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Synthesis, spectral, theoretical studies and in vitro antimicrobial activities of novel diphenyltin(IV) complexes of Schiff bases derived from phenacylamine

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A series of new diphenyltin(IV) complexes of the type Ph_2SnL (L^1: *N*-phenacyl-5-bromosalicylideneimine, Ph_2SnL^1; L^2: *N*-phenacyl-3,5-dichlorosalicylideneimine, Ph_2SnL^2; L^3: *N*–phenacyl-4-methoxysalicylideneimine, Ph_2SnL^3) were synthesized and characterized by elemental analysis, IR, ^1H, ^{13}C, ^{119}Sn NMR spectroscopy and mass spectrometry techniques. The C—Sn—C angles in the complexes were calculated using equations with the $^1J(^{117/119}Sn—^{13}C)$ values from ^{13}C NMR spectra. The possible structures, NMR and electronic properties of the studied molecules were calculated through density functional theory and results compared with experimental data. All the complexes were found to be mildly active against several microorganisms and some fungi. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: diphenyltin(IV); phenacylamine; Schiff base; antimicrobial activity; quantum chemical calculation

Introduction

The synthesis of organotin(IV) complexes derived from Schiff bases has been extensively studied.[1–7] Interest is growing widely as a result of their antimicrobial and antitumor activities.[8–16] These types of compounds have also found application in homogeneous catalysis[17,18] and nonlinear optics.[6,19]

In this paper, we report the synthesis and structural analysis of diorganotin(IV) complexes containing tridentate Schiff base anions derived from 5-bromosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 4-methoxysalicylaldehyde and phenacylamine. The complexes were synthesized starting from Ph_2SnCl_2 and the Schiff base (H_2L) in methanol in the presence of sodium methoxide. The reactions are summarized in Fig. 1. All the diphenyltin(IV) complexes prepared were stable under atmospheric conditions.

The fully optimized equilibrium geometries of Schiff bases and their diphenyltin(IV) complexes were obtained through density functional theory (DFT). A satisfactory correlation was established between theory and experiments.

Antibacterial and antifungal activities of the novel Schiff bases and complexes were also investigated. As the complexes were insoluble in water, solutions in DMSO were used in the activity studies.

Experimental

Materials and Physical Measurements

All chemicals and reagents were of reagent-grade quality. Diphenyltin dichloride, phenacylamine hydrochloride, 5-bromosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 4-methoxysalicylaldehyde and solvents were purchased from Aldrich and used without further purification. ^1H NMR and ^{13}C NMR spectra were obtained in deuterated DMSO and $CDCl_3$ solvents on a Bruker 400 MHz Ultrashield NMR spectrometer with TMS as internal standard. ^{119}Sn NMR spectra were recorded on a Jeol ECX-400 NMR spectrometer. IR spectra were recorded on a Mattson-1000 FT-IR spectrophotometer using KBr pellets, in the range 4000–400 cm^{-1}. Bands were located by means of a microprocessor. API-ES mass spectra were recorded on a Waters 2695 Alliance Micromass ZQ LC-MS spectrometer. Chemical analysis of C, H and N were determined with a LECO CHNS-932 elemental analyzer.

Synthesis of the Ligands

N-Phenacyl-5-bromosalicylideneimine (H_2L^1)

Phenacylamine hydrochloride (2.0 mmol), 5-bromosalicylaldehyde (2.0 mmol) and sodium carbonate (2.0 mmol) dissolved in 50 ml methanol was refluxed for 1 h. The mixture was then filtered to remove NaCl and other insoluble impurities. The precipitate thus formed upon cooling in an ice bath was filtered off. The powder products were crystallized from methanol–dichloromethane (1:1) mixture. Yellow crystals; m.p. 148–152°C. IR (cm^{-1}): 3468 br υ(O—H); 1696 s υ(C=O); 1635 s υ(C=N). ^1H NMR ($CDCl_3$, δ, ppm): 5.10 (s, 2H, H8), 6.87 (d, 1H, ^3J = 9.4, H3), 7.40 (dd, 1H, ^3J = 9.4,

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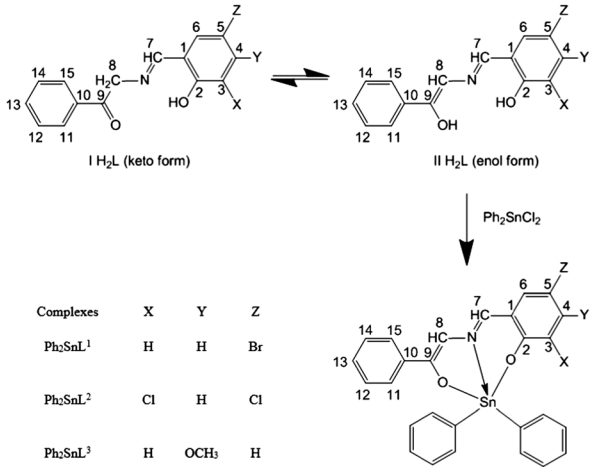

Figure 1. Numbering, preparation of compounds and keto-enol equilibrium.[31]

^4J = 2.5, H4), 7.40 (d, 1H, ^4J = 2.5, H6), 7.51 (dd, 2H, ^3J = 8.0, ^3J = 8.0, H12, H14), 7.62 (dd, 1H, ^3J = 8.0, ^4J = 1.6, H13), 8.01 (dd, 2H, ^3J = 8.0, ^4J = 1.6, H11, H15), 8.33 (s, 1H, H7), 13.04 [s, 1H, (OH)a]. ^{13}C NMR ($CDCl_3$, δ, ppm): 64.17 (C8), 110.23 (C5), 119.31 (C3), 120.20 (C1), 128.35 (C11, C15), 129.01 (C12, C14), 133.85 (C6), 133.94 (C13), 135.28 (C10), 135.51 (C4), 160.23 (C2), 167.50 (C7), 193.92(C9). Mass spectrum (ESI) {*m/z* [assignment] (%)}: 317 $[M]^+$ (5.9). Elemental anal.: found C, 56.52; H, 3.72; N, 4.49%; calcd for $C_{15}H_{12}NO_2Br$: C, 56.63; H, 3.80; N, 4.40%.

H_2L^2 and H_2L^3 were synthesized and purified in a similar method as for H_2L^1.

N-Phenacyl-3,5-dichlorosalicylideneimine (H_2L^2)

Yellow crystals, m.p. 141°C. IR (cm^{-1}): 3469 br υ(O—H); 1689 s υ(C=O); 1650 s υ(C=N). ^{1}H NMR ($CDCl_3$, δ, ppm): 5.09 (s, 2H, H8), 7.19 (d, 1H, ^4J = 2.4, H6), 7.41 (d, 1H, ^4J = 2.4, H4), 7.51 (dd, 2H, ^3J = 7.7, ^3J = 7.7, H12, H14), 7.62 (dd, 1H, ^3J = 7.7, ^4J = 1.6, H13), 7.99 (dd, 2H, ^3J = 7.7, ^4J = 1.6, H11, H15), 8.32 (s, 1H, H7), 15.10 [s, 1H, (OH)a]. ^{13}C NMR ($CDCl_3$, δ, ppm): 63.39 (C8), 119.73 (C1), 122.99 (C3), 128.34 (C11, C15), 129.09 (C12, C14), 129.43 (C4), 131.17 (C5), 132.68 (C6), 134.09 (C13), 136.58 (C10), 156.42 (C2), 167.20 (C7), 193.28(C9). Mass spectrum (ESI) {*m/z* [assignment] (%)}: 307 $[M]^+$ (10.2). Elemental anal.: found C, 58.27; H, 3.40; N, 4.41%; calcd for $C_{15}H_{11}NO_2Cl_2$: C, 58.46; H, 3.60; N, 4.55%.

N-Phenacyl-4-methoxysalicylideneimine (H_2L^3)

Yellow crystals, m.p. 139–140°C. IR (cm^{-1}): 3469 br υ(O—H); 1699 s υ(C=O); 1637 s υ(C=N). ^{1}H NMR ($CDCl_3$, δ, ppm): 3.77 (s, 3H, OCH_3), 5.24 (s, 2H, H8), 6.35 (s, 1H, H3), 6.40 (d, 1H, ^3J = 8.6, H5), 7.31 (d, 1H, ^3J = 8.6, H6), 7.59 (dd, 2H, ^3J = 7.7, ^3J = 7.7 H12, H14), 7.69 (d, 1H, ^3J = 7.7, H13), 8.02 (d, 2H, ^3J = 7.7, H11, H15), 8.42 (s, 1H, H7), 13.88 [s, 1H, (OH)a]. ^{13}C NMR ($CDCl_3$, δ, ppm): 55.18 (OCH_3), 61.57 (C8), 101.17 (C3), 105.96 (C5), 116.11 (C1), 128.03 (C11, C15), 128.87 (C12, C14), 132.86 (C6), 133.45 (C13), 136.02 (C10), 163.70 (C4), 166.36 (C2), 167.28 (C7), 194.00 (C9). Mass spectrum (ESI) {*m/z* [assignment] (%)}: 269 M^+ (43.1). Elemental anal.: found C, 71.11; H, 5.40; N, 5.33%; calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20%.

Preparation of the Complexes

Tin(IV) complexes of the Schiff base ligands were prepared from the diphenyltin(IV) dichloride and the Schiff base as follows. To a solution of Schiff base (2.0 mmol) in 15 ml dry methanol, sodium methoxide (4.0 mmol) in methanol was added and the resulting sodium salt solution of the ligand was filtered to remove any insoluble impurities. To this solution, a solution of Ph_2SnCl_2 (2.0 mmol) in 15 ml dry methanol was added slowly and heated to 50–60°C. The resulting mixture was allowed to cool to room temperature and kept at room temperature overnight. The crystals were filtered off and recrystallized from butanol–dichloromethane (1:1, v/v) mixture. A description of the individual complexes follows.

[N-Phenacyl-5-bromosalicylideneiminato]diphenyltin(IV) (Ph_2SnL^1)

Orange crystals, m.p. 192–194°C. IR (cm^{-1}): 1608 s υ(C=N), 697 υ(Sn—C), 564, υ(Sn—O), 492 υ(Sn—N). ^{1}H NMR ($CDCl_3$, δ, ppm): 6.95 (d, 1H, ^3J = 8.9, H3), 7.05 [s, 1H, $^3J(^{117/119}Sn—^1H)$ = 50.1, H8], 7.15 (d, 1H, ^4J = 2.7, H6), 7.39 (dd, 1H, ^3J = 8.9, ^4J = 2.6, H4), 7.40–7.50 [m, 9H, *meta*-H + *para*-H($SnPh_2$) + H12, H14 + H13], 7.87–7.94 [m, 6H, $^3J(^{117/119}Sn—^1H)$ = 108.0, *ortho*($SnPh_2$) + H11, H15], 8.01 (s, 1H, $^3J(^{117/119}Sn—^1H)$ = 58.9 H7). ^{13}C NMR ($CDCl_3$, δ, ppm): 108.12 (C5), 110.79 (C8), 120.00 (C1), 123.96 (C4), 125.62 (C3), 128.23 (C6), 128.54 (C11, C15,C12, C14), 128.84 [$^3J(^{117/119}Sn—^{13}C)$ = 84.2 Hz, *meta*-C], 129.74 (C13), 130.48 [$^3J(^{117/119}Sn—^{13}C)$ = 17.0 Hz, *para*-C], 134.45 (C10), 136.57 [$^3J(^{117/119}Sn—^{13}C)$ = 54.0 Hz, *ortho*-C], 136.68 [$^1J(^{117}Sn—^{13}C)$ = 970.0 Hz, $^1J(^{119}Sn—^{13}C)$ = 1029.0 Hz, *ipso*-C], 153.06 (C7), 161.43 (C9), 165.79 (C2). ^{119}Sn NMR ($CDCl_3$, δ, ppm):=327.50. Mass spectrum (ESI) {*m/z* [assignment] (%)}: 590 [M +H]$^+$ (^{120}Sn) (13.3), 588 [M+H]$^+$ (^{118}Sn) (8.5), 586 [M+H]$^+$ (^{116}Sn) (3.1), 512 [M−C_6H_5]$^+$ (^{120}Sn) (100.0), 510 [M−C_6H_5]$^+$ (^{118}Sn) (61.0), 508 [M−C_6H_5]$^+$ (^{116}Sn) (26.1), 435 [M−$2C_6H_5$]$^+$ (^{120}Sn) (24.0), 433 [M−$2C_6H_5$]$^+$ (^{118}Sn) (15.9), 431 [M−$2C_6H_5$]$^+$ (^{116}Sn) (6.0), . Elemental anal.: found C, 54.97; H, 3.51; N, 2.40%; calcd for $C_{27}H_{20}NO_2BrSn$: C, 55.05; H, 3.42; N, 2.38%.

[N-Phenacyl-3,5-dichlorosalicylideneiminato]diphenyltin(IV) (Ph_2SnL^2)

Orange crystals, m.p. 230°C. IR (cm^{-1}): 1606 s υ(C=N), 699 υ(Sn—C), 552, υ(Sn—O), 497 υ(Sn—N). ^{1}H NMR ($CDCl_3$, δ, ppm): 6.94 (d, 1H, ^4J = 2.0, H6), 7.09 (s, 1H, $^3J(^{117/119}Sn—^1H)$ = 58.0, H8), 7.39–7.49 (m, 10H, *meta*-H + *para*-H ($SnPh_2$) + H4 + H12, H14 + H13), 7.86–8.10 [m, 6H, $^3J(^{117/119}Sn—^1H)$ = 93,0, *ortho* ($SnPh_2$) + H11, H15], 8.00 (s, 1H, $^3J(^{117/119}Sn—^1H)$ = 47.1, H7). ^{13}C NMR ($CDCl_3$, δ, ppm): 110.99 (C8), 111.63 (C1), 123.89 (C5), 125.72 (C11, C15) ,128.58 (C3), 128.63 (C12, C14), 128.98 [$^3J(^{117/119}Sn—^{13}C)$ = 84.2 Hz, *meta*-C], 129.24 (C13), 129.93 (C6), 130.02 [$^4J(^{117/119}Sn—^{13}C)$ = 17.6 Hz, *para*-C], 132.93 (C4), 134.45 (C10), 136.57 [$^2J(^{117/119}Sn—^{13}C)$ = 54,8 Hz, *ortho*-C], 136.68 [$^1J(^{117}Sn—^{13}C)$ = 980.0 Hz, $^1J(^{119}Sn—^{13}C)$ = 1024.0 Hz *ipso*-C], 152.24 (C7), 159.50 (C9), 162.17 (C2). ^{119}Sn NMR ($CDCl_3$, δ, ppm): −324.40. Mass spectrum (ESI) {*m/z* [assignment] (%)}: 580 [M+H]$^+$ (^{120}Sn) (22.0), 578 [M+H]$^+$ (^{118}Sn) (13.1), 576[M+H]$^+$ (^{116}Sn) (6.2), 502 [M−C_6H_5] $^+$ (^{120}Sn) (100), 500 [M−C_6H_5]$^+$ (^{118}Sn) (66.8), 498 [M−C_6H_5]$^+$ (^{116}Sn) (28.2), 425 [M−$2C_6H_5$]$^+$ (^{120}Sn) (2.0), 423 [M−$2C_6H_5$]$^+$ (^{118}Sn) (1.2), 421 [M−$2C_6H_5$]$^+$ (^{116}Sn) (0.5). Elemental anal.: found C, 56.10; H, 3.27; N, 2.47%; calcd for $C_{27}H_{19}NO_2Cl_2Sn$: C, 56.00; H, 3.31; N, 2.42%.

[N-Phenacyl-4-methoxysalicylideneiminato]diphenyltin(IV) (Ph_2SnL^3)

Reddish-orange crystals, m.p. 195–198°C. IR (cm^{-1}): 1608 s υ(C=N), 686 υ(Sn—C), 544, υ(Sn—O), 499 υ(Sn—N). ^{1}H NMR ($CDCl_3$, δ, ppm): 3.83 (s, 3H, OCH_3), 6.26 (dd, 1H, ^3J = 8.7, ^4J = 2.3, H5), 6.48 (d, 1H, ^4J = 2.3, H3), 6.90 (d, 1H, ^3J = 8.7, H6), 6.97 (s, 1H, $^3J(^{117/119}Sn—^1H)$ = 62.8, H8), 7.32–7.39 [m, 6H, *meta*-H + *para*-H Sn (Ph_2Sn)], 7.39–7.49 (m, 3H, H12, H14 + H13), 7.81–8.0 [m, 4H, $^3J(^{117/119}Sn—^1H)$ = 96.0, *ortho*($SnPh_2$)], 7.85–7.90 (m, 2H, H11, H15), 8.00 (s, 1H, $^3J(^{117/119}Sn—^1H)$ = 51.4, H7). ^{13}C NMR ($CDCl_3$, δ, ppm): 55.47

(OCH_3), 104.22 (C3), 106.96 (C5), 110.52 (C8),112.82 (C1), 125.22 (C11, C15), 128.39 (C12, C14), 128.69 [$^3J(^{117/119}Sn—^{13}C)$ = 88.0 Hz, *meta*-C], 128.94 (C13), 130.22 [$^4J(^{117/119}Sn—^{13}C)$ = 19.8 Hz, *para*-C], 134.75 (C6), 136.29 [$^1J(^{117}Sn—^{13}C)$ = 987.0 Hz, $^1J(^{119}Sn—^{13}C)$ = 1021.0 Hz *ipso*-C], 136.60 [$^2J(^{117/119}Sn—^{13}C)$ = 53.7 Hz, *ortho*-C], 140.63 (C10), 155.00 (C7), 158.62 (C9). 165.52 (C4), 169.56 (C2). ^{119}Sn NMR ($CDCl_3$, δ, ppm): −325.79. Mass spectrum (ESI) {*m/z* [assignment] (%)}:542 $[M+H]^+$ (^{120}Sn) (24.0), 540 $[M+H]^+$ (^{118}Sn) (18.6), 538 $[M+H]^+$ (^{116}Sn) (10.8), 464 $[M-C_6H_5]^+$ (^{120}Sn) (1.0), 462 $[M-C_6H_5]^+$ (^{118}Sn) (0.8), 460 $[M-C_6H_5]^+$ (^{116}Sn) (0.4), 387 $[M\text{-}2C_6H_5]^+$ (0.1). Elemental anal.: found C, 62.33; H, 4.20; N, 2.65%; calcd for $C_{28}H_{23}NO_3Sn$: C, 62.26; H, 4.29; N, 2.59%.

Computational Details

All calculations in this study were carried out using the Gaussian 09 software package,[20] and all molecules were characterized by complete optimization of the molecular geometries in solution with DFT using B3LYP hybrid functional including Becke's three-parameter (B3) gradient corrected exchange functional,[21] Lee, Yang and Parr (LYP)[22] and VWN correlation functionals [functional III],[23] as implemented in Gaussian 09.[24] All calculations were done without any symmetry constraints. Minimum energy geometries of the Schiff base ligands were obtained using 6-311++G(d,p) basis set starting from previously optimized structures at semi-empirical Parametric Model 6[25] level of theory. Diorganotin(IV) complex structures were optimized with mixed-basis set approach using 6-311++G(d,p) basis set for C, H, N, O, X (Cl, Br) atoms and DGDZVP basis set for Sn atom. All stationary points were confirmed as true minima without any negative frequency through analytical vibrational analysis. Cheeseman *et al.*'s GIAO-DFT[26] approach, which can utilize hybrid functionals, used for NMR calculations and solvent effects, are included using the default polarizable continuum model (IEF-PCM) of the software (Solvent: Chloroform). Molecular visualizations are represented with GaussView software.[27]

Antimicrobial Studies

Antibacterial activity

Antibacterial activity of the compounds were investigated against standard strains of Gram-negative bacteria (*Escherichia coli* ATCC (American Type Culture Collection) 35218, *E. coli* ATCC 25922, *Enterobacter cloacae* ATCC 23355, *Serratia marcescens* ATCC 8100, *Pseudomonas aeruginosa* ATCC 27853) and Gram-positive bacteria (*Enterococcus faecalis* ATCC 29212, *Staphylococcus epidermidis* ATCC 12228, *Staphylococcus aureus* ATCC 25923) by Kirby Bauer disc diffusion method.[28] Each bacteria was inoculated onto blood agar plates (Oxoid Ltd, Basingstoke, UK) containing 5% sheep blood and then incubated aerobically at 37°C for 18–24 h. The subsequent growth was used for preparation of bacterial suspension. The turbidity of bacterial suspensions was adjusted with sterile saline to the 0.5 McFarland standards (approximately 1–2 × 10^8 colony-forming units ml^{-1}). Each bacterial suspension was inoculated on to Mueller–Hinton agar plates (Oxoid) using cotton swabs. All compounds were dissolved at a concentration of 200 mg L^{-1} in DMSO. Sterile filter paper discs (diameter 6 mm) (Oxoid) soaked with 25 ml of compounds were placed on the agar plate surface. After incubation at 37°C for 24 h, inhibition zone diameters surrounding the each disc was measured and recorded in millimeters. Gentamicin (10 μg per disc) was used as a positive control disc for bacteria. A sterile distilled-water soaked disc was used as a negative control. The solvent, DMSO, was also tested alone to establish its influence on test performance. Routine quality control testing of commercially prepared Mueller–Hinton agar and blood agar were checked with *Enterococcus faecalis* ATCC 29212.

Antifungal activity

The *in vitro* antifungal activities of compounds were also evaluated against *Aspergillus niger*, *Aspergillus fumigatus*, *Aspergillus flavus* and *Candida albicans* (clinical isolates). Each *Aspergillus* strain was inoculated on to potato dextrose agar (Oxoid) at 35°C for 7 days. Spore suspensions were prepared in sterile saline and adjusted to a turbidity equivalent to that of 0.5 McFarland, corresponding to approximately 10^6 colony-forming units mL^{-1}, then inoculated on to the agar surface using cotton swabs. The agar plates were prepared by using RPMI-1640 medium (Sigma, St Louis, MO, USA) supplemented with 1.5% agar and 2% glucose and buffered to a pH of 7.0 with 0.165 mol L^{-1} MOPS (3-[*N*-morpholino] propanesulfonic acid) (Sigma). For *Candida albicans*, Mueller–Hinton agar supplemented with 2% glucose was used. Sterile filter paper discs (diameter 6 mm) (Oxoid) soaked with 25 ml of compounds were placed on the agar plate surface. Inhibition zone diameters were measured following 24 h incubation at 35°C in ambient air. Fluconazol (25 μg per disc) and amphotericin B (100 U per disc) were used as positive control discs for fungi.

Results and Discussion

NMR Spectra

The ^{1}H NMR spectra of all the ligands display a single signal for the azomethine proton (H-7) at 8.32–8.42 ppm. The H-7 NMR signal of tin(IV) complexes shifted downfield to the range 8.01–8.00 ppm, reflecting the more electropositive nature of the tin atom relative to hydrogen. In the ^{1}H NMR spectra of the ligands, the signals at 13.04–15.10 ppm were assigned to the phenolic proton on the salicylaldehyde moiety (OH) (Fig. 1). The signal disappears in the ^{1}H NMR spectra of the corresponding Sn(IV) complexes, indicating the engagement of phenolic O atoms in complexation. The singlet signal at 5.09–5.24 ppm in ^{1}H NMR spectra indicates the presence of keto form —CH_2 (H8) in solution. The signal shifted to the range 6.97–7.09 ppm in the ^{1}H NMR spectra of the corresponding Sn(IV) complexes. For the diphenyltin(IV) complexes detection of ^3J ($^{117/119}Sn—^1H$) coupling (47.1 and 58.9 Hz) with H7 hydrogen, and ^3J ($^{117/119}Sn—^1H$) coupling (50.1 and 62.8 Hz) with H8 indicates the coordination of enolic oxygen and nitrogen atoms of the ligand with tin. The extent of coupling is comparable with the literature values.[5,13,29] The other protons in the phenyl rings are observed in their normal δ range.

^{3}C-NMR spectral data also confirm the proposed structures. The considerable shifts in the positions of carbon atoms adjacent to the imine nitrogen (C7), phenolic oxygen (C2) and enolic oxygen (C9) and C8 support the proposed coordination sites in the complexes. The shifts in the positions of carbon atoms adjacent to the coordinating atoms clearly indicate the bonding of the imine nitrogen and the two oxygen atoms to the central metal atom. For the Ph_2SnL^1, Ph_2SnL^2 and Ph_2SnL^3, the ^1J ($^{117/119}Sn—^{13}C$) couplings are detected at 970, 980 and 987 Hz, respectively. The magnitude of the coupling constants agrees well with those previously reported for analogous five-coordinate derivatives.[6] Using the equation ^1J ($^{117/119}Sn—^{13}C$) = (15.91 ± 0.72)θ − (1164 ± 84), the C—Sn—C angle in solution can be estimated from the ^1J ($^{117/119}Sn—^{13}C$) coupling constants.[30] Calculated values are 138.1°, 137.8° and 137.6° for Ph_2SnL^1, Ph_2SnL^2 and Ph_2SnL^3, respectively.

In the ^{119}Sn NMR spectra, the observed δ (^{119}Sn) values for Ph_2SnL^1, Ph_2SnL^2 and Ph_2SnL^3 are −327.50, −324.40 and −325.79 ppm, respectively. These ^{119}Sn chemical shifts are in the range reported (90–310 Hz) for five-coordinate tin compounds..[6,13–15,31] These δ (^{119}Sn) values compare well with other diorganotin(IV) complexes containing ONO donor atoms and strongly indicate penta-coordinate nuclei. It is well known that δ (^{119}Sn) values depend on the coordination number of the tin center and the ligand bite angle.[8]

IR Spectra

The infrared spectrum of the ligands is consistent with the keto form [I] (Fig. 1). Stretching vibration bands of C=O and C=N were observed between 1704 and 1686 cm^{-1} and between 1643–1633 cm^{-1}, respectively. The differences are very significant between the IR spectra of the ligands and those of complexes in that that the stretching vibration bands of the C=O and phenolic O—H groups disappear from the spectra of the complexes. This clearly reflects the deprotonation of the phenolic and enolic oxygen atoms on the ligand upon complexation. In the complexes the υ(C=N) band, occurring between 1608 and 1605 cm^{-1}, shifts towards lower frequencies with respect to that of the free Schiff bases, confirming the coordination of the azomethine nitrogen to the organotin moiety. Also Sn—C, Sn—O and Sn—N bands were observed, with ranges of 686–699, 544–564 and 492–499 cm^{-1}, respectively. This is in agreement with the literature values.[9]

Mass Spectra

In the ESI mass spectra of all the compounds, molecular ions and some of the tin-containing fragments are clearly visible and are summarized in the Experimental section. Fragment ions, $[L]^+$, $[RSnL]^+$ and $[SnL]^+$ were also detected in the mass spectra of all the complexes. Fragmentation patterns are also in agreement with the literature reports.[32]

The Sn-containing fragments display the natural abundance of the major Sn isotopes. The experimental isotopic distributions of all the Sn-containing fragment ions were compared with the theoretically calculated one and found to be in agreement with the theoretical relative abundances.

Theoretical Studies

Calculated electronic properties of the compounds are summarized in Table 1.

Our DFT studies revealed that keto-imine forms of the ligands are more stable than enol-imine forms. The Boltzmann distribution equation dictates the ratio of species which varies exponentially depending on the free energy difference and in our case keto:enol tautomer ratios were found to be over 100:1 for the Schiff base ligands. This result indicates predomination of keto forms in solution. Furthermore, calculated HOMO-LUMO gap values of enol-imine forms are remarkably lower than keto-imine tautomers, making them softer species.[34] This may be a key point in reactivity towards complexation of enol tautomers.

Calculated geometric parameters of the compounds are summarized in Table 2 and optimized structures are represented in Figures 2 and 3. The 6-311++G(d,p) basis set, which contains d, p type polarization functions as well as diffusion functions, is a sufficent basis set and led accurate predictions on geometric parameters for such organic parts of the compounds, so that theoretical C=N, C2—O1 and C9—O2 bond lengths of the organotin (IV) complexes are comparable to reported experimental bond lengths in our previous work.[32] However, XRD data are not available for these diphenyltin(IV) complexes' calculated Sn—N, Sn—C, Sn—O1, Sn—O2 bond distances, which are significantly longer than previously reported for some five-coordinated diphenyltin(IV) complexes,[13,35–37] but computational approaches tend to give shorter or longer bond lengths than experimental ones.[38] In this paper a full electron DGDZVP[39] basis set was used to describe the relatively heavy tin element at a non-relativistic level of theory to apply a higher electron correlation. Negletting relativistic effects could cause an increase in relavent bond lengths.[40] Calculated O1—Sn—O2, N—Sn—O1 and N—Sn—O2 bond angles are also in good agreement with the experimental literature data.[13,32,35–37] However, there is no certain proof, but all these findings concerning geometrical parameters are very supportive of experimental and theoretical correlation. C—Sn—C bond angles of optimized structures lie between 125.54° and 127.12° and these values are lower than our experimental values, but underestimation of C—Sn—C bond angles was reported in a similar study.[41]

Theoretical NMR calculations play an important role in assisting spectrum assignment, analyzing experimental spectrum, elucidating structures and exploring the nature of reactive intermediates.[42] Improvements in computer systems and software algorithms are very beneficial for calculating isotropic shielding constants. Clearly, the complex nature of some molecules can lead to incorrect structural propositions even with the assistance of 2D-NMR experiments,[43] so theoretical calculations could become a powerful tool to overcome this problem. An essential point in these calculations is error reduction for better agreement with experimental spectra. On this matter, one of the most successful approach is empirical scaling; in other words, the use of linear regression equations to enhance theoretical prediction accuracy.[44] If there is a reliable, adequate pool of experimental and computational data then this procedure becomes applicable. Since raw data are

Table 1. Calculated properties of the compounds

Compound	*E* (a.u.)[a]	ZPVE[b] (kcal mol^{-1})	$\Delta E_{(Lumo-Homo)}$ (eV)	Dipole moment (Debye)
Schiff bases (enol-imine forms)				
H_2L^1	−3358.3801	145.56	3.44	3.06
H_2L^2	−1704.0784	145.93	3.42	5.22
H_2L^3	−899.3982	171.87	3.47	5.51
Schiff bases (keto-imine forms)				
H_2L^1	−3358.3838	142.63	4.23	6.55
H_2L^2	−1704.0822	139.69	4.32	8.30
H_2L^3	−899.4019	171.69	4.18	6.73
Diphenyltin(IV) complexes				
Ph_2SnL^1	−9845.4065	246.49	3.04	2.44
Ph_2SnL^2	−8191.1067	240.87	3.02	4.44
Ph_2SnL^3	−7386.4249	—[c]	3.13	5.00

[a]Sum of electronic energies in atomic units.

[b]Scaling factor 0.9877 was applied to ZVPE (zero point vibrational energy) value results of Schiff base ligands that were proposed for use with similar basis sets.[33] No scaling factor was applied to ZVPE values of organotin(IV) complexes.

[c]Value could not obtained owing to incomplete analytical frequency calculation, because of scratch space limitation of 32-bit Gaussian 09W.

Table 2. Calculated geometric parameters of ligands and complexes

Bond lengths (Å)						
	H_2L^1	H_2L^2	H_2L^3	Ph_2SnL^1	Ph_2SnL^2	Ph_2SnL^3
C—O	1.343	1.335	1.345	1.314	1.305	1.316
C=O	1.216	1.216	1.216	—	—	—
C N	1.279	1.279	1.283	1.308	1.307	1,310
C—N	1.444	1.445	1.443	1.389	1.388	1.393
Sn—O1	—	—	—	2.125	2.131	2.124
Sn—O2	—	—	—	2.150	2.147	2.150
Sn—C	—	—	—	2.162	2.160	2.164
Sn—N	—	—	—	2.229	2.232	2.217

Bond angles (°)			
	Ph_2SnL^1	Ph_2SnL^2	Ph_2SnL^3
C—Sn—C	126.53	127.12	125.54
O1—Sn—O2	158.79	158.72	159.30
N—Sn—O1	83.27	82.68	83.54
N—Sn—O2	75.52	75.54	75.76

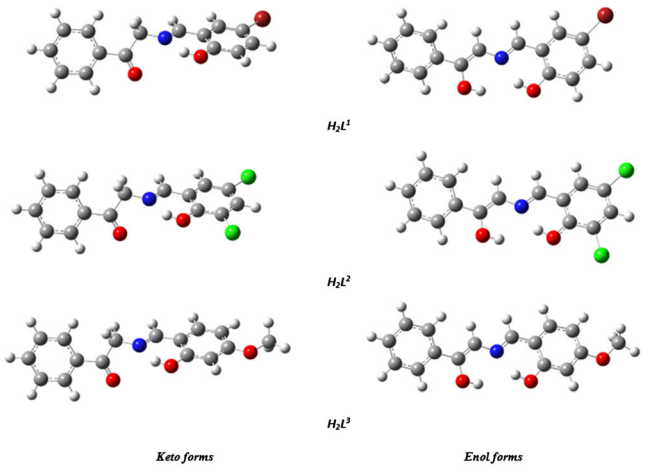

Figure 2. Optimized structures of the Schiff base ligands HL^1, HL^2 and HL^3.

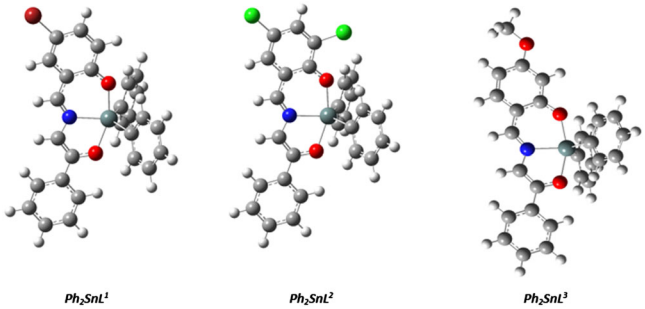

Figure 3. Optimized structures of the organotin(IV) complexes Ph_2SnL^1, Ph_2SnL^2 and Ph_2SnL^3.

known to be contain some systematic errors, linear regression is known to be a one-step solution for reducing them.[42,45] In this work we have successfully applied this method to derive scaling factors for organotin complexes of ONO donor-type Schiff base ligands in solution state. Experimental chemical shift values (δ) were plotted against calculated isotropic shieldings (σ) to obtain linear regression equations with slope and intercept values that were used as scaling factors for our molecular systems. Isotropic shielding values of heavy atom bonded carbons not included in equations which are used to calculate ^{13}C NMR chemical shifts, in order to prevent negative effects over regression quality.[46] In addition, calculated isotropic shieldings have been averaged when experimental distinction not available.[42] Resulting equations and calculated chemical shift values are represented in Table 3, including mean absolute deviation (MAD) and root mean square (RMS) parameters. Results indicate a well-established correlation between experimental spectra and calculated chemical shifts and MAD; RMS values are comparable with the published results of a few studies utilizing DFT and Popple-type basis sets to calculate either ^1H or ^{13}C chemical shifts in organic molecules using the linear regression method.[47–49]

Biological Activity

In this work, the *in vitro* antibacterial and antifungal activities of several Schiff bases and their diphenyltin(IV) complexes were investigated and the results are listed in Table 4.

The data obtained indicate that H_2L^2 had moderate activity against Gram-positive bacteria *Staphylococcus aureus* ATCC 25923, *S. epidermidis* ATCC 12228 and also against the fungus *Candida albicans*. In general, complexes exhibit antibacterial properties higher than those of the corresponding ligands. With regard to the literature, organotin(IV) complexes with Schiff bases often have the higher antibacterial activity than their ligands.[3,50]

All the complexes and ligands were also screened against the Gram-negative bacteria, *E. coli* ATCC 25922, *E. coli* ATCC 35218, *Enertobacter cloacae* ATCC 23355, *Serratia marcescens* ATCC 8100 and *Pseudomonas aeruginosa* ATCC 27853, but no antibacterial activity was observed. Apparently the complexes are only toxic towards Gram-positive strains. The reason probably lies in the difference between the structures of the cell walls. The relatively

Table 3. Calculated ^{1}H, ^{13}C NMR shifts of compounds (δ, ppm), experimental values (in parenthesis) and linear regression equations

Hydrogen	H_2L^1	H_2L^2	H_2L^3	Carbon	H_2L^1	H_2L^2	H_2L^3
C3—H	6.96 (6.87)	—	6.42 (6.35)	1	120.00 (120.20)	119.23 (119.73)	113.29 (116.11)
C4—H	7.41 (7.40)	7.49 (7.41)	—	2	162.41 (160.23)	157.11 (156.42)	164.27 (166.36)
C5—H	—	—	6.28 (6.40)	3	118.29 (119.31)	—	102.66 (101.17)
C6—H	7.41 (7.40)	7.18 (7.19)	7.17 (7.31)	4	135.94 (135.51)	132.33 (129.43)	164.26 (163.70)
C7—H	8.20 (8.33)	8.22 (8.32)	8.34 (8.42)	5	—	—	99.19 (105.96)
C8-H_2	5.04 (5.10)	5.03 (5.09)	4.85 (5.24)	6	135.10 (133.85)	130.53 (132.68)	133.52 (132.86)
C11—H. C15—H	8.34 (8.01)	8.31 (7.99)	8.34 (8.02)	7	167.22 (167.50)	166.70 (167.20)	167.18 (167.28)
C12—H. C14—H	7.65 (7.51)	7.65 (7.51)	7.63 (7.59)	8	66.30 (64.17)	65.96 (63.39)	65.91 (61.57)
C13—H	7.72 (7.62)	7.73 (7.61)	7.68 (7.69)	9	194.82 (193.92)	194.53 (193.28)	195.41 (194.00)
O—H	13.63 (13.04)	14.46 (15.10)	13.52 (13.88)	10	134.17 (135.28)	134.02 (136.58)	134.58 (136.10)
O—CH_3	—	—	3.54 (3.77)	11.15	128.67 (128.35)	128.65 (128.34)	128.44 (128.03)
				12.14	128.45 (129.01)	128.48 (129.09)	128.45 (128.87)
				13	134.09 (133.94)	134.30 (134.09)	134.02 (133.45)
				O—CH_3	—	—	53.77 (55.18)
MAD[a]		*0.17*				*1.33*	
RMS[b]		*0.24*				*1.88*	
Equation		$\delta_{Predicted} = -1.0603\sigma + 33.262$ ($r^2 = 0.99$)				$\delta_{Predicted} = -0.9706\sigma + 175.85$ ($r^2 = 0.99$)	
	Ph_2SnL^1	Ph_2SnL^2	Ph_2SnL^3		Ph_2SnL^1	Ph_2SnL^2	Ph_2SnL^3
C3—H	7.08 (6.95)	—	6.49 (6.48)	1	120.35 (120.00)	120.17 (111.63)	114.22 (112.82)
C4—H	7.25 (7.39)	7.41 (7.44)	—	2	166.23 (161.43)	159.26 (162.17)	167.81 (169.56)
C5—H	—	—	6.10 (6.26)	3	122.91 (125.62)	—	107.36 (104.22)
C6—H	7.03 (7.15)	6.85 (6.94)	6.95 (6.90)	4	136.26 (123.96)	132.29 (132.93)	165.43 (165.52)
C7—H	8.07 (8.01)	7.81 (8.00)	7.76 (8.00)	5	—	—	99.05 (106.95)
C8—H	7.08 (7.05)	7.09 (7.09)	7.05 (6.97)	6	135.47 (128.23)	130.80 (129.93)	135.56 (134.75)
C11—H.C15—H	8.01 (7.90)	8.05 (7.98)	8.06 (7.88)	7	151.19 (153.06)	150.23 (152.24)	152.47 (155)
C12—H.C14—H	7.39 (7.45)	7.41 (7.44)	7.34 (7.43)	8	110.00 (110.79)	110.33 (110.99)	109.64 (110.52)
C13—H	7.39 (7.45)	7.41 (7.44)	7.34 (7.43)	9	159.60 (165.79)	160.66 (159.50)	157.64 (158.62)
O—CH_3	—	—	3.99 (3.83)	10	135.20 (134.45)	134.88 (134.45)	136.24 (140.63)
ortho(Ph_2Sn)	8.01 (7.90)	8.05 (7.98)	8.19 (7.90)	11.15	126.59 (128.54)	125.48 (125.72)	124.60 (125.22)
meta(Ph_2Sn)	7.39 (7.45)	7.41 (7.44)	7.34 (7.36)	12.14	126.59 (128.54)	128.15 (128.63)	127.65 (128.39)
para(Ph_2Sn)	7.39 (7.45)	7.41 (7.44)	7.34 (7.36)	13	129.24 (129.74)	129.52 (129.24)	128.40 (128.94)
				OCH_3	—	—	55.28(55.47)
				Sn—C(*ipso*)	138.33(136.68)	137.47(136.68)	138.95(136.29)
				ortho(Ph_2Sn)	136.27(136.54)	136.27(136.57)	136.19(136.60)
				meta(Ph_2Sn)	128.13(128.84)	128.26(128.98)	127.53(128.69)
				para(Ph_2Sn)	129.84(130.48)	130.01(130.02)	129.02(130.22)
MAD[a]		*0.11*				*1.78*	
RMS[b]		*0.13*				*3.01*	
Equation		$\delta_{Predicted} = -0.896\sigma + 29.099$ ($r^2 = 0.98$)				$\delta_{Predicted} = -0.9585\sigma + 175.1$ ($r^2 = 0.98$)	

[a]Mean absolute deviation values.
[b]Root mean square error values.

Table 4. Antibacterial and antifungal activities of compounds

Microorganism	Inhibiton zone (mm)								
	H_2L^1	H_2L^2	H_2L^3	Ph_2SnL^1	Ph_2SnL^2	Ph_2SnL^3	G	A	F
S. aureus ATCC 25923	—	17	—	20	17	20	22		
S. epidermidis ATCC 12228	—	17	—	19	17	18	25		
E. faecalis ATCC 29212	—	—	—	10	—	13	20		
E. coli ATCC 25922	—	—	—	—	—	—	25		
E. coli ATCC 35218	—	—	—	—	—	—	20		
E. cloacae ATCC 23355	—	—	—	—	—	—	22		
S. marcescens ATCC 8100	—	—	—	—	—	—	24		
P. aeruginosa ATCC 27853	—	—	—	—	—	—	18		
A. niger	—	—	—	16	11	15	—	23	—
A. flavus	—	—	—	18	15	18	—	20	—
A. fumigatus	—	—	—	18	12	18	—	25	—
C. albicans	—	16	—	15	10	15	—	23	25

G, gentamicin (10 μg per disc); A, amphotericin B (100 U per disc); F, fluconazol (25 μg per disc).

more complex walls of Gram-negative cells may prevent the diffusion of chemicals into the cytoplasm of the organisms, which may not be the case for Gram-positive cells. These antibacterial and antifungal activity results are in accordance with those found for other similar diorganotin(IV) complexes.[2,3]

Conclusion

N-Phenacylsalicylideneimine derivatives and their diphenyltin(IV) complexes were prepared and characterized by elemental analyses, NMR spectroscopy, IR spectroscopy and mass spectrometry. The Schiff base ligands remain predominantly as the keto form [I] in solution. In the presence of diphenyltin(IV) chloride they convert to the enolate form, deprotonate and coordinate with the tin atom as uninegatively charged ONO tridentate chelating agents with the elimination of HCl. Five-coordinate geometry is proposed for the organotin(IV) complexes since ^{119}Sn NMR values indicate that and close agreement between experimental and theoretical NMR chemical shifts support that reproduced structures correlate well with the experimental structures. The results of antibacterial screening of the complexes indicate mild inhibitory effects against Gram-positive bacteria.

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