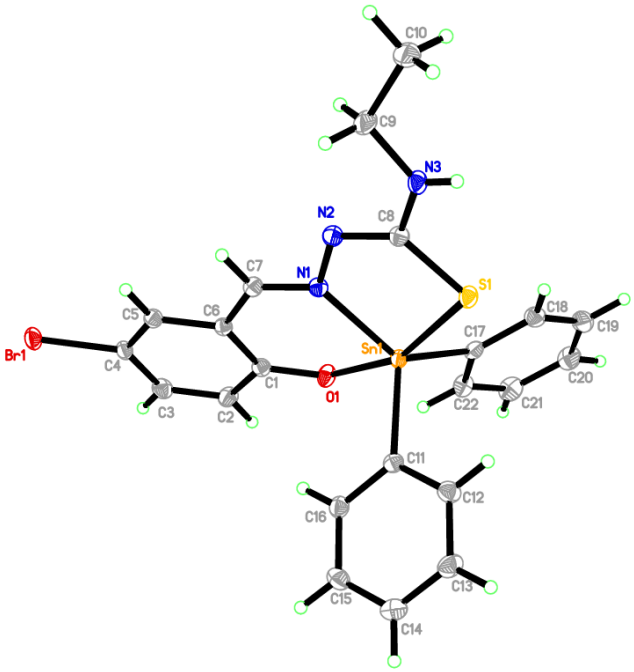

Figure 2. Molecular structure of [Ph_2Sn(BDET)] (**4**) showing displacement ellipsoids at the 50% probability level.

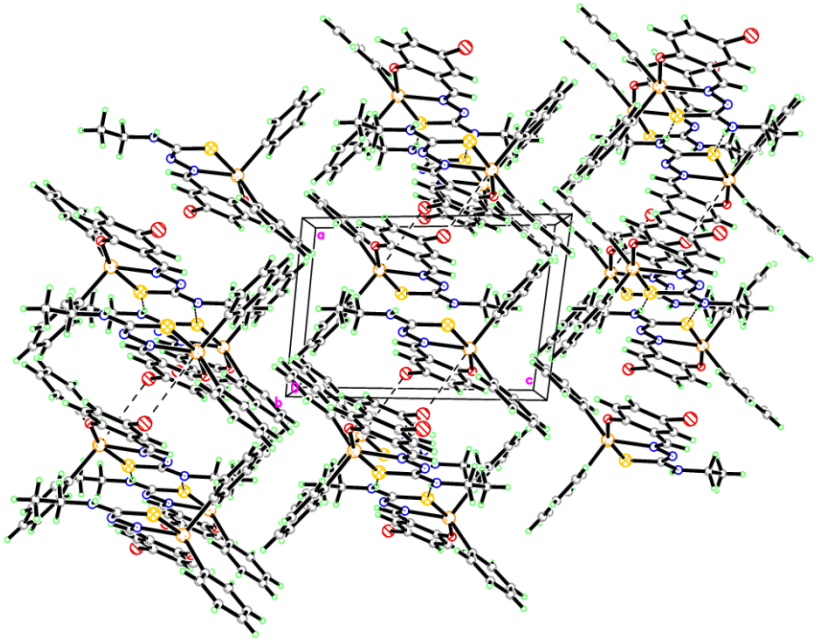

Figure 3. The packing diagram of [Ph_2Sn(BDET)] (**4**) in the crystal lattice, viewed along the *c* axis.