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Dimethyltin (IV) complexes of new thiosemicarbazone ligand with piperazine-1-yimethylene moiety: Synthesis, spectral characterization and antibacterial activity

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Abstract: Three new thiosemicarbazone ligands and their dimethyltin (IV) complexes are reported. The condensation of piperazine-1-carbaldehyde with thiosemicarbazide, 4-methyl-3-thiosemicarbazide, and 4-ethyl-3-thiosemicarbazide was carried out in an ethanol medium using HBr as a catalyst, resulting in the isolation of the ligands (E)-2-(piperazin-1-ylmethylene) hydrazine-1-carbothioamide (HL1), (E)-N-methyl-2-(piperazin-1-ylmethylene) hydrazine-1-carbothioamide (HL2), and (E)-N-ethyl-2-(piperazin-1-ylmethylene) hydrazine-1-carbothioamide (HL3), respectively. The reaction of ligands HL1 - HL3 with dimethyltin (IV) dichloride in ethanol yielded complexes of the general formula [Me2Sn(HLn)Cl2] (n = 1 for 1C, n = 2 for 2C, and n = 3 for 3C). Analytical and spectroscopic analyses confirmed the formation of six-coordinate tin(IV) complexes. Antibacterial studies against six marine pathogenic bacteria and eight human pathogenic bacteria microorganisms belonging to both gram-positive and gram-negative types, using disc diffusion techniques at a concentration of 10 mg/mL with ampicillin as a control, showed that complex 3C possesses enhanced inhibition activity compared to the free ligand HL3.

Keywords: *Antibacterial activity, Piperazine thiosemicarbazone, Synthesis; Spectral characterization, Tin (IV) complexes.*

1. Introduction

The advancements in exploring new synthetic routes played a vital role in developing organic and coordination chemistry [1-3]. The expansion of coordination chemistry has been driven by introducing new chelate systems (complexation agents), particularly small organic species capable of binding various elements, including representative and transition metals [4-6]. As a result, various complexation agents with different donor atoms have been developed and reported [7-10]. Particularly, ligand systems that combine hard donor atoms (nitrogen and oxygen) and soft donor atoms (sulphur, selenium and tellurium) [3, 4]. One interesting class of chelating systems that have significantly contributed to organic and coordination chemistry is Schiff bases [11, 12] which include carbazone and chalcogen-semicarbazone systems [3, 4, 10]. These organic compounds are well known for their robust chelation capabilities towards most metal ions. An interesting example of a chalcogen-semicarbazone system is the thiosemicarbazone compound, which has been the centre of extensive studies due to its remarkable complexation ability, adaptable coordination nature, and diverse pharmacological properties [13, 14]. Furthermore, thiosemicarbazone compounds and their derivatives represent an example of multidentate chelating systems, bearing both the soft sulphur (S) and the hard hydrazine nitrogen (N) donor atoms, which are capable of binding numerous metal ions [10, 15, 16]. These compounds and their coordination complexes play significant roles in the medicinal field due to their diverse biological activities, such as antioxidant, anti-inflammatory, antitumor, antiviral, antitubercular, antibacterial, and antimalarial effects,

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and applications in biomedical molecular imaging [10, 15-19]. As thiosemicarbazone derivatives and their coordination compounds with transition and main group metals exhibit excellent biological properties, they present a promising opportunity to broaden the application of these compounds in various therapeutic areas [20]. One important class of metal complexes is based on organotin (IV), particularly complexes derived from semi- and thiosemicarbazone complexation agents [10]. These complexes featuring bidentate ligand systems with the N, and S donor atoms, have been extensively studied and showed significant interest due to their coordination chemistry and numerous applications, including their role as antibacterial, antifungal, cytotoxic, and biocidal agents [21, 22]. Furthermore, several research groups have focused on exploring the chemistry of these complexes, due to their structural diversity and the range of coordination numbers exhibited by the tin(IV) core [12, 22, 23]. The synthesis of diorganotin (IV) complexes derived from 3-methoxysalicylaldehyde thiosemicarbazone has also been reported, resulting in five-coordinated complexes that exhibit significant cytotoxic and antibacterial activities [24]. Additionally, these complexes are influenced by the nature of the organic moieties bonded to the tin(IV) due to the impact of these groups' electronic and steric effects [25]. As part of our ongoing research into the chemistry of diorganotin (IV), this study investigates the structural and spectral properties of three new thiosemicarbazone ligands and their organotin complexes. Furthermore, the biological efficacy of the ligands and their complexes against marine and human pathogenic bacteria was evaluated.

2. Experimental

2.1. Materials

Reagents used in this work, purchased from Sigma-Aldrich and Across Organics, were employed as received. The analytical-grade solvents were used after distillation according to standard methods.

2.2. Instrumentation

A Carlo Erba 1108 Elemental Analyser (Milan, Italy) and a Shimadzu atomic absorption spectrophotometer (F.A.A) model 680G were used to determine the CHNS analysis of the compounds and the tin(IV) percentage of the complexes. The infrared spectra (FT-IR) were recorded using a Perkin Elmer Spectrum GX spectrophotometer (Perkin Elmer, Waltham, MA, USA) in the range of 4000 to 250 cm^{-1}, using KBr and CsI pellets. The NMR spectra (^{1}H, ^{13}C, and ^{119}Sn) were recorded on a Bruker 400 MHz instrument in DMSO-d_6 solvent, with TMS as the internal reference for ^{1}H-NMR. The uncorrected melting points were determined using a Stewart SMP40. Cyberscan CON 510 conductivity meter measured the complexes' molar conductance.

2.3. Synthesis

2.3.1. Synthesis of Thiosemicarbazone Ligands

Three ligands HL1-HL3 derived from the condensation reaction of piperazine-1-carbaldehyde with thiosemicarbazide, 4-methyl-3-thiosemicarbazide and 4-ethyl-3-thiosemicarbazide were isolated. The condensation reaction was carried out in an ethanol medium using HBr as a catalyst. An outline of the reaction figure is depicted in figure 1.

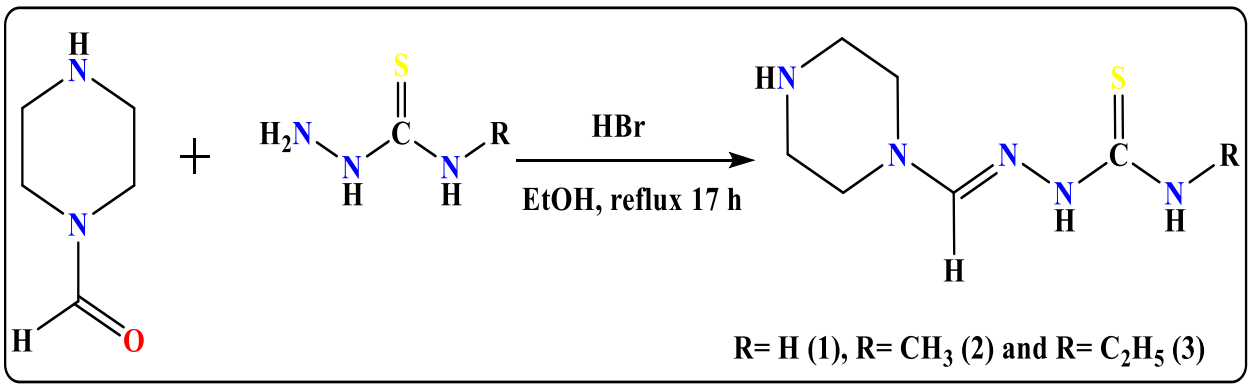

Figure 1.
Reaction pathway of the synthesis of thiosemicarbazone ligands HL1-HL3.

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2.3.1.1. Synthesis of (E)-2-(piperazin-1-ylmethylene)hydrazine-1-carbothioamide (HL1)

Thiosemicarbazide (0.91 g, 10 mmol) was allowed to stir in hot ethanol (20 mL). Subsequently, a mixture of piperazine-1-carbaldehyde (1.14 g 10 mmol) in ethanol (20 mL) was added dropwise with stirring, along with a few drops of concentrated HBr. The resulting mixture was heated under reflux for 17 h and then allowed to cool to room temperature. The solid that formed on cooling was collected by filtration, washed with ethanol (10 mL) and dried in a desiccator over anhydrous silica gel. Colour: white; (yield 1.52 g, 81%), (m.p.; 207-209 °C). $C_6H_{13}N_5S$ (187.27); Elemental Analysis Calc. (%): C 38.48, H 7.00, N 37.40, S 17.12. Found (%): C 38.20, H 6.85, N 37.89, S 17.64. IR (KBr cm^{-1}): ν⁅N(2)-H⁆ 3350; ν⁅N(5)-H⁆ 3275 asy. 3139 sy.; ν⁅N(4)-H⁆ 3032; ν(C=N) 1605; ν(C-N) 1109; ν(N-N) 1057; ν(C=S) 865. ^{1}H NMR (400 MHz; ppm; DMSO-d_6): {9.92 ⁅1H, C(5)H⁆, s}, {8.01 ⁅1H, N(4)H⁆, s}, {7.53 ⁅ 2H, N(5)H⁆, s}, {5.05 ⁅1H, N(2)H⁆, s}, {3.18 ⁅4H, C(1,4)H ⁆, t }, {2.15 ⁅4H, C(2,3)H ⁆, t}. ^{13}C NMR (100.63 MHz; ppm; DMSO-d_6): ⁅178.85 C(6)=S⁆, ⁅145.28 C(5)=N⁆, ⁅25.51 C(1,4)H⁆, ⁅18.03 C(2,3)H⁆.

2.3.1.2. Synthesis of (E)-N-methyl-2-(piperazin-1-ylmethylene) hydrazine-1-Carbothioamide (HL2)

The compound (E)-N-methyl-2-(piperazin-1-ylmethylene) hydrazine-1-carbothioamide was prepared by adopting an analogues procedure used in the preparation of HL1. The substance 4-methyl-3-thiosemicarbazide (1.05 g, 10 mmol) was used instead of thiosemicarbazide and other reagents were adjusted accordingly. A similar worked-up procedure was implemented to give the required compound as a solid. Colour: white. (Yield 1.65g, 83%), (m.p; 227-229°C). $C_7H_{15}N_5S$ (201.29); Elemental Analysis Calc. (%): C 41.77, H 7.51, N 34.79, S 15.93. Found (%): C 41.18, H 7.23, N 35.36, S 16.26. IR (KBr cm^{-1}): ν⁅N(2)-H⁆ 3359; ν⁅N(5)-H⁆ 3225; ν⁅N(4)-H⁆ 3021; ν(C=N) 1604; ν(C-N) 1123; ν(N-N) 1053; ν(C=S) 850. ^{1}H NMR (400MHz; ppm; DMSO-d_6): {9.90 ⁅1H, C(5)H⁆, s}, {8.15 ⁅1H, N(4)H⁆, s}, {5.08 ⁅1H, N(5)H⁆, s}, {4.12 ⁅1H, N(2)H⁆, s}, {3.38 ⁅ 4H, C(1,4)H⁆, t}, {2.95 ⁅3H, C(7)-H⁆, s}, {1.53 ⁅4H, C(2,3,)H⁆, t}. ^{13}C NMR (100.63 MHz; ppm; DMSO-d_6): ⁅178.84 C(6)=S⁆, ⁅142.59 C(5)=N⁆, ⁅31.20 C(1,4)H⁆ , ⁅25.47 (C(7)H)⁆, ⁅18.01 C(2,3)H⁆.

2.3.1.3. Synthesis of (E)-N-ethyl-2-(piperazin-1-ylmethylene) hydrazine-1-carbothioamide (HL3)

The ligand HL3 was synthesised following the same procedure described for HL1, with 4-ethyl-3-thiosemicarbazide (1.19 g, 10 mmol) used instead of the thiosemicarbazide. HL3 was isolated as a white colour solid with a yield of 1.80g (84%), m.p; 243-245°C. $C_8H_{17}N_5S$ (215.32 amu); elemental analysis Calc. (%): C 44.62, H 7.96, N 32.53, S 14.89. Found (%): C 43.99, H 7.53, N 33.11, S 15.18. IR (KBr cm^{-1}): ν⁅N(2)-H⁆ 3360; ν⁅N(5)-H⁆ 3278; ν⁅N(4)-H⁆ 3223; ν(C=N) 1659; ν(C-N) 1109; ν(N-N) 1063; ν(C=S) 857. ^{1}H NMR (400 MHz; ppm; DMSO-d_6): {9.50 ⁅1H, C(5)H⁆, s}, {8.08 ⁅1H, N(4)H⁆, s}, {5.09 ⁅1H, N(5)H⁆, s}, {4.15 ⁅1H, N(2)H⁆, s}, {3.34 ⁅2H, C(7)H⁆, q}, {2.63 ⁅ 4H, C(1,4)H⁆, t}, {1.63 ⁅4H, C(2,3)H⁆, t}, {0.88 ⁅3H, C(8)H⁆, t}. ^{13}C NMR (100.63 MHz; ppm; DMSO-d_6): ⁅177.85 C(6)=S⁆, ⁅143.09 C(5)=N⁆, ⁅30.25 C(1,4)H⁆ , ⁅28.27 C(7)H⁆, ⁅17.55 C(2,3)H⁆, ⁅15.41 C(8)H⁆.

2.3.2. Synthesis of Dimethyltin(IV) Thiosemicarbazone Complexes

The syntheses of dimethyltin(IV) thiosemicarbazone complexes (1C-3C) were achieved using a reported method ⁅26⁆. The general synthetic procedure is shown in Figure 2.

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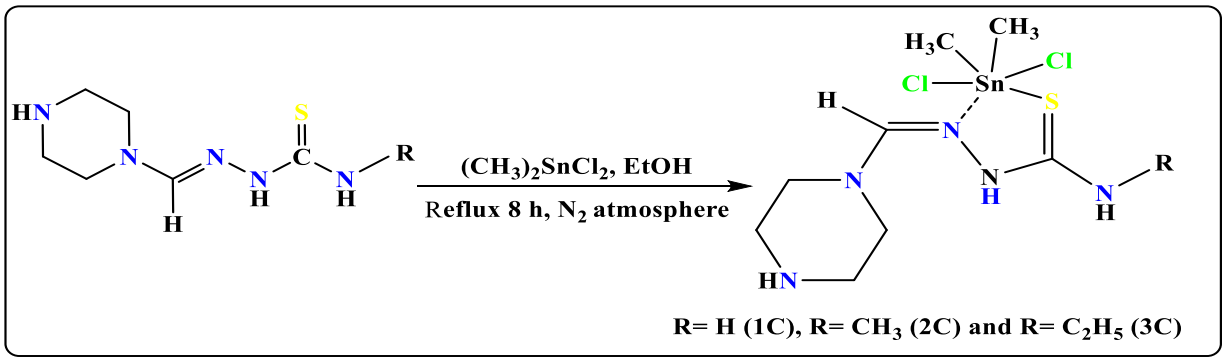

Figure 2.
The synthesis pathway for the formation of dimethyltin(IV) thiosemicarbazon complexes.

2.3.2.1. Synthesis of 1C

To a solution of HL1 (1.87 mg 10 mmol) in 10 mL of ethanol was added slowly with stirring a mixture of (2.19 g, 10 mmol) of $(CH_3)_2SnCl_2$ dissolved in 10 mL of ethanol. The reaction mixture was refluxed for 8 h under N_2 atmosphere. The formed yellow solid was filtered off, washed with cold ethanol (10 mL) and dried over silica. Colour: yellow; (Yield 3.46 g, 85%), (m.p.; 237-239°C). $C_8H_{19}Cl_2N_5SSn$ (406.95); elemental Analysis Calc. (%): C 23.61, H 4.71, N 17.21, S 7.88, Sn 29.17. Found (%): C 23.26, H 4.42, N 17.85, S 8.28, Sn 28.68. IR (KBr CSI cm^{-1}): ν[N(2)-H] 3351; ν[N(5)-H] 3272 asy. 3136 sy.; ν[N(4)-H] 3030; ν(C=N) 1590; ν(C-N) 1091; ν(N-N) 1072; ν(C=S) 844; ν(Sn-C) 685; ν(Sn-N) 450; ν(Sn-S) 335; ν(Sn-Cl) 308. ^{1}H NMR (400 MHz; ppm; DMSO-d_6): {10.39 [1H, C(5)H], s}, { 8.35 [1H, N(4)H], s}, {7.55 [2H, N(5)H], s}, {5.5[1H, N(2)H], s}, {3.25 [4H, C(1,4)H], t}, {2.19 [4H, C(2,3,)H], t}, {1.15 [6H, Sn-CH3], s}. ^{13}C NMR (100.63 MHz; ppm; DMSO-d_6): [172.53 C(6)=S], [153.75 C(5)=N], [25.89 C(1,4)H], [18.37 C(2,3)H], [12.27 C(7,8)H]. ^{119}Sn NMR [DMSO-d6]: (ppm)= -249.79.

2.3.2.2. Synthesis of 2C

The complex 2C was prepared by the same procedure described for the synthesis of 1C, with the use of HL2 (2.01 g, 10 mmol) instead of HL1. Colour: white; (Yield 3.22g, 77%), (m.p.; 284-286°C). $C_9H_{21}Cl_2N_5SSn$ (420.98); elemental Analysis Calc. (%): C 25.68, H 5.03, N 16.64, S 7.62, Sn 28.20. Found (%): C 25.31, H 4.75, N 17.11, S 7.95, Sn 28.81. IR (KBr, CSI cm^{-1}): ν[N(2)-H] 3360; ν[N(5)-H] 3222; ν[N(4)-H] 3023; ν(C=N) 1593; ν(C-N) 1102; ν(N-N) 1077; ν(C=S) thiosemicabazone 821; ν(Sn-C) 670; ν(Sn-N) 443; ν(Sn-S) 342; ν(Sn-Cl) 306. ^{1}H NMR (400MHz; ppm; DMSO-d6): {10.40 [1H, C(5)H], s}, {8.47 [1H, N(4)H], s}, {5.09 [1H, N(5)H], s}, {4.23 [1H, N(2)H], s}, {3.70 [4H, C(1,4)H], t}, {3.20 [3H, C(7)H], s}, {1.80 [4H, C(2,3)H], t},{1.23 [6H, Sn-CH3], s}.^{13}C NMR (100.63MHz; ppm; DMSO-d_6): [171.68 C(6)=S], [150.13 C(5)=N], [31.67 C(1,4)H] , [25.87 C(7)H], [18.53 C(2,3)H], [11.87 C(8,9)H]. ^{119}Sn NMR [DMSO-d6]: (ppm)= -238.22.

2.3.2.3. Synthesis of 3C

The complex 3C was obtained following the same procedure described for 1C, with the use of HL3 (2.15 g, 10 mmol) instead of compound HL1. Colour: white; (Yield 3.39g, 78%), (m.p.; 273-275°C). $C_{10}H_{23}Cl_2N_5SSn$ (435.00); elemental Analysis Calc. (%): C 27.61, H 5.33, N 16.10, S 7.37, Sn 27.29. Found (%): C 27.44, H 5.03, N 16.58, S 7.91, Sn 27.84. IR (KBr, CSI cm^{-1}): ν[N(2)-H] 3361; ν[N(5)-H] 3281; ν[N(4)-H] 3220; ν(C=N) 1642; ν(C-N) 1095; ν(N-N) 1080; ν(C=S) 827; ν(Sn-C) 676; ν(Sn-N) 456; ν(Sn-S) 339; ν(Sn-Cl) 307. ^{1}H NMR (400 MHz; ppm; DMSO-d_6): {9.90 [1H, C(5H], s}, {8.37 [1H, N(4)H], s}, {5.12 [1H, N(5)H], s}, {4.48 [1H, N(2)H], s}, {3.73 [2H, C(7)H], q}, {2.97 [4H, C(1,4)H], t}, {1.85 [4H, C(2,3)H], t,}, {1.21 [3H, C(8)H], t},{1.07 [6H, Sn-CH3], s}. ^{13}C NMR (100.63 MHz; ppm; DMSO-d_6): [172.99 C(6)=S], [152.58 C(5)=N], [30.56 C(1,4)H] , [28.76 C(7)], [18.05 C(2,3)H], [15.92 C(8)H], [11.17 C(9,10)H]. ^{119}Sn NMR [DMSO-d_6]: (ppm)= -244.62. structural formulas of the prepared compounds are depicted in Figure (5).

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3. Results and Discussion

3.1. Synthesis

The synthesis of three new thiosemicarbazone ligands, derived from the reaction of piperazine with thiosemicarbazide derivatives, alongside their organotin(IV) complexes, is reported. The compounds were obtained under reflux conditions and isolated in high yields (77–85%), with the reaction for the complexes performed under a nitrogen atmosphere. Upon complexation with the dimethyltin(IV) precursor, the ligands (HL1-HL3) acted as neutral species, forming six-coordinate complexes. The compounds were characterised using various analytical and spectroscopic techniques, including FTIR, NMR, elemental analysis, melting point determination and molar conductance measurements. Experimental elemental microanalyses of the compounds closely matched the calculated values, confirming the purity of the isolated ligands and their corresponding organotin(IV) complexes, Table 1. The molar conductance values of 11.1, 8.3 and 6.9 S cm^2 mol^{-1} for 1C, 2C and 3C complexes in the DMSO solution confirm their non-electrolyte behaviour [27].

Table 1.
Physical and analytical data of piperazine-based thiosemicarbazone ligands and their dimethyltin (IV) complexes.

No.	Molecular Formula	Mwt	Colour	Yield %	m.p (°C)	Experimental (Calcd) %				
						C	H	N	S	Sn
HL1	$C_6H_{13}N_5S$	187.27	White	81	207-209	38.20 (38.48)	6.85 (7.00)	37.89 (37.40)	17.64 (17.22)	-
1C	$C_8H_{19}N_5SSnCl_2$	406.95	Yellow	85	237-239	23.26 (23.61)	4.42 (4.71)	17.85 (17.21)	8.28 (7.78)	28.68 (29.17)
HL2	$C_7H_{15}N_5S$	201.29	White	83	227-229	41.18 (41.77)	7.23 (7.51)	35.36 (34.79)	16.26 (15.93)	-
2C	$C_9H_{21}N_5SSnCl_2$	420.98	White	77	224-226	25.31 (25.68)	4.75 (5.03)	17.41 (16.64)	7.95 (7.22)	28.81 (28.20)
HL3	$C_8H_{17}N_5S$	215.32	White	84	243-245	43.99 (44.62)	7.53 (7.96)	33.11 (32.53)	15.48 (14.89)	-
3C	$C_{10}H_{23}N_5SSnCl_2$	435.06	White	78	293-295	27.44 (27.61)	5.03 (5.33)	16.58 (16.10)	7.91 (7.37)	27.84 (27.29)

3.2. FTIR spectra

The FTIR spectra of complexes 1C-3C revealed distinct peaks in the range 1642-1590 cm^{-1} attributed to the ν(C=N) group. These bands were shifted to a lower wavenumber, compared with that observed at 1659-1604 cm^{-1} in the spectra of the free ligands (Table 2), confirming the involvement of the nitrogen of the azomethine moiety in the coordination [28, 29]. Additionally, the spectra of 1C-3C revealed peaks in the range 844–821 cm^{-1} that attributed to the ν(C=S) group. These peaks were shifted to a lower wavenumber, compared with that observed at 865–850 cm^{-1} in the spectra of ligands (HL1-HL3) indicating the involvement of the sulphur group in the coordination [30]. Further, the spectra of the free ligands show peaks in the range 3360-3350 cm^{-1}, due to the ν(N-H) piperazine group. These absorptions remain unaltered in the FTIR spectra of the tin(IV) complexes (1C-3C), confirming the non-involvement of this ν(N-H) piperazine group upon coordination. The organotin(IV) complexes display a peak in the range 1080-1072 cm^{-1} due to ν(N–N). These bands appeared at a higher wavenumber than those detected at 1063-1053 cm^{-1} in the free corresponding ligands. The increase of the stretching peak value in the spectra of complexes may account for the rise in the bond order. This is due to the formation of the chelate ring and confirming the involvement of the nitrogen atom of the azomethine in coordination [30]. The FTIR spectra of the tin compounds exhibited new peaks in the range 685–670, 456-443, 342-335 and 308-306 cm^{-1} that were assigned to ν(Sn-C), ν(Sn-N), ν(Sn-S) and ν(Sn-Cl), respectively. A single Sn-Cl peak in the spectra of complexes confirms that the two chloride moieties adopt a *trans* configuration. Figures 3 and 4 represent the infrared spectra of the HL1 and its coordination compound 1C, respectively.

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Table 2.
FTIR spectral data of ligands (HL1–HL3) and their dimethyltin(IV) complexes (1C–3C).

No.	ν(N(2)H)	ν(N(5)H)	ν(N(4)H)	ν(C=N)	ν(N-N)	ν(C=S)	ν(Sn-C)	ν(Sn-N)	ν(Sn-S)	ν(Sn-Cl)
HL1	3350	3275 asym, 3139 sym	3082	1605	1057	865	-	-	-	-
1C	3351	3272 asym, 3136 sym	3080	1590	1072	844	685	450	335	308
HL2	3359	3225	3023	1604	1053	850	-	-	-	-
2C	3360	3222	3023	1593	1107	821	670	443	342	306
HL3	3360	3278	3223	1659	1063	857	-	-	-	-
3C	3361	3281	3220	1642	1080	827	676	456	339	307

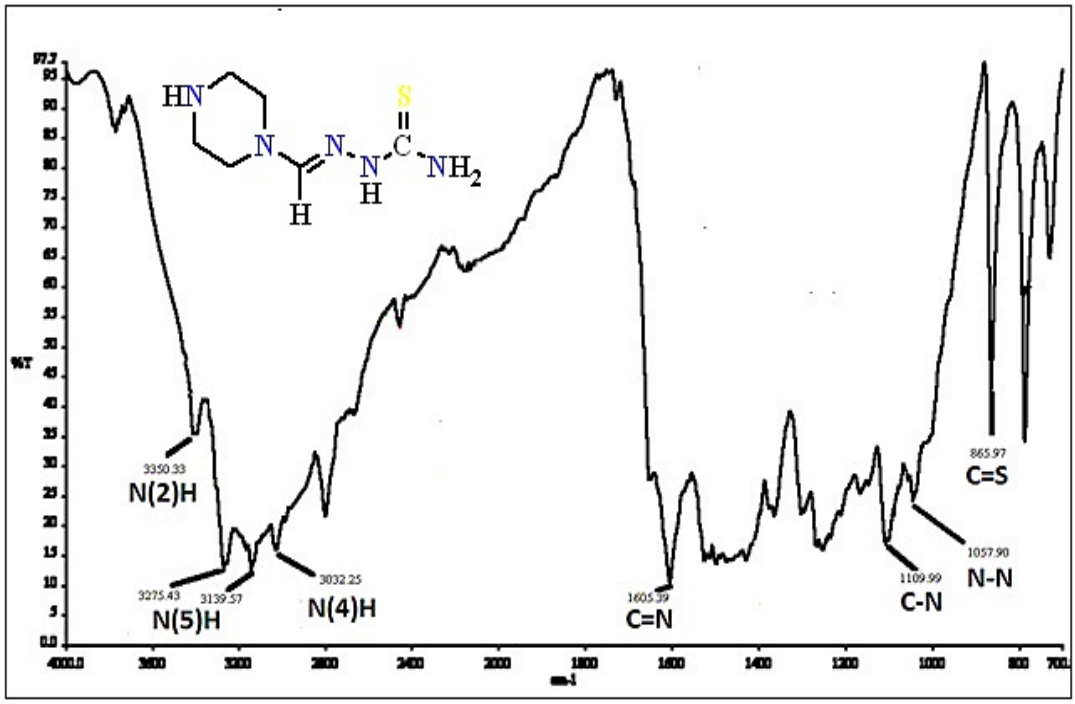

Figure 3.
Infrared spectrum of HL1.

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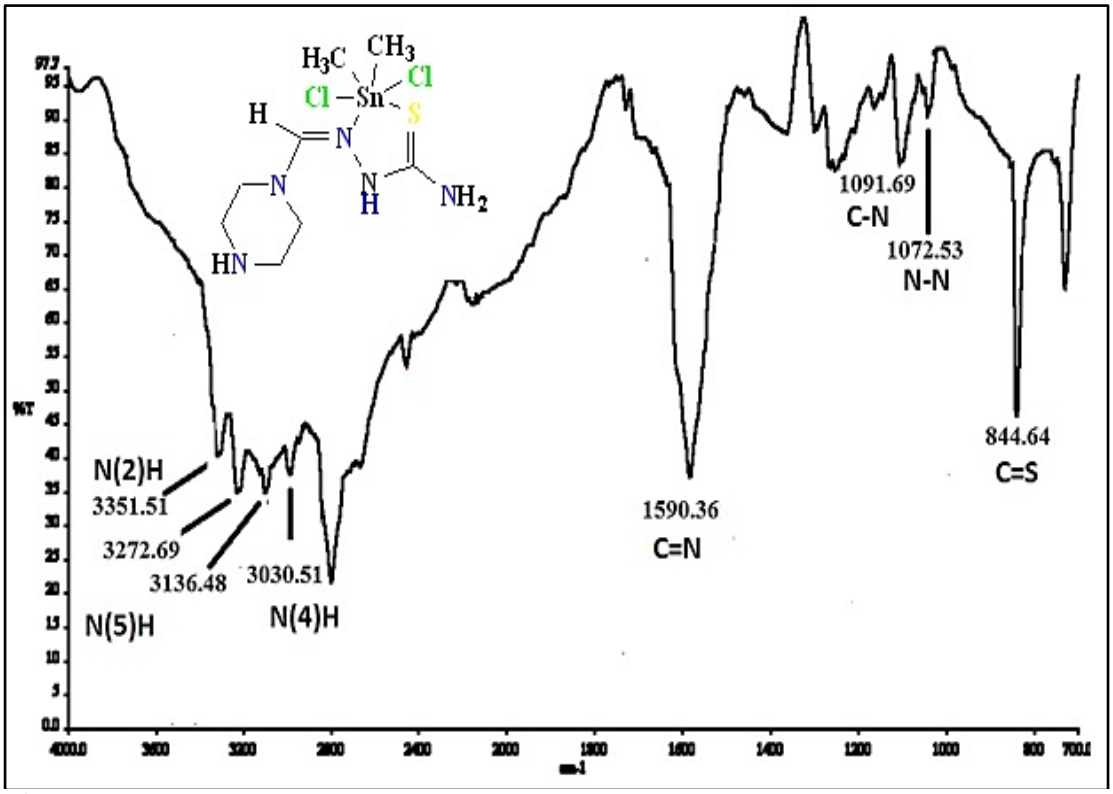

Figure 4.
Infrared spectrum of 1C.

3.3. Nuclear Magnetic Resonance Spectra

The assignment of NMR peaks was based on the numbering scheme shown in Figure 5.

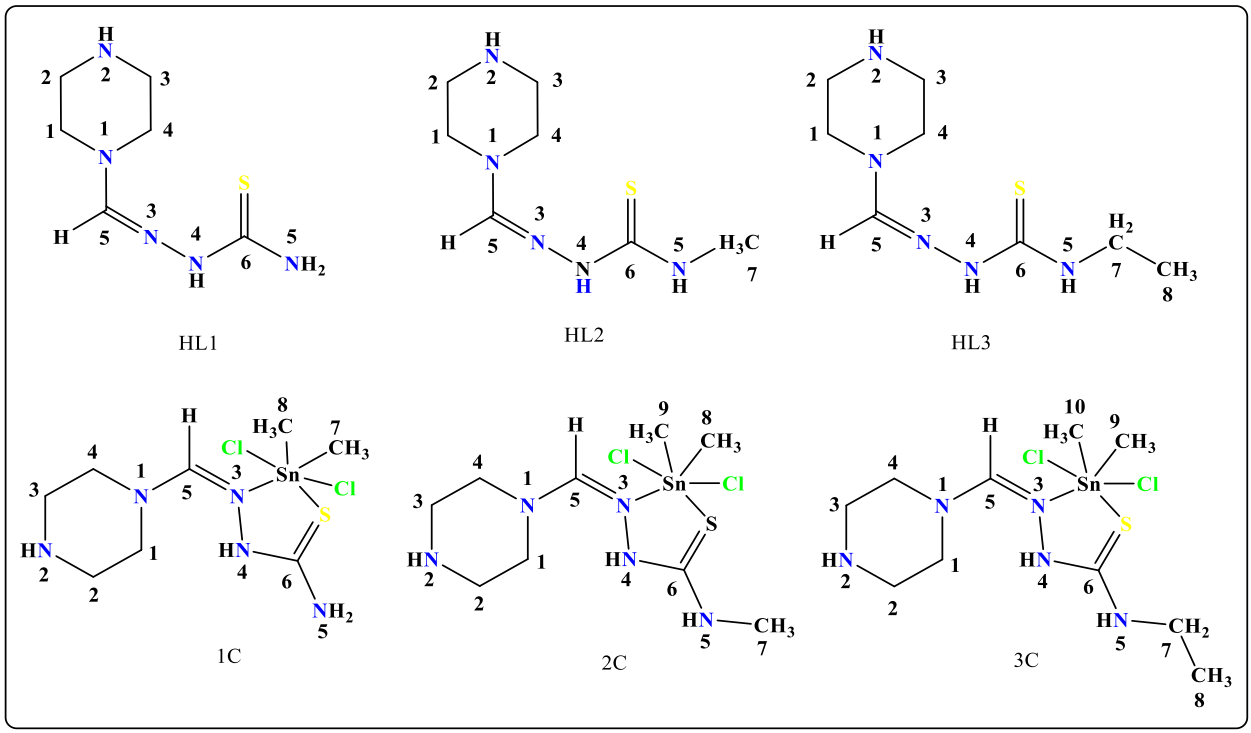

Figure 5.
Numbering scheme for the ligands (HL1-HL3) and their dimethyltin(IV) complexes (1C-3C).

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3.3.1. ^1H NMR spectra

The spectra of complexes 1C-3C showed a chemical shift in the range 10.40-9.90 ppm, which related to the proton of the azomethine moiety. This peak was shifted downfield, compared with that in the free ligands (HL1-HL3). This shift may be attributed to the involvement of the lone pair electron of the azomethine nitrogen in coordination with the tin atom [31]. The ^1H NMR spectrum of 3C exhibits a quartet at 3.37 ppm that is related to the $-CH_2-$ protons. This resonance appeared downfield compared with that in the corresponding ligand. The chemical shift of the methyl groups attached to the tin(IV), in the complexes, appeared as a singlet in the range of 1.23-0.72 ppm [32]. Figures 6 and 7 exhibit the ^1H NMR spectrum of the HL1 and its organotin (IV) complex, respectively.

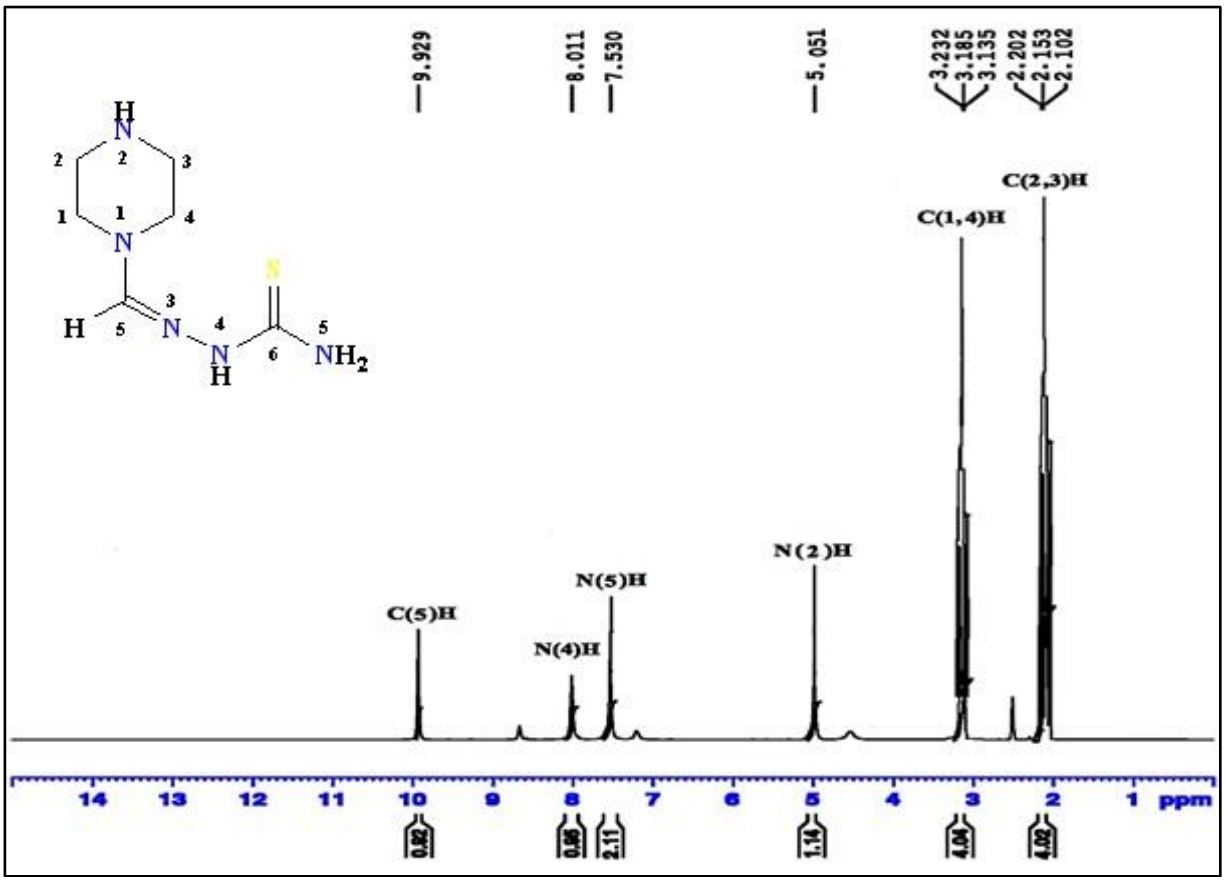

Figure 6.
^1H NMR spectrum of HL1 in DMSO–d_6 solution.

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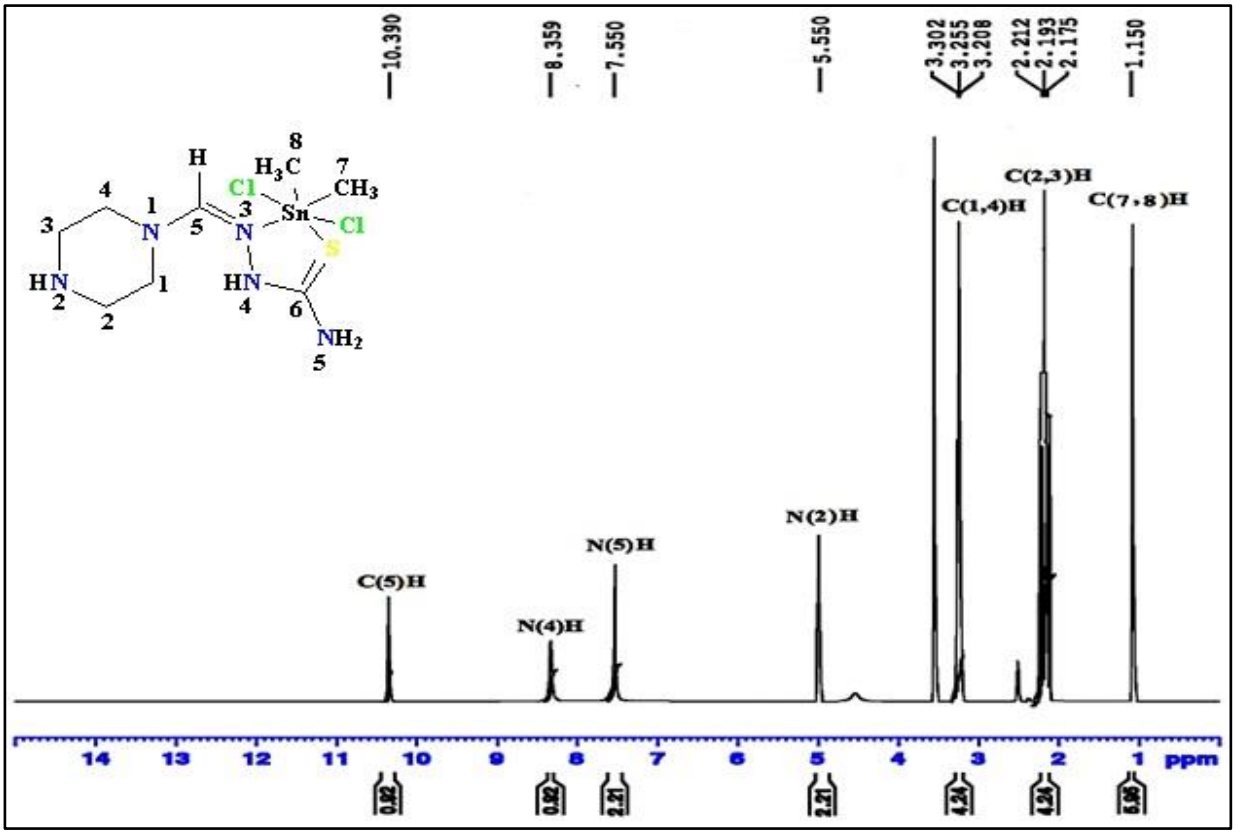

Figure 7.
^{1}H NMR spectrum of 1C in DMSO–d_6 solution.

3.3.2. ^{13}C NMR spectra

The ^{13}C NMR spectral data along with the assignment of characteristic peaks for ligands and their diorganotin(IV) complexes are described in the experimental section. The chemical shifts of the C=S group in the ligands HL1-HL3 were observed at the downfield range 178.85-175.85 ppm and were shifted to upfield at 172.99-171.68 ppm in the complexes 1C-3C due to participation of the C=S group in coordination to tin(IV) atom [12, 22, 23, 32]. The chemical shifts of the C=N moiety in ligands HL1-HL3 were observed at δ 145.28-142.59 ppm, which shifted to the downfield region and appeared at 153.7–150.13 ppm in complexes 1C–3C confirming the participation of the azomethine-N in the coordination to the tin(IV) atom. The δ values of carbon atoms in the aliphatic (methyl and ethyl) groups did not have much changes in the 2C and 3C, compared to the free ligands. Peaks attributed to the methyl groups attached to the tin(IV) core appeared around 15.41-11.17 ppm in the prepared complexes.

3.3.3. ^{119}S NMR spectra

The ^{119}Sn NMR spectra of the organotin(IV) thiosemicarbazone complexes acquired in DMSO–d_6 solutions at room temperature. In these experiments, the NMR solvent acts as a non-coordinating species. The ^{119}Sn NMR spectra of the organotin(IV) complexes (1C-3C) gave a sharp singlet signal in the range –249 to –238 ppm, strongly inductive of a six coordination arrangement around the tin atom and confirming a distorted octahedral geometry [32].

4. Antibacterial Activity of Thiosemicarbazones Ligands and Their Tin Complexes

The antibacterial tests of the thiosemicarbazone ligands and their organotin (IV) complexes against various marine and human bacterial species were evaluated. The percent activity index is included in Table 3 and the minimum inhibition concentration (MIC) data is shown in Table 4. Based on the inhibition zone sizes, ligands HL1 and HL3 showed no appreciable activity against all bacterial strains. However, ligand HL2 displayed moderate antibacterial activity against certain bacterial strains. The organotin(IV) complexes of 1C and 2C revealed moderate antibacterial activity against all tested bacteria, with a

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considerable enhancement in activity compared to their corresponding free ligands. Notably, complex 3C indicated excellent antibacterial activity against *Escherichia coli* (Top 10), *Enterobacter sakazakii*, and *Enterobacter shigella*, as pointed out in both the zone inhibition data (Table 3) and the MIC values (Table 7). The increased activity of the tin complexes compared to their free ligands can be related to the chelation effect, which reduces the central tin atom's polarity by partially sharing its positive charge with the ligand donor atoms. This reduction in polarity enhances the lipophilicity of complexes, facilitating their ability to cross the lipid bilayer of bacterial cell membranes and affecting bacterial growth mechanism [16, 26, 33, 34]. Furthermore, the enhanced antibacterial activity of 3C against *E. coli* and *Enterobacter* species is likely due to its ability to interact effectively with the outer membrane of Gram-negative bacteria, a characteristic often observed in organotin (IV) complexes.

Table 3.
^{1}HNMR spectral data of ligands (HL1-HL3)and their dimethyltin(IV) complexes(1C-3C)

No.	C(5)H	N(4)H	N(5)H	N(2)H	C(1,4)H	C(2,3)H	CH aliphatic
1	9.92(1H,s)	8.01(1H,s)	7.53(2H,s)	5.05(1H,s)	3.18(4H,t)	2.15(4H,t)	
1C	10.39(1H,s)	8.32(1H,s)	7.55(2H,s)	5.06(1H,s)	3.25(4H,t)	2.19(4H,t)	1.15(6H,s)
2	9.90(1H,s)	8.15(1H,s)	5.08(2H,s)	4.12(1H,s)	3.38(4H,t)	1.53(4H,t)	2.95(3H,s)
2C	10.40(1H,s)	8.47(1H,s)	5.09(2H,s)	4.23(1H,s)	3.70(4H,t)	1.80(4H,t)	3.20(3H,s), 1.23(6H,s)
3	9.50(1H,s)	8.08(1H,s)	5.09(2H,s)	4.15(1H,s)	2.63(4H,t)	1.63(4H,t)	3.34(2H,q), 0.88(3H,t)
3C	9.90(1H,s)	8.37(1H,s)	5.12(2H,s)	4.48(1H,s)	2.97(4H,t)	1.85(4H,t)	3.37(2H,q), 1.21(3H,t),1.07(6H,s)

Table 4.
^{13}CNMR spectral data of ligands (HL1-HL3)and their dimethyltin(IV) complexes(1C-3C).

No.	C=S	C=N	CH
1	178.85	145.28	25.51, 18.03
1C	172.53	153.75	25.89, 18.37, 12.27
2	178.84	142.59	31.20, 25.47, 18.01
2C	171.68	150.13	31.67, 25.87, 18.53, 11.87
3	177.85	143.09	30.25, 28.27, 17.55, 15.41
3C	172.99	152.58	30.56, 28.76, 18.05, 15.92, 11.17

Table 5.
^{119}SnNMR spectral data of dimethyltin(IV) complexes(1C-3C).

No.	R	ppm
1C	H	-249.79
2C	Me	-238.22
3C	Et	-244.62

Table 6.
Percent activity index of piperazine-based thiosemicarbazone ligands and their dimethyltin(IV) complexes.

Bacterial strain	HL1	1C	HL2	2C	HL3	3C
L. sp. Gb05(+)	-	33	33	33	-	44
V. ow Gb04(-)	-	23	-	36	-	61
V. alg Gb05(-)	-	27	-	36	-	61
L. sp. Gb03C(-)	-	22	29	40	-	65
V. ow SS1(-)	-	23	30	32	-	71
V. alg SS17(-)	-	31	42	39	-	56
B. sub(+)	-	29	29	22	-	75
E. coli Top 10(-)	-	-	66	66	-	128
E. Sak(-)	-	66	-	72	-	157
E. shg(-)	-	43	59	74	-	120
E. fac(+)	-	25	54	69	-	80
S. typ(-)	-	-	28	32	-	63
E. coli ATCC(-)	-	-	30	36	-	57
B. cer(+)	-	33	22	34	-	42

Note: *Lysinibacillus sp. Gb05* (+), *Vibrio owensii Gb04* (-), *Vibrio alginolyticus Gb05* (-), *Loktanella sp. UKMGb03C* (-), *Vibrio owensii SS1* (-), *Vibrio alginolyticus S17* (-), *Bacillus subtilis* (+), *Escherichia coli* (Top 10) (-), *Enterobacter sakazakii* (-), *Enterobacter shigella* (-), *Enterococcus faecalis* (+), *Salmonella typhimurium* (-), *Escherichia coli* (ATCC) (-), *Bacillus cereus* (+)

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Table 7.
Minimum inhibitory concentration (MIC) piperazine-based thiosemicarbazone ligands and their dimethyltin(IV) complexes (mg/mL).

Bacterial strain	HL1	1C	HL2	2C	HL3	3C
L. sp. Gb05 (+)	-	1.44	1.25	2.41	-	2.51
V. ow Gb04 (-)	-	21.6	-	1.06	-	1.34
V. alg Gb05 (-)	-	21.5	-	1.15	-	1.34
L. sp. Gb03C (-)	-	8.07	1.39	1.06	-	2.06
V. ow SS1 (-)	-	7.98	1.39	5.19	-	1.8
V. alg SS17 (-)	-	3.85	0.83	1.25	-	1.7
B. sub (+)	-	1.52	1.39	4.43	-	1.8
E. coli Top 10 (-)	-	-	0.83	1.82	-	1.7
E. Sak (-)	-	1.67	-	3.85	-	1.34
E. shg (-)	-	0.97	1.52	1.63	-	1.52
E. fac (+)	-	1.67	1.67	1.82	-	3.05
S. typ (-)	-	-	3.88	2.11	-	3.76
E. coli ATCC (-)	-	-	2.22	1.15	-	1.08
B. cer (+)	-	1.37	0.7	0.29	-	2.51

Note: Vibrio owensii SS1 *(-)*, Vibrio alginolyticus SS17 *(-)*, Bacillus subtilis *(+)*, Escherichia coli *(Top 10) (-)*, Enterobacter sakazakii *(-)*, Enterobacter shigella *(-)*, Enterococcus faecalis *(+)*, Salmonella typhimurium *(-)*, Escherichia coli *(ATCC) (-)*, Bacillus cereus *(+)*

5. Conclusion

The successful synthesis and spectral characterization of three new piperazine-based thiosemicarbazone ligands and their organotin(IV) complexes are presented. The identity of the ligands and their tin(IV) complexes was confirmed using a range of analytical and spectroscopic techniques. These include micro-elemental analysis, molar conductance, melting point determination, FT-IR, ^{1}H, ^{13}C NMR and ^{119}Sn NMR spectroscopy. Furthermore, the biological evaluation of the ligands and their Sn(IV) complexes against a range of marine and human bacterial strains was explored. The antibacterial results of the synthesized compounds showed that the tin complexes (1C-3C) exhibited enhanced activity compared with their free ligands (HL1-HL3).

Transparency:

The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.

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