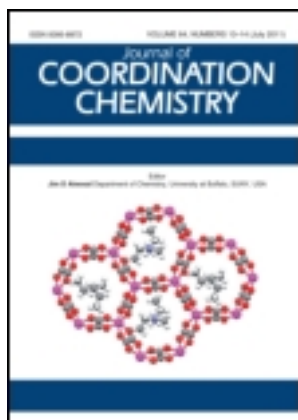


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### Bimetallic organotin(IV) complexes with ferrocene-based azomethines: synthesis, characterization, semi-empirical study, and antibacterial activity

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## Bimetallic organotin(IV) complexes with ferrocene-based azomethines: synthesis, characterization, semi-empirical study, and antibacterial activity

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A series of bimetallic organotin(IV) complexes with ferrocene-based azomethines (Schiff bases) were synthesized by reacting sodium salt of tranexamic acid, 4-amino butanoic acid, and phenyl alanine with trimethyltin and tributyltin chloride in 1:1 molar ratio under inert atmosphere. The synthesized trialkyl organotin complexes condense with formyl ferrocene under inert atmosphere to yield organotin(IV) ferrocenyl Schiff bases. Composition of the organotin(IV) complexes, bonding behavior of donor groups, and structural assignments were studied by elemental analysis, FT-IR,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$  NMR, and mass spectrometry. The spectral data suggest that the ligand is bidentate, coordinating through oxygens. Spectroscopic techniques reveal distorted tetrahedral geometry in solution for the complexes. As solids, the complexes are trigonal bipyramidal, confirmed by semi-empirical study. Mass spectrometric and elemental analysis data support the solid and solution spectroscopic results. Bioactivity screenings show *in vitro* biological potential.

**Keywords:** Bimetallic; Ferrocene-based azomethines; Organotin; IR; NMR; Mass; Semi-empirical; Antibacterial activity

### 1. Introduction

The organometallic compounds containing lead, tin, and mercury are commercially significant [1]. Ferrocene, being readily sublimed, can be used to deposit certain fullerenes, especially carbon nanotubes. Some ferrocenium salts exhibit anticancer activity and an experimental drug has been reported which is a ferrocenyl version of tamoxifen [2].

Azomethines (Schiff bases) can be polymerized and such polymers show superior mechanical, thermal, electrical, and dielectric properties [3]. Schiff bases are potential

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pesticides and herbicidal agents [4]. Schiff bases are used in photoconductive layers in electro photographic photoreceptors, showing improved chargeability, durability, and sensitivity. Ferrocene-containing Schiff bases have been employed in fields such as molecular recognition of biosensors [5], asymmetric catalyst [6], polymer science as redox active polymers and dedrimers [7], non linear optics [8], photochemical systems [9], and pharmacology [10]. Ferrocene-containing Schiff bases and their complexes with different metals are useful in photochemistry, photophysics, chemiluminescence, and electron transfer [11]. Ferrocenyl Schiff bases have shown applications in agriculture and medicines as plant protection agent or antitumor drugs [12]. From the literature [13–15], the replacement of aromatic groups by ferrocenyl moieties in penicillin and cephalosporin drastically improved their antibacterial activity, due to the conformational flexibility of ferrocene backbone in the ligand so it can easily cross the cell membrane. Mono- and di-organotin complexes are biologically less active, whereas tri-organotin complexes are powerful biocides. For improved bactericidal activity upon replacement with ferrocene or ferrocene-derived compounds, we synthesize a new class of potential organometallic-based antibacterial compounds and explore the possibility of their use as biocidal agents.

## 2. Experimental

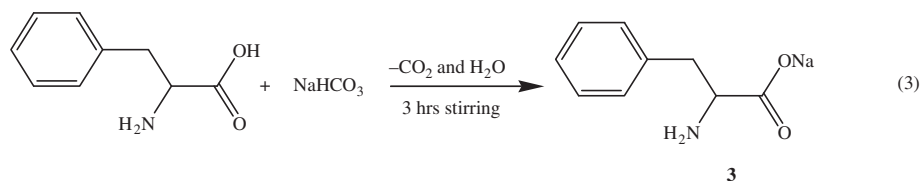
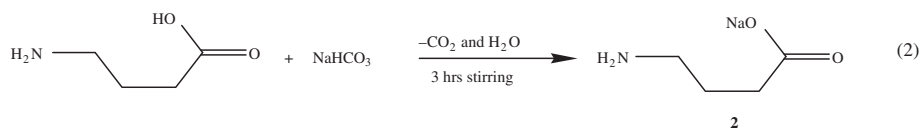
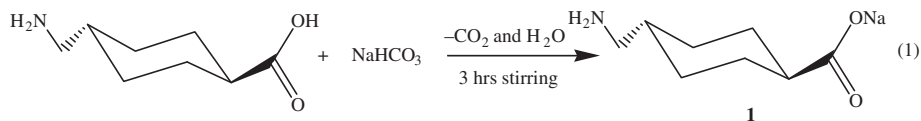
### 2.1. *Materials and methods*

Sodium hydrogencarbonate, tranexamic acid purchased from the market as capsules, 4-amino butanoic acid, phenyl alanine, formyl ferrocene, trimethyltin chloride, tributyltin chloride were purchased from Aldrich and used without purification. Solvents were dried by standard procedure [16]. Melting points were determined by using an electromelting point apparatus model MP-D Mitamura Rikero Kogyo (Japan) and are uncorrected. Elemental analyses (for carbon, hydrogen and nitrogen) were done by a CHNS-932 elemental analyzer, Leco Corporation USA. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker ARC 300-MHz-FT-NMR spectrometer using  $\text{CDCl}_3$  as an internal reference.  $^{119}\text{Sn}$  NMR spectra were recorded on a Bruker AM 250 spectrometer (Germany) with  $\text{Me}_4\text{Sn}$  as external reference. FT-IR spectra were recorded by Hitachi-270-50 IR instrument from 4000 to  $400\text{ cm}^{-1}$ . Mass spectral data were recorded on a MAT 8500 Finnigan 70 eV mass spectrometer (Germany). The structures of **5**, **6**, **8**, and **9** were modeled by MOPAC 2007 [17] using PM6 method [18]. Selected parts of the molecule not containing the metal ion were pre-optimized using molecular mechanics method before subjecting the whole molecule to geometry optimization.

### 2.2. *General procedure for synthesis of sodium salt of tranexamic acid/4-aminobutanoic acid/phenyl alanine 1-3*

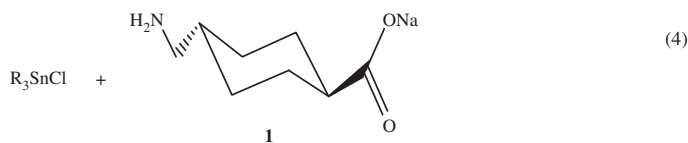
Sodium hydrogencarbonate (1mmol) was added in portions to the solution of 4-(aminomethyl)cyclohexanecarboxylic acid (tranexamic acid)/4-aminobutanoic acid/phenyl alanine (1mmol) in distilled water. The resulting mixture was stirred at room temperature for 3h. The solution was filtered and the solvent was evaporated under vacuum with a rotary evaporator. The solid product was dried in

open air (equations 1–3).

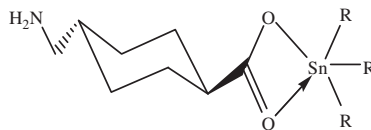


### 2.3. General procedure for synthesis of organotin(IV) derivatives 4–9

The sodium salt of 4-(aminomethyl)cyclohexanecarboxylic acid **1**/4-aminobutanoic acid **2**/phenyl alanine **3** was suspended in 50 mL of dried chloroform in a two-necked round-bottom flask equipped with a magnetic bar and reflux condenser. After stirring for 10 min, 1 mmol of trimethyltin chloride/tributyltin chloride dissolved in 10 mL of dried chloroform (10 mL) was added dropwise. The reaction mixture was refluxed for 6–8 h on a Rota mantle with continuous stirring. The reaction mixture was cooled to room temperature, filtered to remove NaCl, and the solvent was evaporated by rotary evaporator. The solid mass obtained was recrystallized from chloroform:*n*-hexane (1 : 1) (equations 4–6).

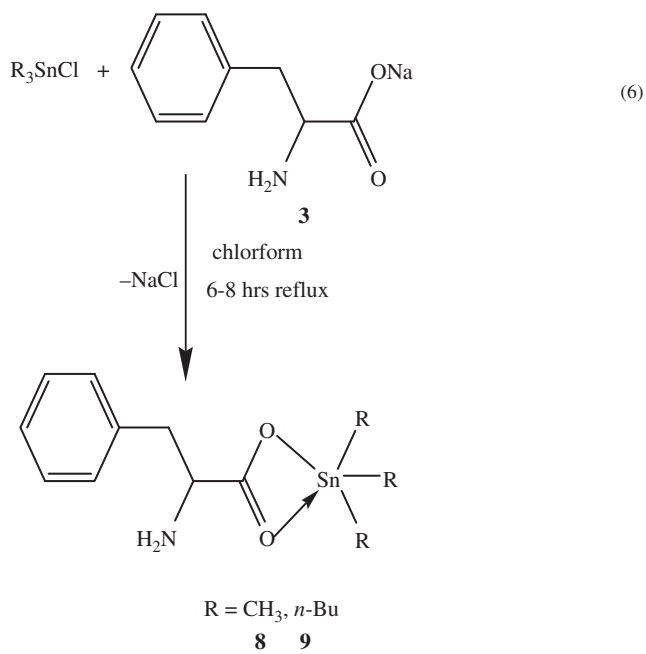
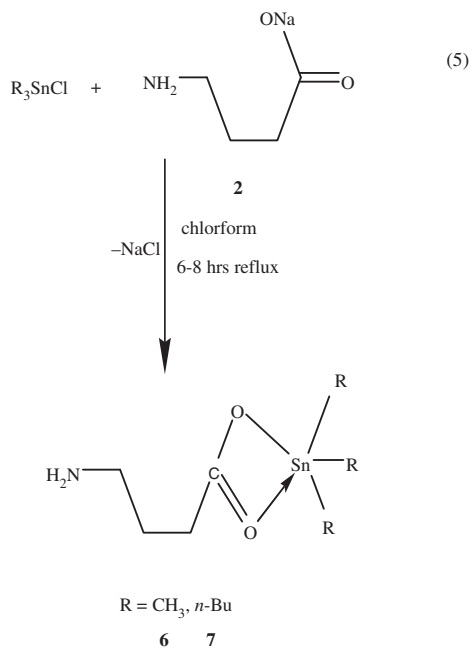


chloroform  
-NaCl  
6-8 hrs reflux



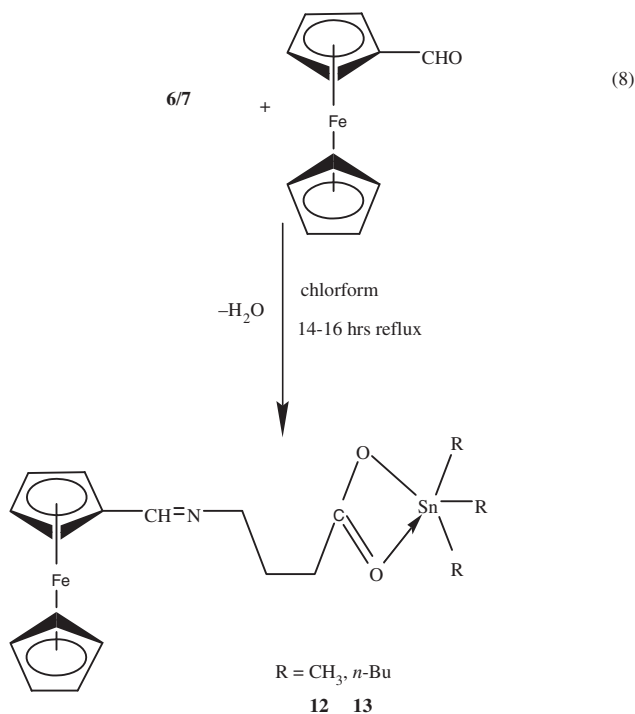
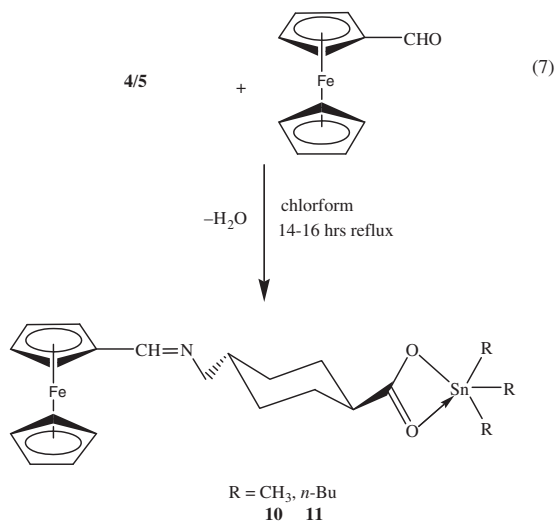
R = CH<sub>3</sub>, *n*-Bu

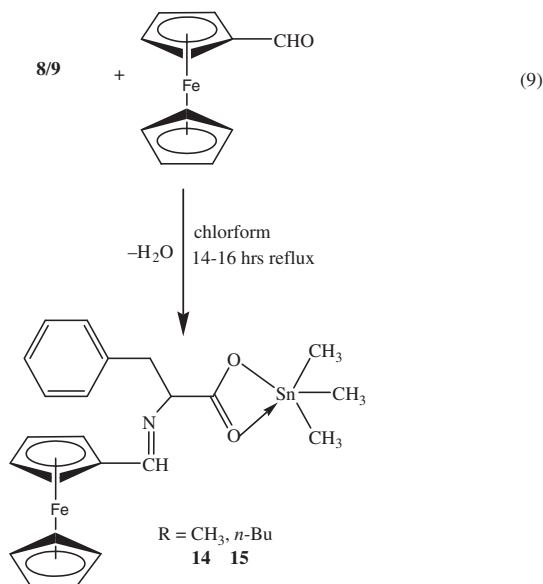
**4**    **5**



#### 2.4. General procedure for synthesis of Schiff bases 10–15

Organotin(IV) derivatives **4–9** and formyl ferrocene were stirred together in 1 : 1 molar ratio, in 80 mL chloroform in a three-necked round-bottom flask along with molecular sieves. The reaction mixture was refluxed at 60°C for 14–16 h under inert atmosphere and then solvent was evaporated with a rotary evaporator under reduced pressure. Solid product obtained was recrystallized in ethanol : *n*-hexane (1 : 1) (equations 7–9).





### 3. Results and discussion

Physical data of synthesized complexes along with the sodium salts are reported in table 1. The complexes are quite stable in air and moisture and are soluble in common organic solvents.

#### 3.1. Infrared spectroscopy

Infrared (IR) spectra of the complexes were recorded from 4000 to 400 cm<sup>-1</sup> and characteristic vibrational frequencies identified. Peaks of prime importance are  $\nu_{\text{CH}=\text{N}}$ ,  $\nu_{\text{COO}}(\text{sym})$ , and  $\nu_{\text{COO}}(\text{asym})$  and data are given in table 2. The new bands  $\nu_{\text{Sn}-\text{C}}$  and  $\nu_{\text{Sn}-\text{O}}$  appear after complex formation.

Carboxylate has two strong C=O stretches which show a strong asymmetric stretching absorption frequency at 1594–1523 cm<sup>-1</sup> and a weaker symmetric stretch at 1458–1409 cm<sup>-1</sup>. By measuring  $\Delta\nu = \nu_{\text{asym}} - \nu_{\text{sym}}$ , the interaction of metal centre with carbonyl group is defined. The coordination geometry of tin, in organotin(IV) carboxylates, adopts a variety of motifs depending on the nature of group attached to the metal and  $\Delta\nu$  value suggests the nature of carboxylate bonding [19]. The complexes show a difference,  $\Delta\nu > 200 \text{ cm}^{-1}$ , which means bidentate carboxylate.  $\nu_{\text{CH}=\text{N}}$  appears in IR spectra of the complexes confirming synthesis of Schiff bases and it does not shift in frequency, suggesting that nitrogen is not involved in bonding with Sn. The appearance of new bands  $\nu_{\text{Sn}-\text{C}}$  and  $\nu_{\text{Sn}-\text{O}}$  at 582–525 and 455–412 cm<sup>-1</sup>, respectively, confirms complexation.



Table 1. Physical data of **1–15**.

Complex No.	Molecular formula	Molecular mass	% Yield	m.p. (°C)	Elemental analysis		
					%C Calcd (found)	%H Calcd (found)	%N Calcd (found)
<b>1</b>	C <sub>8</sub> H <sub>12</sub> NO <sub>2</sub> Na	177.18	65	226	54.23 (54.28)	6.83 (6.87)	7.91 (7.87)
<b>2</b>	C <sub>4</sub> H <sub>8</sub> NO <sub>2</sub> Na	125.1	72	271	38.40 (38.44)	6.45 (6.41)	11.20 (11.16)
<b>3</b>	C <sub>9</sub> H <sub>9</sub> NO <sub>2</sub> Na	186.16	79	262	58.07 (58.12)	4.87 (4.830)	7.52 (7.48)
<b>4</b>	C <sub>11</sub> H <sub>21</sub> NO <sub>2</sub> Sn	318.0	61	122	41.55 (41.59)	6.66 (6.70)	4.40 (4.44)
<b>5</b>	C <sub>20</sub> H <sub>39</sub> NO <sub>2</sub> Sn	444.24	60	88	54.07 (54.03)	8.85 (8.81)	3.15 (3.11)
<b>6</b>	C <sub>7</sub> H <sub>15</sub> NO <sub>2</sub> Sn	263.91	70	132	31.86 (31.82)	5.73 (5.77)	5.31 (5.35)
<b>7</b>	C <sub>16</sub> H <sub>33</sub> NO <sub>2</sub> Sn	390.15	71	154	49.26 (49.22)	8.53 (8.49)	3.59 (3.63)
<b>8</b>	C <sub>12</sub> H <sub>17</sub> NO <sub>2</sub> Sn	325.98	66	112	44.21 (44.25)	5.26 (5.30)	4.30 (4.34)
<b>9</b>	C <sub>21</sub> H <sub>35</sub> NO <sub>2</sub> Sn	452.22	69	145	55.78 (55.82)	7.80 (7.84)	3.10 (3.14)
<b>10</b>	C <sub>22</sub> H <sub>31</sub> NO <sub>2</sub> SnFe	516.04	70	116	51.20 (51.24)	6.05 (6.01)	2.71 (2.75)
<b>11</b>	C <sub>31</sub> H <sub>49</sub> NO <sub>2</sub> SnFe	642.28	64	57	57.97 (57.93)	7.69 (7.65)	2.18 (2.22)
<b>12</b>	C <sub>18</sub> H <sub>25</sub> NO <sub>2</sub> SnFe	461.95	66	123	46.80 (46.76)	5.45 (5.49)	3.03 (3.07)
<b>13</b>	C <sub>27</sub> H <sub>43</sub> NO <sub>2</sub> SnFe	588.19	73	141	55.13 (55.09)	7.37 (7.33)	2.38 (2.42)
<b>14</b>	C <sub>23</sub> H <sub>27</sub> NO <sub>2</sub> SnFe	524.02	68	109	52.72 (52.76)	5.19 (5.23)	2.67 (2.63)
<b>15</b>	C <sub>32</sub> H <sub>45</sub> NO <sub>2</sub> SnFe	650.26	60	162	59.11 (59.07)	6.98 (6.94)	2.15 (2.11)

Table 2. FT-IR data (cm<sup>-1</sup>) of synthesized complexes **1–15**.

Complex No.	$\nu$ CH=N	$\nu$ COO <sub>sym</sub>	$\nu$ COO <sub>asym</sub>	$\Delta\nu$	$\nu$ Sn–C	$\nu$ Sn–O
<b>1</b>	–	1469	1670	201	–	–
<b>2</b>	–	1472	1686	214	–	–
<b>3</b>	–	1489	1695	206	–	–
<b>4</b>	–	1422	1552	130	525	416
<b>5</b>	–	1412	1564	152	532	425
<b>6</b>	–	1424	1538	114	539	434
<b>7</b>	–	1452	1560	108	545	441
<b>8</b>	–	1442	1549	107	551	448
<b>9</b>	–	1432	1580	148	532	444
<b>10</b>	1640	1403	1579	176	572	442
<b>11</b>	1640	1409	1594	185	582	455
<b>12</b>	1640	1414	1593	182	525	412
<b>13</b>	1640	1458	1568	110	530	420
<b>14</b>	1640	1418	1523	105	540	431
<b>15</b>	1640	1454	1592	138	542	436

Table 3.  $^1\text{H}$  NMR<sup>a</sup> shifts (ppm) of organotin(IV) complexes.

Proton No.	4	5	6	7	8	9
2	2.21–2.26 m	2.21–2.27 m	1.37–1.39 m	1.36–1.39 m	2.26–2.33 m	2.26–2.34 m
3	–	–	1.66 d (3.2)	1.66 d (3.2)	1.72 d (3.3)	1.72 d (3.3)
3,3'	1.34–1.38 m	1.32–1.37 m	–	–	–	–
4	–	–	1.92 d (3.5)	1.92 d (3.5)	7.93–7.99 m	7.94–7.97 m
4,4'	1.46–1.54 m	1.46–1.55 m	–	–	–	–
5	4.81–4.92 m	4.82–4.90 m	4.83 s	4.84 s	–	–
5,5'	–	–	–	–	7.21–7.29 m	7.22–7.29 m
6	4.62–4.67 m	4.63–4.69 m	4.26–4.35 m	4.27–4.36 m	–	–
6,6'	–	–	–	–	7.36–7.44 m	7.34–7.43 m
7	4.49 s	4.49 s	–	–	7.15–7.21 m	7.18–7.25 m
NH <sub>2</sub> <sup>+</sup>	8.62 s	8.61 s	8.62 s	8.60 s	8.62 s	8.60 s
$\alpha$	0.95 s [57]	1.35 t [81]	0.92 s [57]	1.36 t [81]	0.88 s [57]	1.34 t [81]
$\beta$	–	1.37–1.44 m	–	1.38–1.45 m	–	1.35–1.41 m
$\gamma$	–	1.24–1.28 m	–	1.25–1.30 m	–	1.21–1.26 m
$\delta$	–	0.90 t (7.4)	–	0.96 t (7.4)	–	0.92 t (7.3)

<sup>a</sup>  $^2J(^{119}\text{Sn}, ^1\text{H})$ ;  $^3J(^1\text{H}, ^1\text{H})$  in hertz are listed in square brackets and parenthesis, respectively. Multiplicity is given as s=singlet, d=doublet, m=multiplet.

Table 4.  $^1\text{H}$  NMR<sup>a</sup> shifts (ppm) of ferrocene based azomethine organotin(IV) complexes.

Proton No.	10	11	12	13	14	15
2	2.21–2.28 m	2.21–2.28 m	1.37–1.42 m	1.36–1.41 m	2.26–2.34 m	2.26–2.33 m
3	–	–	1.66 d (3.2)	1.66 d (3.2)	1.72 d (3.3)	1.72 d (3.3)
3,3'	1.34 m	1.32 m	–	–	–	–
4	–	–	1.92 d (3.5)	1.92 d (3.5)	7.93–7.97 m	7.94–7.99 m
4,4'	1.46 m	1.46 m	–	–	–	–
5	4.81 m	4.82 m	4.83 s	4.84 s	–	–
5,5'	–	–	–	–	7.21–7.28 m	7.22–7.27 m
6	4.62–4.69 m	4.63–4.71 m	–	–	–	–
6,6'	–	–	–	–	7.36–7.39 m	7.34–7.39 m
7	4.49 s	4.49 s	–	–	7.15–7.21 m	7.18–7.21 m
7,7'	–	–	4.35–4.39 m	4.33–4.39 m	–	–
8	–	–	–	–	4.80–4.86 s	4.82–4.88 s
8,8'	–	–	4.61–4.66 m	4.61–4.67 m	–	–
9	–	–	4.75–4.79 m	4.75–4.79 m	–	–
9,9'	4.36–4.39 m	4.37–4.48 m	–	–	–	–
10,10'	4.59–4.67 m	4.58–4.65 m	–	–	4.59–4.62 m	4.56–4.60 m
11	4.72–4.79 m	4.73–4.79 m	–	–	–	–
11,11'	–	–	–	–	4.11–4.17 m	4.14–4.20 m
12	–	–	–	–	4.75–4.77 m	4.79–4.81 m
$\alpha$	0.97 s [57]	1.37 t [81]	0.90 s [57]	1.31 t [81]	0.86 s [57]	1.32 t [81]
$\beta$	–	1.37–1.42 m	–	1.31–1.36 m	–	1.29–1.39 m
$\gamma$	–	1.27–1.35 m	–	1.26–1.29 m	–	1.25–1.28 m
$\delta$	–	0.94 t (7.4)	–	0.94 t (7.4)	–	0.90 t (7.3)

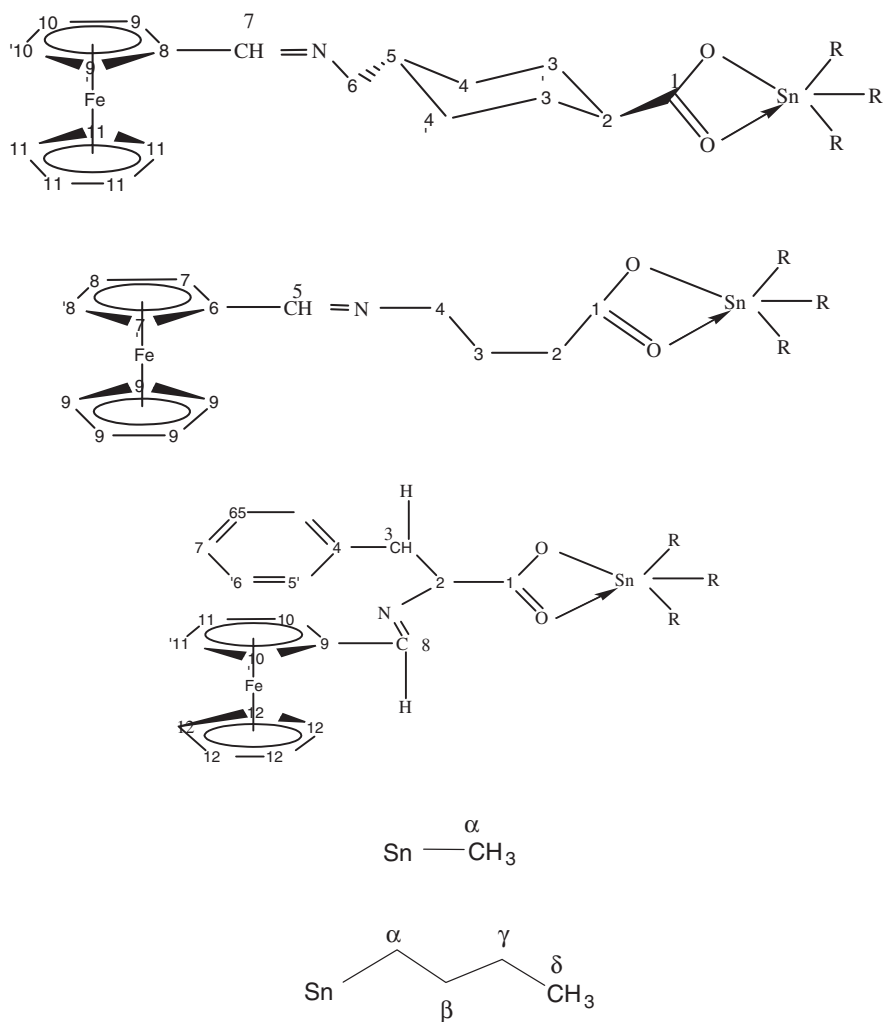
<sup>a</sup>  $^2J(^{119}\text{Sn}, ^1\text{H})$ ;  $^3J(^1\text{H}, ^1\text{H})$  in hertz are listed in square brackets and parenthesis, respectively. Multiplicity is given as s=singlet, d=doublet, m=multiplet.

Table 5.  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR shifts (ppm) of synthesized organotin(IV) complexes.

$^{13}\text{C}$ No.	4	5	6	7	8	9
1	173.8	169.8	168.9	167.9	162.7	167.9
2	43.9	38.1	29.7	32.4	75.9	76.1
3	–	–	27.4	27.8	36.5	37.1
3,3'	29.3	27.8	–	–	–	–
4	–	–	61.3	62.2	129.5	129.5
4,4'	30.6	29.7	–	–	–	–
5	38.1	30.6	–	–	–	–
5,5'	–	–	–	–	128.2	128.2
6	43.9	44.0	–	–	–	–
6,6'	–	–	–	–	126.5	129.0
7	–	–	–	–	126.2	125.3
$\alpha$	18.7	16.9	16.8	13.1	26.4	16.6
	[392]	[397]	[394]	[397]	[392]	[391]
$\beta$	–	15.4	15.1	–	22.4	–
		[20]	[21]		[22]	
$\gamma$	–	14.3	14.6	–	14.7	–
		[63]	[64]		[64]	
$\delta$	–	13.2	13.4	–	13.1	–
$\delta^{119}\text{Sn}$	136.1	107.8	109.9	136.7	107.8	136.9

Table 6.  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR shifts (ppm) of synthesized ferrocene based azomethine organotin(IV) complexes.

$^{13}\text{C}$ No.	10	11	12	13	14	15
1	181.8	181.8	178.9	178.9	176.7	176.9
2	43.9	38.1	29.7	32.4	75.9	76.1
3	–	–	27.4	27.8	36.5	37.1
3,3'	29.3	27.8	–	–	–	–
4	–	–	61.3	62.2	129.5	129.5
4,4'	30.6	29.7	–	–	–	–
5	38.1	30.6	161.3	162.5	–	–
5,5'	–	–	–	–	128.2	128.2
6	43.9	44.0	80.6	80.5	–	–
6,6'	–	–	–	–	126.5	129.0
7	161.0	160.8	–	–	126.2	125.3
7,7'	–	–	129.2	129.8	–	–
8	73.2	73.5	–	–	163.1	163.4
8,8'	–	–	126.4	126.8	–	–
9	–	–	122.2	122.6	138.8	138.7
9,9'	129.6	129.3	–	–	–	–
10	–	–	–	–	–	–
10,10'	128.1	128.6	–	–	129.3	129.4
11	124.2	124.7	–	–	–	–
11,11'	–	–	–	–	128.3	128.3
12	–	–	–	–	126.5	126.3
$\alpha$	18.4 [392]	16.3 [397]	16.4 [394]	13.6 [397]	26.6 [392]	16.4 [391]
$\beta$	–	15.6 [20]	15.8 [21]	–	22.7 [24]	–
$\gamma$	–	14.1 [63]	14.1 [63]	–	14.1 [63]	–
$\delta$	–	13.7	13.6	–	13.6	–
$\delta^{119}\text{Sn}$	136.3	107.4	109.4	136.2	107.5	136.4



Scheme 1. NMR numbering scheme.

### 3.2. NMR spectroscopy

**3.2.1.  $^1\text{H-NMR}$ .**  $^1\text{H}$  NMR spectra of selected compounds have been recorded in deuterated chloroform. The number of signals in the spectra corresponds to the number of magnetically non-equivalent hydrogens. The numbers of protons calculated by integration [20] are in good agreement with those expected. The presence of  $\text{NH}_2^+$  at 8.62–8.60 ppm as singlet in the ligands and absence in complexes confirm the formation of Schiff base. In trimethyltin(IV) compounds,  $\text{CH}_3$  protons give a sharp singlet at 0.86–0.97 ppm with  $^2J(^{119}\text{Sn}-^1\text{H})$  of 57 Hz. The *n*-butyl has triplet for  $\text{Sn}-\text{CH}_2$  (1.35–1.21 ppm) and terminal  $\text{CH}_3$  (at 0.90–0.96 ppm) with  $^3J(^1\text{H}-^1\text{H})$  couplings of 7.4–7.3 Hz with  $^2J(^{119}\text{Sn}-^1\text{H})$  of 81 Hz supporting four-coordinate tin in solution [21].  $^1\text{H}$  NMR chemical shifts are given in tables 3 and 4.

Table 7. Selected bond lengths (Å) and angles (°) for **5**, **6**, **8**, and **9**.

Compound <b>5</b>							
Sn1	O2	2.02			Sn1	O26	2.72
C27	Sn1	2.11			Sn1	C31	2.10
O2	Sn1	C31	112.3	O26	Sn1	C27	147.0
O26	Sn1	C31	87.0	C27	Sn1	C31	109.8
C27	Sn1	C35	109.8	C31	Sn1	C35	114.2
Compound <b>6</b>							
C13	C14	1.40			O11	C12	1.33
Sn2	C7	2.10			O26	Sn2	2.67
O11	Sn2	C1	95.4	O11	Sn2	C3	112.9
C1	Sn2	O26	146.2	C3	Sn2	C7	114.5
C12	O11	Sn2	114.3	C12	O26	Sn2	85.4
Compound <b>8</b>							
Sn1	C18	2.11			Sn1	C31	2.11
Sn1	O44	2.03			C36	C35	1.51
O2	Sn1	C18	112.5	O2	Sn1	C31	100.3
C18	Sn1	O44	99.2	C18	Sn1	O59	150.4
C31	Sn1	O59	90.8	C31	Sn1	O17	149.9
Compound <b>9</b>							
Sn2	O3	2.04			C1	Sn2	2.14
Sn2	C19	2.14			Sn2	C32	2.13
Sn2	C1	C46	111.8	O3	Sn2	C1	94.6
C19	Sn2	C32	114.6	C19	Sn2	O18	85.5
C32	Sn2	O18	89.2	Sn2	C19	C21	113.9

**3.2.2.  $^{13}\text{C}$  NMR.**  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$ . The  $^{13}\text{C}$  NMR spectra of ferrocene show only one signal at 119–121 ppm, while the substituted cyclopentadienyl ring shows three signals at 129.6, 128.4, and 126.3 ppm. These signals do not show a shift on complexation. Signals due to  $\text{C}=\text{N}$  and  $\text{COO}$  at 160.8–163.4 and 181.8–176.7 ppm, respectively, shift downfield by 8–14 ppm on complexation of organotin with ferrocene. The carboxylate carbon shifts to lower field region in organotin(IV) compounds indicating participation of  $\text{COO}$  in coordination to tin. Holeček and coworkers [22] have shown that for four-coordinate trialkyltin compounds, the  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  occur from 325 to 400 Hz, while five-coordinate tin compounds exhibit coupling of 440 to 540 Hz. Here, the trialkyltin compounds show tin–carbon satellites in the range 391–397 Hz in solution, characteristic of tetrahedral tin. Thus bidentate ligand resulting in five coordination in the solid state (FT-IR) is lost in solution.  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR data are given in tables 5 and 6.

The  $^{119}\text{Sn}$  chemical shift values for **4–15** are in the range 107.4–136.9 ppm, characteristic for four-coordinate in non-coordinating solvents [23].

### 3.3. Mass spectrometry

The EI mass spectrum of  $\text{NaL}^1$  was studied as a representative case. Peaks of appreciable intensity were observed at  $m/z$  values 114, 85, 72, 70, 69, 57, and 55. The molecular ion peak was observed at  $m/z$  177.18, in agreement with its molecular weight. In the mass spectral data, most fragment ions occur in groups of peaks as a result of tin isotopes. For simplicity the mass spectral fragmentation data reported here is related to

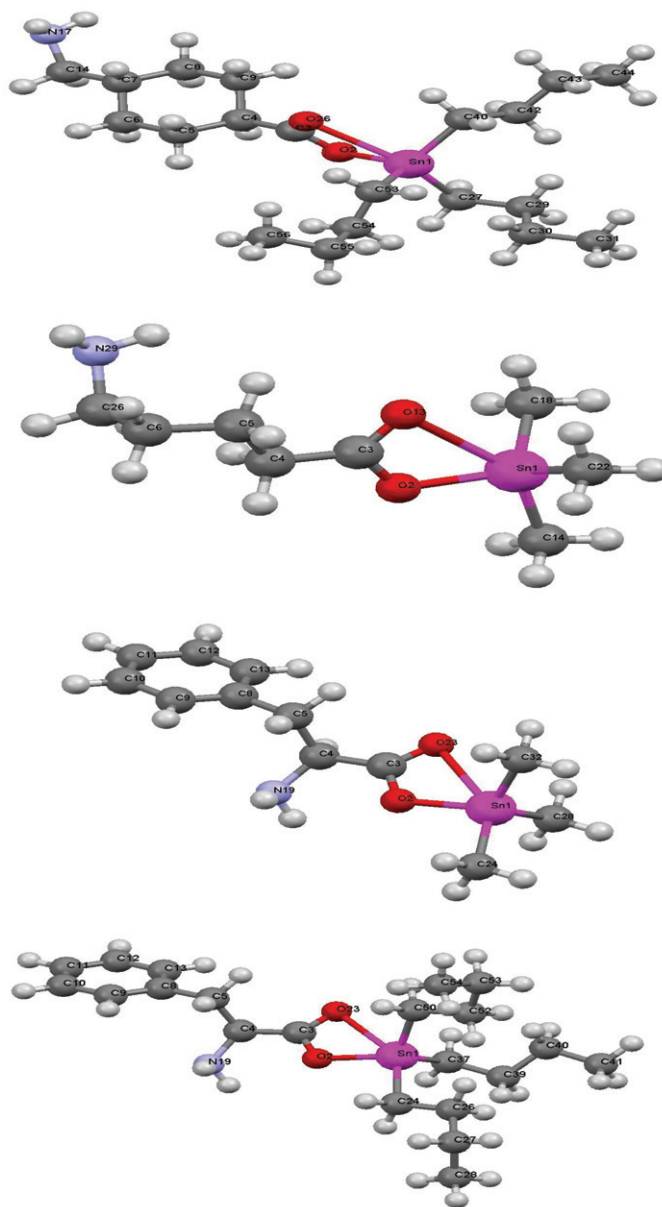


Figure 1. Geometry optimized structures of 5, 6, 8, and 9.

the principal isotope  $^{120}\text{Sn}$  [24]. Molecular ion peak of low intensity was observed for the organotin(IV) derivatives.

### 3.4. Semi-empirical study

The 4-(aminomethyl) cyclohexane, 4-amino butanoate, and 2-amino-3-phenylpropanoate bind bidentate to Sn(IV) in 5, 6, 8, and 9. The three methyl/butyl groups and the

Table 8. Antibacterial activity of ferrocene based azomethine organotin(IV) complexes.

Bacterium	Inhibition zone diameter (mm)				Standard drug
	10	11	12	14	
<i>Escherichia coli</i>	30	34	31	34	35
<i>Bacillus subtilis</i>	32	35	35	33	36
<i>Shigella flexenaria</i>	30	35	31	32	36
<i>Staphylococcus aureus</i>	42	40	40	40	43
<i>Pseudomonas aeruginosa</i>	30	30	32	31	32
<i>Salmonella typhi</i>	38	36	35	33	40

<sup>a</sup>In vitro, agar well diffusion method, conc. 1 mg mL<sup>-1</sup> of DMSO.

<sup>b</sup>Reference drug, Imipenem.

carboxylates are arranged in a distorted trigonal bipyramid. The Sn–O bond distances are 2.02 and 2.72 Å in **5**. O–Sn–O bond angle is  $50 \pm 0.1^\circ$  in **5**, **6**, **8**, and **9**. All bond lengths and angles are comparable to literature values [25]. Selected bond lengths and angles of the optimized structure are tabulated in table 7. The optimized structures are shown in figure 1.

### 3.5. Biological activity

**3.5.1. Antibacterial activity.** Selected compounds were screened for antibacterial activity by the agar-well diffusion method [26]. The zone of inhibition is measured in millimeters and the reference drug used was Imipenem (table 8). All bacterial strains have clinical implication: *Escherichia coli*, infection of wounds, urinary tract, and dysentery; *Bacillus subtilis*, food poisoning; *Shigella flexenari*, blood diarrhea with fever and severe prostration; *Salmonella typhi*, typhoid fever, and localized infection, *Staphylococcus aureus*, food poisoning, scaled skin syndrome, endocarditic, *Pseudomonas aeruginosa*, infection of wounds, eyes, septicemia, and *Salmonella typhi*, typhoid fever, localized infection.

Triorganotin(IV) complexes of the ferrocenyl Schiff base, R<sub>3</sub>SnL, were more active than their parent ligands against the same microorganisms under identical experimental conditions. The reported bimetallic organotin(IV) complexes show enhanced antibacterial activity compared to monometallic organotin(IV) complexes [27–29]. No compound shows better inhibitory action than standard drug.

## 4. Conclusion

IR data suggest bidentate O-coordination of the ligands to Sn moiety, which is confirmed by semi-empirical study. NMR data reveal distorted tetrahedral geometry in solution. Antibacterial results show that the reported complexes do not exhibit better inhibitory action than standard drug, but could be used as conventional bactericides.

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