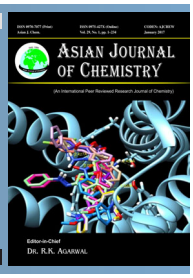
Asian Journal of Chemistry; Vol. 29, No. 3 (2017), 669-674

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20303



Synthesis, Characterization and Antimicrobial Activities of Organotin(IV) Complexes of Schiff Bases Derived from 2,3-Diaminopyridine

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Received: 12 September 2016; *Accepted*: 14 November 2016; *Published online*: 30 December 2016; AJC-18224

A series of hexa-coordinated organotin(IV) complexes of type R_2SnL_n [R = Ph, Bu, Et, Me] has been synthesized from Schiff base ligands (H_2L_{1-3}) derived from 2,3-diaminopyridine and 2-hydroxy-1-naphthaldehyde, salicylaldehyde, 5-bromosalicylaldehyde (where H_2L_1 = 2,2'-(1E,1'E)-(pyridine-2,3-diyl*bis*(azan-1-yl-1-ylidene))*bis*(methan-1-yl-1-ylidene)dinaphthalen-1-ol, H_2L_2 = 2,2'-(1E,1'E)-(pyridine-2,3-diyl*bis*(azan-1-yl-1-ylidene))*bis*(methan-1-yl-1-ylidene)diphenol, H_2L_3 = 2,2'-(1E,1'E)-(pyridine-2,3-diyl*bis*(azan-1-yl-1-ylidene))*bis*(methan-1-yl-1-ylidene)*bis*(4-bromophenol) under inert atmosphere in 1:2 molar ratio. The bonding behaviour, composition and the structural assignment of the synthesized organotin complexes have been characterized by the spectroscopic analysis (^{1}H, ^{13}C and ^{119}Sn NMR, FT-IR, electronic spectra) and elemental analysis. The coordination of the synthesized complexes has been anticipated as hexa-coordinated with the tin atom with ONNO donor system and the ligands are coordinated to the tin atom as tetradentate. The prepared Schiff base ligands and their organotin complexes are evaluated for the antibacterial and antifungal activities against Gram-positive, Gram-negative bacteria and fungi. The complexes show more biological potency in the antimicrobial activities as compared to the ligands.

Keywords: Schiff base ligands, Organotin complexes, Antimicrobial activities.

INTRODUCTION

The organotin compounds containing nitrogen and oxygen donor atoms contribute a noteworthy task commercially [1], medically [2], biologically [3] representing their applications in the coordination and bioinorganic chemistry [4] with both chemical and biological properties. The organotin complexes with Schiff bases are extensively premeditated for the biological applications as antimalarial, anticancer, antitumour [5] and antibacterial [6]. The Schiff bases containing biologically dynamic donor atoms are playing imperative position owing to the better solubility power and the superficial synthesis [7] depending upon the structural variety, type, number and arrangement [8] of donor atoms attached to the tin metal [9]. The Schiff bases have a variety of analytical, clinical applications [10] and furthermore occupy an imperative and substantial role in synthesis, design and biological activity of unsymmetrical atmosphere of Schiff base ligands exhibiting inconsistent stoichiometry and diverse modes of coordination [11]. The pyridine containing ligands have been extensively considered in the coordination chemistry with the metals due to a distinctive position in the synthesis of the compounds with biological potency. On viewing the biological significance, structural variety, chemical properties and industrial importance [12], it has been worthwhile considered to synthesize the organotin compounds with 2,3-diaminopyridine and to evaluate their biological features. As a part of present research work, we are here reporting the synthesis, spectral and biological studies of organotin(IV) complexes of Schiff bases derived from 2,3-diaminopyridine and salicylaldehyde and its derivatives.

EXPERIMENTAL

The reagents and the solvents used were purchased from Sigma Aldrich, used as received without any extra purification and were distilled and dried by the standard ways of purification and thin layer chromatography (TLC) pre-coated with silica gel was used for checking purity of the compounds. The reactions were carried out under anhydrous conditions and thus all the chemicals used and glass equipments have been placed in the moisture free surroundings. The tin estimation was anticipated gravimetrically as SnO_2. The infrared spectra were recorded using KBr pellets having wavelength range with 4000-400 cm^{-1} on Shimadzu IR affinity-I 8000 FT-IR spectro-

meter. The NMR spectra of the compounds were recorded in $CDCl_3$ and DMSO-d_6 on Bruker Avance II 400 MHz NMR spectroscope. Tetra methyl silane (TMS) was used as internal reference and the chemical shift values were reported as parts per million (ppm). The elemental analysis (C, H and N) were analyzed on Perkin-Elmer 2400 instrument (Waltham, Massachusetts).

Preparation of Schiff base ligands (1-3): To the solution of 2,3-diaminopyridine (1 mmol) and salicylaldehyde (2 mmol) in methanol (20 mL), acetic acid (2-3 drops) was added. The reaction mixture in the ratio 1:2 was stirred and refluxed for about 5-6 h at room temperature (TLC, hexane: ethyl acetate, 2:1). The solid product obtained was washed, filtered and recrystallized. A similar procedure was used for the preparation of other Schiff base ligands.

Preparation of organotin(IV) complexes (4-15): To the mixture of Schiff base ligand (1 mmol) in dried methanol, a small piece of sodium metal (44 mg) was added and then this reaction mixture was constantly refluxed for about 2-3 h. To the reaction mixture, the corresponding dialkyltindichloride (R_2SnCl_2) was added and then the reaction mixture was refluxed for 5-6 h. The sticky product was obtained and the stickiness was removed by dry hexane. The solid was collected and dried over vacuum. A similar procedure was used for preparation of other complexes.

2,2'-(1E,1'E)-(Pyridine-2,3-diyl*bis*(azan-1-yl-1-ylidene))*bis*(methan-1-yl-1-ylidene)dinaphthalen-1-ol (1): Yield: 84 %. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.86-6.88 (d, 1H, ArH), 7.22-7.24 (m, 1H, ArH), 7.33-7.35 (d, 1H, ArH), 7.39-7.43 (m, 2H, ArH), 7.53-7.62 (m, 2H, ArH), 7.70-7.71 (m, 1H, ArH), 7.84-7.87 (m, 2H, ArH), 8.01-8.04 (m, 1H, ArH), 8.16-8.18 (m, 1H, ArH), 8.20-8.24 (m, 1H, ArH), 8.43-8.45 (m, 1H, ArH), 8.61-8.63 (m, 1H, ArH), 9.84 (s, 1H, CH=N), 10.01 (s, 1H, CH=N), 14.39 (s, 1H, OH), 15.18 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 118.63, 119.23, 121.48, 124.05, 124.55, 127.32, 127.80, 129.17, 129.53, 132.92, 139.22 (ArC), 160. 13, 160.58 (C-OH), 164.89, 164.93 (C=N). IR (KBr, ν_{max}, cm^{-1}): 3200 (O-H), 1601 (C=N). Anal. calcd. for $C_{27}H_{19}N_3O_2$: (m.w. 417.46), (C, 77.68; H, 4.59; O, 7.67; N, 10.07) %. Found: (C, 77.32; H, 4.21; O, 7.34; N, 9.86) %.

2,2'-(1E,1'E)-(Pyridine-2,3-diyl*bis*(azan-1-yl-1-ylidene))-*bis*(methan-1-yl-1-ylidene)diphenol (2): Yield: 81 %. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.84-6.86 (d, 1H, ArH), 7.21-7.23 (m, 1H, ArH), 7.35-7.37 (d, 1H, ArH), 7.41-7.45 (m, 2H, ArH), 7.57-7.64 (m, 2H, ArH), 7.73-7.75 (m, 1H, ArH), 7.82-7.85 (m, 1H, ArH), 8.03-8.07 (m, 1H, ArH), 8.18-8.20 (m, 1H, ArH), 9.86 (s, 1H, CH=N), 10.03 (s, 1H, CH=N), 14.34 (s, 1H, OH), 15.20 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 118.74, 119.27, 121.56, 124.12, 124.59, 127.38, 127.85, 129.57, 132.95, 139.25 (ArC), 160.18, 160.76 (C-OH), 164.72, 164.87 (C=N). IR (KBr, ν_{max}, cm^{-1}): 3234 (O-H), 1610 (C=N). Anal. calcd. for $C_{19}H_{15}N_3O_2$: (m.w. 317.34), (C, 71.91; H, 4.76; O, 10.08; N, 13.24) %. Found: (C, 71.63; H, 4.42; O, 9.85; N, 12.95) %.

2,2'-(1E,1'E)-(Pyridine-2,3-diyl*bis*(azan-1-yl-1-ylidene))*bis*(methan-1-yl-1-ylidene)*bis*(4-bromophenol) (3): Yield: 82 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 6.81-6.83 (d, 1H, ArH), 7.18-7.20 (m, 1H, ArH), 7.31-7.33 (d, 1H, ArH), 7.42-7.44 (m, 1H, ArH), 7.55-7.57 (m, 1H, ArH), 7.71-7.73 (m, 1H, ArH), 7.85-7.88 (m, 1H, ArH), 8.01-8.04 (m, 1H, ArH), 8.15-8.17 (m, 1H, ArH), 9.84 (s, 1H, CH=N), 10.02 (s, 1H, CH=N), 14.31 (s, 1H, OH), 15.19 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 112.54, 118.74, 119.24, 121.53, 124.09, 124.51, 127.81, 129.52, 132.91, 139.22 (ArC), 160. 21, 160.71 (C-OH), 164.76, 164.92 (C=N). IR (KBr, ν_{max}, cm^{-1}): 3217 (O-H), 1609 (C=N). Anal. calcd. for $C_{19}H_{13}Br_2N_3O_2$: (m.w. 475.13), (C, 48.03; H, 2.76; O, 6.73; N, 8.84; Br, 33.63) %. Found: (C, 47.82; H, 2.41; O, 6.45; N, 8.51; Br, 33.32) %.

(3E,9E)-18,18-Diphenyldinaphtho[1,2-d:2',1'-l]-pyrido[3,2-h][1,3,7,10,2] dioxadiazastannacyclotridecine (4): Yield: 78 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 6.72 (m, 1H, ArH), 6.74-6.75 (d, 1H, ArH), 6.92-6.94 (m, 1H, ArH), 7.04-7.06 (d, 1H, ArH), 7.79 (m, 2H, ArH), 7.89-7.98 (m, 10H, ArH), 8.00 (m, 2H, ArH), 8.03 (m, 1H, ArH), 8.05 (m, 1H, ArH), 8.06 (m, 1H, ArH), 8.07 (m, 2H, ArH), 8.13 (m, 1H, ArH), 8.14 (m, 1H, ArH), 8.15 (m, 1H, ArH), 8.92 (m, 1H, ArH), 8.94 (m, 1H, ArH), 9.94 (s, 1H, CH=N), 10.58 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 112.31, 118.58, 119.17, 121.41, 124.01, 124.53, 126.65, 127.34, 127.85, 129.23, 129.57, 129.94, 130.27, 132.93, 139.22, 150.12 (ArC), 160.43, 161.18 (C-OH), 165.04, 165.18 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -556.03. IR (KBr, ν_{max}, cm^{-1}): 1601 (C=N), 671 (Sn-C), 550 (Sn-O), 437 (Sn→N). Anal. calcd. for $C_{39}H_{27}N_3O_2Sn$: (m.w. 688.36), (C, 68.05; H, 3.95; O, 4.65; N, 6.10; Sn, 17.25) %. Found: (C, 67.83; H, 3.62; O, 4.31; N, 5.87; Sn, 17.03) %.

(3E,9E)-18,18-Dibutyldinaphtho[1,2-d:2',1'-l]pyrido-[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (5): Yield: 75 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.72-0.75 (t, 6H, H-4), 1.13-1.19 (m, 4H, H-3), 1.61-1.64 (m, 4H, H-2), 1.85-1.88 (t, 4H, H-1), 6.75 (m, 1H, ArH), 6.72-6.74 (d, 1H, ArH), 6.90-6.92 (m, 1H, ArH), 7.01-7.03 (d, 1H, ArH), 7.76 (m, 2H, ArH), 8.01 (m, 2H, ArH), 8.05 (m, 1H, ArH), 8.07 (m, 1H, ArH), 8.09 (m, 1H, ArH), 8.11 (m, 2H, ArH), 8.16 (m, 1H, ArH), 8.17 (m, 1H, ArH), 8.19 (m, 1H, ArH), 8.97 (m, 1H, ArH), 8.99 (m, 1H, ArH), 9.98 (s, 1H, CH=N), 10.59 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 12.43, 24.12, 31.45, 42.12, 104.32, 112.27, 118.41, 119.06, 121.37, 124.05, 124.56, 126.62, 127.32, 127.84, 129.28, 129.53, 132.92, 139.25, 150.17 (ArC), 160.54, 161.26 (C-OH), 165.02, 165.13 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -382.18. IR (KBr, ν_{max}, cm^{-1}): 1594 (C=N), 677 (Sn-C), 556 (Sn-O), 439 (Sn→N). Anal. calcd. for $C_{35}H_{35}N_3O_2Sn$: (m.w. 648.38), (C, 64.83; H, 5.44; O, 4.94; N, 6.48; Sn, 18.31) %. Found: (C, 63.52; H, 5.07; O, 4.61; N, 6.14; Sn, 18.03) %.

(3E,9E)-18,18-Diethyldinaphtho[1,2-d:2',1'-l]pyrido-[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (6): Yield: 78 %. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.94 (t, 6H, H-1'), 1.65 (q, 4H, H-2'), 6.73 (m, 1H, ArH), 6.81-6.82 (d, 1H, ArH), 6.93-6.95 (m, 1H, ArH), 7.00-7.02 (d, 1H, ArH), 7.74 (m, 2H, ArH), 7.79 (m, 2H, ArH), 8.02 (m, 1H, ArH), 8.04 (m, 1H, ArH), 8.07 (m, 1H, ArH), 8.10 (m, 2H, ArH), 8.15 (m, 1H, ArH), 8.17 (m, 1H, ArH), 8.19 (m, 1H, ArH), 8.92 (m, 1H, ArH), 8.99 (m, 1H, ArH), 9.96 (s, 1H, CH=N), 10.55 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 9.05, 14.06, 117.79, 118.53, 121.24, 124.19, 127.28, 127.56,

128.39, 128.72, 129.21, 131.36, 132.35, 136.88, 139.25, 150.13 (ArC), 160.59, 161.29 (C-OH), 165.01, 165.18 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -274.11. IR (KBr, ν_{max}, cm^{-1}): 1600 (C=N), 678 (Sn-C), 552 (Sn-O), 436 (Sn→N). Anal. calcd. for $C_{31}H_{27}N_3O_2Sn$: (m.w. 592.27), (C, 62.86; H, 4.59; O, 5.40; N, 7.09; Sn, 20.04) %. Found: (C, 62.52; H, 4.21; O, 5.16; N, 6.83; Sn, 19.86) %.

(3E,9E)-18,18-Dimethyldinaphtho[1,2-d:2',1'-l]pyrido-[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (7): Yield: 74 %. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.92 (s, 6H, H-1"), 6.79 (m, 1H, ArH), 6.87-6.89 (d, 1H, ArH), 6.91-6.93 (m, 1H, ArH), 7.03-7.05 (d, 1H, ArH), 7.78 (m, 2H, ArH), 7.83 (m, 2H, ArH), 7.99 (m, 1H, ArH), 8.02 (m, 1H, ArH), 8.04 (m, 1H, ArH), 8.07 (m, 2H, ArH), 8.13 (m, 1H, ArH), 8.15 (m, 1H, ArH), 8.12 (m, 1H, ArH), 8.87 (m, 1H, ArH), 8.95 (m, 1H, ArH), 9.92 (s, 1H, CH=N), 10.54 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 9.11, 117.63, 118.48, 121.27, 124.16, 127.25, 127.52, 128.34, 128.65, 129.15, 131.29, 132.31, 136.82, 139.28, 150.13 (ArC), 160.45, 161.22 (C-OH), 165.05, 165.16 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -147.23. IR (KBr, ν_{max}, cm^{-1}): 1597 (C=N), 674 (Sn-C), 554 (Sn-O), 439 (Sn→N). Anal. calcd. for $C_{29}H_{23}N_3O_2Sn$: (m.w. 564.22), (C, 61.73; H, 4.11; O, 5.67; N, 7.45; Sn, 21.04) %. Found: (C, 61.49; H, 3.98; O, 5.32; N, 7.18; Sn, 20.87) %.

(5E,11E)-18,18-Diphenyldibenzo[d,l]pyrido[3,2-h][1,3,7,10,2] dioxadiazastannacyclotridecine (8): Yield: 79 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 6.84-6.86 (d, 1H, ArH), 7.21-7.23 (m, 1H, ArH), 7.35-7.37 (d, 1H, ArH), 7.41-7.45 (m, 2H, ArH), 7.51-7.63 (m, 10H, ArH), 7.67-7.69 (m, 2H, ArH), 7.73-7.75 (m, 1H, ArH), 7.82-7.85 (m, 1H, ArH), 8.03-8.07 (m, 1H, ArH), 8.18-8.20 (m, 1H, ArH), 9.86 (s, 1H, CH=N), 10.53 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 112.37, 118.52, 119.12, 121.46, 124.57, 126.69, 127.31, 129.96, 130.21, 132.97, 139.29, 150.14 (ArC), 160.41, 161.25 (C-OH), 165.06, 165.21 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ – 554.97. IR (KBr, ν_{max}, cm^{-1}): 1595 (C=N), 674 (Sn-C), 554 (Sn-O), 431 (Sn→N). Anal. calcd. for $C_{31}H_{23}N_3O_2Sn$: (m.w. 588.24), (C, 63.30; H, 3.94; O, 5.44; N, 7.14; Sn, 20.18) %. Found: (C, 63.12; H, 3.72; O, 5.29; N, 6.82; Sn, 19.82) %.

(5E,11E)-18,18-Dibutylldibenzo[d,l]pyrido[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (9): Yield: 78 %. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.71-0.74 (t, 6H, H-4), 1.11-1.17 (m, 4H, H-3), 1.63-1.67 (m, 4H, H-2), 1.82-1.85 (t, 4H, H-1), 6.81-6.83 (d, 1H, ArH), 7.18-7.20 (m, 1H, ArH), 7.31-7.33 (d, 1H, ArH), 7.38-7.40 (m, 2H, ArH), 7.65-7.67 (m, 2H, ArH), 7.71-7.73 (m, 1H, ArH), 7.79-7.81 (m, 1H, ArH), 7.96-7.98 (m, 1H, ArH), 8.14-8.16 (m, 1H, ArH), 9.81 (s, 1H, CH=N), 10.49 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 12.32, 24.07, 31.42, 42.09, 104.32, 112.22, 118.38, 121.23, 124.01, 126.67, 129.12, 132.87, 139.03, 150.12 (ArC), 160.47, 161.22 (C-OH), 165.09, 165.26 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -324.35. IR (KBr, ν_{max}, cm^{-1}): 1594 (C=N), 679 (Sn-C), 543 (Sn-O), 435 (Sn→N). Anal. calcd. for $C_{27}H_{31}N_3O_2Sn$: (m.w. 548.26), (C, 59.15; H, 5.70; O, 5.84; N, 7.66; Sn, 21.65) %. Found: (C, 58.92; H, 5.38; O, 5.49; N, 7.39; Sn, 21.37) %.

(5E,11E)-18,18-Diethyldibenzo[d,l]pyrido[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (10): Yield: 76 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.95 (t, 6H, H-1') 1.68 (q, 4H, H-2'), 6.82-6.84 (d, 1H, ArH), 7.19-7.21 (m, 1H, ArH), 7.36-7.39 (d, 1H, ArH), 7.43-7.45 (m, 2H, ArH), 7.66-7.68 (m, 2H, ArH), 7.72-7.74 (m, 1H, ArH), 7.81-7.83 (m, 1H, ArH), 8.01-8.04 (m, 1H, ArH), 8.10-8.12 (m, 1H, ArH), 9.83 (s, 1H, CH=N), 10.38 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 9.11, 14.16, 117.71, 121.28, 124.14, 127.23, 128.34, 128.68, 129.25, 136.82, 139.23, 150.09 (ArC), 160.53, 161.21 (C-OH), 165.04, 165.13 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -270.75. IR (KBr, ν_{max}, cm^{-1}): 1600 (C=N), 674 (Sn-C), 552 (Sn-O), 437 (Sn→N). Anal. calcd. for $C_{23}H_{23}N_3O_2Sn$: (m.w. 492.16), (C, 56.13; H, 4.71; O, 6.50; N, 8.54; Sn, 24.12) %. Found: (C, 55.92; H, 4.37; O, 6.27; N, 8.29; Sn, 23.99) %.

(5E,11E)-18,18-Dimethlydibenzo[d,l]pyrido[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (11): Yield: 77 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.92 (s, 6H, H-1"), 6.83-6.85 (d, 1H, ArH), 7.20-7.22 (m, 1H, ArH), 7.32-7.35 (d, 1H, ArH), 7.39-7.41 (m, 2H, ArH), 7.62-7.64 (m, 2H, ArH), 7.69-7.71 (m, 1H, ArH), 7.79-7.81 (m, 1H, ArH), 7.97-7.99 (m, 1H, ArH), 8.12-8.14 (m, 1H, ArH), 9.84 (s, 1H, CH=N), 10.36 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 9.17, 117.64, 121.23, 124.12, 127.25, 128.29, 128.57, 129.12, 136.76, 139.27, 150.13 (ArC), 160.36, 161.25 (C-OH), 165.08, 165.21 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -143.72. IR (KBr, ν_{max}, cm^{-1}): 1598 (C=N), 671 (Sn-C), 559 (Sn-O), 436 (Sn→N). Anal. calcd. for $C_{21}H_{19}N_3O_2Sn$: (m.w. 464.10), (C, 54.35; H, 4.31; O, 6.89; N, 9.05; Sn, 25.58) %. Found: (C, 54.03; H, 4.09; O, 6.57; N, 8.93; Sn, 25.27) %.

(5E,11E)-3,14-Dibromo-18,18-diphenyldibenzo[d,l]-pyrido[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (12): Yield: 78 %. ^{1}H NMR (DMSO-d_6): δ = 6.89-6.71 (d, 1H, ArH), 7.25-7.27 (m, 1H, ArH), 7.38-7.40 (d, 1H, ArH), 7.44-7.47 (m, 1H, ArH), 7.52-7.61 (m, 10H), 7.64-7.66 (m, 2H, ArH), 7.75-7.77 (m, 1H, ArH), 7.84-7.87 (m, 1H, ArH), 8.02-8.04 (m, 1H, ArH), 8.11-8.13 (m, 1H, ArH), 9.82 (s, 1H, CH=N), 10.46 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 112.31, 118.45, 119.06, 121.34, 124.45, 126.61, 127.23, 129.84, 130.14, 132.83, 139.23, 150.05 (ArC), 160.58, 161.18 (C-OH), 165.01, 165.14 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -519.45. IR (KBr, ν_{max}, cm^{-1}): 1602 (C=N), 677 (Sn-C), 551 (Sn-O), 438 (Sn→N). Anal. calcd. for $C_{31}H_{21}N_3O_2SnBr_2$: (m.w. 746.04), (C, 49.91; H, 2.84; Br, 21.42; O, 4.29; N, 5.63; Sn, 15.91) %. Found: (C, 49.62; H, 2.58; Br, 21.19; O, 3.94; N, 5.32; Sn, 15.73) %.

(5E,11E)-3,14-Dibromo-18,18-dibutyldibenzo[d,l]-pyrido[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (13): Yield: 76 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.71-0.74 (t, 6H, H-1) 1.12-1.18 (m, 4H, H-2), 1.64-1.69 (m, 4H, H-3), 1.81-1.84 (t, 4H, H-1), 6.82-6.84 (d, 1H, ArH), 7.19-7.21 (m, 1H, ArH), 7.34-7.36 (d, 1H, ArH), 7.40-7.43 (m, 1H, ArH), 7.63-7.65 (m, 2H, ArH), 7.71-7.73 (m, 1H, ArH), 7.81-7.84 (m, 1H, ArH), 8.01-8.03 (m, 1H, ArH), 8.15-8.18 (m, 1H, ArH), 9.83 (s, 1H, CH=N), 10.39 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 12.29, 23.93, 31.36, 42.01, 104.26, 112.15, 118.34, 121.19, 123.98, 126.58, 129.03, 132.75,

138.93, 150.02 (ArC), 160.48, 161.17 (C-OH), 165.03, 165.19 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ – 322.43. IR (KBr, ν_{max}, cm^{-1}): 1601 (C=N), 671 (Sn-C), 553 (Sn-O), 433 (Sn→N). Anal. calcd. for $C_{27}H_{29}N_3O_2SnBr_2$: (m.w. 706.06), (C, 45.93; H, 4.14; Br, 22.63; O, 4.53; N, 5.95; Sn, 16.81) %. Found: (C, 45.64; H, 3.87; Br, 22.34; O, 4.29; N, 5.68; Sn, 16.56) %.

(5E,11E)-3,14-Dibromo-18,18-diethyldibenzo[d,l]-pyrido[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (14): Yield: 72 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.96 (t, 6H, H-1') 1.67 (q, 4H, H-2'), 6.83-6.85 (d, 1H, ArH), 7.20-7.22 (m, 1H, ArH), 7.35-7.37 (d, 1H, ArH), 7.42-7.44 (m, 1H, ArH), 7.65-7.67 (m, 2H, ArH), 7.72-7.74 (m, 1H, ArH), 7.82-7.85 (m, 1H, ArH), 8.03-8.05 (m, 1H, ArH), 8.17-8.19 (m, 1H, ArH), 9.86 (s, 1H, CH=N), 10.43 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 9.16, 14.23, 117.75, 121.29, 124.20, 127.18, 128.29, 128.53, 129.17, 136.76, 139.18, 150.13 (ArC), 160.38, 161.25 (C-OH), 165.09, 165.18 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -252.95. IR (KBr, ν_{max}, cm^{-1}): 1599 (C=N), 673 (Sn-C), 550 (Sn-O), 431 (Sn→N). Anal. calcd. for $C_{23}H_{21}N_3O_2SnBr_2$: (m.w. 649.95), (C, 42.50; H, 3.26; Br, 24.59; O, 4.92; N, 6.47; Sn, 18.26) %. Found: (C, 42.29; H, 2.98; Br, 24.28; O, 4.68; N, 6.19; Sn, 17.98) %.

(5E,11E)-3,14-Dibromo-18,18-dimethyldibenzo[d,l]-pyrido[3,2-h][1,3,7,10,2]dioxadiazastannacyclotridecine (15): Yield: 75 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.93 (s, 6H, H-1"), 6.81-6.83 (d, 1H, ArH), 7.17-7.19 (m, 1H, ArH), 7.32-7.34 (d, 1H, ArH), 7.40-7.42 (m, 1H, ArH), 7.61-7.63 (m, 2H, ArH), 7.71-7.73 (m, 1H, ArH), 7.81-7.84 (m, 1H, ArH), 8.05-8.07 (m, 1H, ArH), 8.15-8.17 (m, 1H, ArH), 9.89 (s, 1H, CH=N), 10.35 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 9.21, 117.69, 121.29, 124.09, 127.22, 128.24, 128.56, 129.10, 136.72, 139.24, 150.09 (ArC), 160.28, 161.21 (C-OH), 165.04, 165.25 (C=N). ^{119}Sn NMR (149 MHz, DMSO-d_6): δ = -140.74. IR (KBr, ν_{max}, cm^{-1}): 1597 (C=N), 672 (Sn-C), 555 (Sn-O), 436 (Sn→N). Anal. calcd. for $C_{21}H_{17}N_3O_2SnBr_2$: (m.w. 621.90), (C, 40.56; H, 2.76; Br, 25.70; O, 5.15; N, 6.76; Sn, 19.09) %. Found: (C, 40.28; H, 2.32; Br, 25.39; O, 4.97; N, 6.47; Sn, 18.86) %.

RESULTS AND DISCUSSION

The reaction was carried out in 1:2 molar ratio for the synthesized Schiff base ligands, while for the synthesis of complexes it was carried out in 1:1 molar ratio of the prepared ligand and the organotin compound.

Electronic spectra: The electronic spectra of the synthesized Schiff base ligands and their organotin complexes were carried out in chloroform and recorded in the region of 200-500 nm, which showed only intraligand or charge transfer bands. The electronic absorption spectra of the Schiff base ligands exhibited intense bands at 267, 346 and 482 nm. An intense band in high-energy region of the spectrum is due to the π-π* transitions of phenyl rings appeared at 267 nm [13]. The π-π* transitions associated with azomethine (N=C) chromophore showed two other bands at 280-300 nm and the benzene ring secondary bands appeared at 320-360 nm. The ligand to metal bonding may take place because of presence of completely vacant 5*d* orbitals and it occurs by acceptance of lone pair of electrons from nitrogen donor atoms of the ligands.

IR spectra: The IR spectra of all the compounds were recorded using KBr pellets. The presence of hydroxyl group in the Schiff base ligands was confirmed by the presence of a strong and broad absorption band in the stretching frequency at 3300-3200 cm^{-1}. In the IR spectra of the organotin complexes, the absorption bands of the phenolic group were absent. The confirmation for the formation of azomethine group was done by the presence of a strong band in the stretching frequencies of the azomethine group at 1630-1620 cm^{-1} region for the IR spectra of Schiff base ligands. A bathochromic shift was observed in the azomethine stretching frequencies as shift from 1601-1594 cm^{-1} due to delocalization through the coordinated metal [14]. The comparison within the IR spectra of Schiff base ligands and their corresponding organotin(IV) complexes signified the coordination of Schiff base ligands through nitrogen atom of the imino group showing downfield shift in the stretching frequencies of azomethine group of the complexes by 10-15 cm^{-1}. However, the broad band present in this region was due to hydrogen bonding. There appeared presence of some new bands in the stretching frequencies at 439-431 cm^{-1}, 559-543 cm^{-1}, 679-671 cm^{-1} region due to coordination of tin with nitrogen (Sn-N), oxygen (Sn-O), carbon (Sn-C) respectively [15].

NMR spectra

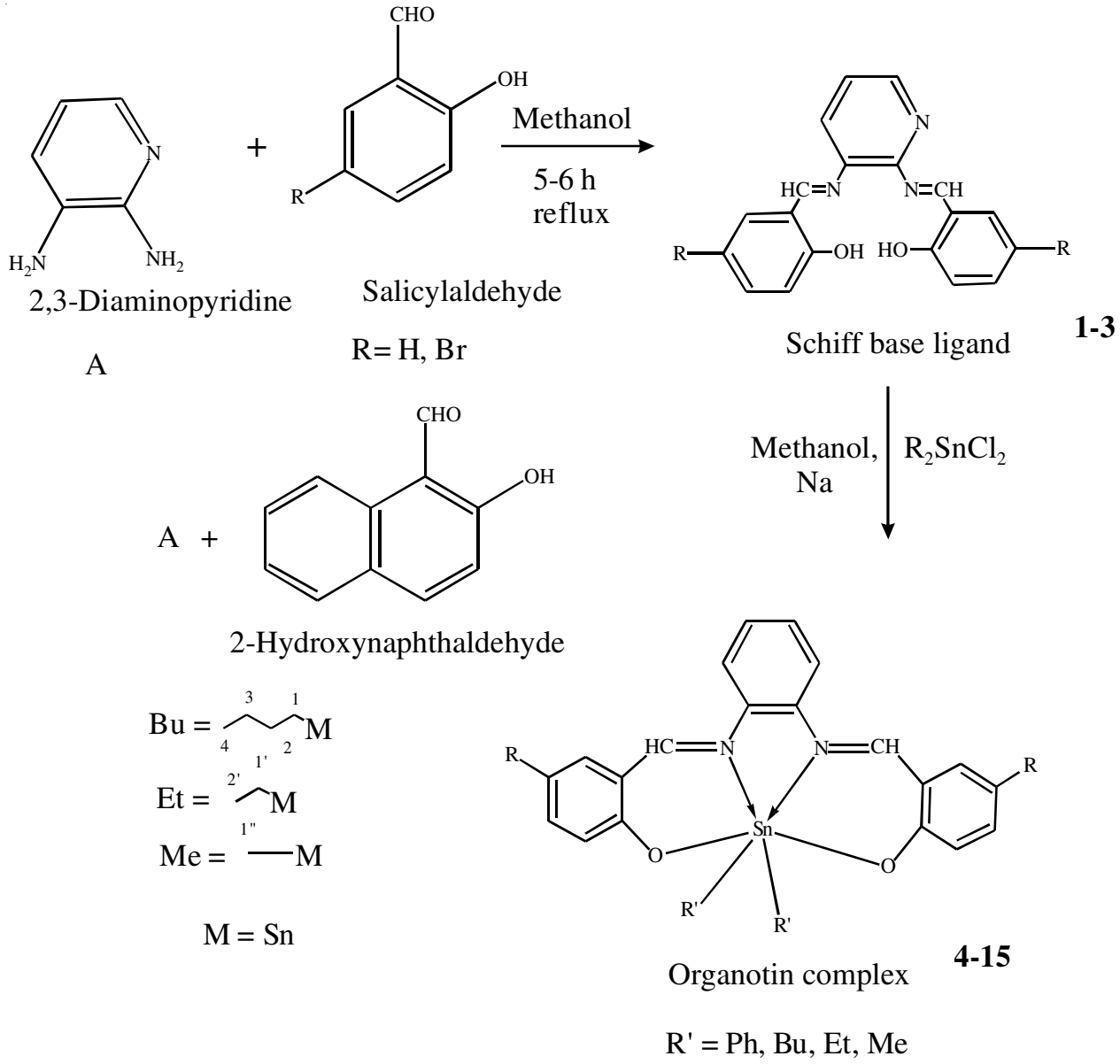
^{1}H NMR spectra: ^{1}H NMR spectral analysis was recorded in $CDCl_3$ and DMSO. In the ligands **1-3**, the OH protons signals appeared at δ 14.31-14.39 ppm are due to the presence of phenolic group in the ligands. Further, there appeared one more signal at δ 15.18-15.20 ppm because of presence of another phenolic group. However, there occurred disappearance of the signals due to OH protons in the tin complexes which indicate the deprotonation with the tin atom on complexation [16]. Also, in the ^{1}H NMR spectra of the ligands **1-3**, the azomethine (–CH=N) proton signals showed a sharp singlet signal at δ 9.84-9.86 ppm due to the presence of azomethine group. Here also, there appeared one more signal at δ 10.01-10.03 ppm due to presence of another azomethine group in the ligands. In the complexes **4-15**, the azomethine proton signals shifted downfield with signal at δ 9.82-9.92 ppm and the other azomethine proton signals shifted with the signal at δ 10.31-10.59 ppm when compared with the ligands due to coordination of nitrogen atom of the azomethine group to the tin atom. The resonance due to the phenyl moiety remains almost unaffected in the complexes. The aromatic protons signals appeared at δ 6.72-8.95 ppm. In the phenyl complexes **4, 8, 12**, the phenyl group protons appeared in the aromatic region. In butyl complexes **5, 9, 13**, the butyl group signals appeared in the aliphatic region at δ 0.71-1.88 ppm. In ethyl complexes **6, 10, 14**, the ethyl group signals appeared in the aliphatic region at δ 0.94-1.68 ppm. In the methyl complexes **7, 11, 15**, the methyl group signals appeared at δ 0.92-0.93 ppm.

^{13}C NMR spectra: ^{13}C NMR spectral analysis was recorded in $CDCl_3$ and DMSO. In the ^{13}C NMR spectra of the ligands **1-3** the singlet signals appeared in the region at δ 160.58-160.71 ppm, δ 164.72-164.89 ppm, δ 164.87-164.92 ppm indicating presence of phenolic group and the two azomethine groups respectively. However, the shifting in the position of phenyl carbon attached to OH group and the carbon atom

attached to the azomethine group in the complexes due to transfer of electron density from the ligands to the tin atom suggest the and formation of tetradendate (ONNO) coordination of oxygen and nitrogen atoms to the tin atom respectively. The R groups attached to tin display single resonance for chemically equivalent carbon, resonances for carbons being overlapped. In the complexes **4, 8, 12**, the new signals due to phenyl group carbon atoms appeared in the aromatic region. In the complexes **5, 9, 13**, the signals due the butyl group carbon atoms appeared in the aliphatic region at δ 12.29-42.21 ppm, while the signals for ethyl complexes **6, 10, 12** and methyl complexes **7, 11, 15**, appeared at δ 9.05-14.23 and δ 9.11-9.21 ppm respectively [17].

^{119}Sn NMR spectra: ^{119}Sn NMR spectral analysis was recorded in $CDCl_3$ and DMSO. In the ^{119}Sn NMR spectra of the complexes, the appearance of a single sharp singlet peak and the chemical shift values have been observed at δ -556.03 to -519.45 ppm, δ -382.18 to -322.43 ppm, δ -274.11 to -252.95 ppm, δ -147.23 to -140.74 ppm for phenyl (**4, 8, 12**), butyl (**5, 9, 13**), ethyl, (**6, 10, 14**), methyl complexes (**7, 11, 15**), which is in good agreement with the chemical shift values for hexa-coordinated states around the tin atoms as earlier reported in the literature [18]. On the basis of the above spectral evidence, the following tentative structure can be proposed for the resulting tin complexes as shown in the **Scheme-I**.

Test microorganisms used: Gram-positive bacteria *Staphylococcus aureus* (MTCC 2901) and *Bacillus cereus* (MTCC 10072), Gram-negative bacteria *Pseudomonas aeruginosa* (MTCC 424), *Escherichia coli* (MTCC 732) and fungi *Aspergillus niger* (MTCC 7678), *Aspergillus flavus* (ITCC 7680).The bacteria were cultivated on nutrient broth, whereas fungi were cultivated on potato dextrose broth (PDB) and DMSO was used as solvent control for the biological activity. The standard antibacterial drug taken was ciprofloxacin and the standard antifungal drug taken was fluconazole.



Scheme-I: General schematic scheme for preparation of Schiff base ligands and Organotin(IV) complexes

TABLE-1
EVALUATION OF *in vitro* ANTIMICROBIAL ACTIVITIES OF SCHIFF BASE LIGANDS AND ORGANOTIN COMPLEXES

S. No.	Compound	Minimum inhibitory concentration (μmol/mL)					
		E. coli (MTCC 732)	*P. aeruginosa* (MTCC 424)	*B. cereus* (MTCC 10072)	*S. aureus* (MTCC NICM 2901)	*A. niger* (MTCC 7678)	*A. flavus* (ITCC 7680)
1	H_2L_1	0.029943	0.014971	0.029943	0.014971	0.007474	0.014971
2	H_2L_2	0.019695	0.019695	0.039390	0.019695	0.009832	0.019695
3	H_2L_3	0.013154	0.013154	0.026309	0.013154	0.006567	0.013154
4	Ph_2SnL_1	0.009080	0.004533	0.004533	0.002266	0.002266	0.004533
5	Bu_2SnL_1	0.009639	0.004812	0.004812	0.005012	0.002406	0.004812
6	Et_2SnL_1	0.021105	0.005268	0.010553	0.010553	0.005268	0.005268
7	Me_2SnL_1	0.011077	0.005530	0.011077	0.011077	0.005530	0.005530
8	Ph_2SnL_2	0.010625	0.005304	0.005304	0.002652	0.002652	0.005304
9	Bu_2SnL_2	0.022799	0.005691	0.005691	0.002845	0.002845	0.005691
10	Et_2SnL_2	0.012699	0.006339	0.012699	0.006604	0.006339	0.006339
11	Me_2SnL_2	0.013467	0.006723	0.013467	0.007003	0.006723	0.006723
12	Ph_2SnL_3	0.016755	0.004182	0.004182	0.002091	0.002091	0.004182
13	Bu_2SnL_3	0.008852	0.004419	0.004419	0.004603	0.008852	0.004419
14	Et_2SnL_3	0.009616	0.009616	0.009616	0.009616	0.002400	0.004800
15	Me_2SnL_3	0.020100	0.010050	0.010050	0.010050	0.002508	0.005017
	Ciprofloxacin	0.004706	0.004706	0.004706	0.004706	–	–
	Fluconazole	–	–	–	–	0.010187	0.010187

Determination of biological assay: The *in vitro* biological activities (antibacterial and antifungal activities) of all the Schiff base ligands and their organotin complexes were evaluated against Gram-positive bacteria *Staphylococcus aureus* (MTCC NICM 2901), *Bacillus cereus* (MTCC 10072), Gram-negative bacteria *Escherichia coli* (MTCC 732), *Pseudomonas aerugenosa* (MTCC 424) and fungi *Aspergillus niger* (MTCC 7678), *Aspergillus flavus* (ITCC 7680) as shown in Table-1. The biological activities of the synthesized compounds were evaluated by the serial dilution method. The concentration for the stock solution of all the compounds was prepared in dry DMSO as 1 mg/mL to form first dilution (50 μg/mL) and the diluted to 0.75 μg/mL. The bacteria and the fungi were inoculated to solution and then it was kept in incubator at 37 °C for 24 h and 7 days in case of bacteria and fungi respectively. Then, the minimum inhibitory concentration (MIC) was determined. Phenyl complexes were shown to be more active than their parent Schiff base ligands under the same experimental conditions against the bacteria and fungi due to lipophilic character favouring the permeation through lipid layer of cell membrane and chelation explained on the basis of chelation theory. Most of the compounds **4, 8, 12** show comparable biological activity with the standard drugs. The electron delocalization of the chelate ring may cause the enhanced biological activities of compounds on complexation [19,20].

Conclusion

We have synthesized the Schiff base ligands and their organotin(IV) compounds derived from 2,3-diaminopyridine and salicylaldehyde derivatives. All the synthesized Schiff bases and the organotin compounds are characterized by spectral techniques and are screened for *in vitro* antibacterial and antifungal activities and compared with the standard drugs. Most of the investigated compounds **4, 5, 8, 9, 12, 13** show moderate to good activity. All the complexes showed biological potency.

ACKNOWLEDGEMENTS

The authors are grateful to CIL, Guru Jambheshwar University of Science & Technology, Hisar, India and SAIF, Punjab University, Chandigarh, India for providing IR and NMR facilities. One of the authors, (AA) is thankful to UGC, New Delhi, India for providing thefinancial support under the scheme RGNF (Rajiv Gandhi National Fellowship).

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