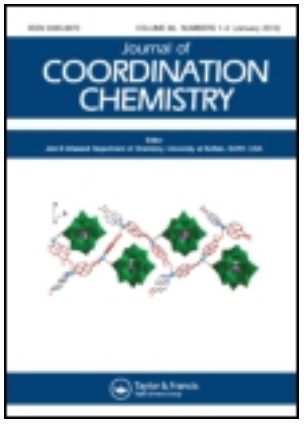

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Tahereh Sedaghat [a], Marjan Monajjemzadeh [a] & Hossein Motamedi [b]

[a] Department of Chemistry, College of Sciences, Shahid Chamran University, Ahvaz, Iran

[b] Department of Biology, College of Sciences, Shahid Chamran University, Ahvaz, Iran

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New diorganotin(IV) complexes with some Schiff bases derived from β-diketones: synthesis, spectral properties, thermal analysis, and antibacterial activity

TAHEREH SEDAGHAT†*, MARJAN MONAJJEMZADEH† and HOSSEIN MOTAMEDI‡

†Department of Chemistry, College of Sciences, Shahid Chamran University, Ahvaz, Iran
‡Department of Biology, College of Sciences, Shahid Chamran University, Ahvaz, Iran

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The Schiff bases H_2L^a, H_2L^b, and H_2L^c have been prepared from the reaction of 2-amino-4-chlorophenol with acetylacetone, benzoylacetone, and dibenzoylmethane, respectively. Organotin(IV) complexes $[SnPh_2(L^a)]$ (**1**), $[SnPh_2(L^b)]$ (**2**), $[SnPh_2(L^c)]$ (**3**), and $[SnMe_2(L^c)]$ (**4**) have been synthesized from the reaction of $SnPh_2Cl_2$ and $SnMe_2Cl_2$ with these Schiff bases. The synthesized complexes have been characterized by elemental analysis and FT-IR, ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. Spectroscopic data suggest the Schiff bases are completely deprotonated and coordinated tridentate to tin *via* imine nitrogen and phenolic and enolic oxygen atoms; the coordination number of tin is five. Thermal decomposition of the complexes has been studied by thermogravimetry. The *in vitro* antibacterial activities of the Schiff bases and their complexes have been evaluated against Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria. H_2L^a, H_2L^c, and all complexes exhibited good activities and have potential as drugs.

Keywords: Diorganotin(IV); Schiff base; Diketones; Thermal analysis; Antibacterial activity

1. Introduction

Schiff bases and their complexes with transition and non-transition metal ions have medicinal, physiological, and pharmaceutical applications, well-known as antibacterial, antifungal, anticancer, antiviral, and herbicidal agents [1–6]. Schiff-base complexes also provide synthetic models for active sites in biological systems [7, 8]. Furthermore Schiff bases offer opportunities for enhancing solubility and stability of their metal complexes and tuning metal centered electronic factors [9]. In many cases, when Schiff bases are administered as their metal complexes, biological activity is enhanced in comparison to the free ligand. Research dealing with complexes of Schiff bases has expanded enormously with increasing attention devoted to Schiff-base complexes of organotin(IV) in view of their chemical properties, biological significance, industrial importance, and structural variety [10–12]. Organotin(IV) complexes possess physical

*Corresponding author. Email: tsedaghat@scu.ac.ir

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and chemical properties for new materials and new metal-based drugs. These chemicals show *in vitro* and *in vivo* antitumor activity, opening a new research sub-area on organotin(IV) compounds [13–15]. Many organotin(IV) compounds have been synthesized and tested for their antitumor activity and found to be as effective as, or even better than, traditional heavy metal anticancer drugs [16–19]. Many studies have been carried out to explore antimicrobial activity of organotin(IV) compounds and the search for antimicrobial agents is of current and growing interest [19–25]. Since biocidal properties of organotin(IV) compounds are dependent on both the organic group and the ligand attached to tin [20, 26], an interesting development is introducing ligands which are themselves bioactive [20, 27–30]. Interaction of organotins has been extensively studied with a variety of Schiff-base ligands due to the importance of their medicinal assays for bactericide and antitumor purposes [17, 31–37]. However, little attention has been paid to systems in which the Schiff bases are derived from β-diketones. Herein, we report the synthesis and spectroscopic characterization of new diorganotin(IV) complexes with Schiff bases derived from acetylacetone and related β-diketones and investigate their thermal behavior and antibacterial activity.

2. Experimental

2.1. *Materials and methods*

All starting materials were purchased from Merck except diphenyltin dichloride which was supplied from Acros Company; all were used as received. All solvents were of reagent grade and used without purification. IR spectra were obtained using a FT BOMEM MB102 spectrophotometer. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded with a Bruker 400 MHz Avance Ultrashield spectrometer. Thermogravimetric analyses (TGA) were carried out using a Perkin-Elmer Diamond thermal analyzer. The heating rates were controlled at 5°C min^{-1} under nitrogen with a 150 mL min^{-1} flow rate; the weight loss was measured from ambient temperature to 1050°C.

2.2. *Synthesis of Schiff bases*

2.2.1. 4-(2-Hydroxy-5-chlorophenylimino)-pentan-2-one (H_2L^a). A solution of 2-amino-4-chlorophenol (2.871 g, 20 mmol) in ethanol (70 mL) was added to a solution of acetylacetone (2.00 g, 20 mmol) in ethanol (50 mL). This solution was refluxed for 8 h. Then the volume of solution was reduced to *ca* 60 mL. H_2L^a precipitates after standing overnight at room temperature, was filtered off, and washed with ethanol (2×5 mL). Finally, H_2L^a was recrystallized from ethanol to give white-brown needle crystals. Yield: 3.204 g (71%); m.p. 159–161°C; Anal. Calcd for $C_{11}H_{12}NO_2Cl$ (%): C, 58.5; H, 5.3; N, 6.2. Found (%): C, 58.9; H, 5.2; N, 6.3. FT-IR (KBr, cm^{-1}): 1547, ν(C=C); 1603, ν(C=O); 2800–3100 br, ν(C–H), ν(O–H)/ν(N–H). ^{1}H NMR (DMSO-d_6): $\delta = 1.98$ (s, 3H, H_{10}), 2.03 (s, 3H, H_{11}), 5.24 (s, 1H, H_8), 6.90 (d, $J = 8.6$ Hz, 1H, H_3), 7.04 (dd, $J = 8.6$, 2.5 Hz, 1H, H_4), 7.27 (d, $J = 2.5$ Hz, 1H, H_6), 10.24 (s, 1H, H_{enolic}), 12.15 (s, 1H, $H_{phenolic}$). ^{13}C NMR (DMSO-d_6): $\delta = 20.0$, C_{10}; 29.4, C_{11}; 98.6, C_8; 117.1, C_3; 122.6, C_4; 124.1, C_6; 125.6, C_5; 128.1, C_1; 149.3, C_2; 159.5, C_7; 195.3, C_9.

2.2.2. 3-(2-Hydroxy-5-chlorophenylimino)-1-phenylbutan-1-one (H_2L^b). H_2L^b was synthesized as described for H_2L^a from benzoylacetone (3.240 g, 20 mmol) and the product was formed as yellow crystals. Yield: 4.60 g (80%); m.p. 186–188°C; Anal. Calcd for $C_{16}H_{14}NO_2Cl$ (%): C, 66.8; H, 4.9; N, 4.9. Found (%): C, 67.1; H, 4.9; N, 4.8. FT-IR (KBr, cm^{-1}): 1576, ν(C=C); 1605, ν(C=O); 2900–3200 br, ν(C–H), ν(O–H)/ν(N–H). ^{1}H NMR (DMSO-d_6): $\delta = 2.20$ (s, 3H, H_{10}), 6.08 (s, 1H, H_8), 6.96 (d, $J = 8.6$ Hz, 1H, H_3), 7.09 (dd, $J = 8.6$, 2.5 Hz, 1H, H_4), 7.37 (d, $J = 2.5$ Hz, 1H, H_6), 7.40–7.61 (m, 3H, $H_{14,15}$), 7.91–7.93 (m, 2H, H_{13}), 10.33 (s, 1H, H_{enolic}), 12.80 (s, 1H, $H_{phenolic}$). ^{13}C NMR (DMSO-d_6): $\delta = 20.6$, C_{10}; 94.8, C_8; 117.2, C_3; 122.7, C_4; 124.4, C_6; 126.0, C_5; 127.3, C_{14}; 128.0, C_{15}; 128.8, C_{13}; 131.5, C_{12}; 139.8, C_1; 149.5, C_2; 162.3, C_7; 187.3, C_9.

2.2.3. 3-(2-Hydroxy-5-chlorophenylimino)-1,3-diphenylpropan-1-one (H_2L^c). Dibenzoylmethane (2.242 g, 10 mmol) was dissolved in ethanol (15 mL) at 65–70°C and mixed with a solution of 2-amino-4-chlorophenol (1.435 g, 10 mmol) in ethanol (10 mL). Then two drops of HCl was added and the solution was refluxed for 10 h. The product was precipitated as bright brown needles after standing overnight at room temperature. Crystals were collected, washed with ethanol, and dried over $CaCl_2$. Yield: 2.448 g (70%); m.p. 73–75°C; Anal. Calcd for $C_{21}H_{16}NO_2Cl$ (%): C, 72.1; H, 4.6; N, 4.0. Found (%): C, 72.5; H, 4.5; N, 4.1. FT-IR (KBr, cm^{-1}): 1567, ν(C=C); 1607, ν(C=O); 3000–3200 br, ν(C–H), ν(O–H)/ν(N–H). ^{1}H NMR (DMSO-d_6): $\delta = 6.18$ (s, 2H, $H_{6,8}$), 6.86 (m, 2H, $H_{3,4}$), 7.44–7.57 (m, 8H, $H_{14,15,17,18,19}$), 8.01 (d, $J = 7.1$ Hz, 1H, H_{13}), 10.41 (s, 1H, H_{enolic}), 12.57 (s, 1H, $H_{phenolic}$). ^{13}C NMR (DMSO-d_6): $\delta = 94.1$, C_8; 98.1, C_3; 117.4, C_4; 122.9, C_6; 124.7, C_5; 128.1-130.9, $C_{13,14,17,18}$; 132.5-136.0, $C_{12,15,16,19}$; 139.9, C_1; 148.7, C_2; 160.7, C_7; 186.2, C_9.

2.3. *Synthesis of organotin(IV) complexes*

2.3.1. $SnPh_2L^a$ (1). H_2L^a (0.056 g, 0.25 mmol) was dissolved in methanol (10 mL) at 50–55°C and KOH (0.028 g, 0.5 mmol) was added. This solution was stirred for 30 min and then $SnPh_2Cl_2$ (0.085 g, 0.25 mmol) in methanol (5 mL) was added. The solution was refluxed for 5 h. A yellow precipitate was formed after evaporating the solvent at room temperature. This precipitate was collected, washed with methanol, and then treated with chloroform (10 mL). The resulted mixture was filtered to remove KCl and then evaporated to dryness. The yellow product was collected and maintained over dry $CaCl_2$. Yield: 0.080 g (65%); m.p. 149–152°C; Anal. Calcd for $C_{23}H_{20}NO_2ClSn$ (%): C, 55.6; H, 4.0; N, 2.8. Found (%): C, 55.7; H, 4.3; N, 3.2. FT-IR (KBr, cm^{-1}): 1527, ν(C=O); 1541, ν(C=N)/ν(C=C); 512, ν(Sn–O); 439, ν(Sn–N). ^{1}H NMR ($CDCl_3$): $\delta = 2.23$ (s, 3H, H_{10}), 2.36 (s, 3H, H_{11}), 5.34 (s, 1H, H_8), 6.98–7.01 (m, 2H, $H_{3,6}$), 7.05 (dd, $J = 8.6$, 2.3 Hz, 1H, H_4), 7.36–7.48 (m, 6H, $H_{m,p}$), 7.82–7.85 [m, 4H, H_o, $^3J(^{119}Sn–^1H) = 84.7$ Hz]. ^{13}C NMR ($CDCl_3$): $\delta = 24.6$, C_{10}; 28.0, C_{11}; 102.0, C_8; 118.7, C_3; 120.2, C_4; 122.6, C_6; 127.2, C_5; 129.1, C_m [$^3J(^{119}Sn–^{13}C) = 85.2$ Hz]; 130.8, C_p; 133.2, C_1; 136.7, C_o [$^2J(^{119}Sn–^{13}C) = 52.8$ Hz]; 138.8, C_i [$^1J(^{119}Sn–^{13}C) = 968.2$ Hz]; 157.1, C_2; 172.7, C_7; 188.3, C_9. ^{119}Sn NMR ($CDCl_3$): $\delta = -302.7$.

2.3.2. $SnPh_2L^b$ (2). H_2L^b (0.071 g, 0.25 mmol) was dissolved in methanol (10 mL) at 45–50°C and a solution of $SnPh_2Cl_2$ (0.085 g, 0.25 mmol) in methanol (5 mL)

was added. This solution was stirred for 30 min and then triethylamine (0.5 mmol) was added. An orange precipitate appeared after 1 h. The mixture was stirred for another 2 h to ensure completion of reaction. The product was filtered, washed with warm methanol, and dried over $CaCl_2$. Yield: 0.097 g (70%); m.p. 169–171°C; Anal. Calcd for $C_{28}H_{22}NO_2ClSn$ (%): C, 60.1; H, 3.9; N, 2.5. Found (%): C, 59.8; H, 3.9; N, 2.6. FT-IR (KBr, cm^{-1}): 1563, ν(C=O); 1586, ν(C=N)/ν(C=C); 544, ν(Sn–O); 447, ν(Sn–N). ^{1}H NMR ($CDCl_3$): $\delta = 2.52$ (s, 3H, H_{10}), 6.09 (s, 1H, H_8), 7.02-7.05 (m, 2H, $H_{3,6}$), 7.08 (dd, $J = 8.9$, 2.1 Hz, 1H, H_4), 7.36–7.43 (m, 6H, $H_{m,p}$), 7.51–7.59 (m, 3H, $H_{14,15}$), 7.85–7.89 [m, 4H, H_o, $^3J(^{119}Sn–^1H) = 84.0$ Hz], 8.04–8.07 (m, 2H, H_{13}). ^{13}C NMR ($CDCl_3$): $\delta = 25.0$, C_{10}; 98.6, C_8; 118.5, C_3; 119.9, C_4; 122.2, C_6 [$^3J(^{119}Sn–^{13}C) = 23.8$ Hz]; 127.0, C_5; 127.2, 128.7, C_{14}; 128.8, C_m [$^3J(^{119}Sn–^{13}C) = 82.5$ Hz]; 129.7, 130.4, C_p [$^4J(^{119}Sn–^{13}C) = 16.8$ Hz]; 131.6, C_{13}; 132.8, C_{15}; 135.0, C_{12}; 136.3, C_o [$^2J(^{119}Sn–^{13}C) = 52.6$ Hz]; 137.8, C_1; 138.3, C_i [$^1J(^{119}Sn–^{13}C) = 973.8$ Hz]; 156.9, C_2; 172.8, C_7; 179.6, C_9. ^{119}Sn NMR ($CDCl_3$): $\delta = -303.3$.

2.3.3. $SnPh_2L^c$ (3). H_2L^c (0.174 g, 0.5 mmol) was dissolved in methanol (10 mL) at 45–50°C and KOH (0.056 g, 1.0 mmol) was added to it. The solution was stirred for 30 min and then $SnPh_2Cl_2$ (0.171 g, 0.5 mmol) in methanol (5 mL) was added dropwise. A red precipitate was formed immediately. After 30 min stirring at the same temperature, the precipitate was filtered, washed with warm methanol, and dried over $CaCl_2$. Yield: 0.254 g (82%); m.p. 164–168°C; Anal. Calcd for $C_{33}H_{24}NO_2ClSn$ (%): C, 63.8; H, 3.8; N, 2.2. Found (%): C, 63.7; H, 3.9; N, 1.7. FT-IR (KBr, cm^{-1}): 1541, ν(C=O); 1584, ν(C=N)/ν(C=C); 568, ν(Sn–O); 448, ν(Sn–N). ^{1}H NMR (DMSO-d_6): $\delta = 5.99$ (s, 1H, H_6), 6.02 (s, 1H, H_8), 6.82 (d, $J = 8.6$ Hz, 1H, H_3), 6.85 (dd, $J = 8.6$, 2.1 Hz, 1H, H_4), 7.28–7.37 (m, 8H, $H_{14,15,17,18,19}$), 7.44–7.57 (m, 6H, $H_{m,p}$), 7.69 [d, 4H, H_o, $^3J_{HH} = 6.7$ Hz, $^3J(^{119}Sn–^1H) = 82.5$ Hz], 8.04 (d, $J = 7.2$ Hz, 2H, H_{13}). ^{13}C NMR (DMSO-d_6): $\delta = 99.8$, C_8; 118.6, C_3; 118.8, C_4; 122.3, C_6; 125.66, C_5; 127.5–129.4, $C_{13,14,17,18}$; 128.5, C_m [$^3J(^{119}Sn–^{13}C) = 82.6$ Hz]; 130.5, C_p; 129.5, 132.0, $C_{15,19}$; 135.6, C_o [$^2J(^{119}Sn–^{13}C) = 50.3$ Hz]; 138.5, C_i [$^1J(^{119}Sn–^{13}C) = 995.8$ Hz]; 134.5, 138.8, $C_{12,16}$; 146.2, C_1; 157.1, C_2; 169.8, C_7; 179.7, C_9. ^{119}Sn NMR ($CDCl_3$): $\delta = -297.9$.

2.3.4. $SnMe_2L^c$ (4). Complex **4** was synthesized as described for **1** from H_2L^c (0.174 g, 0.5 mmol), KOH (0.056 g, 1.0 mmol) and $SnMe_2Cl_2$ (0.109 g, 0.5 mmol). The product was obtained as red solid. Yield: 0.151 g (61%); m.p. 144–146°C; Anal. Calcd for $C_{23}H_{20}NO_2ClSn$ (%): C, 55.6; H, 4.0; N, 2.8. Found (%): C, 55.1; H, 4.3; N, 3.2. FT-IR (KBr, cm^{-1}): 1538, ν(C=O); 1582, ν(C=N)/ν(C=C); 563, ν_{as}(SnC); 553, ν(Sn–O); 506, ν_s(SnC); 444 ν(Sn–N). ^{1}H NMR (DMSO-d_6): $\delta = 0.71$ [s, 6H, H20, $^2J(^{119}Sn–^1H) = 88.1$ Hz], 6.00 (d, $J = 2.5$ Hz, 1H, H_6), 6.06 (s, 1H, H_8), 6.59 (d, $J = 8.5$ Hz, 1H, H_3), 6.73 (dd, $J = 8.6$, 2.5 Hz, 1H, H_4), 7.32–7.55 (m, 8H, $H_{14,15,17,18,19}$), 7.93 (d, $J = 7.1$ Hz, 2 H, H_{13}). ^{13}C NMR (DMSO-d_6): $\delta = 4.2$, C_{20}; 99.4, C_8; 118.2, C_3; 118.4, C_4; 123.0, C_6; 125.4, C_5; 128.0–129.6, $C_{13,14,17,18}$; 130.6, 132.3, $C_{15,19}$; 136.0, 139.2, $C_{12,16}$; 139.4, C_1; 157.8, C_2; 170.9, C_7; 182.0, C_9. ^{119}Sn NMR ($CDCl_3$): $\delta = -117.2$.

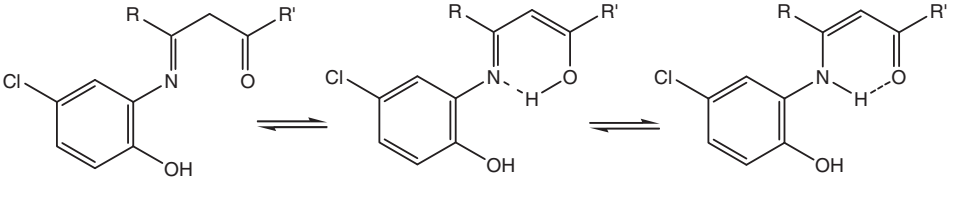
2.4. *Antibacterial tests*

The *in vitro* antibacterial activities of ligands and their corresponding organotin(IV) complexes were investigated against standard strains of two Gram-positive (*Bacillus subtilis* ATCC 12711 and *Staphylococcus aureus* ATCC 6538) and two Gram-negative (*Escherichia coli* ATCC 11303 and *Pseudomonas aeruginosa* ATCC 27853) bacteria. Vancomycin (30 mg/disc), Colistin (2 mg per disc), Nalidixic acid (30 mg per disc), and Erythromycin (15 mg/disc) were used as standard antibacterial drugs. Determination of the antibacterial activity was carried out by paper-disc diffusion. The compounds were dissolved in DMSO at 12.5, 25, 50, and 100 mgmL^{-1} concentration. Muller Hinton broth was used for preparing basal media for the bioassay of the organisms. A lawn culture from 0.5 MacFarland suspension of each strain was prepared on Muller Hinton agar. Blank paper discs (6.4 mm diameter) were saturated with a solution of test compounds (40 μL) and placed on the surface of the agar plates. On one paper disc only DMSO was poured as a control. The plates were incubated at 37°C for 24 h. The inhibition zone diameters around each disc were measured in mm.

3. Results and discussion

3.1. *Synthesis*

The Schiff bases used in this work, H_2L^a, H_2L^b, and H_2L^c, have been synthesized from reaction of 2-amino-4-chlorophenol with acetylacetone, benzoyl acetone and dibenzoyl methane, respectively. In these reactions only 1 : 1 condensation occurred even when an excess of the amine was used. Structural formulae for these Schiff bases are given in figure 1; the forms I–III may be present in tautomeric equilibria as shown. The positions of the keto–enol or amine–imine equilibria and nature of the hydrogen bond in the six-membered chelate ring is a consideration of these Schiff bases. The condensation products of β-dicarbonyl compounds with mono- and diamines exist, in solid state, in keto–amine form III; however, in solution both types of hydrogen bonds, N–H $\cdots$ O or



I II III

	R	R'
H_2L^a	Me	Me
H_2L^b	Me	Ph
H_2L^c	Ph	Ph

Figure 1. Tautomeric forms for Schiff for bases; I: keto-imine, II: enol-limine, III: keto-amine.

N···H–O, have been reported [38–42]. The new organotin(IV) complexes, $[SnPh_2(L^a)]$ (**1**), $[SnPh_2(L^b)]$ (**2**), $[SnPh_2(L^c)]$ (**3**), and $[SnMe_2(L^c)]$ (**4**), were synthesized by the reaction of $SnPh_2Cl_2$ and $SnMe_2Cl_2$ with Schiff bases in the presence of a base. The composition of complexes was confirmed by their analytical data and structures were suggested by spectroscopic investigations.

3.2. *Spectroscopic studies*

In the IR spectra of ligands, the absence of a band in the free C=O stretching region (1700–1770 cm^{-1}) rules out keto–imine form I. The band observed at 1603–1607 cm^{-1} has been assigned as a perturbed carbonyl stretch with the frequency lowering from a free carbonyl, ascribed to conjugation and hydrogen-bonding in keto–amine form III [38, 39]. In the IR spectra of **1–4**, this band shifts to lower frequency providing evidence of participation of oxygen in bonding with tin and so weakening the C=O bond. In the IR spectra of free ligands no band is observed at 3300–3500 cm^{-1} attributable to stretching vibration of free NH or OH indicating inter-/intra-molecular hydrogen-bonding; these bands shift to lower frequency and overlap with the ν(C–H) at 2800–3200 cm^{-1}. This broad band is absent in spectra of **1–4** supporting deprotonation of the ligands during coordination. The appearance of new bands of the complexes at 439–448 and 512–568 cm^{-1}, assigned to ν(Sn–N) and ν(Sn–O), respectively, supports the bonding of nitrogen and oxygen to tin [43–46]. The presence of both ν_s(Sn–C) and ν_{as}(Sn–C) in the IR spectrum of **4** is consistent with a nonlinear C–Sn–C configuration [43, 45, 47, 48].

In the ^{1}H NMR spectra of Schiff bases the integrals of signals establishes only 1 : 1 condensation of diketone and amine. The presence of a signal at 5.2–6.2 ppm (1H) corresponds to the vinylic hydrogen and the absence of a methylene signal near 3 ppm (2H) indicates no participation of keto–imine form I in solution. A sharp singlet at 10 ppm related to enolic proton indicates tautomeric form II in solution; proton transfer to imine nitrogen in form III would lead to broadening of the signal due to interaction with the electronic quadrupole moment of nitrogen [49, 50]. In the spectra of complexes, the absence of both phenolic and enolic signals suggests deprotonation and coordination of dianionic ligands to tin.

The ^{1}H NMR spectrum of **4** shows a singlet at 0.71 ppm for $SnMe_2$ accompanied by satellites with $^2J(^{119}Sn–^1H)$ larger than uncomplexed $SnMe_2Cl_2$ (68.7 Hz). Generally larger coupling constant indicates higher coordination number of tin [51]. Substitution of $^2J(^{119}Sn\text{-}^1H)$ in the Lockhart–Manders equation [52] gives a value of 142.2° for the Me–Sn–Me angle. Therefore in the solution, similar to the solid phase, $SnMe_2$ is not linear.

^{13}C NMR spectral data also support the proposed structures. Shifts in the positions of carbons adjacent to imine nitrogen (C_7) and phenolic and enolic oxygen atoms (C_2, C_9) and also in vinylic carbon (C_8) clearly indicate the bonding of the imine nitrogen and two oxygen atoms to tin [33].

^{119}Sn NMR spectra of all complexes show one sharp singlet at lower frequency than the original $SnMe_2Cl_2$ (+137 ppm) and $SnPh_2Cl_2$ (−32 ppm) [46]. ^{119}Sn chemical shifts are influenced by variation in coordination number, bond angles, and nature of substituents at tin. ^{119}Sn NMR is strongly dependent on the coordination number of tin, and an increase in coordination number produces a large upfield shift. On the basis

Table 1. Thermal decomposition data for **1**–**4**.

Complex	Temperature range (°C)	DTG peak temperature (°C)	Weight loss (%) observed (Calcd)	Evolved product
1	203–365	310	64.6 (65.1)	$C_{11}H_{10}NOCl$, $1.5C_6H_5$
2	234–353	300	40.9 (42.2)	$C_{10}H_9NO$, C_6H_5
	353–396	390	34.1 (33.6)	C_6H_3Cl, C_6H_5
3	181–364	340	41.7 (41.5)	$C_{15}H_{11}NO$, HCl
	364–444	380	32.0 (32.4)	$2C_6H_6$, 1/3SnO
4	155–238	201	7.7 (6.5)	$2CH_4$
	238–402	320	48.9 (48.7)	$C_{15}H_{11}NO$, HCl
	402–1050	900	35.1 (35.3)	CH_4, 6C, 2/3SnO

of the chemical shift ranges for organotin(IV) derivatives, the ^{119}Sn resonances located between −90 and −330 ppm have been empirically related to the five-coordinated tin [17, 43, 53–56]. Thus, it appears reasonable to assume that for all complexes the coordination number of the tin is five in solution.

3.3. *Thermogravimetric analyses*

The TGA of **1**–**4** from ambient temperature to 1050°C are summarized in table 1. Complex **1** shows only one-step decomposition with drastic mass loss at 203–365°C. This process can be readily interpreted as loss of ligand and phenyl groups. The following decomposition of the complex exhibits a gradual mass loss and no obvious peaks in the DTG curve leading to 0.6SnO as final product at 1050°C. Complex **2** decomposed in two steps. The initial weight loss is attributed to removal of one phenyl and part of the ligand. The second step corresponds to the formation of SnO as residue. The thermal degradation of **3** takes place in two stages, the first corresponds to loss of $C_{15}H_{11}NO$ and HCl, while the second may be attributed to removal of two phenyl groups and 1/3SnO. Complex **4** shows three stages of decomposition. First, mass loss corresponds to elimination of two methyl groups. The second step involves HCl and a part of the ligand. The third step takes place to give 1/3SnO as residue.

3.4. *Biological studies*

The *in vitro* antibacterial activities of all Schiff bases and their organotin(IV) complexes were studied along with four standard antibacterial drugs, Vancomycin, Colistin, Nalidixic acid, and Erythromycin. The microorganisms used in this work include *B. subtilis* and *S. aureus* (as Gram-positive bacteria) and *E. coli* and *P. aeruginosa* (as Gram-negative bacteria). The results are presented in table 2. Inhibition zone diameter over 7 mm indicates that all test compounds (except H_2L^b) are active against the bacteria under investigation [57]. Antibacterial activity of compounds is due to either bactericide effects (killing the bacteria) or bacteriostatic effects (inhibiting multiplication of bacteria by blocking their active sites). It may be postulated that antibacterial compounds deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these organisms. It has also been proposed that the ultimate

Table 2. Antibacterial activity data of ligands and **1**–**4**.

	Inhibition zone (mm)																													
	H_2L^a ($mg\,mL^{-1}$)				H_2L^b ($mg\,mL^{-1}$)				H_2L^c ($mg\,mL^{-1}$)				$SnPh_2L^a$ ($mg\,mL^{-1}$)				$SnPh_2L^b$ ($mg\,mL^{-1}$)				$SnPh_2L^c$ ($mg\,mL^{-1}$)				$SnMe_2L^c$ ($mg\,mL^{-1}$)				Standard drugs			
Microorganism	12.5	25	50	100	12.5	25	50	100	12.5	25	50	100	12.5	25	50	100	12.5	25	50	100	12.5	25	50	100	12.5	25	50	100	V	C	N	E
B. subtilis	23	24	22	30	11	15	13	15	11	11	13	20	24	22	23	22	21	19	20	19	25	23	25	22	20	24	26	29	24	30	28	30
S. aureus	20	23	28	32	–	–	–	–	12	13	18	19	22	20	24	22	26	25	26	26	21	22	24	22	14	18	19	21	18	28	16	28
P. aeruginosa	13	13	13	21	–	–	–	–	10	11	14	17	12	12	15	14	–	8	10	8	9	9	13	12	15	16	23	20	–	–	–	–
E. coli	11	11	13	15	–	–	–	–	10	10	11	12	10	9	14	15	14	13	15	14	8	9	10	10	15	18	19	22	18	12	28	20

V = Vancomycin (30 mg per disc), C = Colistin (2 mg per disc), N = Nalidixic acid (30 mg per disc), E = Erythromycin (15 mg per disc), – = no activity.

action of the antibacterial agent is the denaturation of one or more proteins of the cell, which, as a result, impairs normal cellular processes [58]. On comparing the biological activity of the Schiff bases, organotin(IV) complexes and standard drugs, the following results are obtained:

The antibacterial data indicate that H_2L^a has remarkable and H_2L^c has moderate activity toward all bacterial strains while H_2L^b is only effective against *B. subtilis*. The activity of ligands may be due to NH/OH groups inside the Schiff base [59]. According to previous findings, compounds having halogens at different positions of the aromatic ring showed good inhibitory effects [60]. Complexes **2**, **3**, and **4** exhibit more inhibitory effects than the parent ligands. Enhancement in activity may be due to the coordination of ligand to tin leading to electron delocalization and therefore increasing the lipophilic character and efficient diffusion of the metal complexes into bacterial cells [5, 57, 61–65]. All compounds were more toxic toward Gram(+) strains than Gram(−) strains due to difference in the structures of the cell walls. The walls of Gram(−) cells are more complex than those of Gram(+) cells. Lipopolysaccharides form an outer lipid membrane and contribute to the complex antigenic specificity of Gram(−) cells [66]. However, it is important to note that, all compounds (except H_2L^b) have appreciable activities against Gram(−) bacteria, the activity of **4** is significant. It is also interesting that *P. aeruginosa* was inhibited by both Schiff bases (except H_2L^b) and complexes while standard drugs were found to have no activity against it.

4. Conclusion

Four new diorganotin(IV) complexes have been synthesized from the reaction of diorganotin(IV) dichlorides with three Schiff bases derived from 1 : 1 condensation of 2-amino-4-chlorophenol with various β-diketones. On the basis of analytical and spectral data, Schiff bases are completely deprotonated and coordinated to tin tridentate *via* imine nitrogen and phenolic and enolic oxygen atoms (figure 2). The synthesized organotin complexes inhibit both Gram-positive (*B. subtilis* and *S. aureus*)

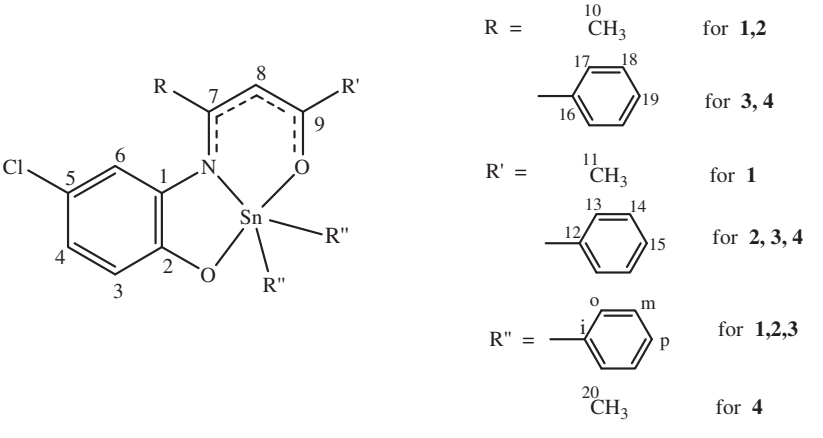


Figure 2. Suggested structure for **1**–**4** with numbering for NMR assignments.

and Gram-negative (*E. coli* and *P. aeruginosa*) bacterial species. Most research for new anti-tumor drugs depends on antibiotics affecting Gram-negative bacteria [67], making it possible that these new organotin(IV) complexes have anti-tumor effects. With regard to data published on tin derivatives, $[R_2Sn(IV)]^{2+}$ compounds generally exhibit higher antitumor activity than those of the corresponding mono-, tri- and tetraorganotin(IV) or inorganic tin derivatives; within the diorganotin(IV) class, the highest activity is exerted by $[Et_2Sn(IV)]^{2+}$ and $[Ph_2Sn(IV)]^{2+}$ complexes [20]. Di-phenyl-tin(IV) derivatives often are less toxic than other di-organo-tin(IV) derivatives [17, 68, 69]. Therefore, **1**–**3** may be good candidates for cytotoxicity studies. This research shows that both the nature of organic groups (R) bound to tin and the substituents in the donor ligand (L) can change the biological activity of R_2SnL derivatives. This study shows a further aspect of the structural chemistry and thermal and biological properties of organotin(IV) complexes with multidentate Schiff-base ligands.

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