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Synthetic, structural, theoretical and biological study of triorganotin(IV) Schiff base complexes derived from amino acids

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ABSTRACT

A new series of triorganotin(IV) complexes of monofunctional bidentate Schiff base have been synthesized and characterized through elemental analysis, conductance measurements, molecular weight determinations, UV-visible, multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR spectroscopy, FT-IR, X-ray powder diffraction and theoretical calculations. On the basis of these techniques, it is proposed that the ligands are bounded to the tin atom through the azomethine nitrogen and carboxylate oxygen. The data reveal that triorganotin(IV) complexes have penta-coordination with trigonal bi-pyramidal geometry. Molecular modeling has been provided in support of the geometry of complexes. The synthesis organotin(IV) compounds have been tested against various Gram-positive and Gram-negative bacteria (Bacillus cereus, E. coli, Klebsiella spp. and Staphylococcus spp.). The results obtained show that the synthesized organotin(IV) complexes have promising activity against all the tested microorganisms.

Keywords: Isatin, Chloroisatin, spectroscopy, organotin(IV) complexes, theoretical calculations, X-ray powder diffraction, Antimicrobial activity.

INTRODUCTION

Amino acids and their compounds with different metal ions play an important role in biology, pharmacy and industry [1-4]. A number of *in-vivo* studies have indicated that biologically active compounds become more bacteriostatic and carcinostatic upon chelation. Such interaction of transition metal ions with amino acids and peptides is of immense pharmaceutical and biologically importance [5-10]. A considerable research effort is devoted to synthesis of new Schiff base complexes with metal ions, to further develop applications in the area of material science, biological and pharmaceutical chemistry [11-13]. Isatin is an endogenous molecule identified in human beings that has anticonvulsant, antimicrobial, analgesic and various other pharmacological activities. Extensive literature review has been made regarding the activities of the isatin, especially for its anticonvulsant, antimicrobial and anti-inflammatory activity. Schiff's bases of isatin were reported to possess anticonvulsant activity and various other pharmacological activities [14-17].

The complexes of organotin(IV) compounds with nitrogen and oxygen donor ligands have been studied extensively not only driven by their interesting coordination chemistry but also due to the potential applications in the field of material science, agriculture, biological activities and pharmaceutical chemistry. Biological activity of organotin complexes is believed to be independent on the structure of molecule and coordination number of the metal [18-21]. It has also been noted that many di and triorganotin(IV) carboxylates display interesting antitumor activities [22]. As a part of our continuing efforts to synthesis and characterize tributyltin chelates using simple inexpensive amino acid Schiff bases, in the paper we describe the synthesis, characterization and antimicrobial studies of stable tributyltin(IV) complexes.

EXPERIMENTAL SECTION

All reagents were purchased from Aldrich and Merck and were used as such. The solvents were purified and dried according to the literature method [23]. All the reactions were carried out under anhydrous and oxygen free nitrogen atmosphere. Melting points were determined in an open glass capillaries and were uncorrected. The ligands were prepared by the condensation of isatin and 5-chloroisatin with amino acids (isoleucine, valine, methanine and histidine) as described earlier [18].

Analytical Methods and Spectral Measurements

Tin was estimated gravimetrically as SnO_2. CHN analyses were carried out on a Perkin Elmer 2400 Elemental Analyzer. The elemental and spectral analyses of synthesized compounds have been carried out at SAIF Punjab University, Chandigarh. The purity of compounds was checked on thin layers of silica gel in various non-aqueous solvent systems, e.g. benzene: ethylacetate (9:1), benzene: ethylacetate (8:2). Molecular weight determinations were carried out by the Rast camphor method. Molar conductance measurements were made in anhydrous dimethylformamide at 25±5 °C using a Systronics conductivity bride model 305. The electronic spectra were recorded in DMSO on a Thermo UV1 spectrophotometer. IR spectra were recorded on a Perkin Elmer Spectrum SP-2 Fourier transform spectrophotometer using KBr pellets (4000–400 cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance II (400 MHz) FTNMR spectrometer using DMSO-d_6 as solvent at 400 MHz and 100 MHz, respectively. TMS was used as internal reference for ^1H NMR and ^{13}C NMR. The ^{119}SnNMRspectra with proton noise decoupling were recorded on a Bruker Avance II spectrometer using dry DMSO as the solvent at 149.21 MHz and tetramethyltin (TMT) as an external standard. X-ray powder patterns were obtained with a SIEMENS D-5000 X-ray diffractometer using CuKα radiation (l = 1.5405984 Å) and setting of 30 kV and 15 mA. The geometry optimization of the compound (1b) and (2b) from the experimental structures was carried out with DFT method. B3LYP at 6-31G basis sets were performed with the Gaussian 03 software package, and Gauss view visualization program [24] to conduct the DFT calculations. B3LYP methods at 6.31G basis sets calculation level were employed in investigation of the optimized molecular structures.

Syntheses of Tributyltin(IV) Complexes

Bis(tri-*n*-butyltin) oxide (2.5 mmol) was added to the calculated amount of the ligands (5.0 mmol) in 1:2 molar ratio in dry benzene (70 ml), methanol (30 ml) mixture as reaction medium. The contents were refluxed on a fractionating column for about 6 - 8 hours. The water librated in the reaction was removed azeotropically with benzene. On completion of the reaction, the resulting products were rendered free from solvent and then washed repeatedly with dry cyclohexane. The crystalline solids were separated out and purified by recrystallization from the same solvent. The products so formed were finally dried in vacuum at 40±5 °C for 2 - 3 hours. The purity of the complexes was checked by TLC using silica gel-G as adsorbent. Their physical properties and analytical data are given below:

Compound [**2a]**: Yield: 72.05 %; m.p. 220 °C; colour: yellowish; Anal. Calcd. for $C_{26}H_{42}N_2O_3Sn$: Sn, 21.61; C, 56.85; H, 7.71; N, 5.10. Found: Sn, 21.53; C, 56.97; H, 7.68; N, 5.15; IR (KBr, cm^{-1}): 1610s (C=N- stretching vibration), 1728s (-C=O stretching of carboxylate group), 1600m (COO asymmetric stretching of COO), 1325m (COO symmetric stretching of COO), 545m (Sn←N), 434s (Sn-O), 656m (Sn-C); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 3.98 (1H, *d*, *J* = 7.2 Hz, N-C<u>H</u>-CH-), 2.08-2.16 (1H, *m*, CH_2-C<u>H</u>-CH_3), 0.80 (3H, d, *J* = 7.2 Hz, CH-C<u>H_3</u>), 1.48-1.57 (2H, *m*, -CH-C<u>H_2</u>-CH_3), 0.95 (3H, *t*, *J* = 7.3 Hz, CH_2-C<u>H_3</u>), 8.10 (1H, *s*, NH) 7.22-7.80 (4H, *m*, aromatic ring); 1.65-1.21(6H, *m*, -$(CH_2)_3$-); 0.80 (3H, *t*, *J* = 7.4 Hz, C<u>H_3</u> of butyl group); ^{13}C-NMR (100 MHz, DMSO, δ / ppm): 185.2 (-COO), 66.6 (-CH), 154.3 (-C=N), 21.3 (-CH_2), 17.5 (-CH_3), 167.5, 146.1, 133.0, 130.6, 126.4, 124.2, 120.2 (aromatic carbons); 27.4, 27.9, 24.6, 13.5 (Sn-Bu); ^{119}Sn-NMR (149.21 MHz, DMSO, δ / ppm): 125.38.

Compound [**2b]**: Yield: 83.09 %; m.p. 230 °C; colour: light brown; Anal. Calcd. for $C_{25}H_{39}ClN_2O_3Sn$: Sn, 20.84; C, 52.70; H, 6.90; N, 4.92. Found: Sn, 20.92; C, 52.61; H, 6.97; N, 4.87; IR (KBr, cm^{-1}): 1618s (C=N- stretching vibration), 1724s (-C=O stretching of carboxylate group), 1604s (COO asymmetric stretching of COO), 1322m (COO symmetric stretching of COO), 540w (Sn←N), 430m (Sn-O), 638m (Sn-C); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.38 (2H, *t*, N-CH-C); 8.12(2H, *s*, NH); 7.17-7.83(4H, *m*, aromatic); 0.76 (3H, *t*, CH_3, Sn-Bu); 1.25-1.90 (6H, *m*, -$(CH_2)_3$-, Sn-Bu); ^{119}Sn-NMR (149 MHz, DMSO, δ / ppm):132.15.

Compound [**2c]**: Yield: 69.57 %; m.p. 160 °C; colour: light brown; Anal. Calcd. for $C_{25}H_{40}N_2O_3SSn$: Sn, 20.92; C, 52.92; H, 7.11; N, 4.94; S, 5.65. Found: Sn, 20.78; C, 52.79; H, 7.05; N, 4.91; S, 5.57; IR (KBr, cm^{-1}): 1612s (C=N- stretching vibration), 1726s (-C=O stretching of carboxylate group), 1596m (COO asymmetric stretching of COO), 1322m (COO symmetric stretching of COO), 550w (Sn←N), 455m (Sn-O), 668s (Sn-C); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.46(1H, *t*, -CH-); 3.30(2H, *d*, -CH_2); 7.08-7.82(5H, *m*, aromatic); 1.72-1.18 (6H, *m*, -$(CH_2)_3$-); 0.76, (3H, *t*, CH_3 of butyl group); ^{13}C-NMR (100 MHz, DMSO, δ / ppm): 184.2 (-COO), 60.1 (-CH), 153.7 (-C=N),

30.8 (-CH_2), 17.5 (-CH_3), 157.0, 144.6, 136.4, 132.2, 129.3, 122.8, 117.5 (aromatic carbons); 27.1, 28.7, 25.2, 13.9 (Sn-Bu).

Compound [**2d]**: Yield: 72.90 %; m.p. 210 °C; colour: light brown; Anal. Calcd. for $C_{26}H_{37}ClN_4O_3Sn$: Sn, 19.53; C, 51.38; H, 6.14; N, 9.22. Found: Sn, 19.67; C, 51.22; H, 6.08; N, 9.14; IR (KBr, cm^{-1}): 1608s (C=N- stretching vibration), 1722s (-C=O stretching of carboxylate group), 1595m (COO asymmetric stretching of COO), 1318m (COO symmetric stretching of COO), 555s (Sn←N), 442w (Sn-O), 645s (Sn-C); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.42(1H, *t*, N-CH-); 3.29 (2H, *d*, *J* = 7.6 Hz, -CH_2-); 7.05-7.75 (5H, *m*, aromatic); 1.76-1.20 (6H, *m*, -$(CH_2)_3$-); 0.80 (3H, *t*, CH_3 of butyl group); ^{119}Sn-NMR (149.21 MHz, DMSO, δ / ppm):128.25.

Compound [**2e]**: Yield: 80.27 %; m.p. 216 °C; colour: light brown; Anal. Calcd. for $C_{25}H_{39}ClN_2O_3SSn$: Sn, 19.73; C, 49.89; H, 6.53; N, 4.65; S, 5.33. Found: Sn, 19.58; C, 49.74; H, 6.50; N, 4.58; S, 5.30; IR (KBr, cm^{-1}): 1605s (C=N- stretching vibration), 1734s (-C=O stretching of carboxylate group), 1590s (COO asymmetric stretching of COO), 1315m (COO symmetric stretching of COO), 560m (Sn←N), 450m (Sn-O), 662m (Sn-C); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.81 (1H, *t*, N-CH-CH_2-); 2.30 (4H, *m*, -$(CH_2)_2$-); 1.72 (3H, *s*, -CH_3); 8.14 (1H, *s*, NH); 6.97-7.80 (4H, *m*, aromatic); 1.88-1.20 (6H, *m*, -$(CH_2)_3$-); 0.85 (3H, *t*, CH_3 of butyl group); ^{119}Sn-NMR (149.21 MHz, DMSO, δ / ppm):125.38.

Antibacterial Assay

Synthesized compounds were screened for their antibacterial activity against *B. cereus*, *E. coli*, *Klebsiella spp*. and *Staphylococcus spp*. at various concentrations 100 µg/ml and 200 µg/ml by the agar well diffusion method [25]. 5 ml aliquot of nutrient broth was inoculated with the test organisms and incubated at 30 °C for 24 hours. Sterile nutrient agar plates were also prepared and holes of 5 mm diameter were cut using a sterile cork borer ensuring proper distribution. The test organisms after 24 hours of incubation were spread onto separate agar plates. The chemical compounds were dissolved in DMSO were poured into appropriately labeled holes using a pipette in aseptic conditions. A hole containing DMSO served as a control. Triplicate plate of each bacterial strain was prepared. The plates were incubated aerobically at 30 °C for 24 h. The antimicrobial activity was determined by measuring the diameter of the zone (mm) showing complete inhibition with respect to control (DMSO).

RESULTS AND DISCUSSION

Bis(tri-*n*-butyltin) oxide reacts with the Schiff bases in 1:2 molar ratio in dry benzene and methanol to give the complexes under azeotropic removal of water (Scheme 1). The reactions were found to be quite facile and were complete within 6–8 h of refluxing. The resulting solid complexes were obtained in good yields (70–90 %). The solid complexes were soluble in methanol, DMSO and DMF and sparingly soluble in chloroform and other organic solvents. The compounds were dissolved in DMF and molar conductance 10^{-3} M of solution at 25 °C was measured. The molar conductance valves of the complexes fall in the range 04.85 to 08.14 Ω^{-1} cm^2 mol^{-1}, indicating their non-electrolytic nature.

IR spectral study

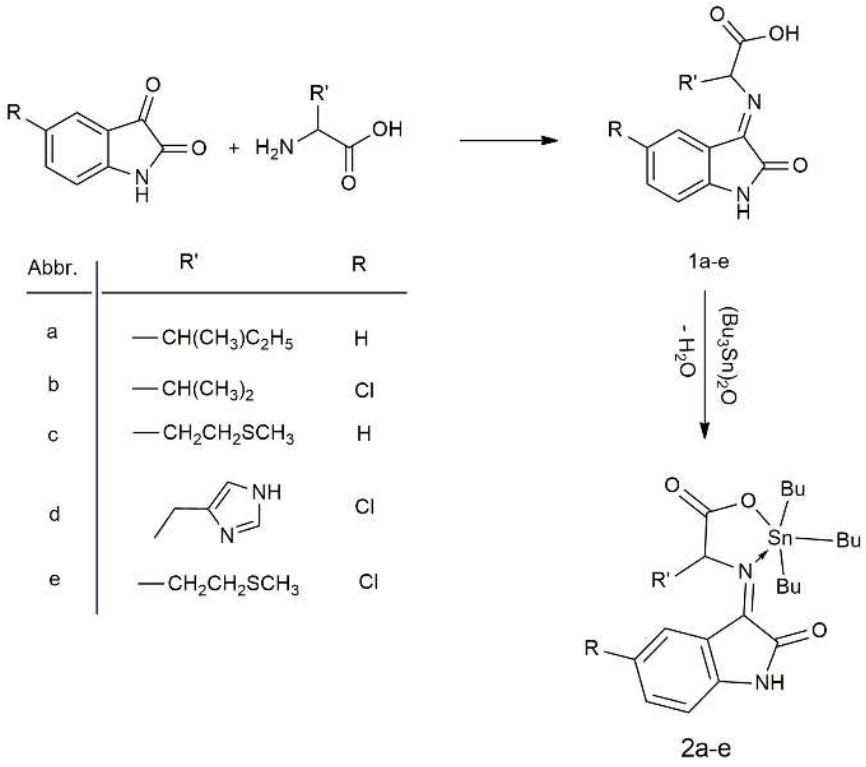
The characteristic infrared absorption frequencies (cm^{-1}) and their assignments for the ligand and their triorganotin(IV) complexes are given in experimental section. In all the tributyltin(IV) Schiff base complexes studied, absorption bands in the range of 1605 – 1618 cm^{-1}, due to the ν(C=N) undergo a substantial lowering when compared with the free ligands (1622-1632 cm^{-1}), indicating coordination by the azomethine group to the central tin atom [18]. The new bands appeared in the region of 545±10 cm^{-1} in the spectra of the complexes, are assigned to stretching frequencies of ν(Sn←N) [18] bond formations.

The spectra of the ligands contain a broad absorption band appeared in the region 3110-2750 cm^{-1} which is assigned to hydrogen bonded ν(OH) [25]. The disappearance of broad band in the spectra of the tin complexes, which was present in all the free ligands, suggests the deprotonation of the free COOH group upon complexation [20]. The appearance of a new band in the spectra of all tin complexes in the region 440-460 cm^{-1}, which may be assigned to ν(Sn−O), further, supports the bonding of carboxylate group to the tin atom. The complexation of organotin(IV) with the ligands are confirmed by the presence of Sn←N, Sn-O and Sn-C bonds.

Electronic spectral study

The spectra of the ligands and their complexes were recorded in dry DMSO. The various bands observed were assigned to inter-ligand and charge transfer of n-π* transition according to their energies and intensities. Electronic spectra of the complexes exhibit three bands in the region 200-235, 250-345 and 365-430 nm, which may be due to the π-π* transition of benzenoid, π-π* transition of COO and π-π* transition of the >C=N- chromophore, respectively. Further, there was a sharp band observed in the 252±5 nm region in the spectra of the complexes,

which could be assigned as a charge transfer band. It has been reported that a metal is capable of forming dπ-pπ* bonds with ligands containing nitrogen or oxygen as the donor atoms. Since tin atom has its 5d orbitals completely vacant, L-M bonding can take place by the acceptance of a pair of electrons from nitrogen or oxygen atoms of the ligands.



Scheme 1. Representative equation illustrating the formation of Schiff bases and their triorganotin(IV) complexes.

[1]H NMR spectral study

The characteristic resonance peaks in the ^{1}H NMR spectra of the complexes, recorded in DMSO-d_6, are given in experimental section. A signal appears at δ 11.39 – 12.28 ppm in the spectra of ligands due to the carboxylic proton is absent in the spectra of the corresponding tin complexes, indicating the involvement of the carboxylic oxygen in bonding to tin atom. The ligands give a complex multiplet signal in the region δ 6.95 - 7.89 ppm (m) for the aromatic protons and these remain almost at the same position in the spectra of the tin complexes. The complexes, however, show additional signals at δ 1.65 – 1.21 ppm owing to the protons of the butyl group. The CH_3 protons of tributyltin compounds are significant as a triplet at δ 0.78-82 ppm, while –CH_2- protons appear as a multiplet. The protons in the complexes have been identified and the total numbers of protons calculated from the integration curves are in agreement with the proposed molecular formulae.

[13]C NMR spectral study

The ^{13}C NMR spectral data for few represented ligands and their corresponding tin complexes have been recorded in dry DMSO (experimental section). The complexes exhibited a δ (COO) signal in the range of ~δ 185 ppm. The ^{13}C NMR spectra of complexes showed that the chemical shift of the δ(COO) signal in each complexes was shifted downfield compared to that of their parent ligands (~δ 178 ppm), indicating the involvement of the carboxylic oxygen in coordination to the tin atom. The occurrence of resonances in the range of 110 -150 ppm in the ^{13}C NMR spectra of the complexes and ligands defined as benzene signals. The carbon of the butyl group is observed at (δ 7.4-13.5 ppm) position comparable to other similar compounds [26].

[119]Sn NMR spectral study

The value of δ(^{119}Sn) define the coordination number of the central tin atom. All the complexes, ^{119}Sn NMR spectra show only a sharp singlet indicating the formation of a single species. For organotin(IV) complexes, the δ(^{119}Sn) value for four-coordinated complexes fall in the range between δ +200 to δ -60 ppm; for five-coordinated complexes fall in the range between δ -90 to δ -190 ppm and for six-coordinated complexes fall in the range between δ -210 to δ -400 ppm. Complexes of tributyltin(IV) exhibited δ(^{119}Sn) values at ~ δ□-125.38 ppm which lie in the range of δ -

90 to δ -190 ppm, hence, indicating that the tin atom in all the complexes have five-coordinated and have a trigonal bipyramidal geometry [18,21,27].

On the basis of the above mentioned different spectral studies, it is suggested that the bonding through the azomethine nitrogen and carboxylate oxygen atoms to the tin atom. Finally, distorted trigonal bipyramidal geometries around the tin atom have been proposed.

X-ray powder diffraction study

The X-ray diffraction studies have been performed on PANalytical X-ray powdered diffractometer. The experimental conditions employed in reading the pattern were as follow: the operating target voltage 30kV, the tube current 15 mA. The X-ray from copper target was filtered with nickel and monochromatic Kα line of wavelength 1.5406 Å was obtained. Filtration reduces noise due to white radiation and increases resolution also. The X–ray diffraction of L^1H and its metal complexes indicates crystalline nature of ligand (1a) and there tin complex (2a). All the reflection has been indexed for D (particle size) using Scherrers equation. Basically crystallite size is reflected in the broadening of a particular peak in a diffraction pattern associated with a particular planar reflection from within the crystal unit cell. It is inversely related to the FWHM of an individual peak, the more narrow the peak, the larger the crystallite size. The individual crystallite domains are periodic and in phase, the diffraction of the X-Ray beam is reinforced, resulting in a tall narrow peak. The crystals are defect free and periodically arranged, the X-ray beam is diffracted to the same angle even through multiple layers of the specimen. The crystals are more randomly arranged or have low degrees of periodicity; the result is a broader peak. The average particle size is 30.879 nm and 38.281 nm, respectively for ligand (1a) and its triorganotin(IV) complex (2a). These values of particle size and 2θ for each peak have been calculated with the help of the cell parameters and corresponding FWHM values. The lattice spacing, FWHM and particle size for L^1H and its tin complex has been found out and are given in Table 1 and Table 2, respectively. The diffractogram of compounds are shown in Figure 1 and 2.

Table 1. X-ray powder diffraction data of the ligand (1a)

S.No.	2θ	d (Å) (Obs.)	d (Å) (Calc.)	FWHM	D*
1	13.503	6.55203	6.55240	0.4765	28.897
2	14.925	5.93080	5.93086	0.3792	36.255
3	16.827	5.26461	5.26449	0.3960	34.637
4	21.464	4.13654	4.13651	0.5075	26.843
5	22.025	4.03257	4.03256	0.4712	28.884
6	22.540	3.94156	3.94157	0.3691	36.841
7	23.880	3.72325	3.72323	0.5726	23.691
8	27.269	3.26781	3.26772	0.4268	31.571
9	28.452	3.13454	3.13449	0.4278	31.417
10	31.937	2.79998	2.79997	0.4940	26.984
11	34.510	2.59690	2.59692	0.3935	33.650

**D = Crystallite size (in Å), d = lattice spacing*

Table 2. X-ray powder diffraction data of the tributyltin(IV) complex (2a)

S.No.	2θ	d (Å) (Obs.)	d (Å) (Calc.)	FWHM	D*
1	10.124	8.72982	8.73059	0.1219	113.300
2	23.436	3.79274	3.77783	0.4567	29.727
3	25.992	3.42537	3.42538	0.3084	43.808
4	27.990	3.18518	3.18516	0.4240	31.731
5	30.336	2.94399	2.94401	0.3471	38.555
6	34.711	2.58227	2.58230	0.4063	32.572
7	36.697	2.44696	2.44695	0.4208	31.275
8	40.473	2.22696	2.22694	0.3648	35.662
9	44.328	2.04184	2.04183	0.3797	33.818
10	49.998	1.82276	1.82276	0.5497	22.861
11	50.419	1.80853	1.80851	0.4367	28.726
12	59.364	1.55557	1.55556	0.4664	25.828
13	62.831	1.47781	1.47782	0.3972	29.791

**D = Crystallite size (in nm), d = lattice spacing*

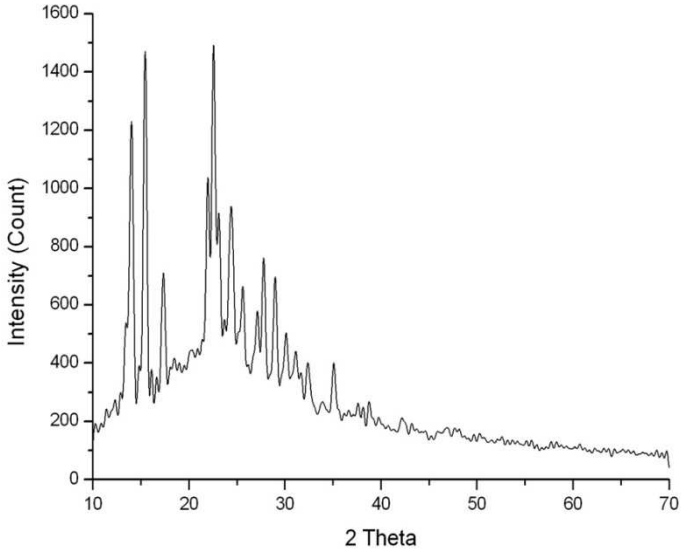


Fig. 1 X-ray diffraction pattern of compound (1a)

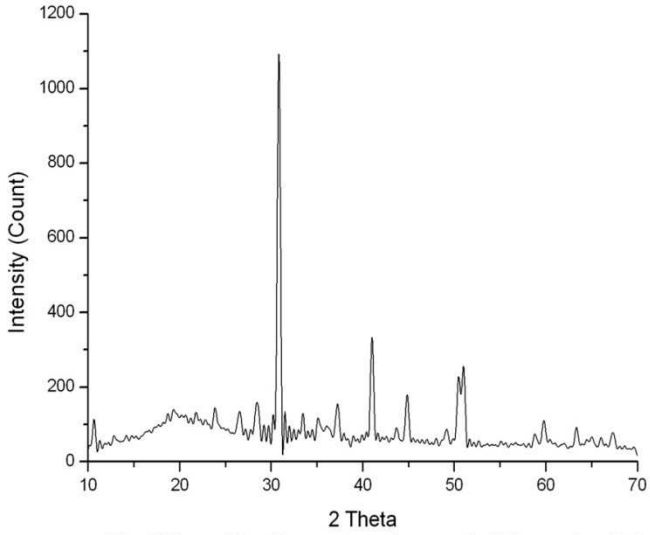


Fig. 2 X-ray diffraction pattern of organotin (IV) complex (2a)

Theoretical calculations

B3LYP (6-31G) calculations were performed for ligand and its complex. The optimized molecular structure of the most stable form is shown in Figure 3 and 4, respectively. The deprotonated ligand is coordinated as bidentate ligand *via* the carboxylate oxygen, and azomethine nitrogen atoms. The five coordination number is completed by three carbon atoms of butyl groups. The organic molecule acts as anionic bidentate with the ON donors placed in the same side. Since the synthesized compounds are related and differ only in substituted R group, one compound (2b) was theoretically studied. Based upon spectroscopic data, Sn(IV) compounds with ON ligands generally adopt distorted trigonal bypyramidal geometry. The optimized structure for the compound (2a) is shown in Figure 4. The bond angles around tin atom, for example C(26)-Sn(1)-C(32) angle of 93.4°, N(5)-Sn(1)-O(2) angle of 78.1°, C(26)-Sn(1)-C(32) angle of 103.1°, C(26)-Sn(1)-N(5) angle of 91.6°, C(26)-Sn(1)-O(2) angle of 156.4°, C(26)-Sn(1)-C(29) angle of 100.5°, C(32)-Sn(1)-N(5) angle of 146.8°, C(32)-Sn(1)-O(2) angle of 84.5°, C(29)-Sn(1)-N(5) angle of 108.2°, C(26)-Sn(1)-N(5) angle of 91.6°, C(29)-Sn(1)-O(2) angle of 102.9° in $Bu_3Sn(L^2)$ are the representative of the trigonal bipyramidal structure. The Sn-O bond distances are close to be identical values. The calculated Sn-O bond distances of 2.0452 Å in compound (2b), are also close to the already reported Sn-O distances in tris[(2-methyl-2-phenyl)propyl](2,4-dinitro-phenolato)tin (2.048) [28]. The different Sn-C distances of Sn(1)-C(26)/Sn(1)-C(29)/Sn(1)-C(32) and Sn-N distance of Sn(1)-N(5) in compound (2b) are 2.181/2.177/2.189 Å and 2.095 Å, which are similar to the already reported structures [29], SaleanH_2Sn 2.0535(9), 2.0369(8) Å.

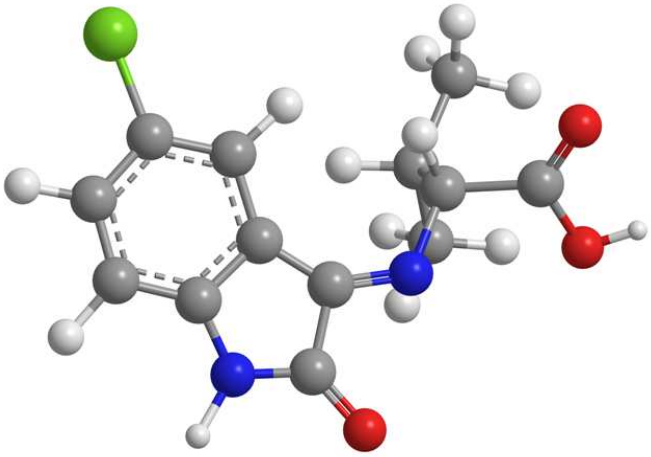


Fig. 3 Optimized Structure of the Ligand (1b)

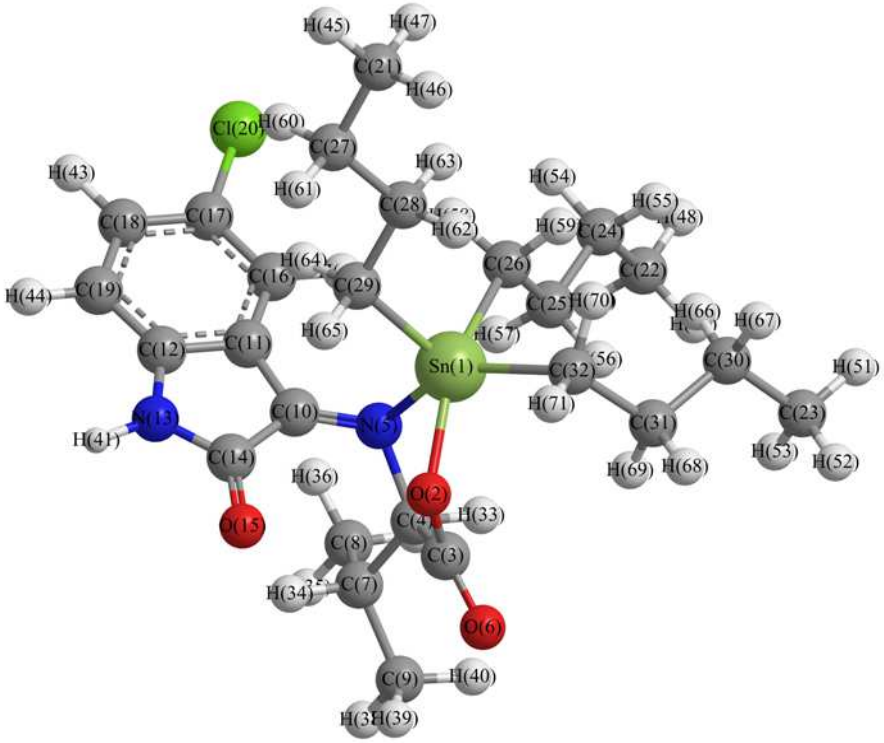


Fig. 4 Optimized Structure of the organotin(IV) complex (2b)

Molecular orbital calculations provided a detailed description of the orbitals including the spatial characteristics, nodal patterns and individual atom contributions. The contour plots of the frontier orbitals for the ground state of (1b) and (2b) are shown in Figure 5 and Figure 6 together with the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). It was interesting that both orbitals were substantially distributed over the conjugation plane. In addition, it can be observed that the HOMO orbitals were located on the substituted molecule, while the LUMO orbitals resembled those obtained for the unsubstituted molecule. Therefore, the substitution influenced the electron donation ability while imposing only a small impact on the electron acceptance ability.

The orbital energy levels of the HOMO and LUMO of (1b) and (2b) are shown in Figure 5 and Figure 6. An electronic system with a larger HOMO-LUMO gap should be less reactive than one having a smaller gap. In the present study, the HOMO-LUMO gap values of (1b)/(2b), were -8.305/-4.301 and -8.122/-5.254 eV, respectively.

The lower value in the HOMO and LUMO energy gap would explain the eventual charge-transfer interaction taking place within the molecules. The low HOMO values for compound (1b) indicated that this molecule had low ionisation energies, suggesting that it could lose electrons easily.

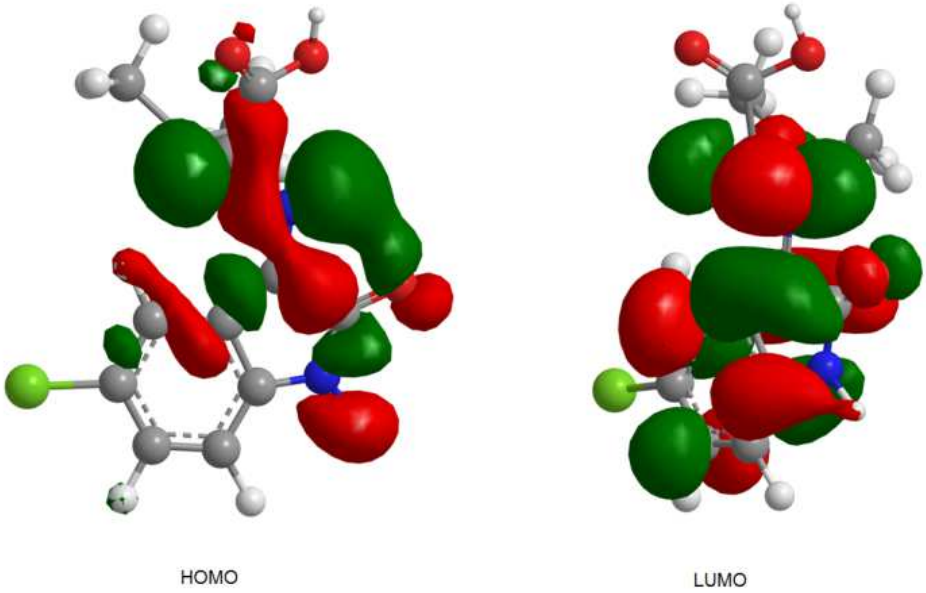


Fig. 5 Frontier orbitals of the compound (1b)

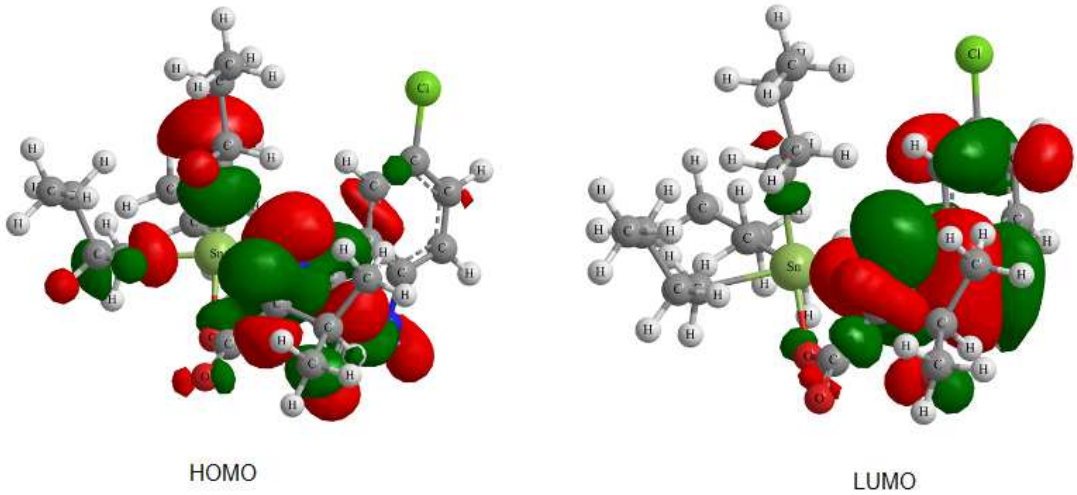


Fig. 6 Frontier orbitals of the organotin(IV) complex (2b)

Antimicrobial results

Newly synthesized organotin(IV) compounds were tested by the well diffusion method [25] for their antimicrobial activities at a concentration of 100 µg/ml and 200 µg/ml. *Bacillus cereus*, *E. coli*, *Klebsiella spp*. and *Staphylococcus spp*. (bacteria) were used as the test organisms. Streptomycin was used as positive control to compare its activity with synthesized complexes. The data in Table 3 show the complexes exhibit significant antibacterial activity as compared to the free ligand. The antibacterial screening results show that organotin(IV) complexes are more active as compared to the ligands, which indicate that metallation increases the activity. All the complexes tested were found to be highly active against all the micro-organisms. This may be due to the greater lipophilic nature of the complexes [30]. Comparison of the activities of synthesized complexes with standard drug and with compounds already reported in literature [31] showed that some complexes are more potent but some are less active than standard drug against different test microorganisms. Comparison of activity indices reveals that compounds (1b) and (2b) are more active than the other compounds against *E. coli*, *Klebsiella spp.* and compounds (1c) and (2c) are found to possess greater activity than the other complexes against *Bacillus cereus*. Compound (1a)

and (2a) are found to p**o**ssess greater activity than the other compounds against *Staphylococcus spp*. The above studies indicate clearly that the complexes synthesized in the present studies are highly active against all these pathogens.

Table 3. Antibacterial Activity of ligands their triorganotin(IV) complexes

Compds	Inhibition Zone[a] (Activity index)[b]							
	E. coli		*Klebsiella spp*		*Bacillus cereus*		*Staphylococcus spp*	
	100 µg/ml	200 µg/ml	100 µg/ml	200 µg/ml	100 µg/ml	200 µg/ml	100 µg/ml	200 µg/ml
1a	11.7 (0.71)	13.9 (0.69)	8.6 (0.57)	11.6 (0.60)	10.2 (0.58)	12.6 (0.57)	12.1 (0.67)	15.1 (0.67)
2a	16.3 (0.99)	19.8 (0.98)	13.5 (0.89)	15.5 (0.81)	15.8 (0.90)	18.8 (0.86)	18.2 (1.01)	20.9 (0.93)
1b	10.5 (0.64)	13.5 (0.67)	8.2 (0.54)	11.2 (0.58)	11.4 (0.65)	14.6 (0.66)	8.7 (0.48)	11.9 (0.53)
2b	15.7 (0.96)	20.3 (1.00)	15.3 (1.01)	19.1 (0.99)	16.9 (0.97)	19.7 (0.90)	13.6 (0.76)	16.2 (0.72)
1c	13.7 (0.84)	15.0 (0.74)	5.6 (0.37)	7.2 (0.38)	11.1 (0.63)	15.0 (0.68)	10.2 (0.57)	12.9 (0.57)
2c	16.8 (1.02)	18.8 (0.93)	11.5 (0.76)	15.6 (0.81)	17.2 (0.98)	20.2 (0.92)	14.6 (0.81)	16.9 (0.75)
1d	5.9 (0.36)	6.7 (0.33)	6.4 (0.42)	8.1 (0.42)	4.8 (0.27)	6.5 (0.30)	5.6 (0.31)	6.7 (0.30)
2d	8.6 (0.52)	10.2 (0.50)	9.7 (0.64)	11.7 (0.61)	9.2 (0.53)	11.2 (0.51)	14.8 (0.82)	20.0 (0.89)
1e	5.6 (0.34)	6.7 (0.33)	4.3 (0.29)	6.4 (0.34)	7.9 (0.45)	9.6 (0.44)	7.8 (0.43)	9.4 (0.42)
2e	12.5 (0.76)	14.8 (0.73)	10.6 (0.70)	14.7 (0.77)	15.2 (0.87)	18.2 (0.83)	13.6 (0.76)	16.9 (0.75)

[a] *IZ = Inhibition zone (in mm).*

[b] *(AI) = Activity index = Inhibition zone of test compounds/Inhibition zone of standard.*

CONCLUSION

In the present study, the triorganotin(IV) complexes of Schiff bases were prepared and characterized by elemental analysis, molar conductance, and spectroscopic techniques, and its geometric structure. The results showed that the structure of the complexes are distorted trigonal bipyramidal in which the (1a-e) acts as monofunctional bidentate ligands in a N, O^- manner, via the deprotonated carboxylate oxygen and the azomethine nitrogen. The XRD patterns indicate crystalline nature of the complexes. Furthermore, the theoretical calculations are in close agreement with the X-ray data of the reported similar compounds. These compounds exhibited significant activity against all the tested microorganisms.

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