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Research Article

Hypercoordinated Organosilicon(IV) and Organotin(IV) Complexes: Syntheses, Spectral Studies, and Antimicrobial Activity *In Vitro*

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This paper deals with the syntheses and structural features of some new diorganosilicon(IV) and diorganotin(IV) complexes having general formulae $(CH_3)_2MCl(L^1)$, $(CH_3)_2MCl(L^2)$, $(CH_3)_2M(L^1)_2$, and $(CH_3)_2M(L^2)_2$ with new Schiff bases (M = Si and Sn). The Schiff bases HL^1 and HL^2 have been derived from the condensation of 3-bromobenzaldehyde with 4-amino-3-ethyl-5-mercapto-1,2,4-triazole and 4-amino-5-mercapto-3-propyl-1,2,4-triazole, respectively. The compounds have been characterized by the elemental analyses, molar conductance, and spectral (UV, IR, ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR) studies. The resulting complexes have been proposed to have trigonal bipyramidal and octahedral geometries. *In vitro* antimicrobial activities of the compounds have been carried out.

1. Introduction

The chemistry of complexes with hypercoordinated silicon and tin atoms is interesting from many points of view such as reactivity, biological activity, and structural features as reported in several reviews [1–3]. The Schiff bases bearing additional donor groups represent the most important class of heteropolydentate ligands capable of forming mono-, bi-, and polynuclear complexes with different metal ions. Enhanced reactivities of silicon complexes due to increased coordination number as well as modified electronic properties as a result of modified ligand sphere and coordination geometries have been reported [4, 5]. Singh et al. recently reported the activity of Schiff base complexes with silicon against pathogenic fungi and bacteria [6, 7]. The insecticidal and nematicidal activities were also reported for some hypercoordinated silicon complexes [8]. Organosilicon compounds of N- and S-containing ligands are well known for their anticarcinogenic, tuberculostatic, antimicrobial, and acaricidal activities [9, 10]. Similarly organotin(IV) compounds have been receiving increasing attention in the area of inorganic and metal organic chemistry due to the important industrial [11] (pesticides, antifouling paints, and fire retardants), pharmacological [12, 13] (antifungal, antibacterial, and antitumor drugs), and environmental applications. Organotin(IV) complexes are extensively studied due to their coordination geometries as well as structural diversity (Monomeric, dimeric, hexameric, and oligomeric) [14]. So by keeping in mind the various applications of the organosilicon(IV) and organotin(IV) complexes and further continuation of our work [15, 16], we report here the syntheses, characterization, and biological activity of some new silicon and tin complexes of the Schiff bases derived from the condensation of 3-bromobenzaldehyde with different triazoles.

2. Experimental

2.1. Materials. Adequate care was taken to keep chemicals, glass apparatus, and organosilicon(IV) and organotin(IV) complexes free from moisture. All the chemicals and solvents were used under dry conditions. To attain dry conditions, all the apparatus used during the experimental work were fitted with Quickfit interchangeable standard ground

joints. All the reagents, namely, dimethylsilicondichloride (Acros), dimethyltindichloride (TCI-America), and 3-bromobenzaldehyde (Spectrochem) were used as such.

2.2. Analytical Methods and Physical Measurements. Silicon and tin were determined gravimetrically as SiO_2 and SnO_2. Melting points were determined on a capillary melting point apparatus. Molar conductance measurements of 10^{-3} M solution of metal complexes in dry DMF were measured at room temperature (25 ± 1°C) with a conductivity bridge type 305 Systronics model. Carbon, hydrogen, nitrogen, and sulfur were estimated using the elemental analyzer Heraeus Vario EL-III Carlo Erba 1108 at the Central Drug Research Institute, Lucknow, India. The electronic spectra of the ligands and their metal complexes were recorded in dry methanol, on a Systronics, Double Beam spectrophotometer 2203, in the range of 600–200 nm. The IR spectra of the ligands and metal complexes were recorded in Nujol mulls/KBr pellets using BUCK scientific M5000 grating spectrophotometer in the range of 4000–350 cm^{-1}. Nuclear magnetic resonance spectra (^1H, ^{13}C) were recorded on Bruker-300ACF, and ^{29}Si and ^{119}Sn were recorded on Bruker-400ACF spectrometer in DMSO-d_6 using Me_4Si as an internal standard for ^1H, ^{13}C, ^{29}Si, and Me_4Sn for ^{119}Sn spectra.

2.3. Syntheses of Ligands. 4-Amino-3-ethyl-5-mercapto-1,2,4-triazole and 4-amino-5-mercapto-3-propyl-1,2,4-triazole were synthesized by the reported method (Figure 1) [17].

2.3.1. 4-(3-Bromobenzylidene-Amino)-3-Ethyl-5-Mercapto-s-Triazole (HL^1). A solution of 4-amino-3-ethyl-5-mercapto-1,2,4-triazole (2.0 g, 14 mmol) in ethanol (40 mL) was treated with 3-bromobenzaldehyde (2.57 g, 14 mmol). The reaction mixture was refluxed for 4 h. After the completion of the reaction, the reaction mixture was kept overnight at room temperature, and the product was filtered, washed, and recrystallized from the same solvent:

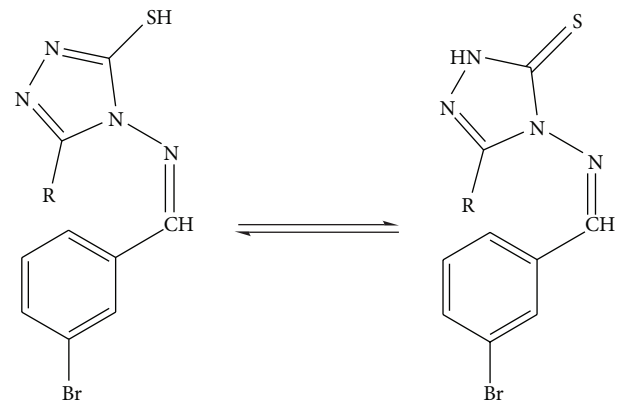
m.p. 198°C, greenish white, yield: 86%, (found: C, 42.30; H, 3.02; N, 18.73; S, 10.71%. Calcd. for $C_{11}H_{11}BrN_4S$: C, 42.45; H, 3.56; N, 18.00; S, 10.30%).

2.3.2. 4-(3-Bromobenzylidene-Amino)-5-Mercapto-3-Propyl-s-Triazole (HL^2). An ethanolic solution of 3-bromobenzaldehyde (2.34 g, 13 mmol) was added with stirring to an ethanolic solution of 4-amino-5-mercapto-3-propyl-1,2,4-triazole (2.0 g, 13 mmol) and refluxed for 4 h. After the completion of the reaction, the reaction mixture was kept overnight at room temperature, and the product was filtered, washed, and recrystallized from the same solvent:

m.p. 188°C, light green, yield: 83%, (found: C, 44.30; H, 4.19; N, 17.23; S, 9.87%. Calcd. for $C_{12}H_{13}BrN_4S$: C, 44.32; H, 4.03; N, 17.23; S, 9.86%).

2.4. Synthesis of Organometallic Complexes

2.4.1. Synthesis of 1:1 Organosilicon Complexes. To the Me_2SiCl_2 (0.100 g, 0.8 mmol) in ~30 mL of dry methanol, was added the sodium salt of the corresponding ligands in 1:1 molar ratio. The sodium salts of the ligands were prepared by dissolving the sodium metal (0.018 g, 0.8 mmol), HL^1 (0.242 g, 0.8 mmol), and HL^2 (0.252 g, 0.8 mmol) in ~30 mL dry methanol. The reaction mixture was refluxed for about 12 h and then allowed to cool at room temperature. Sodium chloride formed during the reaction was separated by filtration through sintered funnel. The excess of solvent was removed under reduced pressure by vacuum pump, and the resulting solid was repeatedly washed with 5–10 mL dry cyclohexane and again dried under vacuum:



R = $-CH_2-CH_3$(HL^1), $-CH_2-CH_2-CH_3$(HL^2)

Figure 1: Structure of Schiff bases.

$Me_2SiCl(L^1)$: m.p. 210°C, yellow, yield: 78%, (found: C, 38.81; H, 4.01; N, 13.78; S, 7.71; Si, 5.42%. Calcd. for $C_{13}H_{16}BrClN_4SSi$: C, 38.67; H, 3.99; N, 13.87; S, 7.94; Si, 6.96%).

$Me_2SiCl(L^2)$: m.p. 232°C, yellow, yield: 81%, (found: C, 41.24; H, 3.35; N, 13.44; S, 7.70; Si, 5.73%. Calcd. for $C_{14}H_{18}BrClN_4SSi$: C, 40.24; H, 4.34; N, 13.41; S, 7.67; Si, 6.72%).

2.4.2. Synthesis of 1:2 Organosilicon Complexes. To the Me_2SiCl_2 (0.100 g, 0.8 mmol) in ~30 mL of dry methanol, was added the sodium salt of the corresponding ligands in 1:2 molar ratio. The sodium salts of the ligands were prepared by dissolving the sodium metal (0.036 g, 1.6 mmol), HL^1 (0.282 g, 1.6 mmol), and HL^2 (0.504 g, 1.6 mmol), in ~30 mL dry methanol. The reaction mixture was refluxed for about 12 h and then allowed to cool at room temperature. Sodium chloride formed during the reaction was separated by filtration through sintered funnel. The excess of solvent was removed under reduced pressure by vacuum pump, and the resulting solid was repeatedly washed with 5–10 mL dry cyclohexane and again dried under vacuum:

$Me_2Si(L^1)_2$: m.p. 242°C, brown, yield: 74%, (found: C, 42.12; H, 3.80; N, 16.48; S, 9.39; Si, 4.91% Calcd. for $C_{24}H_{26}Br_2N_8S_2Si$: C, 42.48; H, 3.86; N, 16.51; S, 9.45; Si, 4.14%).

$Me_2Si(L^2)_2$: m.p. 246°C, light green yield: 82%, (found: C, 43.20; H, 4.11; N, 15.83; S, 9.11; Si, 3.02% Calcd. for $C_{26}H_{30}Br_2N_8S_2Si$: C, 44.19; H, 4.28; N, 15.86; S, 9.08; Si, 3.97%).

2.4.3. Synthesis of 1:1 Organotin Complexes. The sodium salts of the ligands were prepared by dissolving the sodium metal (0.011 g, 0.46 mmol) and HL^1 (0.142 g, 0.46 mmol), HL^2 (0.148 g, 0.46 mmol) in ~30 mL dry methanol. Then, to the Me_2SiCl_2 (0.100 g, 0.46 mmol) in ~30 mL of dry methanol, was added the sodium salt of the corresponding ligands in 1:1 molar ratio. The reaction mixture was refluxed for about 12 h and then allowed to cool at room temperature. Sodium chloride formed during the reaction was separated by filtration through sintered funnel. The excess of solvent was removed under reduced pressure by vacuum pump, and the resulting solid was repeatedly washed with 5–10 mL dry cyclohexane and again dried under vacuum:

$Me_2SnCl(L^1)$: m.p. 204°C, off-white, yield: 75%, (found: C, 31.50; H, 3.29; N, 11.30; S, 6.51; Sn, 23.22% Calcd. for $C_{13}H_{16}BrClN_4SSn$: C, 31.58; H, 3.26; N, 11.33; S, 6.49; Sn, 24.01%).

$Me_2SnCl(L^2)$: m.p. 252°C, off-white, yield: 83%, (found: C, 33.11; H, 3.50; N, 11.12; S, 6.29; Sn, 22.39%. Calcd. for $C_{14}H_{18}BrClN_4SSn$: C, 33.07; H, 3.57; N, 11.02; S, 6.31; Sn, 23.35%).

2.4.4. Synthesis of 1:2 Organotin Complexes. To the Me_2SnCl_2 (0.100 g, 0.46 mmol) in ~30 mL of dry methanol, was added the sodium salt of the corresponding ligands in 1:2 molar ratio. The sodium salts of the ligands were prepared by dissolving the sodium metal (0.022 g, 0.92 mmol) and HL^1 (0.281 g, 0.92 mmol), HL^2 (0.296 g, 0.92 mmol) in ~30 mL dry methanol. Sodium chloride formed during the reaction was separated by filtration through sintered funnel. The reaction mixture was refluxed for about 12 h and then allowed to cool at room temperature. The excess of solvent was removed under reduced pressure by vacuum pump, and the resulting solid was repeatedly washed with 5–10 mL dry cyclohexane and again dried under vacuum:

$Me_2Sn(L^1)_2$: m.p. 262°C, light yellow, yield: 79%, (found: C, 37.51; H, 3.31; N, 14.53; S, 8.40; Sn, 14.49%. Calcd. for $C_{24}H_{26}Br_2N_8S_2Sn$: C, 37.48; H, 3.41; N, 14.57; S, 8.34; Sn, 15.43%).

$Me_2Sn(L^2)_2$: m.p. 206°C, light yellow, yield: 78%, (found: C, 39.20; H, 3.86; N, 14.12; S, 8.08; Sn, 13.91%. Calcd. for $C_{26}H_{30}Br_2N_8S_2Sn$: C, 39.17; H, 3.79; N, 14.06; S, 8.04; Sn, 14.89%).

3. Results and Discussion

The resulting complexes have been obtained as colored solids which are soluble in DMSO, DMF, and MeOH but insoluble in other organic solvents. The ligands show a sharp melting point, while the complexes decompose in a range of temperature (204–262°C). The molar conductivity values measured for 10^{-3} M solutions in anhydrous DMF are in the range of 10–17 Ω^{-1} cm^2 mol^{-1}, showing that all 1:1 and 1:2 complexes are nonelectrolytic in nature [3].

3.1. Electronic Spectra. The electronic spectra of ligands HL^1 and HL^2 exhibit maxima at 365 nm and 364 nm, respectively, which could be assigned to the n-π^* transition of the azomethine group. These bands show a blue shift in 1:1 and 1:2, Si(IV) and Sn(IV) metal complexes and appear at 359 nm, 355 nm, 352 nm, and 355 nm, for $Me_2SiCl(L^1)$, $Me_2Si(L^1)_2$, $Me_2SiCl(L^2)$, and $Me_2Si(L^2)_2$ and at 358 nm, 355 nm, 356 nm, and 358 nm for $Me_2SnCl(L^1)$, $Me_2Sn(L^1)_2$, $Me_2SnCl(L^2)$, and $Me_2Sn(L^2)_2$, respectively. This blue shift is due to the polarization within the >C=N chromophore group caused by the metal-ligand interaction which clearly indicates the coordination of azomethine nitrogen atom to the metal atom [18]. Further, the electronic spectra of both the ligands exhibit medium intensity band at 260 nm due to π-π^* transition which remain unchanged in the spectra of metal complexes.

3.2. IR Spectra. The IR spectra of the free ligands were compared with the spectra of organosilicon(IV) and organotin(IV) complexes in order to study the binding mode of the Schiff bases to the metal ions in the new complexes. Several significant changes with respect to the ligands are observed in the corresponding organometallic complexes, which are listed in Table 1. The IR spectra of the ligands HL^1 and HL^2, show medium intensity bands in the region of 3109 cm^{-1} and 2754 cm^{-1} which may be assigned to ν(N–H) and ν(S–H) vibrations, respectively. Other bands in the region of 1165 cm^{-1} due to ν(C=S) [19] suggest that ligands exist as in the thiol-thione tautomerism (Figure 1). The disappearance of these bands in the corresponding metal complexes and the appearance of a new band ~770 cm^{-1} due to ν(C–S) indicate the deprotonation of the thiol group of triazole which support the complexation through sulfur atom. The metal sulphur bond formation is further supported by a band at ~446 cm^{-1} and ~420 cm^{-1} for ν(Si–S) and ν(Sn–S) in the spectra of organosilicon(IV) and organotin(IV) complexes, respectively [20]. A sharp and strong band in the region of 1582 cm^{-1} for ν(N=CH) in case of ligands was shifted to a higher wavelength number and appears in the region of 1602–1610 cm^{-1} in the spectra of metal complexes, indicating the coordination of ligands through azomethine nitrogen to the metal atom. The metal nitrogen bond was further supported by the presence of a band at about ~562 cm^{-1} for ν(Si–N) and ~538 cm^{-1} for ν(Sn–N) [21]. A strong band in the region of 412–362 cm^{-1} was assigned to ν(M–Cl) for 1:1 metal complexes.

3.3. ^{1}HNMR Spectra. The proton magnetic resonance spectra of the ligands and their corresponding organosilicon and organotin complexes were recorded in DMSO-d_6 using TMS as internal standard. The bonding pattern is further supported by ^{1}HNMR spectral studies of the ligands and their corresponding organometallic complexes. The chemical

Table 1: IR-spectroscopic data (cm^{-1}) of the ligands and their metal complexes.

Compound	ν(N–H)	ν(–C=N)	ν(C=S)[a]/ν(C–S)[b]	ν(S–H)	ν(M–S)	ν(M–N)	ν(M–Cl)
HL^1	3109	1582	1165	2754	—	—	—
$Me_2SiCl(L^1)$	—	1605	765	—	454	576	422
$Me_2Si(L^1)_2$	—	1602	741	—	442	562	—
$Me_2SnCl(L^1)$	—	1600	725	—	420	536	362
$Me_2Sn(L^1)_2$	—	1610	771	—	432	542	—
HL^2	3109	1582	1165	2770	—	—	—
$Me_2SiCl(L^2)$	—	1607	779	—	449	564	418
$Me_2Si(L^2)_2$	—	1603	779	—	446	558	—
$Me_2SnCl(L^2)$	—	1605	771	—	421	538	378
$Me_2Sn(L^1)_2$	—	1610	756	—	423	544	—

a: Ligands.
b: Complexes.

Table 2: ^{1}HNMR chemical shifts of the ligands and their metal complexes.

Compound	–C**H**=N	–S**H**	Aromatic–**H**	Triazole–C**H**$_2$–C**H**$_3$, C**H**$_2$–C**H**$_2$–C**H**$_3$
HL^1	10.56	11.66	7.35–8.15(s, d, t)	2.85–2.92(q), 1.35–1.40(t)
$Me_2SiCl(L^1)$	10.89	—	7.20–8.04(s, d, t)	2.27–2.38(q), 1.12–1.17(t)
$Me_2Si(L^1)_2$	11.22	—	7.34–8.05(s, d, t)	2.29–2.37(q), 1.15–1.20(t)
$Me_2SnCl(L^1)$	11.04	—	7.31–8.05(s, d, t)	2.28–2.39(q), 1.12–1.20(t)
$Me_2Sn(L^1)_2$	10.87	—	7.16–8.05(s, d, t)	2.27–2.35(q), 1.13–1.22(t)
HL^2	10.54	11.57	7.35–8.04(s, d, t)	2.81–2.85(t), 1.79–1.86(m), 1.03–1.08(t)
$Me_2SiCl(L^2)$	10.98	—	7.34–8.13(s, d, t)	2.63–2.68(t), 1.37–1.66(m), 0.90–0.92(t)
$Me_2Si(L^2)_2$	10.81	—	7.33–7.98(s, d, t)	2.76–3.06(t), 1.25–1.56(m), 0.98–1.07(t)
$Me_2SnCl(L^2)$	11.05	—	7.16–8.05(s, d, t)	2.72–2.91(t), 1.59–1.74(m), 0.86–0.91(t)
$Me_2Sn(L^1)_2$	10.94	—	7.27–8.04(s, d, t)	2.59–2.64(t), 1.53–1.67(m), 0.89–0.94(t)

shift values (δ, ppm) of the different protons are given in Table 2. The ^{1}HNMR spectra of the ligands exhibit peaks at δ 11.66 ppm (s, 1H) and δ 11.57 ppm (s, 1H) characteristic of the –SH proton of triazole for HL^1 and HL^2, respectively [16]. The disappearance of the signal due to –SH proton in the spectra of metal complexes indicates the deprotonation of the thiol group and that supports the coordination of ligand through sulphur atom to the central metal atom. A signal at δ 10.56 ppm (s, 1H) and 10.54 (s, 1H) ppm was observed due to azomethine proton in the spectra of free ligands HL^1 and HL^2, respectively, which moves downfield in the ^{1}HNMR spectra of metal complexes [22] and indicates the bonding through the azomethine nitrogen atom to the central metal atom. Other peaks that are found around the δ value 7.16–8.15 (4H) are due to aromatic protons. The signal in the region δ 0.6–1.5 ppm is also observed in the spectra of complexes due to CH_3-M group. Some additional signals, due to the aliphatic chain attached to the triazole moiety, also appeared in the ^{1}HNMR spectra of the ligands and their metal complexes, as reported in Table 2.

3.4. ^{13}CNMR Spectra. The ^{13}CNMR spectral data of ligands HL^1 and HL^2 and their corresponding 1 : 1 and 1 : 2 metal complexes were also recorded in DMSO-d_6 and reported in Table 3. The proposed coordination in these complexes has been supported by the shifting in chemical shift values of the carbon atoms attached to the azomethine nitrogen atom and thiolic sulfur atom. The other carbon atoms remain almost undisturbed [15]. The new signal due to the methyl groups attached to the metal atom in the spectra of complexes has also been reported in Table 3. All these data also support the coordination of the ligands through nitrogen and sulfur atoms to the central metal atom.

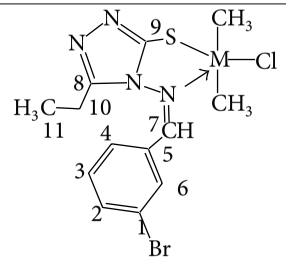
3.5. ^{29}Si and ^{119}Sn NMR Spectra. The ^{29}Si and ^{119}Sn NMR chemical shifts are very sensitive to the coordination number of the silicon and tin. So in order to propose the geometry of the complexes, ^{29}Si and ^{119}Sn NMR spectra of the organosilicon and organotin complexes of ligand HL^1 were recorded (Figure 2). These ^{29}Si and ^{119}Sn NMR chemical shift values greatly shifted upfield on bonding to the Lewis base. The ^{29}Si NMR spectra of $\{Me_2SiCl(L^1)\}$ and $\{Me_2Si(L^1)_2\}$ give sharp signals at δ −103.35 ppm, δ −110.40 ppm, respectively, which clearly indicates the penta- and hexa-coordinated environment around the silicon atom. Similarly, the observed ^{119}Sn NMR chemical shifts of the studied complexes, $\{Me_2SnCl(L^1)\}$ and $\{Me_2Sn(L^1)_2\}$, are in the range of penta- and hexa-coordinated environment, which appears at δ −172.14 ppm, δ −240.30 ppm, respectively [23].

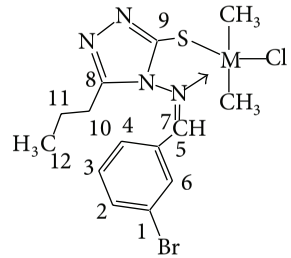
4. Biological Assay

4.1. Test Microorganisms. Four bacteria, *Staphylococcus aureus* (MTCC 96), *Bacillus subtilis* (MTCC 121) (Gram positive), *Escherichia coli* (MTCC 1652), and *Pseudomonas*

Table 3: ^{13}C NMR chemical shifts of the ligands and their metal complexes.

Compound	C_1/C_2	C_3/C_4	C_5/C_6	C_7/C_8	C_9/C_{10}	C_{11}/C_{12}	$M–CH_3$
HL^1	123.18/127.64	130.46/130.87	135.12/134.75	162.36/153.96	158.47/10.29	18.90	—
$Me_2SiCl(L^1)$	122.06/128.04	130.68/130.96	136.93/135.42	166.84/147.99	154.43/20.19	12.78	31.43
$Me_2Si(L^1)_2$	121.93/127.05	130.72/130.81	136.26/133.92	167.25/147.09	153.23/21.81	12.05	29.34
$Me_2SnCl(L^1)$	122.27/127.32	129.92/131.03	136.43/133.98	165.23/149.06	153.92/19.53	12.89	33.89
$Me_2Sn(L^1)_2$	122.67/127.08	130.77/130.97	136.39/134.41	164.89/149.48	153.54/18.97	14.44	31.54
HL^2	123.18/127.58	130.47/130.93	135.13/134.75	162.38/152.88	158.50/13.62	19.47/26.97	—
$Me_2SiCl(L^2)$	122.94/127.43	129.78/131.25	136.78/134.17	163.79/151.56	154.26/22.12	15.65/22.14	30.45
$Me_2Si(L^2)_2$	122.71/127.49	131.75/131.13	136.91/135.54	164.21/150.97	155.03/19.96	24.97/18.58	33.86
$Me_2SnCl(L^2)$	123.69/127.39	130.98/131.06	136.79/134.23	164.02/151.39	154.89/23.53	19.06/19.36	32.42
$Me_2Sn(L^1)_2$	121.91/127.26	130.74/130.74	137.13/134.72	163.89/152.03	154.38/21.26	23.02/14.77	34.53





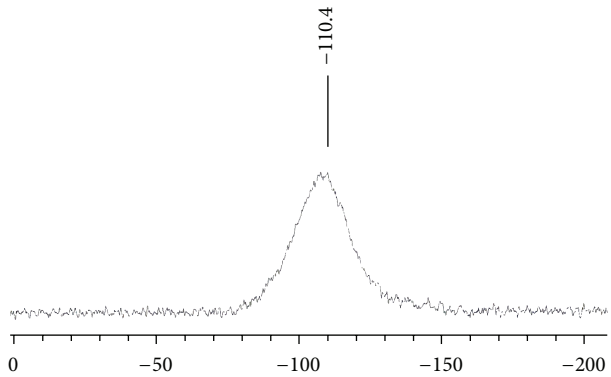


Figure 2: ^{29}Si NMR spectra of Si (1 : 2) metal complex of ligand (HL^1).

aeruginosa (MTCC 741) (Gram negative), were procured from MTCC, Chandigarh; and two fungi, *A. niger* and *A. flavus*, the ear pathogens isolated from the patients of Kurukshetra, were used in the present study.

4.2. In Vitro Antibacterial Activity. All the newly synthesized Schiff bases and their organometallic complexes were screened for their antibacterial activities against test bacteria, namely, *S. aureus*, *B. subtilis* (Gram positive), *E. coli*, and *P. aeruginosa* (Gram negative). The activity is determined by reported agar well-diffusion method [24]. All the cultures were adjusted to 0.5 McFarland standards, which are visually comparable to a microbial suspension of approximately 1.5×10^8 cfu/mL. 20 ml of Mueller-Hinton agar medium was poured into each Petri plate, and the agar plates were swabbed with 100 μL inocula of each test bacterium and kept for 15 min for adsorption. Using sterile cork borer of 8 mm diameter, wells were bored into the seeded agar plates, and these were loaded with a 100 μL volume with concentration of 2.0 mg/mL of each compound reconstituted in the dimethylsulphoxide (DMSO). All the plates were incubated at 37°C for 24 hr. Antibacterial activity of each compound was evaluated by measuring the zone of growth inhibition against the test organisms with zone reader (Hi antibiotic zone scale). DMSO was used as a negative control, whereas ciprofloxacin was used as a positive control. This procedure was performed in three replicate plates for each organism.

4.3. Determination of Minimum Inhibitory Concentration (MIC). MIC is the lowest concentration of an antimicrobial compound that will inhibit the visible growth of a microorganism after overnight incubation. MIC of the various compounds against bacterial strains was tested through a modified agar well-diffusion method [25]. In this method, a twofold serial dilution of each chemically synthesized compound was prepared by first reconstituting the compound in DMSO followed by dilution in sterile distilled water to achieve a decreasing concentration range of 256 to 0.5 μg/mL. A 100 μL volume of each dilution was introduced into wells (in triplicate) in the agar plates already seeded with 100 μL of standardized inoculums (10^6 cfu/mL) of the test microbial strain. All test plates were incubated aerobically at 37°C for 24 hr and observed for the inhibition zones. MIC, taken as the lowest concentration of the chemical compound that completely inhibited the growth of the microbe, showed by a clear zone of inhibition, was recorded for each test organism. Ciprofloxacin was used as the positive control.

4.4. In Vitro Antifungal Activity. The ligands and their metal complexes were also screened for their antifungal activity against two fungi, namely, *A. niger* and *A. flavus*, the ear pathogens isolated from the patients of Kurukshetra [26], by poison-food technique [27]. The moulds were grown on Sabouraud dextrose agar (SDA) at 25°C for 7 days and used as inocula. The 15 mL of molten SDA (45°C) was poisoned by the addition of 100 μL volume of each compound having concentration of 4.0 mg/mL, reconstituted in the DMSO, poured into a sterile Petri plate, and allowed it to solidify at room temperature. The solidified poisoned agar plates were inoculated at the center with fungal plugs (8 mm diameter) obtained from the colony margins and incubated at 25°C for 7 days. DMSO was used as the negative control whereas fluconazole was used as the positive control. The experiments were performed in triplicates. The diameter of fungal colonies was measured and expressed as percent mycelial inhibition by applying the formula:

$$\text{percent inhibition of myelial growth} = \frac{(dc - dt)}{dc} \times 100, \quad (1)$$

dc = average diameter of fungal colony in negative control sets,

dt = average diameter fungal colony in experimental sets.

4.5. Observations. The antibacterial data reveals that the free ligands and their metal complexes are active against gram-positive bacteria (*S. aureus* and *B. subtilis*) and inactive against gram-negative bacteria (*E. coli* and *P. aeruginosa*). It has also been observed that the organometallic complexes are more affective as compared to the free ligands. Efficacy of all the compounds was found to be more potent inhibitors of bacterial growth as compared to the fungal culture. Among the synthesized compounds tested, 1 : 1 and 1 : 2 complexes of silicon and tin, that is, $Me_2SiCl(L^1)$, $Me_2Si(L^1)_2$, $Me_2Si(L^2)_2$, $Me_2SnCl(L^2)$, and $Me_2Sn(L^2)_2$ show more antibacterial activity that is near to standard drug (ciprofloxacin) (Table 4). In the series, the MIC of the compounds ranged between 64 and 128 μg/mL against gram-positive bacteria. Compound $Me_2Sn(L^1)_2$ and $Me_2SnCl(L^2)$ show highest MIC of 64 μg/mL against *S. Aureus* and *B. Subtilis* (Table 5). The antifungal activity of compounds (Figure 3) shows more than 50% inhibition of mycelia growth against *A. Niger* and *A. flavus* (Table 6). Thus, it can be postulated that further studies of these complexes in this direction could lead to more interesting results.

5. Conclusions

Trigonal bipyramidal and octahedral geometries have been proposed for 1 : 1 and 1 : 2 organosilicon(IV) and organotin(IV) complexes (Figure 4) with the help of various spec-

Table 4: *In vitro* antibacterial activity of the ligands and their metal complexes.

Compounds	Zone of inhibition (mm)[a]			
	S. Aureus	*B. Subtilis*	*E. Coli*	*P. Aeruginosa*
HL^1	16.3	16.6	—	—
$Me_2SiCl(L^1)$	17.6	18.6	—	—
$Me_2Si(L^1)_2$	16.6	19.6	—	—
$Me_2SnCl(L^1)$	17.3	16.8	—	—
$Me_2Sn(L^1)_2$	16.9	15.3	—	—
HL^2	16.3	15.3	—	—
$Me_2SiCl(L^2)$	17.6	17.3	—	—
$Me_2Si(L^2)_2$	18.6	15.6	—	—
$Me_2SnCl(L^2)$	16.9	19.6	—	—
$Me_2Sn(L^2)_2$	16.6	18.0	—	—
Ciprofloxacin	26.6	24	25.0	22.0

—: No activity.
[a] Values, including diameter of the well (8 mm), are means of three replicates.

Table 5: Minimum inhibitory concentration (MIC) (μg/mL) of the ligands and their metal complexes.

Compounds	*S. Aureus*	*B. Subtilis*
HL^1	128	128
$Me_2SiCl(L^1)$	128	64
$Me_2Si(L^1)_2$	64	128
$Me_2SnCl(L^1)$	64	128
$Me_2Sn(L^1)_2$	64	64
HL^2	128	128
$Me_2SiCl(L^2)$	64	64
$Me_2Si(L^2)_2$	128	128
$Me_2SnCl(L^2)$	64	64
$Me_2Sn(L^2)_2$	64	128
Ciprofloxacin	5	5

Table 6: *In vitro* antifungal activity of the ligands and their metal complexes.

Compounds	Mycelial growth inhibition (%)	
	A. niger	*A. flavus*
HL^1	46.6	44.4
$Me_2SiCl(L^1)$	51.3	55.6
$Me_2Si(L^1)_2$	49.5	50.5
$Me_2SnCl(L^1)$	54.7	49.4
$Me_2Sn(L^1)_2$	59.1	50.9
HL^2	41.1	45.5
$Me_2SiCl(L^2)$	48.8	62.5
$Me_2Si(L^2)_2$	56.6	48.4
$Me_2SnCl(L^2)$	54.8	63.3
$Me_2Sn(L^2)_2$	49.5	55.7
Fluconazole	81.1	77.7

tral studies like UV, IR, ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR. The antimicrobial studies suggested that all the Schiff bases were found to be biologically active and their metal complexes showed significantly enhanced antibacterial and antifungal activity against microbial strains in comparison to the free ligands, thus, exhibiting their broad spectrum nature and can be further used in pharmaceutical industry.

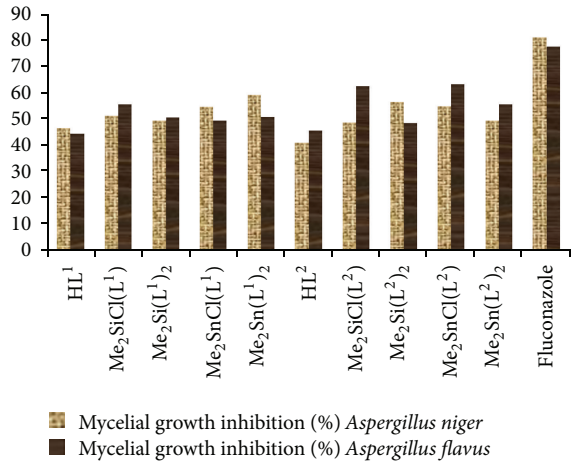


Figure 3: Comparison of antifungal activity of compounds with commercial antibiotic.

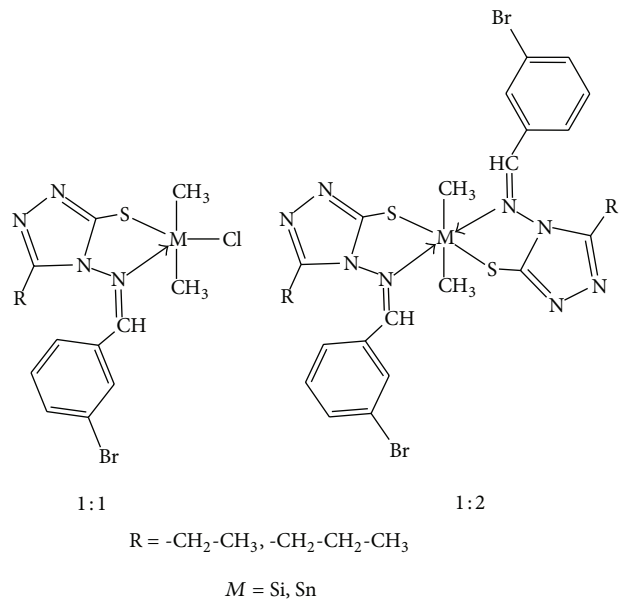


Figure 4: Proposed structures of the 1 : 1 and 1 : 2 complexes.

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