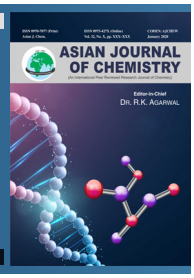
Asian Journal of Chemistry; Vol. 32, No. 10 (2020), 2553-2558

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22819



Antimicrobial and Antioxidant Activities of Diorganotin(IV) Complexes Synthesized from 1,2,4-Triazole Derivatives

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Received: 7 May 2020; *Accepted*: 22 June 2020; *Published online*: 25 September 2020; AJC-20068

Novel diorganotin(IV) complexes were synthesized from 1,2,4-triazole Schiff base ligands which were synthesized by reaction between the 4-amino-5-phenyl-1,2,4-triazole-3-thiol and salicyaldehyde derivatives. The bonding and geometry of the diorganotin(IV) complexes were evaluated by using different spectroscopic techniques such as FT-IR, mass, ^{1}H, ^{13}C & ^{119}Sn NMR. The different spectroscopic techniques revealed the tridentate (ONS) mode of chelation of Schiff base ligands and pentacoordinated environment around the central tin metal which was satisfied with azomethine nitrogen, phenolic oxygen, thiolic sulfur and metal-carbon bond of alkyl/aryl group. The Schiff base ligands and their organotin(IV) complexes were tested for their *in vitro* antimicrobial and antioxidant activities to examine the biological outline of complexes in comparison to standard drugs. The results of activities data revealed that diorganotin(IV) complexes are more active than Schiff base ligands and some diorganotin(IV) complexes are even more active than the standard drugs. In all the synthesized complexes, compound **9** (Bu_2SnL^2) and **10** (Ph_2SnL^2) were most potent and can be used in future clinical trials.

Keywords: Triazole, Scavenger, Chelates, Antioxidant, Diorganotin(IV) complexes.

INTRODUCTION

Infections caused by bacteria, fungi, yeast and/or viruses results in death. Firstly, it occurs in small part of body and then spread to whole body parts. To inhibit the growth of infection caused by pathogen, some drugs are developed called as antibiotics. The unstoppable appearance of antibiotic resistant bacteria is now becoming a global threat as there are fewer or even no helpful antibiotic available for pathogens [1,2]. This issue highlights the urgent requirement of effective and selective antimicrobial drugs. In order to develop the effective, non-resistance drugs researchers tested a library of organic and inorganic compounds and found that metal complexes are most potent and tin metal complexes play a vital role in this field [3,4].

Organotin(IV) compounds known to show a ample variety of biological applications and most demanding class of organometallic compound due to its biomedical efficacy as antimicrobial, antifouling and pesticidal agents [5]. Organotin(IV) compounds shows broad spectrum of antimicrobial activity, higher toxicity to microbes and low toxicity to mammals. They are used from industrial to biomedical field and also have wide application in biological field such as antioxidant, antibacterial, antifungal, anticancer, antituberculorsis, antiviral, antileshminial, anti-diabetic, antianalgesic, antinematicidal, DNA cleavage and binding, *etc*. [6-10]. These biological applications of organotin(IV) compounds were affected by oxidation number, coordination number, geometry of tin metal and kinetic stability of complexes.

1,2,4-Triazole and its detivatives belongs to isothiocyanates class and possess different pharmacological activities. 1,2,4-Triazole as a unit present in the different market selling drugs such as fluconazole (antifungal drug), ribavirin (antiviral drug), trazodone (antidepressant drug), vorozole, anasterozole and letrozole (anticancer drugs) [11-14]. Organotin(IV) complexes with 1,2,4-triazole Schiff base ligands resulted in the enchancement in activity as compared to free ligand according to Tweedy's chelation theory [15]. In the current work, diorganotin(IV) complexes with halo derivatives of salicylaldehyde and 4-amino-5-phenyl-1,2,4-triazole-3-thiol were synthesized. The structure elucidation of all compounds were done by using UV-visible, FT-IR, ^{1}H, ^{13}C & ^{119}Sn NMR and mass spectro-

scopic analysis. All the synthesized compounds were demonstrated for antimicrobial activity against some Gram-positive, Gram-negative bacteria and fungus and calculated the MIC values. Further, antioxidant activity of synthetic complexes was evaluated by calculating their percentage of radical scavenging values.

EXPERIMENTAL

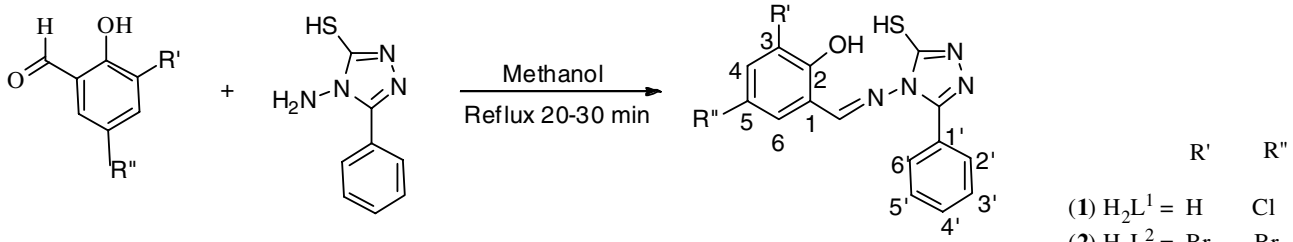
Chemicals like 4-amino-5-phenyl-1,2,4-triazole-3-thiol, 5-chlorosalicylaldehyde, 3,5-dibromosalicylaldehyde, dimethyltin dichloride, diethyltin dichloride, dibutyltin dichloride and diphenyltin dichloride were obtained from Sigma-Aldrich, USA. All solvents used in experimental were of analytical grade and used after drying with standard procedure [16]. FT-IR spectra was recorded using Shimadzu IR Affnity-I 8000 FT-IR spectrophotometer by KBr pellets method in the range of 4000-400 cm^{-1}. The NMR spectra (^{1}H, ^{13}C & ^{119}Sn) of Schiff base ligands and their diorganotin(IV) complexes were recorded on Bruker Avance II 400 MHz NMR spectrometer using DMSO-d_6 and $CDCl_3$ solvent and tetramethylsilane (TMS) and tetramethyltin as internal standard. Chemical shifts (δ) and coupling constants (*J*) value were reported in ppm and Hz, respectively. Mass spectra of Schiff base ligands and complexes were carried on SCIEX-QTOF in methanol solvent. Electronic spectra were recorded in DMSO at room temperature using UV-Vis-NIR Varian Cary-5000 spectrometer. Molar conductance was recorded using conductivity bridge type model- 306 Systronic in DMF at room temperature.

Synthesis of Schiff base ligands (1-2): 5-Chlorosalicylaldehyde/3,5-dibromosalicylaldehyde (0.469 g/0.837 g, 3 mmol) was refluxed with 4-amino-5-phenyl-1,2,4-triazole-3-thiol (0.576 g, 3 mmol) in 35 mL of methanol after adding 2-3 drops of glacial acetic acid. The progress of reaction was checked by thin layer chromatography (TLC). On completion of reaction different coloured solid products were formed, which were filtered, recrystallized in methanol and dried in vacuum (**Scheme-I**).

4-Chloro-2-(((3-mercapto-5-phenyl-4*H*-1,2,4-triazol-4-yl)imino)methyl)phenol (H_2L^1, 1): Yield: 95%, yellow solid; m.p.: 222-224 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 12.68, MS: *m/z* (M^+) cacld. for $C_{15}H_{11}N_4OSCl$: 330.79; found: 331.80 $(M+H)^+$. ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 14.021 (s, 1H, SH), 12.20 (s, 1H, OH), 10.25 (s, 1H, -N=C-H), 8.626-8.619 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 2.8 Hz), 8.31-8.28 (1H, dd, C_4-Ar-H, $J_{ortho,meta}$ = 9.2Hz, 2.8Hz), 7.88-7.85 (2H, m, $C_{2',6'}$-Ar-H), 7.60-7.54 (3H, m, $C_{3',4',5'}$-Ar-H), 7.20-7.18 (1H, d, C_2 - Ar-H, $^3J_{HH}$ = 9.2Hz) : ^{13}C NMR (100 MHz, DMSO, δ ppm): 160.23 (HC=N), 157.47 (C-SH), 154.07 (C-OH), 151.09 (C-Cl). FT-IR (KBr, ν_{max}, cm^{-1}): 3420 (O-H, br), 2369 (S-H), 1606 (C=N, m).

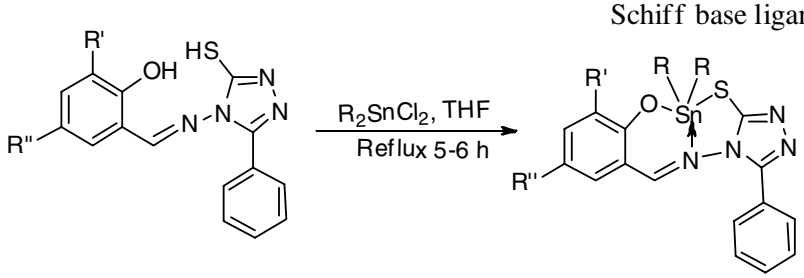
2,4-Dibromo-6-(((3-mercapto-5-phenyl-4*H*-1,2,4-triazol-4-yl)imino)methyl)phenol, H_2L^2, 2): Yield: 93%, yellow solid; m.p.: 220-222 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 12.19, MS: *m/z* (M^+) cacld. for $C_{15}H_{10}N_4OSBr_2$: 454.14; found: 455.13 $(M+H)^+$. ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 15.007 (s, 1H, SH), 13.14 (s, 1H, OH), 10.76 (s, 1H, -N=C-H), 8.726-8.720 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 2.4Hz), 8.42-8.38 (1H, dd, C_4-Ar-H, $J_{otho,meta}$ = 9.0 Hz, 2.4 Hz), 7.93-7.90 (2H, m, $C_{2',6'}$-Ar-H), 7.72-7.68 (3H, m, $C_{3',4',5'}$-Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6, δ ppm): 162.46 (HC=N), 159.30, (C-SH), 151.68 (C-OH), 150.04 (C-Br). FT-IR (KBr, ν_{max}, cm^{-1}): 3422 (O-H, br), 2371 (S-H), 1607 (C=N, m).

Synthesis of diorganotin(IV) complexes (3-10): Schiff base ligand H_2L^1 (0.341g, 1 mmol) was stirred with triethylamine (0.278 mL, 2 mmol) in THF (20 mL) solvent for 20 min.



Schiff base ligands (**1-2**)

	R'	R"
(**1**) H_2L^1 =	H	Cl
(**2**) H_2L^2 =	Br	Br



Diorganotin(IV) complexes (**3-10**)

(**3**) R'= H R"= Cl	R= Me	(**7**) R' = Br	R" = Br	R= Me
(**4**) R' = H R'' = Cl	R= Et	(**8**) R' = Br	R''= Br	R= Et
(**5**) R' = H R'' = Cl	R= Bu	(**9**) R' = Br	R" = Br	R= Bu
(**6**) R' = H R'' = Cl	R= Ph	(**10**) R' = Br	R" = Br	R= Ph

Scheme-I: Synthesis of Schiff base ligands (**1-2**) and their diorganotin(IV) complexes (**3-10**)

The above solution was refluxed with THF solution of dimethyltin(IV) dichloride (2.19 g, 1 mmol) for 5-6 h. The white coloured precipitate of Et_3NHCl salt was formed on completion of reaction which was then filtered and evaporates solvent under reduced pressure. Solid products were formed which was recrystallized from the dry hexane and dried in desiccator (**Scheme-I**).

Me_2SnL^1 (3): Yield: 82%, yellow solid; m.p.: 160-162 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 11.21, MS: *m/z* (M^+) calcd. for $C_{17}H_{15}N_4OSClSn$: 477.56; found: 478.58 $(M+H)^+$. ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 10.27 (s, 1H, -N=C-H), 8.628-8.621 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 2.8Hz), 8.33-8.29 (1H, dd, C_4-Ar-H, $J_{ortho,\ meta}$ = 9.2 Hz, 2.8 Hz), 7.89-7.86 (2H, m, $C_{2',6'}$-Ar-H), 7.62-7.59 (3H, m, $C_{3',4',5'}$-Ar-H), 7.20-7.18 (1H, d, C_2-Ar-H, $^3J_{HH}$ = 9.2Hz), 0.85 (s, 6H, Me). ^{13}C NMR (100 MHz, DMSO-d_6, δ ppm): 160.89 (HC=N), 157.86 (C-SH), 154.90 (C-OH), 9.19 (Me). ^{119}Sn NMR (400 MHz, DMSO-d_6, δ ppm): −139.22. FT-IR (KBr, ν_{max}, cm^{-1}): 1597 (C=N, m), 543 (Sn-N), 657 (Sn-O).

Et_2SnL^1 (4): Yield: 76%, yellow solid; m.p.: 159-161 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 12.13, MS: *m/z* (M^+) calcd. for $C_{19}H_{19}N_4OSClSn$: 505.61; found: 506.60 $(M+H)^+$.^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 10.29 (s, 1H, -N=C-H), 8.629-8.621 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 3.2Hz), 8.35-8.30 (1H, dd, C_4-Ar-H, $J_{ortho,meta}$ = 9.3 Hz, 3.2 Hz), 7.90-7.87 (2H, m, $C_{2',6'}$-Ar-H), 7.63-7.60 (3H, m, $C_{3',4',5'}$-Ar-H), 7.22-7.20 (1H, d, C_2-Ar-H, $^3J_{HH}$ = 9.3 Hz), 1.17-1.13 (12H, m, Sn-CH_2CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ ppm): 161.02 (HC=N), 158.10 (C-SH), 155.27 (C-OH), 34.19 (Et-C), 9.18 (Et-C). ^{119}Sn NMR (400 MHz, DMSO-d_6, δ ppm): −161. FT-IR (KBr, ν_{max}, cm^{-1}): 1595 (C=N, m), 550 (Sn-N), 664 (Sn-O).

Bu_2SnL^1 (5): Yield: 76%, yellow solid; m.p.: 150-153 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 12.22, MS: *m/z* (M^+) calcd. for $C_{23}H_{27}N_4OSClSn$: 561.71; found: 562.72 $(M+H)^+$. ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 10.28 (s, 1H, -N=C-H), 8.627-8.620 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 2.8 Hz), 8.33-8.29 (1H, dd, C_4-Ar-H, $J_{ortho,meta}$ = 9.3 Hz, 2.8 Hz), 7.90-7.87 (2H, m, $C_{2',6'}$-Ar-H), 7.63-7.60 (3H, m, $C_{3',4',5'}$ -Ar-H), 7.21-7.19 (1H, d, C_2-Ar-H, $^3J_{HH}$ = 9.3 Hz), 1.29-1.23 (14H, m, Sn-CH_2CH_3), 1.02-0.99 (4H, m, Sn-CH_2). ^{13}C NMR (100 MHz, DMSO-d_6, δ ppm): 161.00 (HC=N), 158.17 (C-SH), 155.27 (C-OH), 37.33 (Bu-C), 29.18 (Bu-C), 9.18 (Bu-C). ^{119}Sn NMR (400 MHz, DMSO-d_6, δ ppm): −244.22. FT-IR (KBr, ν_{max}, cm^{-1}): 1596 (C=N, m), 546 (Sn-N), 663 (Sn-O).

Ph_2SnL^1 (6): Yield: 78%, yellow solid; m.p.: 163-165 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 13.01, MS: *m/z* (M^+) cacld. for $C_{27}H_{19}N_4OSClSn$: 601.69; found: 602.70 $(M+H)^+$. ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 10.28 (s, 1H, -N=C-H), 8.626-8.620 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 2.4 Hz), 8.35-8.32 (1H, dd, C_4-Ar-H, $J_{ortho,meta}$ = 8.8 Hz, 2.4 Hz), 7.87-7.85 (2H, m, $C_{2',6'}$-Ar-H), 7.60-7.57 (3H, m, $C_{3',4',5'}$-Ar-H), 7.25-7.23 (1H, d, C_2-Ar-H, $^3J_{HH}$ = 8.8 Hz), 7.07-7.04 (10H, m, Sn-Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ ppm): 161.66 (HC=N), 158.33 (C-SH), 155.19 (C-OH), 120-115 (Ph-C).^{119}Sn NMR (400 MHz, DMSO-d_6, δ ppm): −341.03. FT-IR (KBr, ν_{max}, cm^{-1}): 1593 (C=N, m), 549 (Sn-N), 667 (Sn-O).

Me_2SnL^2 (7): Yield: 83%, yellow solid; m.p.: 146-148 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 11.94, MS: *m/z* (M^+) cacld. for $C_{17}H_{14}N_4OSBr_2Sn$: 600.90; found: 601.90 $(M+H)^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.78 (s, 1H, -N=C-H), 8.728-8.722 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 2.4Hz), 8.44-8.40 (1H, dd, C_4-Ar-H, $J_{ortho,\ meta}$ = 9.0 Hz, 2.4 Hz), 7.97-7.94 (2H, m, $C_{2',6'}$-Ar-H), 7.74-7.70 (3H, m, $C_{3',4',5'}$-Ar-H), 1.01 (s, 6H, Me). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.22 (HC=N), 160.05 (C-SH), 153.11 (C-OH), 8.86 (Me). ^{119}Sn NMR (400 MHz, $CDCl_3$, δ ppm): −132. FT-IR (KBr, ν_{max}, cm^{-1}): 1597 (C=N, m), 571 (Sn-N), 671 (Sn-O).

Et_2SnL^2 (8): Yield: 79%, orange solid; m.p.: 150-152 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 12.13, MS: *m/z* (M^+) cacld. for $C_{19}H_{18}N_4OSBr_2Sn$: 628.96 ; found: 629.95 $(M+H)^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.78 (s, 1H, -N=C-H), 8.725-8.720 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 2.0Hz), 8.44-8.40 (1H, dd, C_4-Ar-H, $J_{ortho,\ meta}$ = 9.2 Hz, 2.0 Hz), 7.95-7.92 (2H, m, $C_{2',6'}$-Ar-H), 7.70-7.66 (3H, m, $C_{3',4',5'}$-Ar-H), 1.18-1.14 (m, 4H), 1.04-1.02 (t, 6H, $^3J_{HH}$ = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.22, (HC=N), 160.05, (C-SH), 153.21 (C-OH), 37.12 (Et-C), 9.66 (Et-C). ^{119}Sn NMR (400 MHz, $CDCl_3$, δ ppm): −171.11. FT-IR (KBr, ν_{max}, cm^{-1}): 1593 (C=N, m), 565 (Sn-N), 667 (Sn-O).

Bu_2SnL^2 (9): Yield: 75%, yellow solid; m.p.: 141-143 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 12.23, MS: m/z (M^+) Cacld. for $C_{23}H_{26}Br_2N_4OSSn$: 685.06; found: 686.08 $(M+H)^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.78 (s, 1H, -N=C-H), 8.726-8.720 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 2.4Hz), 8.40-8.36 (1H, dd, C_4-Ar-H, $J_{ortho,\ meta}$ = 9.0 Hz, 2.4 Hz), 7.94-7.90 (2H, m, $C_{2',6'}$-Ar-H), 7.70-7.64 (3H, m, $C_{3',4',5'}$-Ar-H), 1.41-1.38 (m,14H, Sn-CH_2CH_3), 0.87-0.84 (t, 4H, $^3J_{HH}$ = 7.8 Hz). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 164.57, (HC=N), 160.44, (C-SH), 153.42 (C-OH), 44.05 (Bu-C), 31.05 (Bu-C), 22.22 (Bu-C), 8.90 (Bu-C). ^{119}Sn NMR (400 MHz, $CDCl_3$, δ ppm): −247.09. FT-IR (KBr, ν_{max}, cm^{-1}): 1597 (C=N, m), 568 (Sn-N), 646 (Sn-O).

Ph_2SnL^2 (10): Yield: 81%, yellow solid; m.p.: 200-203 ºC, Conductivity: (ohm^{-1} cm^2 mol^{-1}) in DMF: 12.45, MS: *m/z* (M^+) Cacld. for $C_{27}H_{18}N_4OSBr_2Sn$: 725.04; found: 726.06 $(M+H)^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.79 (s, 1H, -N=C-H), 8.735-8.729 (1H, d, C_6-Ar-H, $^4J_{HH}$ = 2.4Hz), 8.53-8.49 (1H, dd, C_4-Ar-H, $J_{ortho,\ meta}$ = 9.0 Hz, 2.4 Hz), 7.95-7.92 (2H, m, $C_{2',6'}$-Ar-H), 7.79-7.66 (3H, m, $C_{3',4',5'}$-Ar-H), 7.28-7.24 (m, 10H, Sn-Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ ppm): 164.22, (HC=N), 160.05, (C-SH), 153.21 (C-OH), 124.15-120.12 (Ph-C). ^{119}Sn NMR (400 MHz, $CDCl_3$, δ ppm): −346.09. FT-IR (KBr, ν_{max}, cm^{-1}): 1598 (C=N, m), 574 (Sn-N), 667 (Sn-O).

Antimicrobial activity: All synthesized compounds were evaluated for *in vitro* antibacterial activity against Gram-positive bacteria (*Staphylococcus aureus* (NCIM 5021) and *Bacillus subtilus* (NCIM 2063); Gram-negative bacteria (*Escherichia coli* (MTCC 723) and *Pseudomonas aeruginosa* (MTCC 7093)) and antifungal activity against *Aspergillus niger* (MTCC 9933) and *Candida albicans* (MTCC 227) using DMSO as a negative, ciprofloxacin and fluconazole as positive control. The antimicrobial activity was tested by using serial dilution method and minimum inhibitory concentrations (MIC) were calculated. The method adopted for carrying activity was described earlier [17].

Radical scavenging activity: All the compounds (**1-10**) were tested for radical scavenging activity by using 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay. The procedure used for carry

out this experiment is same as reported earlier [18]. The percentage scavenging activity was calculated by using the following equation:

$$\text{Radical scavenging activity (\%)} = \frac{B-S}{B} \times 100$$

where, B is absorbance of blank and S is absorbance of sample.

RESULTS AND DISCUSSION

In present work, two Schiff base ligands were synthesized from 4-amino-5-phenyl-1,2,4-triazole-3-thiol and halo derivative of salicylaldehyde. Diorganotin(IV) complexes of these Schiff bases (**3-10**) were also synthesized by using above Schiff base with R_2SnCl_2 (R= methyl, ethyl, butyl and phenyl) in THF solvent. The complexes were soluble in chloroform, DMSO, DMF, methanol, acetonitrile, ethylacetate and insoluble in water and hexane. The molar conductivity values are less than 16, which suggests the non-electrolytic nature of the compounds. The results of characterizations data convinced that Schiff base bound to tin metal in tridentate manner (ONS) and form pentacoordinated environment around metal atom through phenolic oxygen, thiol sulfur and nitrogen of azomethine group.

Electronic spectra: The UV-vis spectra of compounds were taken in DMSO solvent. In the spectra of Schiff base ligands, band appeared at 302 and 413 nm due to π-π* and n-π* transition in azomethine group. On complexation, these bands undergoes red shift at 296 and 431 nm, which tells the formation of coordinated bonds between tin metal and nitrogen of azomethine.

IR spectra: In IR spectra, a broad band at 3422-3420 cm^{-1} and a sharp band at 2371-2369 cm^{-1} due to hydroxyl ν(OH) and thiol ν(SH) groups in ligands which gets disappeared on complexation, indicating deprotonation and binding of oxygen and sulfur with tin metal [19]. The indicative band at 1607-1602 cm^{-1} due to azomethine group, shifted to lower value on complexation suggested the donation of electron density by nitrogen to tin metal and formation of tin nitrogen bond. Furthermore, in complexes some new bands at 565-527 and 671-646 cm^{-1} assigned to ν(Sn-N) and ν(Sn–O), respectively which confirm the coordination of nitrogen and oxygen with the tin metal.

^{1}H NMR spectra: In the ^{1}H NMR spectra, singlet signal at δ 14.02-15.00 ppm and δ 12.20-13.14 ppm due to thiol (S-H) and hydroxyl (OH) protons, gets vanished on complexation indicated the bond between sulfur and oxygen with the metal atom [20]. A characteristic signal at δ 10.25-10.76 ppm due to azomethine proton (CH=N) , gets shifted to higher value at δ 10.27-10.79 ppm on complexation, indicated involvement of azomethine group in bonding. The signals at δ 7.18-8.72 ppm due to aromatic proton in Schiff base ligands which unaffected on complexation formation.

Some extra signals in diorganotin(IV) complexes appeared due to presence of alkyl and aryl groups. The singlet signal at δ 0.85-1.01 ppm due to methyl protons, multiplet signal at δ 1.02-1.18 ppm due to ethyl protons, signals at δ 0.84-1.41 ppm for butyl protons and signals of phenyl protons are in the range of δ 7.04-7.24 ppm, respectively which confirmed the formation of metal carbon bond.

^{13}C NMR spectra: The ^{13}C NMR spectral data of compounds show the coordination of ligands through nitrogen and oxygen donor atom with the tin metal and gives the supported information regarding the complexation. In Schiff base ligands, signal at δ 160.17-161.42 ppm consigned to azomethine (-CH=N) carbon, 161.39 -159.86 ppm due to sulfur carbon and δ 150.99-152.15 ppm for hydroxyl carbon, all gets shifted to lower value in tin complexes confirmed the coordination of these carbon with tin metal as observed in IR and proton NMR spectra. Signals at δ 116-129.39 ppm due to aromatic carbon remains unchanged on complexation, predicts their non-laxity during complexation.

Additionally, some more signals emerges in the complexes which signifies the presence of carbon atom directly attached to tin metal other than Schiff base carbon signals. Signal at δ 8.79-9.01 due to methyl carbon, ethyl carbon signals at δ 44.27-47.13 and δ 8.29-9.26, signal at δ 46.45-51.40, 25.26-32.83, 25.26-28.36 and 9.02-9.40 ppm due to carbon of butyl group and phenyl carbon signal appeared at δ 126.69-129.15 ppm.

^{119}Sn NMR spectra: The value of chemical shift ^{119}Sn NMR indicates about the coordination number and number of signal in tin spectra gives information about the involvement of number of tin metal in complexes. A sharp singlet at δ -132 to -132.16 ppm for methyl, -161 to -171.11 ppm for ethyl, -244 to -247.09 ppm for butyl, -341.03 to -346.09 ppm for phenyl complexes, respectively. These values of chemical shifts present in the range of pentacoordinated structure in complexes [21].

Antimicrobial activity: The synthesized compounds (**1-10**) are evaluated for *in vitro* antimicrobial activity against two Gram-positive bacteria (*Staphylococcus aureus* and *Bacillus subtilus*); two Gram-negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*) and two fungus (*Aspergillus niger,* and *Candida albicans*) using serial dilution method and their MIC values are calculated. Ciprofloxacin and fluconazole are used as positive control for antibacterial and antifungal activity and DMSO as negative control. The results of microbial activity are summarized in Table-1.

The literature survey on the antimicrobial activity of compounds revealed that the activity was due to azomethine bond (-CH=N) in Schiff base ligands and metal-complexes. After complexation, the activity was increased which was described by Tweedy′s theory and Overtone concept of cell permeability where, during chelation electron delocalization and sharing of charge take place between the ligand and the metal, which results in the increase in the lipophilicity of complex so that it easily passes through the cell membrane. After the permeability of complex it inhibits the growth of microbes by disrupting any of three cellular processes: (i) enzyme-metal binding activity, (ii) respiration, (iii) protein formation [22,23]. Additionally, the activity of complexes is also affected by the nature of substituent attached, the donation effect of ligands, molecular weight of compound and the geometry of complexes.

From the microbial data, it is revealed that the ligands are more active than their starting material, which is due to presence of electron withdrawing group on benzene ring which increase the lipophilicity of compounds. The order of antimicrobial activity of Schiff base ligands: $H_2L^2 > H_2L^1$.

TABLE-1
MINIMUM INHIBITORY CONCENTRATION (MIC, μmol/mL) OF COMPOUNDS (**1-10**) AGAINST BACTERIAL AND FUNGAL STRAINS

Compounds	Gram-positive bacteria		Gram-negative bacteria		Fungi	
	S. aureus	*B. subtilis*	*E. coli*	*P. aeruginosa*	*A. niger*	*C. albicans*
1	0.074	0.037	0.018	0.037	0.037	0.018
2	0.054	0.006	0.013	0.006	0.027	0.013
3	0.052	0.026	0.026	0.026	0.026	0.013
4	0.048	0.024	0.024	0.024	0.024	0.024
5	0.022	0.022	0.011	0.022	0.022	0.011
6	0.040	0.020	0.010	0.020	0.020	0.010
7	0.020	0.010	0.010	0.010	0.010	0.010
8	0.020	0.010	0.010	0.010	0.010	0.010
9	0.009	0.004	0.004	0.004	0.004	0.004
10	0.008	0.004	0.004	0.004	0.004	0.004
Ciprofloxacin	0.0047	0.0047	0.0047	0.0047	–	–
Fluconazole	–	–	–	–	0.0102	0.0051

*4-Amino-5-phenyl-1,2,4-triazole-3-thiol MIC value = 0.035 μM/mL

In complexes, diphenyl complexes are found more active due to delocalization of π-electron cloud to chelate ring [24]. The general trend for the antimicrobial activity is: Ph > Bu > Et ≥ Me. Complexes are found more active than the free Schiff base ligand which was explain by chelation theory.

In all the synthesized compounds **2**, **9** and **10** are found to most potent with MIC values 0.054-0.004 μmol/mL. Compound **9** (Bu_2SnL^2) and **10** (Ph_2SnL^2) were found to be most efective than the standard ciprofloxacin and fluconazole.

Antioxidant activity: The *in vitro,* antioxidant activity tested for the compounds by using free radical DPPH , purple colour that changes its colour by accepting an electron from other compound and results in decrease in absorbance of 517 nm. The results of activity revealed that percentage scavenging activity increase with the concentration.

The percentage scavenging activity in Schiff base ligands presents in the range of 57.80-67.91% but on complexation the value of percentage scavenging increases upto 81.24 at 100 μg/mL concentration. In Schiff base ligand, compound **1** (H_2L^1) possess more value of percentage scavenging 67.91 at 100 μg/mL concentration as compared to other ligand (Table-2). The trend followed by the radical scavenging activity in Schiff base ligand is: $H_2L^1 > H_2L^2$.

TABLE-2
in vitro ANTIOXIDANT ACTIVITY OF SCHIFF BASE LIGANDS AND THEIR DIORGANOTIN(IV) COMPLEXES (**1-10**) SHOWING PERCENTAGE SCAVENGING ACTIVITY AT 100 μg/mL

Compounds	Scavenging (%)	Compounds	Scavenging (%)
1	67.91	**6**	70.53
2	58.99	**7**	74.20
3	69.26	**8**	77.53
4	69.86	**9**	80.89
5	70.21	**10**	81.24
Ascorbic acid	95.03		

In diorganotin(IV) complexes, compound **9** (Bu_2SnL^2) and **10** (Ph_2SnL^2) are found to be more active with 80.89 and 81.24% value of percentage scavenging (Table-2). The general trend for antioxidant activity is Ph ≥ Bu > Et > Me. In all the synthesized compound, compound **9** and **10** are most active but less than the standard ascorbic acid (95.03%).

Conclusion

The synthesis of Schiff base ligands (**1-2**) with 1,2,4-traizole and halo salicylaldehyde derivatives and their diorganotin(IV) complexes (**3-10**) is reported in this work. Spectroscopies techniques revealed about the coordination number and geometry around the tin metal. A pentacordinated environment around the tin metal with tridentates Schiff base ligands (NOS) and the Schiff base ligands bound tin metal through azomethine nitrogen, thiolic sulfur and phenolic oxygen. The *in vitro* antimicrobial and antioxidant studies of the compounds exhibited that on complexation activity enhance as compared to the free Schiff base ligands. Compounds **9** (Bu_2SnL^2) and **10** (Ph_2SnL^2) displayed promising antimicrobial and antioxidant activity.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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