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Synthesis, characterization, biological activities of dimethyltin(IV) complexes of Schiff bases with ONO-type donors

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ABSTRACT

Four different dimethyltin(IV) complexes of Schiff bases derived from 2-amino-3-hydroxypyridine and different substituted salicylaldehydes have been synthesized. The compounds, with the general formula [Me_2Sn(2-OArCH=NC_5H_3NO)], where Ar = $-C_6H_3$(5-CH_3) [Me_2SnL^1], $-C_6H_3$(5-NO_2) [Me_2SnL^2], $-C_6H_2$(3,5-Cl_2) [Me_2SnL^3], and $-C_6H_2$(3,5-I_2) [Me_2SnL^4], were characterized by IR, NMR (^{1}H and ^{13}C), mass spectroscopy and elemental analysis. Me_2SnL^3 was also characterized by X-ray diffraction analysis and shows a fivefold C_2NO_2 coordination with distorted square pyramidal geometry. H_3C–Sn–CH_3 angles in the complexes were calculated using Lockhart's equations with the $^1J(^{117/119}Sn–^{13}C)$ and $^2J(^{117/119}Sn–^1H)$ values (from the ^{1}H-NMR and ^{13}C-NMR spectra). The *in vitro* antibacterial and antifungal activities of dimethyltin(IV) complexes were also investigated.

1. Introduction

An important class of organotin(IV) complexes are those derived from ligands containing nitrogen and oxygen donor atoms. Especially, organotin(IV) complexes of deprotonated Schiff bases are known [1–9]. Recently organotin(IV) compounds have received considerable attention because of their biological properties [10], particularly antitumour [11–16], antibacterial [17–21] and antifungal activity [20–22]. In addition to their biological activity, the organotin(IV) complexes have also found application in catalysts [23] and nonlinear optics [9,24].

Generally, tin atoms in complexes derived from ONO terdentate ligands are penta-coordinate with a trigonal bipyramidal (TBP) or square pyramidal (SP) geometry [3,4,6,19,24–28]. In these geometries, the metal center can act as a Lewis acid, which allows to increase its coordination number by addition of molecules having electron donating atoms (e.g. solvent molecules) [3,4,6,25–27], changing the geometry to distorted octahedral. For that reason, five-coordinate tin complexes frequently form Sn···O intermolecular bonds in the solid state, thus giving dimeric aggregates through the formation of a Sn_2O_2 four-membered ring [24,28,29].

As part of our investigation dealing with the study of dimethyltin(IV) species derived from Schiff base ligands, we describe herein the synthesis and structural analysis of derivatives containing terdentate ONO-donor Schiff base ligands (H_2L). The ligands are derived from four different salicylaldehyde and 2-amino-3-hydroxypyridine. The complexes have been synthesized under mild conditions from dimethyltin(IV) dichloride and H_2L in methanol in the presence of triethylamine, Fig. 1.

We have also investigated antibacterial and antifungal activities of these complexes, together with those of dimethyltin(IV) complexes which we synthesized and characterized in our previous studies [30–32].

2. Experimental

2.1. Analytical methods and physical measurements

All chemicals and reagents were of reagent-grade quality. Dimethyltin dichloride, 2-amino-3-hydroxypyridine, 5-methylsalicylaldehyde, 5-nitrosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 3,5-diiodosalicylaldehyde and solvents were purchased from Aldrich and used without further purification.

The ^{1}H-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. The infrared spectra

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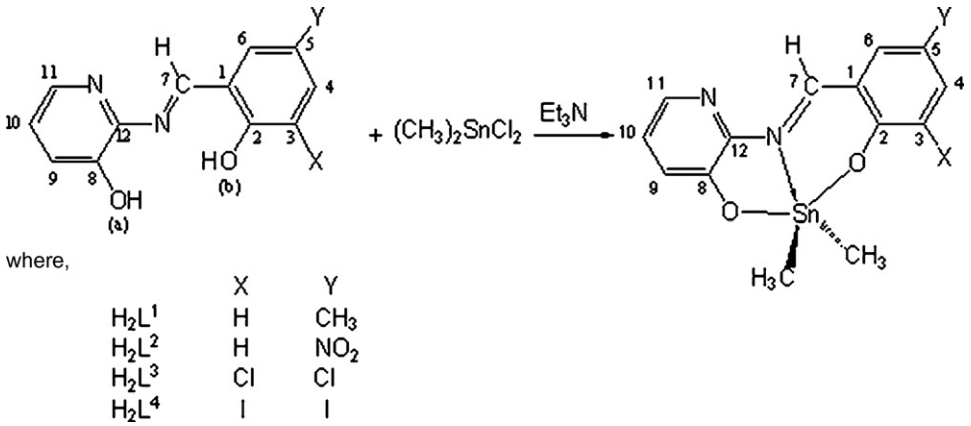

Fig. 1. Numbering and preparation of compounds.

were recorded on a Mattson-1000 FTIR spectrophotometer using KBr pellets, in the range of 4000–400 cm^{-1}. Bands were located by means of a microprocessor. ESI-mass spectra were recorded on a AGILENT 1100 MSD LC–MS spectrometer. Melting points were determined with in hot-stage Leica DM EP Polarizing Microscope System. Chemical analysis of C, H and N were determined with LECO CHNS-932 elemental analyzer. Intensity data for Me_2SnL^3 were measured at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo Kα (λ = 0.71073 Å) radiation and using the ω-2θ scan technique. Full-matrix least-squares refinement method was carried out on F^2 of the positional and anisotropic thermal parameters of the non-hydrogen atoms and of the positional parameters of the hydrogen atoms, which were assigned fixed isotropic thermal parameters. SHELXS-97 and SHELXL-97 [33] programs were used to solve and refine the structure. The molecular diagram and crystal structure showing the crystallographic unit cell were drawn with the program ORTEPIII [34]. A summary of crystal data and refinement results were given in Table 1.

Table 1
Crystal data and structure refinement parameters for $C_{14}H_{12}Cl_2N_2O_2Sn$.

Empirical formula	$C_{14}H_{12}Cl_2N_2O_2Sn$
Formula weight	429.88
Crystal system	Monoclinic
Space group	P 2_1/n
a = 9.6010(10) Å b = 15.861(3) Å c = 10.9800(10) Å	β = 113.825(7)°
Volume (Å^3)	1529.6(4)
Z	4
D_{calc} (g cm^{-3})	1.867
μ(Mo Kα) (mm^{-1})	0.27
T (K)	293(2)
Crystal description	Prism
Colour	Transparent orange
Crystal sizes	0.50 × 0.25 × 0.20
Radiation Mo Kα (λ, Å)	0.71073
θ_{min}–θ_{max} (°)	2.4–26.3
Absorption correction	Psi-scan
F(0 0 0)	840
Index rangers	$-10 \le h \le 11$, $-19 \le k \le 0$, $-13 \le l \le 0$
Reflections collected	3250
Number of refined parameters	194
Number of reflection used	3090
Observed data [$I > 2\sigma(I)$]	2608
R [$F^2 > 2\sigma(F^2)$]	0.027
R_w (F^2)	0.082
$w = 1/[\sigma^2(Fo^2) + (0.0617P)^2 + 0.4100P]$	Where $P = (Fo^2 + 2Fc^2)/3$
Goodness-of-fit on F^2	0.955
Largest diff. peak and hole (eÅ^{-3})	0.749, −0.845

2.2. Antimicrobial studies

2.2.1. Antibacterial activity

The dimethyltin(IV) complexes were screened for their antibacterial activities 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 [35]. All compounds were dissolved at a concentration of 200 mg/L in methanol. 0.5 McFarland suspension of each strain was swabbed on Mueller Hinton agar (Oxoid Limited, Hampshire, England). Paper discs with a diameter of 6 mm (Oxoid Limited, Hampshire, England) were saturated with 25 mL of a solution of test compounds and placed on the surface of the agar plates. After incubation at 37 °C for 24 h, inhibition zone diameters surrounding the each disc were measured and recorded in millimeter. Gentamicin (10 μg/disc) was used as a positive control disc for bacteria.

2.2.2. Antifungal activity

The *in vitro* antifungal activities of dimethyltin(IV) complexes were also evaluated against *Aspergillus niger*, *Aspergillus fumigatus*, *Aspergillus flavus*, and *Candida albicans* (clinical isolates). Each *Aspergillus* strain was inoculated onto potato dextrose agar (Oxoid Limited, Hampshire, England) 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, then inoculated to the agar surface. The agar plates were prepared by using RPMI-1640 medium (Sigma, St. Louis, USA) supplemented with 1.5% agar and 2% glucose and buffered to a pH of 7.0 with 0.165 mol/L MOPS (3-[N-morpholino] propanesulfonic acid) (Sigma, St. Louis, USA). For *C. albicans*, Mueller Hinton agar supplemented with 2% of glucose was used. Paper discs with a diameter of 6 mm (Oxoid Limited, Hampshire, England) were saturated with 25 mL of a solution of test compounds and placed on the surface of the agar plates. Inhibition zone diameters were measured following 24 h of incubation at 35 °C in ambient air. Fluconazol (25 μg/disc) was used as a positive control disc for fungi.

2.3. Preparation of the ligands

The Schiff bases were synthesized by mixing equimolar amounts of 2-amino-3-hydroxypyridine with the appropriate salicylaldehyde, both dissolved in methanol. The reaction mixture was

refluxed for 1 h and the precipitate thus formed upon cooling in an ice bath was filtered off. The solid residue was crystallized from methanol–dichloromethane (1/1, v/v) mixture. The description of the individual products was as follows:

N-(3-hydroxypyridine-2-yl)-5-methylsalicylideneimine, H_2L^1. Orange crystals, m.p.: 149–151 °C. Mass spectrum (ESI) {*m*/*z* [assignment] (%)}: 229 $[M+H]^+$ (100.0). Elemental anal.: found C, 68.30; H, 5.42; N, 12.33%. Calcd. for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27%. IR (cm^{-1}): 2690 br υ(O–H); 1623 s υ(C=N).

N-(3-hydroxypyridine-2-yl)-5-nitrosalicylideneimine, H_2L^2. Yellow crystals, m.p.: >300 °C. Mass spectrum (ESI) {*m*/*z* [assignment] (%)}: 260 $[M+H]^+$ (1.1). Elemental anal.: found C, 55.47; H, 3.55; N, 16.38%. Calcd. for $C_{12}H_9N_3O_4$: C, 55.60; H, 3.50; N, 16.21%. IR (cm^{-1}): 2997 br υ(O–H), 1612 vs. υ(C=N).

N-(3-hydroxypyridine-2-yl)-3,5-dichlorosalicylideneimine, H_2L^3. Orange crystals, m.p.: 233–235 °C. Mass spectrum (ESI) {*m*/*z* [assignment] (%)}: 283 $[M+H]^+$ (4.9). Elemental anal.: found C, 50.90; H, 2.58; N, 10.05%. Calcd. for $C_{12}H_8Cl_2N_2O_2$: C, 50.91; H, 2.85; N, 9.89%. IR (cm^{-1}): 3013 br υ(O–H), 1625 vs. υ(C=N).

N-(3-hydroxypyridine-2-yl)-3,5-diiodosalicylideneimine, H_2L^4. Orange crystals, m.p.: >300 °C. Mass spectrum (ESI) {*m*/*z* [assignment] (%)}: 467 $[M+H]^+$ (15.0). Elemental anal.: found C, 30.77; H, 1.81; N, 6.15%. Calcd. for $C_{12}H_8I_2N_2O_2$: C, 30.93; H, 1.73; N, 6.01%. IR (cm^{-1}): 3045 br υ(O–H), 1621 vs. υ(C=N).

2.4. Preparation of the complexes

All the complexes were similarly prepared from dimethyltin(IV) dichloride and the appropriate Schiff base ligands as follows. To a solution of Schiff base (2.0 mmol) in 15 mL dry methanol, a few drops of triethylamine were added and the resulting triethylammonium salt solution of the ligand was filtered to remove any insoluble impurities.

To this solution, a solution of $(CH_3)_2SnCl_2$ (2.0 mmol) in 15 mL of dry methanol was added slowly and heated (50–60 °C). The resulting mixture was cooled at room temperature overnight. The reddish-orange crystals were filtered off and recrystallized from butanol–dichloromethane (1/1, v/v) mixture. The description of the individual complexes was as follows:

[*N-(3-hydroxypyridine-2-yl)-5-methylsalicylideneiminato*]*dimethyltin(IV)*, Me_2SnL^1. Red crystals, m.p.: 182–184 °C. Mass spectrum (ESI) {*m*/*z* [assignment] (%)}: 377 $[M+H]^+$ (^{120}Sn) (97.1), 375 $[M+H]^+$ (^{118}Sn) (79.9), 373 $[M+H]^+$ (^{116}Sn) (52.1), 346 $[M-2CH_3]^+$ (^{120}Sn) (3.3), 344 $[M-2CH_3]^+$ (^{118}Sn) (3.0), 342 $[M-2CH_3]^+$ (^{116}Sn) (1.5). Elemental anal.: found C, 47.99; H, 4.39; N, 7.28%. Calcd. for $C_{15}H_{16}N_2O_2Sn$: C, 48.04; H, 4.30; N, 7.47%; IR (cm^{-1}): 1604 s υ(C=N), 621 υ(Sn–C), 525, 532 υ(Sn–O), 467 υ(Sn–N).

[*N-(3-hydroxypyridine-2-yl)-5-nitrosalicylideneiminato*]*dimethyltin(IV)*, Me_2SnL^2. Brown crystals, m.p.: 259–261 °C. Mass spectrum (ESI) {*m*/*z* [assignment] (%)}: 408 $[M+H]^+$ (^{120}Sn) (14.9), 406 $[M+H]^+$ (^{118}Sn) (14.8), 404 $[M+H]^+$ (^{116}Sn) (6.3). Elemental anal.: found C, 41.37; H, 3.35; N, 10.25%. Calcd. for $C_{14}H_{13}N_3O_4Sn$: C, 41.42; H, 3.23; N, 10.35%. IR (cm^{-1}): 1610 υ(C=N), 691 υ(Sn–C), 525, 544 υ(Sn–O), 471 υ(Sn–N).

[*N-(3-hydroxypyridine-2-yl)-3,5-dichlorosalicylideneiminato*]*dimethyltin(IV)*, Me_2SnL^3. Red crystals, m.p.: 226–228 °C. Mass spectrum (ESI) {*m*/*z* [assignment] (%)}: 431 $[M+H]^+$ (^{120}Sn) (56.8), 429 $[M+H]^+$ (^{118}Sn) (35.6), 427 $[M+H]^+$ (^{116}Sn) (12.7), 151 $[(CH_3)_2SnH]^+$ (^{120}Sn) (4.3), 149 $[(CH_3)_2SnH]^+$ (^{118}Sn) (3.7), 147 $[(CH_3)_2SnH]^+$ (^{116}Sn) (1.8), 135 $[CH_3Sn]^+$ (^{120}Sn) (3.1), 133 $[CH_3Sn]^+$ (^{118}Sn) (2.8), 131 $[CH_3Sn]^+$ (^{116}Sn) (1.8). Elemental anal.: found C, 39.25; H, 2.90; N, 6.45%. Calcd. for $C_{14}H_{12}Cl_2N_2O_2Sn$: C, 39.12; H, 2.81; N, 6.52%. IR (cm^{-1}): 1600 s υ(C=N), 689 υ(Sn–C), 581, 542 υ(Sn–O), 473 υ(Sn–N).

[*N-(3-hydroxypyridine-2-yl)-3,5-diiodosalicylideneiminato*]*dimethyltin(IV)*, Me_2SnL^4. Red crystals, m.p.: 216–218 °C. Mass spectrum

Table 2
^{1}H chemical shifts (δ in ppm) and coupling constants (J in Hz) of the ligands and dimethyltin(IV) complexes.

Compound	H(3)	H(4)	H(6)	H(7)	H(9)	H(10)	H(11)	OH(a)	OH(b)	CH_3	$SnMe_2$
H_2L^1	6.98 1H, d ^3J=8.4	7.25 1H, dd ^3J=8.4, ^4J=1.4	7.37 1H, d ^4J=1.4	9.40 1H, s	7.35 1H, dd ^3J=8.2, ^4J=1.3	7.20 1H, dd ^3J=8.2, ^4J=4.5	8.09 1H, dd ^3J=4.4, ^4J=1.3	9.55 1H, s	12.01 1H, s	2.41 3H, s	–
H_2L^2	6.97 1H, d ^3J=9.4	8.21 1H, dd ^3J=9.4, ^4J=2.9	8.85 1H, d ^4J=2.9	9.66 1H, s	7.43 1H, dd ^3J=8.1, ^4J=1.3	7.31 1H, dd ^3J=8.1, ^4J=4.5	8.04 1H, dd ^3J=4.5, ^4J=1.3	10.27 1H, s	15.2 1H, s	–	–
H_2L^3	–	7.69 1H, d ^4J=2.6	7.85 1H, d ^4J=2.6	9.48 1H, s	7.43 1H, dd ^3J=8.1, ^4J=1.5	7.29 1H, dd ^3J=8.1, ^4J=4.5	8.02 1H, dd ^3J=4.5, ^4J=1.5	10.13 1H, s	15.4 1H, s	–	–
H_2L^4	–	8.14 1H, d ^4J=1.5	8.10 1H, d ^4J=1.6	9.36 1H, s	7.43 1H, dd ^3J=8.0, ^4J=1.4	7.29 1H, dd ^3J=8.0, ^4J=4.6	8.02 1H, dd ^3J=4.6, ^4J=1.4	10.72 1H, s	15.70 1H, s	–	–
Me_2SnL^1	6.77 1H, d ^3J=8.4	7.22 1H, dd ^3J=8.4, ^4J=1.9	7.26 1H, d ^4J=2.0	9.48 1H, s	7.09 1H, dd ^3J=8.1, ^4J=1.5	7.12 1H, dd ^3J=8.1, ^4J=4.3	7.76 1H, dd ^3J=4.3, ^4J=1.5	–	–	2.28 3H, s	0.83 6H, s
Me_2SnL^2	6.80 1H, d ^3J=9.4	8.25 1H, dd ^3J=9.4 ^4J=2.6	8.45 1H, d ^4J=2.6	9.64 1H, s	7.14 1H, dd ^3J=8.0 ^4J=1.4	7.20 1H, dd ^3J=8.0 ^4J=4.4	7.82 1H, dd ^3J=4.4 ^4J=1.4	–	–	–	0.92 6H, s
Me_2SnL^3	–	7.59 1H, d ^4J=2.5	7.31 1H, d ^4J=2.5	9.49 1H, s	7.12 1H, dd ^3J=8.2, ^4J=1.4	7.17 1H, dd ^3J=8.2, ^4J=4.4	7.79 1H, dd ^3J=4.3, ^4J=1.4	–	–	–	0.90 6H, s
Me_2SnL^4	–	8.18 1H, d ^4J=2.2	7.64 1H, d ^4J=2.1	9.40 1H, s	7.12 1H, dd ^3J=8.2, ^4J=1.5	7.16 1H, dd ^3J=8.2, ^4J=4.4	7.72 1H, dd ^3J=4.4, ^4J=1.5	–	–	–	0.89 6H, s

Table 3
^{13}C-NMR spectral data (δ in ppm) of the ligands and their corresponding organotin(IV) complexes.

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	CH_3	$SnMe_2$
H_2L^1	118.72	159.16	117.01	135.46	128.91	133.81	164.94	146.46	123.78	124.16	140.40	145.78	20.35	–
H_2L^2	117.51	169.16	120.32	130.90	138.24	131.24	159.70	147.36	125.24	125.35	139.59	140.68	–	–
H_2L^3	118.97	160.44	121.04	133.15	123.89	130.24	158.06	147.26	124.68	124.25	138.87	142.65	–	–
H_2L^4	119.35	164.87	79.40	149.80	92.04	142.29	159.06	147.42	125.21	125.29	139.54	140.81	–	–
Me_2SnL^1	116.92	168.18	122.34	135.34	126.30	139.58	163.92	153.73	125.10	125.26	135.44	143.69	20.09	1.77
Me_2SnL^2	115.95	173.95	123.29	131.45	138.09	133.46	163.20	154.02	126.14	126.58	136.32	142.48	–	2.43
Me_2SnL^3	118.07	162.92	120.55	136.25	127.37	132.97	162.74	154.12	125.94	126.28	136.04	142.83	–	2.40
Me_2SnL^4	118.36	166.18	95.74	152.57	99.54	144.38	162.44	154.09	125.88	126.20	136.08	142.83	–	2.42

(ESI) {*m*/*z* [assignment] (%)}: 615 $[M+H]^+$ (^{120}Sn) (61.7), 613 $[M+H]^+$ (^{118}Sn) (49.8), 611 $[M+H]^+$ (^{116}Sn) (28.3). Elemental anal.: found C, 27.36; H, 2.10; N, 4.67%. Calcd. for $C_{14}H_{12}I_2N_2O_2Sn$: C, 27.44; H, 1.97; N, 4.57%. IR (cm^{-1}): 1585 s υ(C=N), 677 υ(Sn–C), 570 υ(Sn–O), 465 υ(Sn–N).

3. Results and discussions

In the present work, we report the synthesis, characterization, antibacterial and antifungal activities of R_2SnL, where R = Me, L = deprotonated Schiff bases derived from substituted salicylaldehydes with 2-amino-3-hydroxypyridine. Schiff bases and their dimethyltin(IV) complexes were characterized by their elemental analysis, ^{1}H, ^{13}C-NMR, IR and mass spectral data.

3.1. NMR spectra

Because of the low solubility in $CDCl_3$, the NMR spectra of the Schiff bases (except H_2L^1) were made in deuterated DMSO. The NMR spectra of the organotin(IV) complexes were recorded in $CDCl_3$. 2D COSY homonuclear, HETCOR and HMBC heteronuclear correlation techniques were made use of for signal assignments. The ^{1}H-NMR and ^{13}C-NMR data for the ligands and their tin(IV) complexes were summarized in Tables 2 and 3.

In the ^{1}H-NMR spectra of the ligands, the signals at 9.55–10.72 ppm [$(OH)_a$ proton on the pyridine moiety] and 12.01–15.70 ppm [$(OH)_b$ proton on the salicylaldehyde moiety] disappeared in the ^{1}H-NMR spectra of the corresponding Sn(IV) complexes, indicating the engagement of phenolic O atoms in complexations. The ^{1}H-NMR spectra of the ligands show a single signal for H-7 that appears between 9.36 and 9.66 ppm, as well as the corresponding signals for the iminic salicylidene moiety [15,18,19,36]. The H-7 signal of tin(IV) complexes appear in the range of 9.40–9.64 ppm. The $^3J(^{117/119}Sn–^1H)$ coupling (48.6–50.5 Hz) due to NMR-active Sn isotopes is visible and this is a strong indication to the ligation of azomethine nitrogen to Sn atom. The extent of coupling is comparable with literature values [4,18,29]. For the ligands and complexes, the signals of H-4 and H-6 protons (for H_2L^3, H_2L^4 and their complexes) are confirmed by two-dimensional heteronuclear-correlated NMR technique (2D ^{13}C–^{1}H HMBC) in addition to 2D ^{1}H–^{1}H COSY experiments. Other protons in the phenyl rings are found in their normal δ range [37–39]. The spectra of the complexes display additional signals due to methyl protons ($(CH_3)_2$Sn moiety) that appear at 0.83–0.92 ppm range. The two methyl-group protons appear to be equivalent and again, two-bond ^{1}H–^{117}Sn and ^{1}H–^{119}Sn couplings (77.6–86.0 Hz) are observable. These values are typical of the five-coordinated tin(IV) species.

^{13}C-NMR spectral data also support the authenticity of the proposed structures. The considerable shifts in the positions of carbon atoms adjacent to the imine nitrogen (C-7) and phenolic/pyridilic oxygen (C-2, C-8) support the proposed coordination 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 two oxygen atoms to the central metal atom. The $^1J(^{117/119}Sn–^{13}C)$ couplings (629.6–658.6 Hz) are clearly visible. The magnitude of the coupling constants agree well with those previously reported for analogous five-coordinate derivatives [4,43]. The $^2J(^{117/119}Sn–^{13}C)$ couplings were not observed in the complexes, as is the case for similar structures [4].

The C–Sn–C angles were calculated using Lockhart's equation $\{\theta(Me–Sn–Me) = 0.0161 \times [^2J(^{117/119}Sn–^1H)]^2 - 1.32 \times [^2J(^{117/119}Sn–^1H)] + 133.4\}$ with known $^2J(^{117/119}Sn–^1H)$ values as well as with the equation $\{^1J(^{117/119}Sn–^{13}C) = 10.7\theta - 778\}$ by inserting $^1J(^{117/119}Sn–^{13}C)$ values [40,41]. The results of the calculation obtained by $^2J(^{117/119}Sn–^1H)$ values for Me_2SnL^3 (139.0°), was closer to the true value [141.28(18)°], compared to the estimated angle based on $^1J(^{117/119}Sn,^{13}C)$ data (134.3°). Calculated values on the basis of the Lockhart's equations and a sample X-ray diffraction value for Me_2SnL^3 are displayed in Table 4.

3.2. IR spectra

Selected IR data for all compounds are reported in Section 2. The differences is obvious rather than remarkable between the IR spectra of the ligands and those of dimethyltin(IV) complexes is that the stretching vibration bands of the phenolic and pyridilic O–H groups disappear from the spectra of the complexes. This is assigned to deprotonation of the phenolic and pyridilic oxygen atoms of the ligand upon complexation with the tin atom. This was also confirmed by the appearances of a band at 570–525 cm^{-1} due to Sn–O stretching vibration.

In the complexes the υ(C=N) band, occurring between 1610 and 1585 cm^{-1}, is considerably shifted towards lower frequencies with respect to that of the free Schiff bases (1625–1612 cm^{-1}), confirming the coordination of the azomethine nitrogen to the organotin moiety. Also the Sn–C and Sn–N bands were observed at 691–621

Table 4
The $^3J(^{117/119}Sn–^1H)$, $^2J(^{117/119}Sn–^1H)$, and $^1J(^{117/119}Sn–^{13}C)$ values (Hz) and the Me–Sn–Me angles of the dimethyltin complexes.

Compound	^3J(Sn–H) CH=N	^2J(Sn–H) Me_2Sn	θ(Me–Sn–Me)[a]	^1J(Sn–C) Me_2Sn	θ(Me–Sn–Me)[b]	θ(Me–Sn–Me)[c]
Me_2SnL^1	48.6	78.4	128.9°	629.6	131.6°	–
Me_2SnL^2	49.2	77.6	127.9°	640.0	132.5°	–
Me_2SnL^3	49.6	86.0	139.0°	658.6	134.3°	141.28°
Me_2SnL^4	50.5	79.2	129.9°	656.6	134.1°	–

[a] Calculated from $\theta(Me–Sn–Me) = 0.0161 \times [^2J(^{117/119}Sn–^1H)]^2 - 1.32 \times [^2J(^{117/119}Sn–^1H)] + 133.4$.
[b] Calculated from $^1J^{117/119}Sn–^{13}C = 10.7\theta(Me–Sn–Me) - 778$.
[c] From X-ray data.

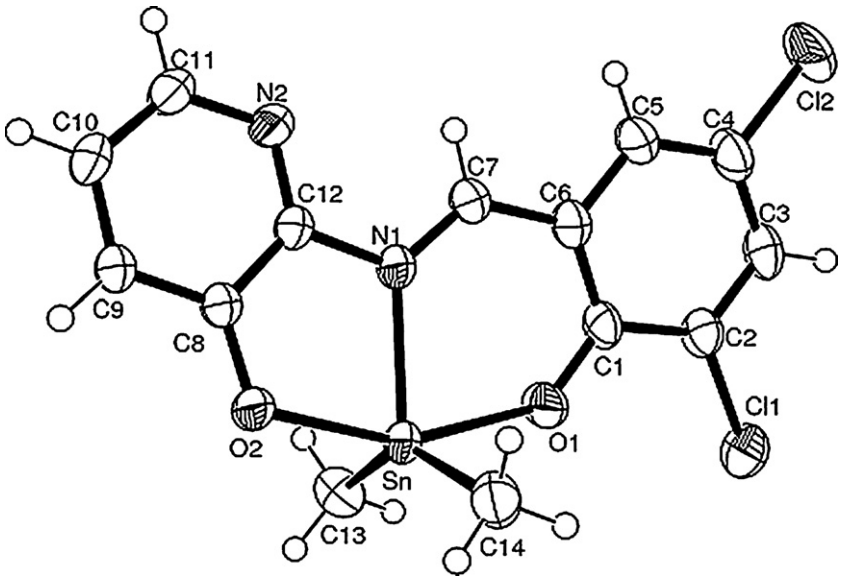

Fig. 2. The molecular structure of Me_2SnL^3 showing the atom numbering scheme. The displacement ellipsoids are plotted at the 50% probability level.

and 473–465 cm^{-1} correspondingly [15]. These findings clearly suggest the coordination of imino nitrogen, deprotonated phenolic and pyridilic oxygen donor sites to the central tin atom and therefore terdentate dibasic nature of the coordinated ligand may be accepted.

3.3. Mass spectra

The Schiff bases and their dimethyltin(IV) complexes were also characterized by mass spectrometry using electrospray ionization technique. The $[M+H]^+$ ion peaks of the complexes are given in Section 2. 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 in agreement with the theoretical relative abundances. As an example, the $[M+H]^+$ ion peak with the characteristic tin isotopes of Me_2SnL^1 was measured (theoretical relative abundances in parentheses): *m*/*z* 373, 53.6% (43.1%); 374, 33.1% (29.8%); 375, 82.3% (75.5%); 376, 42.4% (37.6%); 377, 100% (100%); 378, 20.8% (16.6%); 379, 16.7% (15.0%); 380, 3.0% (2.2%); 381, 18.8% (16.5%); 382, 4.8% (2.7%). The fragmentation pattern is in agreement with the literature reports [5,8,11].

3.4. Crystal structure of Me_2SnL^3

The molecular structure and the atom numbering scheme for compound [N-(3-hydroxypyridine-2-yl)-3,5-dichlorosalicylideneiminato]dimethyltin(IV), Me_2SnL^3 is shown in Fig. 2. A list of the bond lengths and angles for the complex is given in Table 5.

The coordination around tin in the complex is defined by two carbon atoms from methyl groups, two oxygen atoms forming a bridge to phenyl and pyridyl rings through the tin atom and imino nitrogen atom found in the ligand which is in phenol-imine form. The metal atom is in a distorted square pyramidal geometry. To quantify the extent of distortion from the ideal square pyramidal geometry towards the trigonal bipyramidal, the trigonal index, τ, was computed [7,42,43]. The τ value is defined as $\tau = (\beta - \alpha)/60$, α and β being the two largest donor–metal–donor angles in the five-coordinated environment. For a perfectly square pyramidal geometry, τ should be equal to 0, while it becomes unity for a perfect trigonal bipyramidal geometry. For the complex Me_2SnL^3, τ value was found 0.25. Thus for compound, square pyramidal geometry predominates over trigonal bipyramidal geometry. In the complex, the two carbon atoms and two oxygen atoms constitute the square base and the imino nitrogen atom occupies the apical position. The following bond angles may be given as an evidence of distorted square-pyramidal conformation. O1–Sn–O2: 156.16(8); O1–Sn–N1: 80.17(9); O2–Sn–N1: 75.99(9); N1–Sn–C13: 109.46(14); N1–Sn–C14: 108.51(14); C13–Sn–C14: 141.28(18); O1–Sn–C14: 89.77(14); O1–Sn–C13: 89.39(14); O2–Sn–C13: 97.96(14); O2–Sn–C14: 98.21(13). The distortion is mainly due

Table 5
Selected bond lengths and angles (Å, °).

Sn–O1	2.179(2)	O1–C1	1.293(4)
Sn–O2	2.131(2)	O2–C8	1.333(4)
Sn–N1	2.213(3)	N1–C7	1.295(4)
Sn–C13	2.103(4)	N1–C12	1.425(4)
Sn–C14	2.095(3)	C6–C7	1.430(5)
O1–Sn–O2	156.16(8)	N1–Sn–C13	109.46(14)
O1–Sn–N1	80.17(9)	N1–Sn–C14	108.51(14)
N1–Sn–O2	75.99(9)	C13–Sn–C14	141.28(18)
O1–Sn–C13	89.39(14)	Sn–O1–C1	132.3(2)
O1–Sn–C14	89.77(14)	Sn–O2–C8	115.3(2)
O2–Sn–C13	97.96(14)	Sn–N1–C7	129.1(2)
O2–Sn–C14	98.21(13)		

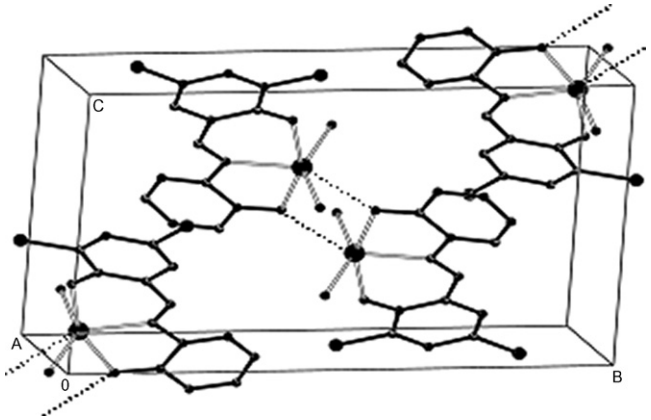

Fig. 3. The packing diagram of Me_2SnL^3.

Table 6
Antibacterial and antifungal activities of compounds.

Microorganism	Inhibition zone (mm)									
	Me_2SnL^1	Me_2SnL^2	Me_2SnL^3	Me_2SnL^4	Me_2SnL^{5a}	Me_2SnL^{6a}	Me_2SnL^{7a}	Me_2SnL^{8a}	G	F
S. aureus ATCC 25923	16	22	32	–	17	–	18	–	22	
S. epidermidis ATCC 12228	12	22	24	–	14	–	12	–	25	
E. faecalis ATCC 29212	16	–	15	–	15	–	14	–	14	
E. coli ATCC 25922	16	–	–	–	14	–	16	–	19	
E. coli ATCC 35218	15	–	–	–	11	–	15	–	–	
E. cloacae ATCC 23355	14	–	–	–	16	–	16	–	25	
S. marcescens ATCC 8100	10	–	–	–	11	–	13	–	24	
P. aeruginosa ATCC 27853	–	–	–	–	–	–	–	–	18	
A. niger	12	–	15	–	10	–	–	–	–	–
A. flavus	13	–	20	–	12	–	–	–	–	–
A. fumigatus	12	–	20	–	12	–	–	–	–	–
C. albicans	–	–	–	–	–	–	–	–	–	25

G: gentamicin; F: fluconazol.
[a] Me_2SnL^5, [N-(3-hydroxypyridine-2-yl)-salicylideneiminato]dimethyltin(IV); Me_2SnL^6, [N-(3-hydroxypyridine-2-yl)-5-bromosalicylideneiminato]dimethyltin(IV); Me_2SnL^7, [N-(3-hydroxypyridine-2-yl)-5-hydroxysalicylideneiminato]dimethyltin(IV); Me_2SnL^8, [N-(3-hydroxypyridine-2-yl)-5-chlorosalicylideneiminato]dimethyltin(IV).

to the rigidity of chelate rings, together with the large covalent radius of tin(IV). These geometric results are in agreement with the results of similar tin(IV) complexes [3,4,30,31,44].

Five- and six-membered rings form upon chelation of the Sn atom to the ligands. The organic parts of the five-membered and six-membered rings are nearly planar (the torsion angles, O2–C8–C13–N1: −0.6(5)°; C1–C6–C7–N1: −5.3(6)°; O1–C1–C6–C7: −1.7(6)°) but the tin atom is out of these planes as indicated by the torsion angles, Sn–O2–C8–C12: 10.6(4)°; N1–Sn–O2–C8: −11.4(2)°; Sn–O1–C1–C6: 20.4(6); Sn–N1–C7–C6: −5.9(6).

From Fig. 3 it can be seen that in the compound the tin atom environment is six-coordinate in a centrosymmetric arrangement leading to a Sn_2O_2 core connected by the Sn–O bond, and the Sn···O2 bond distance of 2.839(2) Å is markedly greater than the sum of the covalent radii for Sn–O (2.13 Å), but is considerably less than the sum of the Van der Waals radii (3.70 Å). The O···Sn bonding occurs with the oxygen atom at the five-membered ring. It is shown that the O2 atom makes weak interactions with the Sn atom of the second complex. Two molecules form a weak-bridged dimer with weak contacts of Sn···O bonding. The large C–Sn–C bond angle (141.28(18)°) allows for the formation of Sn···O intermolecular interaction, giving rise to a dimeric organization. The dimeric assembly occurs via the formation of a Sn_2O_2 four-membered ring. This fact modifies the coordination around the tin atom which show a distorted octahedral geometry with Sn···O interaction distances [4,19,24,28,29,45,46].

3.5. Biological activity

In the literature, the organotin(IV) complexes of Schiff bases containing pyridine moiety were tested on different microbial species including bacteria, yeast and molds. Some of the complexes showed appreciable antimicrobial activities and lack of genotoxicity [47].

In this work, the antibacterial and antifungal activities of the synthesized dimethyltin(IV) complexes and the others which were characterized our previous studies [30–32] are listed in Table 6.

The results show that Me_2SnL^1, Me_2SnL^5 and Me_2SnL^7 were found effective against all bacterial strains except *P. aeruginasa* ATCC 27853 while, Me_2SnL^3 was only effective against Gram positive bacteria. Compound Me_2SnL^3 also showed higher activity against *S. aureus* ATCC 25923 than the standard drug gentamisin. Me_2SnL^4, Me_2SnL^6 and Me_2SnL^8 were found to have no activity against the all tested strains. On the other hand Me_2SnL^2 showed antibacterial activity only against *S. aureus* ATCC 25923 and *S. epidermidis* ATCC 12228. The results of the antifungal disc diffusion susceptibilities tests revealed that Me_2SnL^1, Me_2SnL^3 and Me_2SnL^5 had antifungal activity against all *Aspergillus* spp., whereas no activity was observed against *C. albicans*. The change of a substituent in the ligand may lead to enhanced antibacterial and antifungal activities of these dimethyltin(IV) complexes. These antibacterial and antifungal activity results are in accordance with those found for other similar dimethyltin(IV) complexes [20,48].

4. Conclusion

In summary, four new dimethyltin(IV) compounds of N-(3-hydroxypyridine-2-yl)-salicylideneimine derivatives have been synthesized and characterized by IR, NMR, mass spectroscopy and elemental analysis. The crystal structure of Me_2SnL^3 has also been determined by X-ray single crystal diffraction analyses. It has found that the tin atoms are five-coordinated in a square pyramidal geometry. The monomeric Me_2SnL^3 units are linked into dimers by weak intermolecular interactions with Sn···O bonding. The *in vitro* antibacterial and antifungal tests of the synthesized dimethyltin complexes have been carried out. Me_2SnL^3 showed higher activity against *S. aureus* ATCC 25923 than the standard drug gentamisin. The results of antifungal screening, indicated that Me_2SnL^3 also showed more activity against all *Aspergillus* spp. than the other complexes.

5. Supplementary material

More details of the crystal structure determinations have been deposited with the Cambridge Crystallographic Data Centre with the deposition number: CCDC 674907.

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