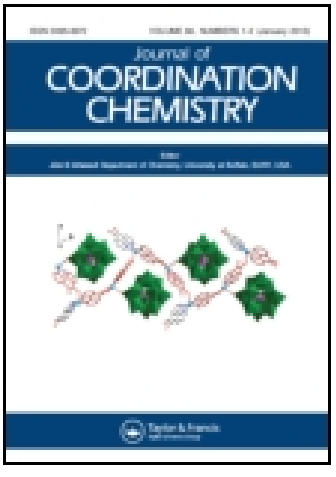

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Synthesis, characterization, HOMO-LUMO study, and antimicrobial activity of organotin(IV) complexes of 4-piperidine carboxamide and its Schiff base

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Synthesis, characterization, HOMO–LUMO study, and antimicrobial activity of organotin(IV) complexes of 4-piperidine carboxamide and its Schiff base

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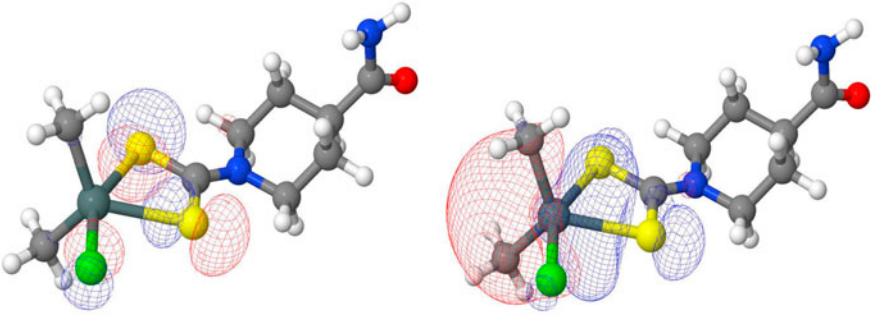

A series of organotin(IV) complexes has been synthesized by reacting 4-piperidine carboxamide with CS_2 and R_2SnCl_2/R_3SnCl in 1 : 1 M/L ratio at room temperature. The synthesized complexes were further treated with benzaldehyde to synthesize Schiff bases under stirring. All the complexes were characterized by elemental analysis, FT-IR, ^1H and ^{13}C NMR. FT-IR and semi-empirical study confirm the bidentate nature of ligand. The complexes exhibit four-coordinate geometry in solution. Thermodynamic parameters and molecular descriptors were calculated by using semi-empirical PM3 method. HOMO–LUMO calculations show that chlorodiorganotin complexes are more susceptible to nucleophilic attack when compared with triorganotin complexes. Negative heats of formation at 298 K demonstrate that **1**, **4,** and **7** are thermodynamically stable. The antimicrobial results have shown that complexes containing Schiff base exhibit significantly better activity compared to complexes with carboxamide derivatives.

Keywords: 4-Piperidine carboxamide; Schiff base; Organotin complexes; Spectroscopic studies; Semi-empirical study; HOMO–LUMO calculations; Biological activity

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1. Introduction

Organotin(IV) complexes are of interest because of their biomedical and commercial applications [1]. Several organotin complexes are effective as antifouling, antimicrobial [2], and antiviral agents. Applications of metal complexes in the treatment of numerous human diseases are a vigorously expanding area in biomedical and inorganic chemistry [3, 4].

There has been interest in coordination chemistry of Schiff bases because of ease of syntheses of various metal complexes [5, 6] and stabilization in various oxidation states. Schiff-base complexes have been used as models for biological systems [7, 8]. In addition to antitumor activities, organotin(IV) complexes with Schiff bases present an interesting variety of structural possibilities [9].

As an extension of our previous work with Schiff bases [10–12], the present studies have been undertaken to investigate organotin(IV) derivatives of 4-piperidine carboxamide and its Schiff base to compare the biological activities.

2. Experimental

2.1. *Chemicals and instrumentation*

All reagents and solvents were purchased from Sigma, Aldrich, and Merck. The solvents were dried [13] prior to use. The melting points of complexes were determined by electrothermal melting point apparatus using open capillaries (Stuart-SMP, USA). Elemental analyses were carried out on a CHNS elemental analyzer Leco (USA). Infrared spectra were recorded as KBr/CsBr disks using a Perkin Elmer spectrophotometer from 4000 to 250 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer using $CDCl_3$ as an internal standard.

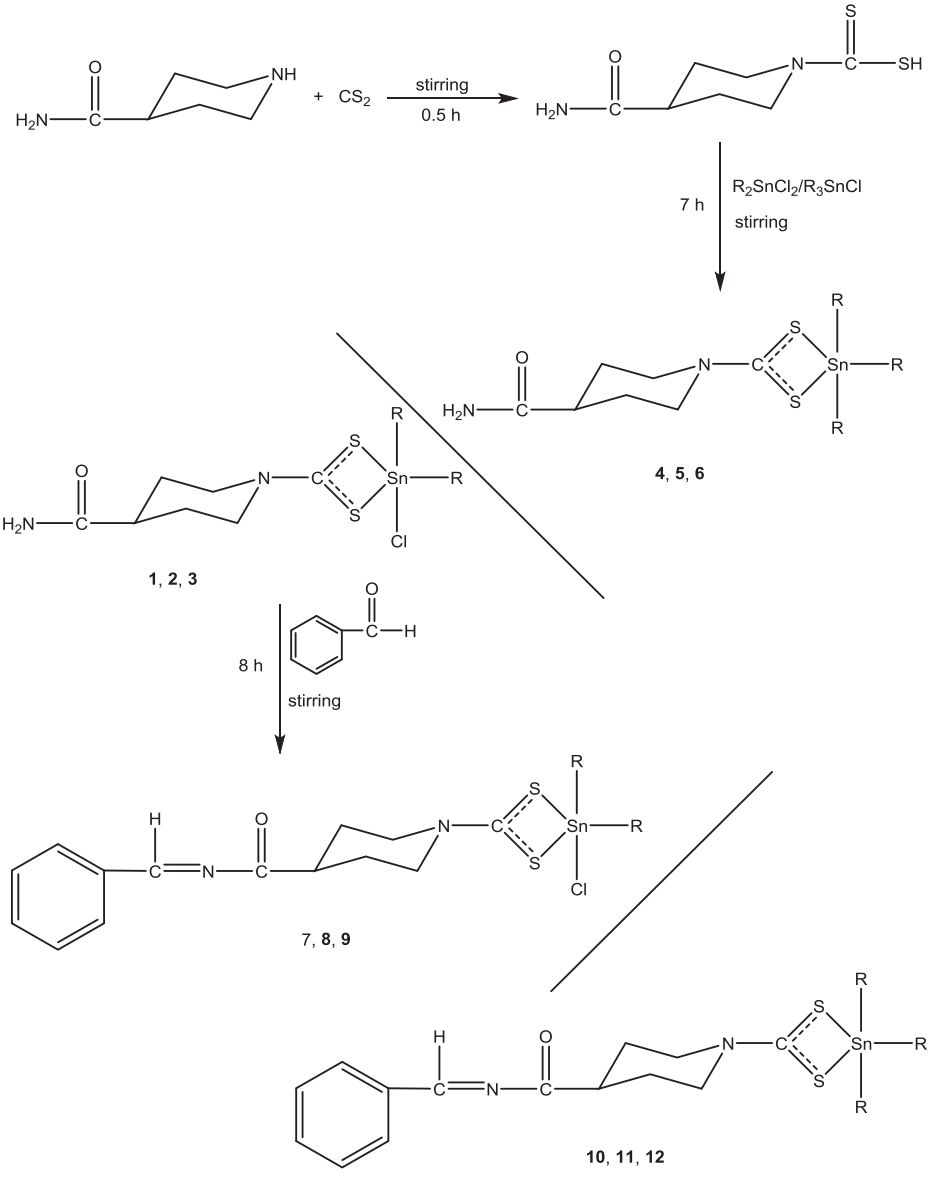
The molecules were modeled by MOPAC 2007 program [14] in the gas phase using PM3 method [15], based on the premise that atoms prefer an arrangement which has the minimum energy and hence most stable. Selected parts of the complexes not containing tin were pre-optimized using molecular mechanics methods. Several cycles of energy minimization had to be carried out for each molecule. The structures were optimized by Eigen Vector. The root mean square gradient for molecules was less than one. Self-consistent field was attained in each case. Absences of imaginary frequencies were checked.

2.2. *General procedure for synthesis of organotin(IV) complexes*

2.2.1. Step-I. 4-Piperidine carboxamide (1 mM) was dissolved in ethanol (20 mL) in a round bottom flask (250 mL) with continuous stirring and then CS_2 (1 mM) was added dropwise. The reaction mixture was stirred at room temperature for 0.5 h. Then R_2SnCl_2/R_3SnCl (1 mM) was added as solid in portions in the above reaction mixture and stirred continuously for 7 h. Solvent was evaporated and the solid product obtained was recrystallized in ethanol : pet. ether (1 : 1).

2.2.2. Step-II. The product obtained in step-I (1 mM) was dissolved in ethanol (15 mL) with continuous stirring at room temperature and benzaldehyde (1 mM) was added dropwise. The reaction mixture was further stirred for 8 h at room temperature.

Solvent was evaporated and the product obtained was recrystallized in ethanol : pet. ether (1 : 1).



R = Me, *n*-Bu, Ph

R	Me	*n*-Bu	Ph
Compound	**1**,**4**,**7**,**10**	**2**,**5**,**8**,**11**	**3**,**6**,**9**,**12**

3. Results and discussion

The synthesized complexes have sharp melting points and are soluble in common organic solvents. Elemental analysis data reveal that the observed values are in agreement with calculated values. Physical data are given in table 1.

3.1. *Infrared spectroscopy*

In order to study the binding mode of the ligand with tin(IV), spectra of the complexes were compared with that of ligand [16]; data are given in table 2. The disappearance of the S–H band in spectra of all synthesized complexes confirms the complexation of organotin(IV) through sulfur. It has been reported [17] that observation of a single ν(C=S) at 1000 cm^{-1} is indicative of dithiocarbamate groups bonded symmetrically or bidentate. A strong ν(C–S) is at 1004–1056 cm^{-1}, while ν(C=S) is at lower frequency, 939–993 cm^{-1}.

Schiff base formation was confirmed due to the occurrence of ν(C=N) bands at 1614–1697 cm^{-1} in **7–12**. The spectral band due to –NH at 3248–3296 cm^{-1} in ligand and **1–6** illustrates that –NH does not coordinate [18] and disappearance of this band in **7–12** confirms formation of Schiff base.

New bands at 528–563 cm^{-1}, 461–492 cm^{-1}, and 221–242 cm^{-1} are assigned to ν(Sn–C), ν(Sn–S), and ν(Sn–Cl), respectively [19, 20]; ν(Sn–C) band appears at 263, 254, 251, and 261 cm^{-1} for **3**, **6**, **9**, and **12**, respectively, which are di- and triphenyltin derivatives.

3.2. *^{1}H NMR spectroscopy*

^{1}H NMR spectral data of the ligand and **1–12** are given in tables 3 and 4 along with their coupling values. The absence of the −SH proton resonance in the complexes confirms deprotonation. All the protons present in **1–12** have been identified in position and number with the protons calculated from the incremental method [21]. The NH_2 protons are sharp singlet at 8.73 in HL and do not show any shift in **1–6**, confirming that this group does not participate in complexation. Disappearance of this signal in spectra of **7–12** confirms reaction of NH_2 with benzaldehyde to yield the Schiff base. The CH_3 protons in **1** and **7** are singlets at 1.13 and –0.01 ppm with tin satellites having $^2J[^{119}Sn–^1H] = 96$ and 98 Hz, respectively, supporting five-coordinate tin in solution [17].

In **2** and **8**, the methylene protons of butyl are multiplets at 1.26–1.87 and 0.56–0.90 ppm. The terminal CH_3 group of butyl gives triplets at 0.87 and 0.20 ppm with $^3J[^1H–^1H]$ of 7.2 Hz for **2** and **8**, respectively. The methyls in **4** and **10** attached to Sn give singlets at 0.39 and 0.50 ppm.

In triphenyltin(IV) derivatives, the phenyl protons consisted of two groups of peaks. The *ortho* protons were observed at 6.86–7.30 and 6.98–7.42 ppm and those for the *meta* and *para* protons (6.69–6.92 and 6.82–6.95 ppm) for **6** and **12**.

3.3. *^{13}C NMR spectroscopy*

Tables 5 and 6 list the ^{13}C chemical shifts and tin–carbon coupling constants for **1–12**. In **7–12**, the chemical shift of C-1 attached with sulfur (–CSS) was at 194.4–194.6 ppm [22].

Table 1. Physical data of organotin(IV) complexes.

Complex no.	Molecular formula	MW	MP (°C)	% Yield	Elemental analysis			
					% C Calcd (found)	% H Calcd (found)	% N Calcd (found)	% S Calcd (found)
HL	$C_7H_{12}N_2OS_2$	204	214–215	76	41.17(41.14)	5.92(5.96)	13.72(13.68)	31.37(31.32)
1	$C_9H_{17}N_2OS_2SnCl$	387.2	168–170	70	27.89(27.93)	4.42(4.40)	7.23(7.19)	16.52(16.56)
2	$C_{15}H_{29}N_2OS_2SnCl$	471.2	115–118	74	38.20(38.24)	6.20(6.15)	5.94(5.90)	13.58(13.54)
3	$C_{19}H_{21}N_2OS_2SnCl$	511.68	182–183	85	44.60(44.55)	4.14(4.10)	5.47(5.51)	12.53(12.57)
4	$C_{10}H_{20}N_2OS_2Sn$	367.1	98–100	80	32.72(32.77)	5.49(5.42)	7.63(7.68)	17.45(17.41)
5	$C_{19}H_{38}N_2OS_2Sn$	493.1	110–112	80	46.20(46.16)	7.76(7.71)	5.68(5.71)	12.99(13.04)
6	$C_{25}H_{26}N_2OS_2Sn$	553.7	166–167	76	54.27(54.31)	4.74(4.70)	5.06(5.01)	11.57(11.52)
7	$C_{16}H_{21}N_2OS_2SnCl$	475.2	141–143	61	40.40(40.36)	4.45(4.41)	5.89(5.94)	13.45(13.49)
8	$C_{22}H_{33}N_2OS_2SnCl$	559.2	122–124	63	47.21(47.24)	5.94(5.90)	5.00(5.04)	11.44(11.48)
9	$C_{26}H_{25}N_2OS_2SnCl$	599.78	171–172	78	52.07(52.12)	4.20(4.24)	4.67(4.71)	10.69(10.63)
10	$C_{17}H_{24}N_2OS_2Sn$	455.2	160–163	80	44.86(44.90)	5.31(5.35)	6.15(6.11)	14.07(14.02)
11	$C_{26}H_{42}N_2OS_2Sn$	581.4	102–105	77	53.72(53.76)	7.28(7.25)	4.82(4.86)	11.02(11.01)
12	$C_{32}H_{30}N_2OS_2Sn$	641.4	113–115	89	59.92(60.06)	4.71(4.67)	4.37(4.42)	10.00(10.05)

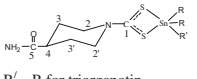
Table 2. Infrared absorption bands (cm^{-1}) of organotin(IV) complexes.

Complex no.	ν(S–H)	ν(C=S)	ν(C–S)	ν(NH)	ν(C=N)	ν(Sn–C)	ν(Sn–S)	ν(Sn–Cl)
HL	2796	997	947	3248	–	–	–	–
1	–	968	1024	3265	–	545	492	242
2	–	978	1012	3296	–	544	472	239
3		952	1032	3285	–	263	474	230
4	–	947	1056	3207	–	555	479	–
5	–	942	1045	3271	–	535	472	–
6	–	993	1023	3290	–	254	461	–
7	–	941	1045	–	1685	530	464	234
8	–	976	1004	–	1697	536	469	239
9		972	1015	–	1626	251	480	221
10	–	964	1050	–	1690	540	483	–
11	–	945	1043	–	1614	528	469	–
12	–	939	1030	–	1650	261	487	–

Table 3. ^{1}H NMR data[a–c] of organotin(IV) complexes.

	Chemical shift (ppm)						
Proton no.	**HL**	**1**	**2**	**3**	**4**	**5**	**6**
2, 2′	1.83–1.88m	1.82–1.86m	1.82–1.87m	1.82–1.87m	1.82–1.87m	1.81–1.87m	1.81–1.86m
3, 3′	2.85–2.96m	2.82–2.86m	2.82–2.87m	2.84–2.85m	2.82–2.86m	2.81–2.85m	2.82–2.87m
NH_2	8.73s	8.74s	8.73s	8.74s	8.74s	8.74s	8.74s
SH	1.62s	–	–	–	–	–	–
R	–	1.13s[96]	0.87t(7.2) 1.26–1.34m 1.61–1.87m	6.52–6.83m 6.12–7.50m	0.39s[77.8]	0.92t(7.7) 1.63–1.68m 1.72–1.77m	6.69–6.92m 6.86–7.30m

[a]Chemical shifts (δ) in ppm. $^{n}J(^{1}H,^{1}H)$ and $^{n}J[^{119}Sn,^{1}H]$ in Hz are listed in parenthesis and square brackets, respectively.
[b]Multiplicity is given as, s = singlet, t = triplet, and m = multiplet.
[c]



R′ = R for triorganotin
R′ = Cl for diorganotin
R = Me, *n*-Bu, Ph

The C=O in **1–6** give signal at 175.56–175.98 ppm, upfield in **7–12** due to condensation of NH_2 with benzaldehyde to 169.8–169.8 ppm. The $^{1}J(^{119}Sn–^{13}C)$ for **4**, **6**, **8**, **10**, and **11** are 395.6, 638.1, 558.3, 378.6, and 578.6 Hz, respectively, indicative of four-coordinate geometry [23] in solution. In **1** and **7**, signals at 28.5 ppm and 28.7 ppm were due to methyl bound to Sn. In **12**, phenyl carbon signals were observed at 128.7–137.2 ppm [24, 25].

3.4. *Semi-empirical study*

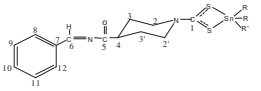
In the geometry optimized structures, one sulfur of the ligand bonds bidentate to tin. The other positions are occupied by methyl or phenyl groups. Selected bond angles (°) and bond lengths (Å) are given in Supplementary material (Supplemantal data can be accessed http://dx.doi.org/10.1080/00958972.2013.869584) and are typical [26]. The piperidine molecule adopts a chair-like configuration in all the complexes.

Computed negative heats of formation indicate that **1**, **4,** and **7** are thermodynamically stable (Supplementary material). The calculated HOMO and LUMO of **1**, **3**, **4**, **6**, **7**, **9**,

Table 4. ^{1}H NMR data[a–c] of organotin(IV) complexes.

	Chemical shift (ppm)					
Proton no.	**7**	**8**	**9**	**10**	**11**	**12**
2,2′	2.78–2.87m	2.77–2.86m	2.78–2.87m	2.78–2.87m	2.78–2.87m	2.77–2.86m
3,3′	1.83–1.86m	1.82–1.87m	1.82–1.86m	1.82–1.87m	1.83–1.87m	1.85–1.86m
4	2.42–2.47m	2.41–2.46m	2.42–2.46m	2.41–2.47m	2.43–2.47m	2.45–2.46m
6	7.44s	7.43s	7.45s	7.44s	7.44s	7.46s
8,12	7.27–7.40m	7.26–7.39m	7.26–7.40m	7.27–7.41m	7.27–7.39m	7.28–7.40m
9,11	6.81–6.93m	6.80–6.95m	6.81–6.94m	6.82–6.90m	6.82–6.95m	6.80–6.95m
10	7.27s	7.28s	7.27s	7.26s	7.27s	7.28s
R	−0.01 ^{2}J[98]	0.56–0.90m 0.20t(7.2)	6.72–6.87m 6.92–7.52m	0.50s ^{2}J[82]	0.64–1.1m 0.23t(7.2)	6.82–6.95m 6.98–7.42m

[a]Chemical shifts (δ) in ppm. $^{n}J(^{1}H,^{1}H)$ and $^{n}J[^{119}Sn,^{1}H]$ in Hz are listed in parenthesis and square brackets, respectively.
[b]Multiplicity is given as, s = singlet and m = multiplet.
[c]

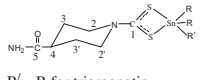


R′ = R for triorganotin; R′ = Cl for diorganotin
R = Me, *n*-Bu, Ph

Table 5. ^{13}C NMR data[a–c] of organotin(IV) complexes.

	Chemical shift (ppm)						
Carbon no.	**HL**	**1**	**2**	**3**	**4**	**5**	**6**
1	211.6	195.7	195.0	195.5	195.6	195.2	195.4
2, 2′	42.9	42.8	42.8	42.7	42.8	42.7	42.8
3, 3′	28.9	28.5	28.7	28.6	28.6	28.3	28.7
4	39.8	39.8	39.9	39.8	39.8	39.8	39.8
5	175.7	175.6	175.6	175.5	175.8	175.9	175.6

[a]Compound **1**: Sn-CH_3Cl, (C-α) 28.5 ^{1}J[299]; Compound **2**: Sn-C_4H_9Cl, (C-α) 28.1 ^{1}J[551], (C-β) 27.2 ^{2}J[24], (C-γ) 26.5 ^{3}J[65], (C-δ) 14.1; Compound **3**: Sn-C_6H_5Cl, (C-α) 147.3 ^{1}J[434], (C-β) 137.8 ^{2}J[34], (C-γ) 135.6 ^{3}J[43], (C-δ) 129.6; Compound **4**: Sn-CH_3, (C-α) –2.0 ^{1}J[395]; Compound **5**: Sn-C_4H_9, (C-α) 28.8 ^{1}J[573], (C-β) 26.80 ^{2}J[23], (C-γ) 25.4 ^{3}J[65], (C-δ) 14.2; and Compound **6**: Sn-C_6H_5, (C-α) 142.1 ^{1}J[638], (C-β) 136.0 ^{2}J[47.8], (C-γ) 135.9 ^{3}J[58], (C-**δ**) 129.2.
[b]Chemical shifts (δ) in ppm. $^{n}J[^{119}Sn,^{13}C]$ in Hz are listed in square brackets.
[c]



R′ = R for triorganotin
R′ = Cl for diorganotin
R = Me for 1, 3, Bu for 2, 4, Ph for 5

10, and **12** are shown in figure 1 and Supplementary material. The HOMO is primarily located on sulfur and chloride, while the LUMO is located on Sn, which indicates that Sn is highly susceptible to nucleophilic attack. The calculated HOMO and LUMO energies are shown in Supplementary material. A large HOMO–LUMO gap indicates stable molecule with low chemical reactivity, while a small energy of HOMO is associated with unstable molecule with high chemical reactivity. Energy of HOMO for **3** and **10** shows that **3** is least stable with high reactivity while **10** is most stable with less reactivity. The ability of the molecule to donate electrons, (Ionization Potential), E_{LUMO} represents (Electron Affinity), and electrophilicity values ($\omega = \mu^2/2\eta$) [27], chemical potential values $\mu = -(I + A)/2$ [28], global hardness ($\eta = I - A/2$) values [29] and

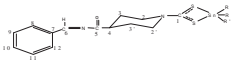
Table 6. ^{13}C NMR data[a–c] of organotin(IV) complexes.

	Chemical shift (ppm)					
Carbon no.	**7**	**8**	**9**	**10**	**11**	**12**
1	194.6	194.4	194.3	194.6	194.5	194.6
2,2′	43.4	43.4	43.4	43.4	43.4	45.4
3,3′	28.9	28.9	28.9	28.9	28.9	28.9
4	39.0	39.0	39.0	39.0	39.0	39.0
5	169.8	169.8	169.8	169.8	169.8	169.8
6	161.2	161.1	161.2	161.1	161.1	161.1
7	131.5	131.5	131.4	131.5	131.5	136.5
8,12	129.4	129.3	129.2	129.5	129.5	129.2
9,11	128.2	128.2	128.2	128.2	128.2	128.2
10	136.0	136.0	136.0	136.0	136.0	136.0

[a]Compound **7**: Sn-CH_3Cl; (C-α) 28.7 ^1J[297]; Compound **8**: Sn-$CH_2CH_2CH_2CH_3Cl$, (C-α) 20.9 ^1J[558], (C-β) 28.6 ^2J[33], (C-γ) 27.6 ^3J[86], (C-δ) 14.0; Compound **9**: Sn-C_6H_5Cl, (C-α) 137.0 ^1J[438], (C-β) 129.2 ^2J[36], (C-γ) 136.2 ^3J[46], (C-δ) 128.2; Compound **10**: Sn-CH_3, 2.2 ^1J[378]; Compound **11**: Sn-$CH_2CH_2CH_2CH_3$, (C-α) 22.6 ^1J[578], (C-β) 28.7 ^2J[34], (C-γ) 27.6 ^3J[87], (C-δ) 14.2; and Compound **12**: Sn-C_6H_5, (C-α) 137.2 ^1J[642], (C-β) 129.8 ^2J[49], (C-γ) 136.5 ^3J[62], (C-δ) 128.7.

[b]Chemical shifts (δ) in ppm. ^nJ[^{119}Sn,^{13}C] in Hz are listed in square brackets.

[c]



$R^/$ = R for triorganotin
$R^/$ = Cl for diorganotin

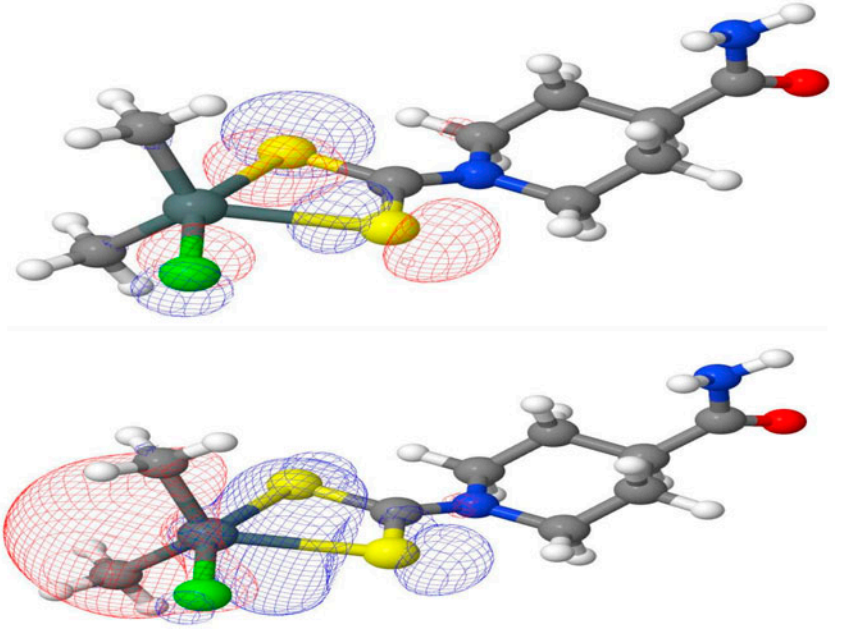


Figure 1. HOMO–LUMO of **1**.

global softness values ($S = 1/2\eta$) [30] have been calculated in each case (Supplementary material). The presence of a chloride instead of a methyl or phenyl increases the electrophilic character of the molecule. In other words, the chlorodiorganotin complexes

Table 7. Antibacterial activity[a–c] of organotin(IV) complexes.

Complex no.	Zone of inhibition (mm)			
	B. subtilus	*S. aureus*	*P. multocida*	*E. coli*
HL	$18.5^{e} \pm 0.9$	$14.5^{f} \pm 0.9$	$20.5^{e} \pm 0.9$	$17^{f} \pm 1$
1	$22.0^{d} \pm 0.00$	$21^{de} \pm 1$	$21.5^{de} \pm 0.5$	$19.5^{e} \pm 0.9$
2	$22.5^{d} \pm 0.9$	$22.0^{cd} \pm 0.00$	$21.7^{de} \pm 0.4$	$20.0^{e} \pm 0.00$
3	$24.0^{cd} \pm 0.00$	$24.6^{bc} \pm 0.8$	$25.2^{bc} \pm 0.8$	$22^{cd} \pm 1$
4	$23.3^{cd} \pm 0.8$	$23^{cd} \pm 1$	$23.5^{cd} \pm 0.8$	$21.3^{de} \pm 0.8$
5	$26.0^{ab} \pm 0.9$	$21^{de} \pm 1$	$26^{b} \pm 1$	$26.0^{ab} \pm 0.00$
6	$24.0^{cd} \pm 0.00$	$24.7^{bc} \pm 0.8$	$25.3^{bc} \pm 0.8$	$22^{cde} \pm 1$
7	$24.0^{cd} \pm 1.4$	$24.0^{bcd} \pm 0.00$	$24.0^{c} \pm 0.00$	$23.5^{bcd} \pm 0.5$
8	$26.0^{b} \pm 0.00$	$25.3^{bc} \pm 0.8$	$25^{bc} \pm 1$	$24^{bc} \pm 3$
9	$28^{a} \pm 1$	$26^{ab} \pm 2$	$29^{a} \pm 1$	$27.3^{a} \pm 0.8$
10	$25^{bc} \pm 1$	$19^{e} \pm 1$	$26.5^{b} \pm 0.9$	$24.5^{bc} \pm 0.9$
11	$26.7^{ab} \pm 0.8$	$23^{bcd} \pm 1$	$27^{b} \pm 1$	$26.0^{ab} \pm 0.00$
12	$28^{a} \pm 1$	$26^{ab} \pm 2$	$29^{a} \pm 1$	$27.5^{a} \pm 0.9$
Rifampicin	$26^{ab} \pm 1$	$24.0^{a} \pm 0.5$	$24^{bc} \pm 1$	$26^{a} \pm 1$

[a]Rifampicin = Standard drug.
[b]Values are mean ± SD of three samples analyzed individually in triplicate at ($p < 0.01$).
[c]Different letters in superscript indicate significant and nonsignificant differences within sample.

are more susceptible to nucleophilic attack when compared with triorganotin complexes. Substituting chloride for methyl/phenyl makes the molecule less hard due to lower HOMO–LUMO gap.

3.5. *Antibacterial activity*

The ligand and organotin(IV) complexes were screened for their antibacterial activity against *B. subtilus*, *P. multocida*, *S. aureus*, and *E. coli* test by the disk diffusion method [31]. Rifampicin was used as positive control to compare its activity with synthesized complexes. The data in table 7 show the complexes exhibit significant antibacterial activity as compared to free ligand.

The antibacterial activities of **7–12** containing the Schiff base were better than **1–6**, suggesting the imine group enhances activity of complexes [7, 8]. This may be due to the greater lipophilic nature of the complexes [32–35]. Comparison of the activities of synthesized complexes with standard drug and with compounds already reported in literature [36–45] showed that some complexes are more potent but some are less active than standard drug against different test microorganisms.

3.6. *Antifungal activity*

The antifungal activities of organotin(IV) complexes along with the ligand were checked against selected fungal strains *A. niger*, *A. flavus*, *G. lucidum*, and *A. alternata*. Standard drug showed highest antifungal activity against all selected fungi. Data are given in table 8. The results show that **7–12** have better fungicidal activity compared to **1–6** without Schiff base. The better fungicidal activity is due to formation of Schiff base in **7–12** which enhances the activity on coordination with tin [46]. Greater fungicidal activity of organotin (lV) complexes when compared to free ligand may be due to chelation.

Table 8. Antifungal activity[a–c] of organotin(IV) complexes.

Complex no.	Zone of inhibition (mm)			
	A. niger	*A. flavus*	*A. alternata*	*G. lucidum*
HL	$05.5^{h} \pm 0.9$	$7^{f} \pm 1$	00.0^{f}	$07.5^{f} \pm 0.9$
1	$12.5^{g} \pm 0.9$	$12.0^{d} \pm 0.00$	$17^{e} \pm 1$	$14.0^{e} \pm 0.00$
2	00.0^{i}	00.0^{g}	00.0^{f}	00.0^{g}
3	$18^{b} \pm 1$	$16.5^{b} \pm 0.00$	$19.3^{b} \pm 0.4$	$17.6^{b} \pm 0.4$
4	$13.5^{fg} \pm 0.5$	$14.0^{c} \pm 0.00$	$17.7^{de} \pm 0.4$	$14.0^{e} \pm 0.00$
5	$15.0^{cd} \pm 0.00$	$14.0^{cd} \pm 0.8$	$18.5^{b} \pm 0.5$	$17.0^{bc} \pm 0.5$
6	$14.0^{ef} \pm 0.00$	$10.5^{e} \pm 0.9$	$18.5^{cd} \pm 0.9$	$15.5^{d} \pm 0.5$
7	$14.5^{def} \pm 0.5$	$13.5^{e} \pm 0.9$	$17.5^{de} \pm 0.5$	$15.7^{d} \pm 0.4$
8	$15.2^{cde} \pm 0.4$	$14.2^{c} \pm 0.4$	$18.0^{de} \pm 0.00$	$16.0^{d} \pm 0.00$
9	$19^{b} \pm 1$	$16.9^{b} \pm 0.00$	$19.9^{b} \pm 0.4$	$17.9^{b} \pm 0.4$
10	$15.5^{cd} \pm 0.5$	$14.7^{bc} \pm 0.8$	$18.2^{cd} \pm 0.4$	$16.5^{cd} \pm 0.5$
11	$16.0^{c} \pm 0.00$	$14.7^{bc} \pm 0.8$	$19.2^{bc} \pm 0.4$	$17.2^{bc} \pm 0.4$
12	$18^{b} \pm 1$	$16.0^{b} \pm 0.00$	$19.7^{b} \pm 0.4$	$17.7^{b} \pm 0.4$
Fluconazol	$20^{a} \pm 1$	$19^{a} \pm 1$	$22.0^{a} \pm 0.00$	$17^{a} \pm 1$

[a]Fluconazol = Standard drug.
[b]Values are mean ± SD of three samples analyzed individually in triplicate at ($p < 0.01$).
[c]Different letters in superscript indicate significant and nonsignificant differences within sample.

4. Conclusion

We have synthesized organotin(IV) complexes with 4-piperidine carboxamide and its Schiff base with benzaldehyde under stirring. IR and semi-empirical study confirms the bidentate nature of ligand. Complexes are five-coordinate geometry in the solid state. NMR data reveal four-coordinate geometry in solution. HOMO–LUMO calculations show that chlorodiorganotin complexes are more susceptible to nucleophilic attack when compared with triorganotin complexes. Computed negative heat of formation shows that **1**, **4,** and **7** are thermodynamically stable. Antimicrobial results reveal that activity is enhanced upon coordination with tin. The antimicrobial activity further increases upon coordination with Schiff base. Difference in behavior towards bacterial and fungal strains suggests different mode of action and activity controlling factors in either case.

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