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# Binuclear organotin(IV) complexes with adipic dihydrazones: Synthesis, spectral characterization, crystal structures and antibacterial activity

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ABSTRACT

New organotin(IV) complexes, $(R_2Sn)_2L$ [L = $L^a$: R = Me (**1**), Ph (**2**); L = $L^b$: R = Me (**3**), Ph (**4**)] have been synthesized by reaction of dihydrazone ligands, bis(5-bromosalicylaldehyde) adipicdihydrazone ($H_4L^a$) and bis(2-hydroxynaphthaldehyde) adipicdihydrazone ($H_4L^b$) with $R_2SnCl_2$ (R = Me or Ph). The synthesized compounds have been investigated by elemental analysis and IR, $^1$H NMR, and $^{119}$Sn NMR spectroscopy. The structures of **1** and **4** have been also confirmed by X-ray crystallography. The results show that the dihydrazone acts as a tetrabasic ligand in the enolic form and is coordinated to two diorganotin moiety via the imine nitrogen and phenolic and enolic oxygen atoms. All complexes are binuclear and the coordination number of each tin is five. The *in vitro* antibacterial activity of ligands and complexes has been evaluated against Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria and compared with standard drugs. All complexes exhibit more inhibitory effects than the parent ligands.



## 1. Introduction

Acylhydrazones and their metal complexes have attracted great and growing interest due to their interesting biological properties, such as antibacterial, antifungal and antitumor activities. These compounds have been found to have therapeutic activity for example in the treatment of tuberculosis and Fe overload disease. Also, they have been used as fluorescent materials, pigments, analytical reagents and polymer-coating [1–5]. In the field of hydrazone chemistry, a special place is held by bis-acylhydrazones for several reasons [6]: (i) The presence of two coordinating unit in these ligands may yield supramolecular architectures or better coordinative properties than those a sole coordinative unit, (ii) a ditopic ligand enables the properties of its complexes to be modulated by the degree of deprotonation, and (iii) metal complexes of dihydrazones may be able to mimic bimetallic sites in various enzymes. Among the research dealing with complexes of hydrazones, increasing attention has been devoted to organotin(IV) complexes in view of chemical properties, biological significance, industrial importance, and structural variety of organotin(IV) compounds [7]. Since biocidal properties of organotin(IV) compounds are dependent on both the organic group and the ligand attached to tin [8,9], an interesting development is introducing ligands which are themselves bioactive [8,10–12]. Up to now many organotin complexes with a variety of hydrazones have been studied due to the importance of their medicinal assays for bactericide and antitumor purposes [13–15] and also because of an interesting variety of structural possibilities. However, less attention has been paid to organotin complexes with diacylhydrazones as multidentate ligands [16–18].

As part of our investigation dealing with the study of diorganotin(IV) complexes with Schiff bases, this paper reports the syntheses, crystal structures, spectral properties and antibacterial activities of diphenyl- and dimethyltin(IV) complexes with bis-acylhydrazones derived from condensation of adipic dihydrazide with 5-bromosalicylaldehyde and 2-hydroxynaphthaldehyde, $H_4L^a$ and $H_4L^b$, respectively, Fig. 1.

## 2. Experimental

### 2.1. Materials and methods

All starting materials were purchased from Merck while diphenyltin dichloride was supplied from Acros Company and were all used as received. All solvents were of reagent grade and used

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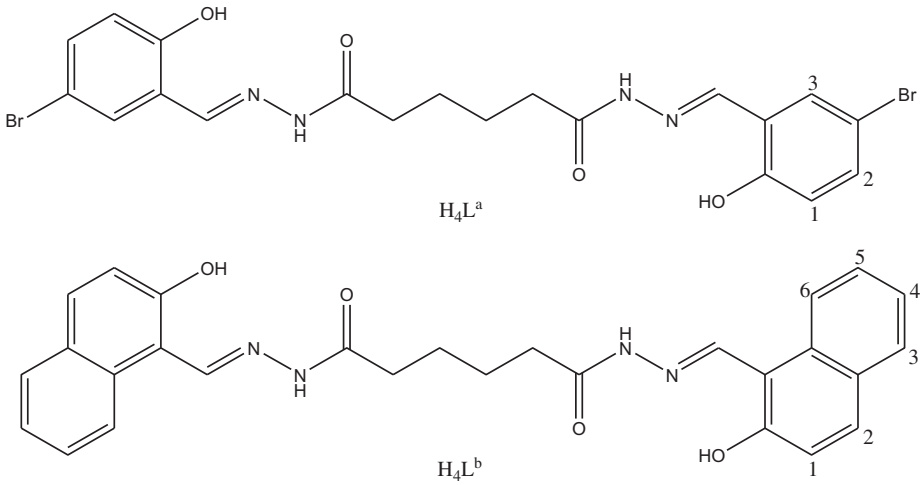


**Fig. 1.** Structure of dihydrazone ligands with numbering for $^1$H NMR assignments.

without further purification. IR spectra were obtained using a FT BOMEM MB102 spectrophotometer. The $^1$H and $^{119}$Sn NMR spectra were recorded with a Bruker 400 MHz Avance Ultrashield spectrometer.

### 2.2. Synthesis of bis(5-bromosalicylaldehyde)adipicdihydrazone ($H_4L^a$)

A mixture of adipic dihydrazide (0.043 g, 0.25 mmol) and 5-bromosalicylaldehyde (0.125 g, 0.625 mmol) was refluxed in ethanol for 3 h. After this time the white product was filtered and washed with ethanol. Yield: 0.133 g (90%); m.p. 287 °C; IR (KBr, cm$^{-1}$): $\nu$(NH/OH), 3100–3200 br; $\nu$(C=O), 1679; $\nu$(C=N), 1611. $^1$H NMR (DMSO-d$_6$): $\delta$ = 1.62 (t, br, 4H, CH$_2$), 2.63 (t, br, 4H, CH$_2$), 6.86 (d, 2H, H1, $^3J_{HH}$ = 8.7 Hz), 7.40 (dd, 2H, H2, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz), 7.72 (d, 2H, H3, $^4J_{HH}$ = 2.3 Hz), 8.31 (s, 2H, HC=N), 11.22 (s, 2H, NH), 11.69 (s, 2H, OH).

### 2.3. Synthesis of bis(2-hydroxynaphthaldehyde)adipicdihydrazone ($H_4L^b$)

A mixture of adipic dihydrazide (0.174 g, 1 mmol) and 2-hydroxynaphthaldehyde (0.430 g, 2.5 mmol) was refluxed in ethanol for 5 h. After this time the milky precipitate was filtered and washed with ethanol. Yield: 0.310 g (65%); m.p. 220 °C; IR (KBr, cm$^{-1}$): $\nu$(NH/OH), 3100–3200 br; $\nu$(C=O), 1659; $\nu$(C=N), 1615. $^1$H NMR (DMSO-d$_6$): $\delta$ = 1.70 (t, br, 4H, CH$_2$), 2.33 (t, br, 4H, CH$_2$), 7.20 (d, 2H, H1, $^3J_{HH}$ = 8.7 Hz), 7.40 (t, 2H, H4, $^3J_{HH}$ = 7.6 Hz), 7.58 (t, 2H, H5, $^3J_{HH}$ = 7.7 Hz), 7.87 (m, 4H, H2, 3), 8.20 (d, 2H, H6, $^3J_{HH}$ = 8.6 Hz), 9.16 (s, 2H, HC=N), 11.75 (s, 2H, NH), 12.65 (s, 2H, OH).

### 2.4. Synthesis of $(Me_2Sn)_2L^a$ (**1**)

Triethylamine (0.4 mmol) was added to a solution of $H_4L^a$ (0.054 g, 0.1 mmol) in ethanol (20 mL). This solution was stirred for 30 min. Then a solution of $Me_2SnCl_2$ (0.055 g, 0.25 mmol) in ethanol (10 mL) was added. The solution was refluxed for 4 h. After this time the yellow product was filtered and washed with ethanol. Yield: 0.024 g (30%). The solid was recrystallized from chloroform/ethanol and yellow lozenge single crystals suitable for X-ray crystallography were formed by slow evaporation at room temperature. Anal. Calc. for $C_{24}H_{28}N_4O_4Br_2Sn_2$: C, 34.56; H, 3.36; N, 6.72%; Found: C, 34.80; H, 2.95; N, 6.95. IR (KBr, cm$^{-1}$): $\nu$(C=N), 1609; $\nu_{as}$(Sn–C), 650; $\nu$(Sn–O), 570; $\nu_s$(Sn–C), 528; $\nu$(Sn–N), 457. $^1$H NMR ($CDCl_3$): $\delta$ = 0.79 [s, 12H, SnMe$_2$, $^2J(^{119}Sn-^1H)$ = 78.2 Hz], 1.72 (t, br, 4H, CH$_2$), 2.34 (t, br, 4H, CH$_2$), 6.65 (d, 2H, H1, $^3J_{HH}$ = 9.0 Hz), 7.21 (d, 2H, H3, $^4J_{HH}$ = 2.5 Hz), 7.36 (dd, 2H, H2, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.5 Hz), 8.46 [s, 2H, HC=N, $^3J(^{119}Sn-^1H)$ = 45.4 Hz]. $^{119}$Sn NMR ($CDCl_3$): $\delta$ = −151.

### 2.5. Synthesis of $(Ph_2Sn)_2L^a$ (**2**)

Complex **2** was synthesized as described for compound **1** from $Ph_2SnCl_2$ (0.086 g, 0.25 mmol). Yield: 0.068 g (63%). Anal. Calc. for $C_{44}H_{36}N_4O_4Br_2Sn_2$: C, 48.82; H, 3.33; N, 5.17%. Found: C, 48.12; H, 2.95; N, 4.67%. IR (KBr, cm$^{-1}$): $\nu$(C=N), 1607; $\nu$(Sn–O), 572; $\nu$(Sn–N), 445. $^1$H NMR (DMSO-d$_6$): $\delta$ = 1.71 (t, br, 4H, CH$_2$), 2.35 (t, br, 4H, CH$_2$), 6.82 (d, 2H, H1, $^3J_{HH}$ = 9.0 Hz), 7.27–7.37 [m, 12H, H$_{m,\ p}$ (Ph$_2$Sn)], 7.37 (d, 2H, H3, $^4J_{HH}$ = 2.5 Hz), 7.54 [m, 8H, H$_o$(Ph$_2$Sn)], 7.75 (d, br, 2H, H2, $^3J_{HH}$ = 7.2 Hz), 8.56 [s, 2H, HC=N, $^3J(^{119}Sn-^1H)$ = 50.9 Hz]. $^{119}$Sn NMR (DMSO-d$_6$): $\delta$ = −425.

### 2.6. Synthesis of $(Me_2Sn)_2L^b$ (**3**)

Triethylamine (0.4 mmol) was added to a solution of $H_4L^b$ (0.048 g, 0.1 mmol) in methanol (20 mL). This solution was stirred for 30 min. Then a solution of $Me_2SnCl_2$ (0.055 g, 0.25 mmol) in methanol (10 mL) was added. The solution was refluxed for 5 h. After this time the yellow product was filtered and washed with methanol. Yield: 0.032 g (41%); Anal. Calc. for $C_{32}H_{34}N_4O_4Sn_2$: C, 49.5; H, 4.38; N, 7.22; Found: C, 49.64; H, 3.99; N, 7.42%. IR (KBr, cm$^{-1}$): $\nu$(C=N), 1610; $\nu_{as}$(Sn–C), 637; $\nu$(Sn–O), 566; $\nu_s$(Sn–C), 530; $\nu$(Sn–N), 459. $^1$H NMR (DMSO-d$_6$): $\delta$ = 0.65 [s, 12H, SnMe$_2$, $^2J(^{119}Sn-^1H)$ = 86.0 Hz], 1.67 (t, br, 4H, CH$_2$), 2.33 (t, br, 4H, CH$_2$), 6.88 (d, 2H, H1, $^3J_{HH}$ = 9.1 Hz), 7.28 (t, 2H, H4, $^3J_{HH}$ = 7.6 Hz), 7.46 (t, 2H, H5, $^3J_{HH}$ = 7.7 Hz), 7.87 (m, 2H, H3, $^3J_{HH}$ = 8.0 Hz), 7.83 (m, 2H, H2, $^3J_{HH}$ = 9.1 Hz), 8.16 (d, 2H, H6, $^3J_{HH}$ = 8.7 Hz), 9.45 [s, 2H, HC=N, $^3J(^{119}Sn-^1H)$ = 40.4 Hz]. $^{119}$Sn NMR (DMSO-d$_6$): $\delta$ = −209.

### 2.7. Synthesis of $(Ph_2Sn)_2L^b$ (**4**)

Complex **2** was synthesized as described for compound **1** from $Ph_2SnCl_2$ (0.086 g, 0.25 mmol) and in ethanol. Yield: 0.065 g (63%). The yellow needle single crystals suitable for X-ray crystallography were obtained after recrystallization from chloroform/ethanol. Anal. Calc. for $C_{52}H_{42}N_4O_4Sn_2$: C, 60.85; H, 3.90; N, 5.46%. Found: C, 61.13; H, 3.51; N, 6.52%. IR (KBr, cm$^{-1}$): $\nu$(C=N), 1603; $\nu$(Sn–O), 572; $\nu$(Sn–N), 465. $^1$H NMR ($CDCl_3$): $\delta$ = 1.98 (s, 4H, CH$_2$), 2.51 (s, 4H, CH$_2$), 6.88 (d, 2H, H1, $^3J_{HH}$ = 9.1 Hz), 7.34 (t, 2H, H4, $^3J_{HH}$ = 7.2 Hz),

7.38–7.44 [m, 12H, $H_{m,p}$ ($Ph_2Sn$)], 7.46 (t, 2H, H5, $^3J_{HH} = 8.0$ Hz), 7.73 (m, 2H, H3, $^3J_{HH} = 7.7$ Hz), 7.85 [m, 8H, H2, $H_o$($Ph_2Sn$)], 8.01 (d, 2H, H6, $^3J_{HH} = 8.6$ Hz), 9.58 [s, 2H, HC=N, $^3J(^{119}Sn-^1H) = 55.8$ Hz]. $^{119}Sn$ NMR ($CDCl_3$): $\delta = -330$.

### 2.8. X-ray structure determination

Data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using MoKα radiation ($\lambda = 0.71073$ Å). Data collection, cell refinement, data reduction and absorption correction were performed using multiscan methods with Bruker software [19]. The structures were solved by direct methods using SIR2004 [20]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on $F^2$ using SHELXL [21]. All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collection and analysis are reported in Table 1.

### 2.9. Antibacterial tests

The *in vitro* antibacterial activity of ligands and their corresponding organotin(IV) complexes was investigated against the standard strains of two Gram-positive (*Bacillus subtilis* ATCC 6633 and *Staphylococcus aureus* ATCC 6538) and two Gram-negative (*Escherichia coli* ATCC 35218 and *Pseudomonas aeruginosa* ATCC 27853) bacteria. In order to compare the results, Nalidixic acid (30 mg/disc) and Vancomycin (30 mg/disc) were used as standard antibacterial drugs. Determination of the antibacterial activity was carried out by paper-disc diffusion method. The compounds were dissolved in DMSO at 10, 20 and 40 mg/mL concentration. Muller Hinton broth was used for preparing basal media for the bioassay of the organisms. A lawn culture from 0.5 MacFarland suspension of each strain was prepared on Muller Hinton agar. Blank paper discs (6.4 mm diameter) were saturated with a solution of test compounds and placed on the surface of the agar plates. On one paper disc only DMSO was poured as a control. The plates were incubated at 37 °C for 24 h. The inhibition zone diameters around each disc were measured in mm.

**Table 1**
Crystallographic and structure refinement data for **1** and **4**.

| | **1** | **4** |
|---|---|---|
| Empirical formula | $C_{24}H_{28}Br_2N_4O_4Sn_2$ | $C_{52}H_{42}N_4O_4Sn_2$ |
| Formula weight | 833.70 | 1024.28 |
| $T$ (K) | 293(2) | 296(2) |
| Wavelength, $\lambda$ (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic |
| Space group | P-1 | C2/c |
| Crystal size ($mm^3$) | 0.20 × 0.18 × 0.12 | 0.19 × 0.07 × 0.06 |
| $a$ (Å) | 6.626 | 37.333(9) |
| $b$ (Å) | 10.030 | 12.410(3) |
| $c$ (Å) | 12.089 | 9.888(2) |
| $\alpha$ (°) | 67.42 | 90 |
| $\beta$ (°) | 74.67 | 102.874(14) |
| $\gamma$ (°) | 86.04 | 90 |
| $V$ ($Å^3$) | 715.0 | 4465.8(18) |
| $Z$ | 1 | 4 |
| $D_{calc.}$ ($Mg\ m^{-3}$) | 1.936 | 1.523 |
| $\theta$ Ranges for data collection (°) | 1.89 to 29.00 | 2.64 to 27.00 |
| $F$(000) | 402 | 2056 |
| Absorption coefficient ($mm^{-1}$) | 4.577 | 1.169 |
| Index ranges | $-9 \le h \le 9$ | $-47 \le h \le 47$ |
| | $-13 \le k \le 13$ | $-15 \le k \le 15$ |
| | $-16 \le l \le 16$ | $-12 \le l \le 12$ |
| Reflections collected | 29,685 | 39,095 |
| Independent reflections | 3791 | 4876 |
| | [$R$(int) = 0.0284] | [$R$(int) = 0.07361] |
| Data/restraints/parameters | 3791/0/163 | 4876/0/280 |
| Goodness-of-fit on $F^2$ | 1.057 | 1.026 |
| Final $R$ indices [I > 2σ(I)] | $R_1 = 0.0317$ | $R_1 = 0.0371$ |
| | $wR_2 = 0.0873$ | $wR_2 = 0.0586$ |
| R indices (all data) | $R_1 = 0.0360$ | $R_1 = 0.0994$ |
| | $wR_2 = 0.0918$ | $wR_2 = 0.0773$ |
| Largest diff. peak and hole ($e.A^{-3}$) | 1.423 and −1.166 | 0.335 and −0.385 |

## 3. Results and discussion

Bis-acylhydrazone ligands, $H_4L^a$ and $H_4L^b$, were obtained from the reaction of adipic dihydrazide with 5-bromosalicylaldehyde and 2-hydroxynaphthaldehyde, respectively. These compounds have four ionizable protons and can potentially act as hexadentate ligands with two tridentate domain connected by a flexible linker group. The dinuclear complexes **1**–**4** were prepared by reaction of dihydrazone ligand, $R_2SnCl_2$ (R = Me or Ph) and in presence of triethylamine in 1:2:4 ratio with a slight excess of diorganotin dichloride. The new complexes were characterized by elemental analysis and IR and $^1H$ and $^{119}Sn$ NMR spectroscopy. The structure of **1** and **4** has been also determined by X-ray diffraction.

### 3.1. Spectroscopic studies

In the IR spectra of complexes the disappearance of $\nu_{O-H}$ and $\nu_{N-H}$ shows complete deprotonation of the ligand during coordination to the tin atoms. The absence of $\nu_{C=O}$ in complexes confirms that the ligand coordinates with tin in the enol form [18]. The $\nu$(C=N) band at 1611 and 1615 $cm^{-1}$ for ligands is shifted to a lower energy in the spectra of complexes. This observation indicates that the imine nitrogen atom is involved in coordination to the tin atom. The appearance of new bands in the IR spectra of the synthesized complexes assigned to $\nu$(Sn–N) and $\nu$(Sn–O) supports the bonding of nitrogen and oxygen to the tin atom [22–25]. Presence of both $\nu_s$(Sn–C) and $\nu_{as}$(Sn–C) in the IR spectrum of **1** and **3** is consistent with a nonlinear Me–Sn–Me configuration.

The signals at 11.22–12.65 ppm in the spectra of free ligands may be attributed to acidic protons, –NH–N= and Ar–OH groups. In the $^1H$ NMR spectra of the complexes, the complete absence of these signals suggests the deprotonation of ligand and coordination to the tin in the enol form. The signal attributed to imine protons in the spectrum of free ligands is shifted downfield and accompanied by satellites in complexes due to $^3J(^{119}Sn-H)$ coupling. This is an indication that the two imine nitrogen atoms is coordinated to tin(IV) centers. The $^1H$ NMR spectrum of dimethyl complexes shows a singlet at low frequency for $SnMe_2$ protons accompanied by satellites with $^2J(^{119}Sn-^1H)$ larger than uncomplexed $SnMe_2Cl_2$ (68.7 Hz) indicates the higher coordination number of tin [26]. Substitution of $^2J(^{119}Sn-^1H)$ in the Lockhart–Manders equation

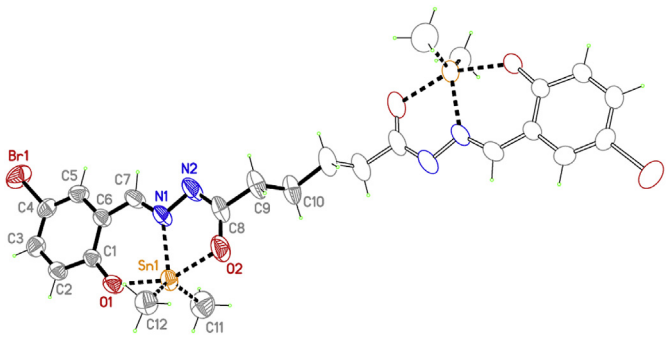


**Fig. 2.** Perspective view of compound **1** constituted by the asymmetric unit (filled drawings) showing the numbering scheme and the centrosymmetric half part (empty drawings). Thermal ellipsoids are drawn at the 50% probability level, while the hydrogen size is arbitrary.

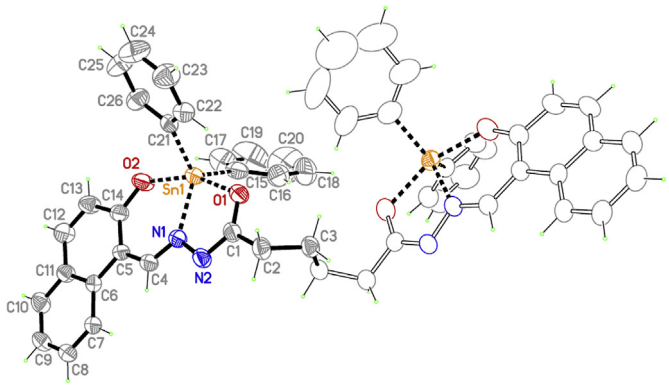


**Fig. 3.** View of compound **4** evidencing the 2-fold axis passing through the C3 and C3′ atoms and showing the numbering scheme of the asymmetric unit denoted by filled drawings. Thermal ellipsoids are drawn at the 30% probability level, while the hydrogen size is arbitrary.

[27], gives a value of 128.7° and 140.0° for Me–Sn–Me angle in **1** and **3**, respectively.

The $^{119}Sn\{^{1}H\}$ NMR spectra of all complexes show only one sharp singlet significantly at lower frequency than that of the original $SnMe_2Cl_2$ (+137 ppm) and $SnPh_2Cl_2$ (−32 ppm) [26]. Appearance of only one signal indicates the similar environment for two tin centers in complex. On the basis of the chemical shifts ranges proposed empirically [28–30], the coordination number of tin atoms is five taking into consideration that this chemical shift is located in lower frequency of the range for phenyltin complexes and also for complexes in DMSO.

**Table 2**
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **1**.

| | |
|---|---|
| Sn(1)–C(12) | 2.097(4) |
| Sn(1)–O(1) | 2.096(2) |
| Sn(1)–C(11) | 2.102(5) |
| Sn(1)–N(1) | 2.185(3) |
| Sn(1)–O(2) | 2.152(3) |
| O(1)–C(1) | 1.313(4) |
| C(6)–C(7) | 1.427(4) |
| C(7)–N(1) | 1.288(5) |
| N(1)–N(2) | 1.398(4) |
| N(2)–C(8) | 1.304(6) |
| C(8)–O(2) | 1.296(5) |
| C(8)–C(9) | 1.498(5) |
| C(9)–C(10) | 1.474(6) |
| C(12)–Sn(1)–O(1) | 93.99(14) |
| C(12)–Sn(1)–C(11) | 134.1(2) |
| O(1)–Sn(1)–C(11) | 96.99(18) |
| C(12)–Sn(1)–N(1) | 117.04(15) |
| O(1)–Sn(1)–N(1) | 83.53(10) |
| C(11)–Sn(1)–N(1) | 108.47(17) |
| C(12)–Sn(1)–O(2) | 92.88(14) |
| O(2)–Sn(1)–O(1) | 155.58(12) |
| C(11)–Sn(1)–O(2) | 94.95(18) |
| N(1)–Sn(1)–O(2) | 72.49(11) |
| O(1)–C(1)–C(6) | 124.2(3) |
| O(2)–C(8)–N(2) | 125.6(3) |
| N(1)–C(7)–C(6) | 126.4(3) |
| C(8)–N(2)–N(1) | 110.7(3) |
| C(7)–N(1)–Sn(1) | 128.5(2) |
| N(2)–N(1)–Sn(1) | 116.8(2) |
| C(8)–O(2)–Sn(1) | 114.5(2) |
| C(1)–O(1)–Sn(1) | 132.4(2) |
| Sn(1)–O(1)–C(1)–C(6) | −4.9(5) |
| Sn(1)–N(1)–N(2)–C(8) | −0.1(4) |
| Sn(1)–N(1)–C(7)–C(6) | 2.6(6) |
| Sn(1)–O(2)–C(8)–N(2) | 1.1(6) |

**Table 3**
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **4**.

| | |
|---|---|
| Sn(1)–C(21) | 2.100(4) |
| Sn(1)–O(1) | 2.119(3) |
| Sn(1)–C(15) | 2.100(5) |
| Sn(1)–N(1) | 2.135(3) |
| Sn(1)–O(2) | 2.082(3) |
| O(1)–C(1) | 1.298(4) |
| C(4)–C(5) | 1.423(5) |
| C(4)–N(1) | 1.300(4) |
| N(1)–N(2) | 1.404(4) |
| N(2)–C(1) | 1.295(4) |
| C(14)–O(2) | 1.319(4) |
| C(1)–C(2) | 1.492(5) |
| C(2)–C(3) | 1.528(5) |
| C(21)–Sn(1)–O(2) | 94.24(14) |
| C(21)–Sn(1)–C(15) | 123.64(15) |
| O(1)–Sn(1)–C(21) | 95.10(14) |
| C(21)–Sn(1)–N(1) | 119.67(13) |
| O(2)–Sn(1)–N(1) | 82.87(11) |
| C(15)–Sn(1)–N(1) | 116.54(14) |
| C(15)–Sn(1)–O(2) | 96.37(18) |
| O(2)–Sn(1)–O(1) | 156.39(10) |
| C(15)–Sn(1)–O(1) | 96.39(18) |
| N(1)–Sn(1)–O(1) | 73.82(11) |
| O(2)–C(14)–C(5) | 124.4(4) |
| O(1)-C(1)–N(2) | 125.0(4) |
| N(1)–C(4)–C(5) | 127.6(4) |
| C(1)–N(2)–N(1) | 111.0(3) |
| C(4)–N(1)–Sn(1) | 129.2(3) |
| N(2)–N(1)–Sn(1) | 116.2(2) |
| C(1)–O(1)–Sn(1) | 113.8(2) |
| C(14)–O(2)–Sn(1) | 133.4(2) |
| Sn(1)–N(1)–N(2)–C(1) | −1.7(4) |
| Sn(1)–O(1)–C(1)–N(2) | 3.8(5) |
| Sn(1)–N(1)–C(4)–C(5) | −1.1(6) |
| Sn(1)–O(2)–C(14)–C(5) | 5.4(6) |

### 3.2. X-ray structures

The molecular structures of **1** and **4** are given in Figs. 2 and 3. Selected bond lengths and angles are listed in Tables 2 and 3. Complex **1** is crystallized in the P-1 triclinic space group and one molecule is present in a unit cell, whereas complex **4** is crystallized in the C2/c monoclinic space group with four molecules in a unit cell. The structure of two complexes is binuclear and complex **1** is centrosymmetry. The alkyl linker chain shows *anti–anti–anti* conformation in **1** while *gauche–anti-gauche* in **4**. Structural parameters are completely similar for two parts of one molecule. The C–O and C–N bond lengths in the amide functionality are consistent with the enolate form of the hydrazinic moiety in complexes [18,31,32]. The Schiff base is completely deprotonated and acts as a tetrabasic ligand in the enolic form. The each tin center is surrounded by imine nitrogen, enolic oxygen and phenolic oxygen of ligand and two carbons of organic groups, therefore the coordination number of both tin is five. To quantify the extent of distortion from either ideal square pyramid or trigonal bipyramid, the index of trigonality, $\tau$, have been found from $\tau = (\alpha - \beta)/60$ [33], $\alpha$ and $\beta$ are the two largest bond angles around the metal atom in the five-coordinated environment. For a perfectly square pyramidal geometry, $\tau$ should be equal to zero, while it becomes unity for ideal trigonal bipyramidal geometry. The $\tau$ value is 0.358 for **1** and therefore the metal coordination geometry is described as highly distorted square pyramid with imine nitrogen atom occupies the apical position. The nitrogen is chosen as apex because any the four donor atoms which define the two largest angles $\alpha$ and $\beta$ should not be in axial position. The $\tau$ value for **4** obtains 0.545 and indicates the geometry of the complex is between square-pyramidal and

trigonal-bipyramidal. But with particular precision, trigonal-bipyramidal predominates over square-pyramidal geometry. Therefore, the geometry around the tin atom may be considered as a highly distorted trigonal-bipyramidal with phenolic and enolic oxygens in axial and azomethine nitrogen and two *ipso*-carbons from phenyl groups in equatorial positions. This distortion from perfect geometries is mainly due to the rigidity of chelate rings, and facilitated by the large covalent radius of tin(IV) [34,35]. The coordination part of ligand forms six and five membered chelate rings. These chelate rings are not planar but torsion angles are very small (Tables 2 and 3). The Sn–N1 bond length is 2.185(3) and 2.135(3) Å for **1** and **4**, respectively, which are very similar to the sum of the covalent radii of Sn–N (2.15 Å), but are considerably shorter than the sum of Van der Waals radii (3.75 Å). Sn–$O_{phenolic}$ and Sn–$O_{enolic}$ distances are also similar to the sum of the covalent radii of Sn–O (2.10 Å). Therefore, there is very strong covalent bond between tin with oxygen and nitrogen atoms. In complex **1,** the slight difference between the C–Sn–C angle from X-ray data, 134.1 (2)°, and the empirical estimation in solution (128.7°) may be related to removing the crystal network pressure in solution.

### 3.3. Biological studies

The *in vitro* antibacterial activities of Schiff base and its complexes were studied along with two standard antibacterial drugs, *viz*, Nalidixic acid and Vancomycin. The microorganisms used in this work include *B. subtilis* and *S. aureus* (as Gram-positive bacteria) and *E. coli* and *P. aeruginosa* (as Gram-negative bacteria). The results are presented in Table 4. Comparing the biological activity of the ligands, organotin(IV) complexes and standard drugs, indicate that all complexes exhibit more inhibitory effects than the parent ligands and complex **2** show more inhibition on bacterial growth than others. Generally, biological activity of organotin(IV) complexes is influenced both by donor ligand and by the number and nature of the organic groups bound to tin. A mechanism postulated for action of antibacterial compounds is deactivation of various cellular enzymes or denaturation of one or more proteins of the cell, which, as a result, impairs normal cellular processes and metabolic pathways of these organisms. It may involve the hydrolysis of organotin compound and formation of bonds between Sn and donor atoms at active biological centers [36–39]. However, permeability across the bacterial cell wall is prior necessity for the effectiveness of the biocide compounds against different microorganisms. Therefore the enhancement in activity of the ligand on complexation with organotins may be due to electron delocalization over the whole chelate ring upon complexation. Such chelation increases the lipophilic character and enhances the permeation of the complexes through the lipid layer of the bacterial cell membrane (chelation theory) [40–43]. It is apparent that toxicity toward Gram-positive bacteria is more than Gram(−) strains. The reason is the difference in the structures of the cell walls. The walls of Gram(−) cells are more complex than those of Gram(+) cells. Lipopolysacharides form an outer lipid membrane and contribute to the complex antigenic specificity of Gram(−) cells. However, it is remarkable that the bacteria of the genus *Pseudomonas* are a group of resistant microorganism that many standard drugs were found to have no activity against it [44,45]. Therefore it is interesting that *P. aeruginosa* was inhibited by these complexes.

**Table 4**
Antibacterial activity data of ligands and their complexes.

| Compound | Conc. (mg/mL) | Inhibition zone (mm) | | | |
|---|---|---|---|---|---|
| | | *E. coli* | *P. aeruginosa* | *S. aureus* | *B. subtilis* |
| $H_4L^a$ | 10 | 10 | 10 | 12 | 12 |
| | 20 | 11 | 12 | 14 | 13 |
| | 40 | 12 | 13 | 16 | 15 |
| $H_4L^b$ | 10 | 11 | n.a. | 13 | 9 |
| | 20 | 12 | n.a. | 15 | 11 |
| | 40 | 13 | n.a. | 16 | 13 |
| **1** | 10 | 10 | 15 | 13 | 14 |
| | 20 | 13 | 16 | 16 | 16 |
| | 40 | 15 | 17 | 18 | 17 |
| **2** | 10 | 16 | 13 | 15 | 15 |
| | 20 | 17 | 14 | 18 | 19 |
| | 40 | 22 | 15 | 23 | 23 |
| **3** | 10 | n.a. | 12 | 19 | 13 |
| | 20 | 12 | 13 | 20 | 15 |
| | 40 | 13 | 14 | 22 | 16 |
| **4** | 10 | 10 | n.a. | 14 | 14 |
| | 20 | 12 | n.a. | 16 | 15 |
| | 40 | 13 | n.a. | 17 | 17 |
| Vancomycin | | 13 | n.a. | 17 | 23 |
| Nalidixic acid | | 24 | n.a. | 12 | 22 |

n.a. = no activity.

## 4. Conclusion

On the basis of spectral and structural investigations, dihydrazones are completely deprotonated and coordinated to diorganotin moiety as tetrabasic ligands via imine nitrogen and phenolic and enolic oxygens. All complexes are binuclear and on the basis of $^{119}$Sn NMR data, coordination number of both tin retains five in solution. The synthesized organotin complexes are evaluated in inhibiting both Gram-positive (*B. subtilis* and *S. aureus*) and Gram-negative (*E. coli* and *P. aeruginosa*) bacteria. All complexes exhibit more inhibitory effects than the parent ligands and in some cases than the standards. Therefore these compounds have a potential to be used as drugs.

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## Appendix A. Supplementary material

CCDC 893775 and 879031 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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