Synthesis, Spectral, Biological and Theoretical Investigation of Some New Sn (IV) Complexes with Schiff Base Ligands Containing NNOS Coordination Sphere

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Abstract

New tin (**IV**) complexes of empirical formula, $[Cl_2Me_2Sn(H_2L)^{1-3}]$, where $((H_2L)^{1-3}$: Methyl-2-{[1-methyl-2-(2-hydroxy-3-methoxyphenyl)methylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate [H2cd3OMesalMeen], Methyl-2-{[1-methyl-2-(2-hydroxy-4-methoxyphenyl)methylidynenitrilo]ethyl}amino-1-cyclopentenedithiocar-boxylate, $[H_2cd4OMesalMeen]$, Methyl-2-{[1-methyl-2-(2-hydroxy-5-methoxyphenyl)-methylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate, $H_2cd5OMesalMeen$]) have been prepared and fully characterized by a variety of physico-chemical techniques. Spectroscopic data suggest that in three complexes the Schiff base ligand is coordinated through oxygen. The Schiff base ligands and their Sn (IV) complexes were tested against two pathogenic bacteria (Staphylococcus aureus as Gram-positive bacteria and Escherichia coli as Gram-negative bacteria). All the complexes exhibit higher antibacterial activity than the free ligands. Computation analyses at the level of DFT with Becke's three parameter hybrid methods were performed to study the geometrics, electronic structures; HOMO- LUMO energy gap, dipole moment and its calculated vibrational frequencies were investigated. An excellent agreement between the experimental and calculated results obtained from the two spectra methods.

Keywords: *Tin (IV) complexes, Antibacterial, Schiff base ligand, Theoretical methods.*

Introduction

Schiff bases are well-known an intensive area of research due to their simple synthesis, versatility and diverse range of application. These types of chemical ligands have wide application in food industry, dye industry,

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analytical chemistry, catalysis, fungicidal, agrochemical and biological activities [1-5]. Schiff base played a key role in the development of coordination chemistry as the readily form stable complexes with most transition metals. The fields of Schiff base complexes have been fast growing on account of the wide variety of possible structures for the ligands depending upon the ketones, aldehydes and amines. The interest in sulfur chelating Schiff base has been stimulated by their interesting physical and chemical properties and potentially useful bioactivities. However, in the past, most work on Schiff base containing Sulfur donor atom involved their complexes with transition metal ion [6-10].The complexes of this ligand with non transition metal ions have not received as much attention. Organotin complexes of Schiff base have been synthesized and studied for some times because they have some characteristics properties like manifestations of novel structures, thermal stability, relevant biological properties and synthesis flexibility, medicinal utility and commercial applications [11-14]. The development of these complexes resulted in an advance research activity in the field of coordination chemistry leading to very interesting conclusions. Keeping these developments in mind, we have synthesized some organotin (IV) complexes, as potential antibacterial agents and as a conformationally flexible ligand containing both hard and soft donor atoms O, N and S. The compounds

were characterized by elemental analysis, IR, NMR, and UV-Vis techniques. Also, the structure of the complexes was studied by the density functional theory to find the electronically stable structure. The theoretical goal of this study focuses on these features of the chemistry. The comparison between the experimental and the theoretical results about the title compound have also been revealed in the paper.

Experimental

Materials

All chemicals and reagents were of reagent grade quality. All the reagents, viz., 3-methoxysalicylaldehyde, 4-methoxysalicylaldehyde, 5-methoxysalicylaldehyde 1,2- diaminopropane, ammonia solution, carbon disulfide, dimethylsulfate, cyclopentanone, dimethyltin (**IV**) dichloride (Merck) dibutyltin (**IV**) dichloride and diphenyltin (**IV**) dichloride (Alfa Aesar) were used as received.

Apparatus and Techniques

The infrared spectra of the solid compounds were recorded on a Shimadzu FTIR 8300 spectrophotometer in the range 4000-200 cm^{-1} from KBr discs. The melting points were determined in open capillaries with electronic melting point apparatus. C, H, N, S analyses were carried on a Termo Fininngan-Flash-1200. The ^{1}H and ^{119}Sn NMR spectra data were obtained on Bruker Avance DPZ 500

MHz spectrometer using TMS and SnMe$_4$ as references and chemical shift are expressed in ppm. The conductivity were performed using Jenway 4310 conductivity meter and a diptype cell with a platinized electrode in DMF having 10^{-3} M solutions of the metal complexes at room temperature. UV-Vis spectra were recorded in DFT with T80 UV-Vis spectrophotometers.

Preparation of ligands and corresponding complexes

The unsymmetrical Schiff base ligands has been synthesized by stirring at room temperature a 1:1 molar ratio mixture of methyl-2-(1-methyl-2'-amino-ethane)amino-1-cyclopentenedithiocarboxylate [HcdMeen] and 3, -4, 5- methoxysalicylaldehyde in methanolic solution following a reported method [15-17]. The resultant yellow powder was recrystallized from methanol/chloroform 2:1 (V:V). To a stirred solution of methyl-2-{[1-methyl-2-(2-hydroxy-3-methoxyphenyl) methylidynenitrilo]ethyl}amino-1-cyclo-pentenedithiocarboxylate [H$_2$cd3OMesalMeen], methyl-2-{[1-methyl-2-(2-hydroxy-4-methoxyph-enyl)methylidynenitrilo]ethyl} amino-1-cyclopentenedithiocarboxylate, [H$_2$cd4OMesalMeen] and methyl-2-{[1-me-thyl-2-(2-hydroxy-5-methoxyphenyl)methylidynenitrilo]ethyl}amino-1-cycl-openten-edithiocarboxylate, [H$_2$cd5OMesalMeen] (1 mmol) in 15 mL of chloroform/methanol 2:1(V:V), a solution of Me$_2$SnCl$_2$ (1 mmol) in 15 mL of methanol was added slowly at r.t. The mixture was then stirred for 4-6 h.

During this period, the yellow solid precipitate formed was filtered and washed with petroleum ether (Sheme 1). Similar procedure with some change was employed for the reaction of dibutyl- and diphenyltin (IV) dichloride. All attempts for preparing of these complexes were unsuccessful.
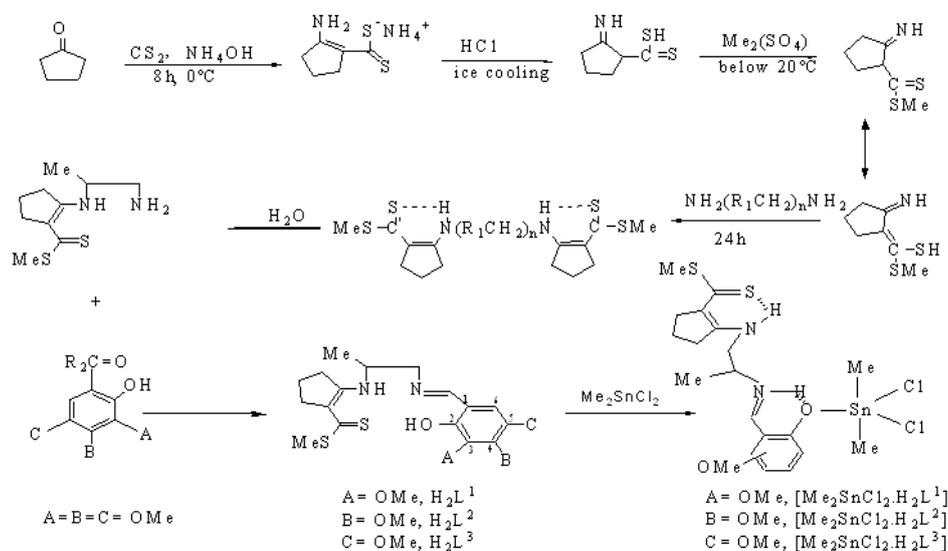
Scheme 1.

Determination of bacteriological activity

Bioactivities were investigated using agar-well diffusion method [18]. The synthesized Schiff base ligands and their tin (IV) complexes were screened for their biological activities by using two bacteria namely Staphylococcus aureus and Escherichia coli by the reported method. The bacteria were subculured in agar medium. Recommended concentration (100 µL) of the test sample 1mg/mL in DMSO was introduced in the respective wells. The Petri dishes were incubated immediately for 24 hours at 37ºC. Activity was determined by measuring the diameter of the zone showing complete inhibition (mm). Growth inhibition was compared with standard drugs. In order to clarify the role of DMSO on the biological screening, separate studies were carried out with solvent DMSO only and it showed no activity against any microbial strains.

Theoretical methods

The quantum chemical calculations were performed using Gaussian 03 package [19]. The local minimum energy, dipole moment, HOMO- LUMO energy and its band gap of the optimized structures for Sn(IV) complexes was computed at Becke three parameter hybrid function (B3LYP) using LANL2DZ basis set for all atoms including tin [20]. The calculated vibrational spectra of the optimized complexes were assigned based on vibrational mode analysis with the aid of the DFT method.

Results and discussion

Elemental analysis

The structural formula of the three Sn(IV) complexes was obtained according to the following fact. The empirical formula for these complexes is $C_{20}H_{30}N_2Cl_2O_2SnS_2$ and formula weight for of them is 584.185. Experimental and calculated elemental compositions of the complexes are given in Table 1. The analytical data are in good agreement with the proposed stoichiometry of the complexes. Solutions of these complexes no react with silver nitrate indicating the existence of chloride in inside coordination's sphere of the tin ion.

Molar conductance

The tin (**IV**) complexes under investigation are quite stable at ambient temperature. They are sparingly soluble in donor solvents such as DMF and DMSO. The molar conductance of these complexes (Table 1) indicating that it is essentially a non-electrolyte in this solvent [21]. The very low conductance for these complexes is strong evidence that the Schiff base is coordinated to the tin atom as an un-negatively charged ligand and that the two chloro ligands are also coordinated to the tin ion.

Table 1. Analytical data and some physical properties of the tin(IV) complexes.

Complexes	Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)	Yeild (%)	m.p. (°C)	Anal. Found (Calc.)(%)			
				C	H	N	S
[Me$_2$SnCl$_2$.H$_2$L^1]	14	48	145	41.35(41.12)	5.53(5.18)	4.98(4.80)	11.02(10.98)
[Me$_2$SnCl$_2$.H$_2$L^2]	11	46	168	40.93(41.12)	5.32(5.18)	5.16(4.80)	10.86(10.98)
[Me$_2$SnCl$_2$.H$_2$L^3]	20	53	173	41.22(41.12)	5.46(5.18)	4.66(4.80)	10.76(10.98)

Infrared spectra

The IR spectra give enough information to elucidate the nature of bonding of the ligand to the metal ions. The IR spectra of free Schiff base were compared with the spectra of the tin (IV) complexes in order to study the binding mode of the Schiff base to Sn(IV) ion in the new complexes. In Table 2 the main infrared bands and their assignments are shown. In this spectra of free ligand and new complexes no band is observed in the region 3500-3600 cm^{-1} attributable to the stretching vibration of the free phenolic OH group indicating that the ring formed by the intramolecular hydrogen bond in the ligand which, is retained in complexes. Weak broad absorption bands appearing in the range of 2800-2900 cm^{-1} for the free Schiff base ligands are assigned to υ(O-H) and υ(N-H) overlapping with the υ(C-H) [17]. These bands are observed to shift slightly to higher frequency due to the coordination of phenolic oxygen atom with tin and changes in hydrogen bonding [22]. The strong bands at 1624-1635 cm^{-1}, which can be attributed to υ(C=N) stretching frequency on Schiff base ligands [17]. This band showed a major shift to higher frequency (1647-1659 cm^{-1}) is suggesting the complex formation and the proton transfer from phenolic oxygen atom to the imine nitrogen atom [23]. In the spectra of tin (IV) complexes a sharp peak at 1549-1558 cm^{-1} due to the υ(C O) providing evidence of participation of the phenolic oxygen in the tin-ligand bonding [24]. The aromatic υ(C=C) stretching frequency occurs at 1472-1485 cm^{-1} [25]. The characteristic sulfur vibration of υ(C-S) appearing at 790 cm^{-1} [17]. In the spectra of complexes these bands are shifted. New bands in the range of 580-590 cm^{-1} which are not present in the Free Schiff base are due to υ(Sn-O) vibration [26] and the appearance of the vibrations support the involvement of the oxygen atoms of phenolic group complaxation with the tin ion under investigations.

Table 2. Selected experimental and calculated vibrational frequencies (cm^{-1}) of the Sn(IV) Schiff base. omplexes.

	Complexes	υ(Sn-O) m	υ(C=S) br,m	υ(C=C) s	υ(C⋯O) s	υ(C=N) vs	υ(C-H) m
Experimental frequencies	[Me$_2$SnCl$_2$.H$_2$L^1]	587	790	1484	1553	1647	2850
	[Me$_2$SnCl$_2$.H$_2$L^2]	580	787	1472	1549	1641	2847
	[Me$_2$SnCl$_2$.H$_2$L^3]	584	790	1485	1558	1659	2853
Calculated frequencies	[Me$_2$SnCl$_2$.H$_2$L^1]	589	787	1738,1560,1489	1550	1652	2857
	[Me$_2$SnCl$_2$.H$_2$L^2]	575	788	1722,1560,1481	1550	1650	2851
	[Me$_2$SnCl$_2$.H$_2$L^3]	589	785	1750,1560,1490	1561	1663	2857

vs: very strong; s: strong; m: medium; w: weak; br: broad.

^{1}H and ^{119}Sn NMR spectra

The NMR spectrum is recorded to confirm the binding sites during the complexation. The NMR data are given in Table 3. The chemical shift observed for the –OH and –NH protons in free Schiff base ligands (δ 12.45-13.53 ppm) and (δ 12.37-12.38 ppm) was observed in all complexes. The shielding of this group and shifted up field in complexes may be due to bonding of the oxygen to the tin (IV) ion which lead to increase of the density of electrons on the hydroxyl group. The same results were confirmed by the IR spectroscopy. The signal at 8-9 ppm were assigned to imine proton (HC=N) is not flanked by satellites, this is an indicating that the N atom is not coordinated to tin(IV) [27]. The lack of down field shift in the position of the signal attributable to S-CH3 (δ 2.56 ppm in free ligand) indicates little or no participation of the –C=S group in binding [28]. The ligand shows multiple signals in the region δ 6.40-7.24 ppm for the aromatic protons and these values are remains almost same position in the spectra of Sn(IV) complexes. 1HNMR spectra of Schiff base ligands and their complexes show two peaks at chemical shift ca.1.37-1.39 and 3.77-3.90 ppm, these singlet peak with three proton integration has been assigned to the methyl group on diamine bridge and methyl moiety of the methoxy group. The high field regions in the spectra of dimethyl tin show signal at 1.15 ppm for all complexes and these are due to the methyl groups in the organotin fragment. These signals have satellites due to coupling with tin (^{2}J ^{119}Sn-H 71.0 and 77.1 Hz). The data describe above are all consistent with those observed for the other five coordinated diorganotin complexes containing Schiff base ligands [29].

Table 3. ^{1}H and [119] NMR spectral data of the tin (IV) complexes (δ/ppm, DMSO- d_6).

	[Me$_2$SnCl$_2$.H$_2$L^1]	[Me$_2$SnCl$_2$.H$_2$L^2]	[Me$_2$SnCl$_2$.H$_2$L^3]
^{1}H NMR data	1.12 (s, 6H, Sn-Me), 1.39 (3H, d, Me), 2.56 (3H, s, SMe), 3.48-3.56 (3H, m, H^{en}), 3.90 (3H, s, OMe), 6.81-6.92 (2H, m, H^{4,5}), 6.95 (1H, d, H^6), 8.30 (1H, s, CH=N), 12.05 (1H, br, NH), 13.12 (1H, br, OH);	1.12 (s, 6H, Sn-Me), 1.37 (3H, d, Me), 2.56 (3H, s, SMe), 2.76-3.52 (3H, m, H^{en}), 3.81 (3H, s, OMe), 6.40 (1H, s, H^3), 6.53 (1H, d, H^5), 7.09 (1H, d, H^6), 8.16 (1H, s, CH=N), 12.11 (1H, br, NH), 13.13 (1H, br, OH)	1.12 (s, 6H, Sn-Me), 1.39 (3H, d, Me), 2.56 (3H, s, SMe), 3.52-3.55 (3H, m, H^{en}), 3.77 (3H, s, OMe), 6.73 (1H, s, H^6), 6.86 (1H, d, H^4), 7.24 (1H, d, H^3), 8.11 (1H, s, CH=N), 12.14 (1H, br, NH), 12.05 (1H, br, OH)
^{119}Sn NMR data	-271.37	-267.41	-283.55

The value of chemical shift [119]Sn spectra expresses the coordination number of the nucleus in the related metal complexes. Although the shift ranges are dependent on the nature of substituents at the tin atom, the 119Sn resonance of tin complexes gives sharp signals between -90 and -330 ppm have been empirically related to the five coordination of tin atom in methyltin derivatives [22, 30,31]. Thus on the basis of the above evidences it is suggested that the geometry of the resulting tin complexes be characterized as trigonal by pyramidal. The proposed structures of newly synthesized complexes are shown in Scheme 1. Therefore, it is clear from these results that the data obtained from the elemental analysis, IR and NMR spectral measurements are in agreement with each other.

synthesized ligands and their complexes at very low concentrations (~10^{-4} M range) are recorded in DMF solution. The ligands exhibit the band at 312-314 and 392-398 nm can be assigned to intra ligand to π→π* and n→π* transition [17]. Complex formation with dimethyltin(IV)dichloride results changes of the spectra took place in the UV-Vis region (250-500 nm) of π→π* and n→π* absorption band upon this is interaction. The original peaks of the Schiff base ligands not changed (n→π*) and a new peak is appeared in 400-450 nm region. It seems that this is an LMCT from nO to Sn(IV) via coordination of Schiff base ligand to dimethyltindichloride. After coordination of Schiff base to Me$_2$SnCl$_2$, the π→π* transition in 312-314 nm region has a red shift [32].

UV-Vis absorption spectra

The Electronic absorption spectra of all the

Table 4. Electronic spectral data (λmax, nm, DMF) of the Schiff bases and their complexes.

Complexes	π-π*	n-π*	LMCT transition
[Me$_2$SnCl$_2$.H$_2$L^1]	٣٣٠	393	٤٣٥
[Me$_2$SnCl$_2$.H$_2$L^2]	323	398	٤٣٧
[Me$_2$SnCl$_2$.H$_2$L^3]	327	398	٤٣٥

Antibacterial activity results

The free Schiff base ligands and their corresponding tin(IV) complexes were tasted against the selected bacteria E.coli (G-) and S. aureus (G+). The measured zones of inhibition against of various microorganisms are summarized in Table 5. All the tested compounds showed good biological activity against microorganism. It is found that the complexes have higher antimicrobial activity than the free ligands. This can be explained on the Tweedy's chelation theory [33]. The lipid membrane that surrounds the cell favors the passage of only lipid soluble materials due to which lipophilicity is an important factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with the donor groups. Further, it increases the delocalization of p-electron over the whole chelate ring and hence enhances the liposolubility of the complexes. This increased liposolubility enhances the penetration of the complexes into the lipid membrance, the lipophilic group to derive the compound through the semipermeable of the cell, and blocks the metal binding sites in the enzymes of the microorganism

Table 5. The Growth inhibition zone (diameter in millimeter) of the Sn(IV) Schiff base complexes.

| Compounds	E. Coli	S. Aureus
Streptomycin (standard)	24	22
H$_2$L^1	21	18
H$_2$L^2	19	17
H$_2$L^3	21	20
[Me$_2$SnCl$_2$.H$_2$L^1]	27	26
[Me$_2$SnCl$_2$.H$_2$L^2]	25	24
[Me$_2$SnCl$_2$.H$_2$L^3]	27	28

Computational details

Structural parameters

The molecular properties of the structures under investigation were determined by density functional theory (B3LYP functional) with LANL2DZ basis sets. The optimized

structures are shown in Figure 1. Coordination around the Sn(IV) ion is defined by the two Cl, two C atoms of methyl group and O atom of the H2L ligand. The two Sn-Cl42 and Sn-Cl432 bond lengths are similar and the calculated value is longer than Sn-C44, Sn-C45 and Sn-O38 (0.25-0.63Å) (See Table 6). The coordination geometry can be views as a trigonal by pyramidal with the two C atoms and O atom remains in the equatorial position and two Cl atoms in the axial position. In view of the bond angle, Cl42-Sn-Cl43 angles make approximately a 180º angle and the calculated C45-Sn-C44, C45-Sn-O38 and C44-Sn-O38 angles are 120º respectively. On the basis of the results the TBP structure was confirmed. Some important optimized bond lengths and bond angles of complexes are summarized in Table 6.

(a)

(b)

(c)
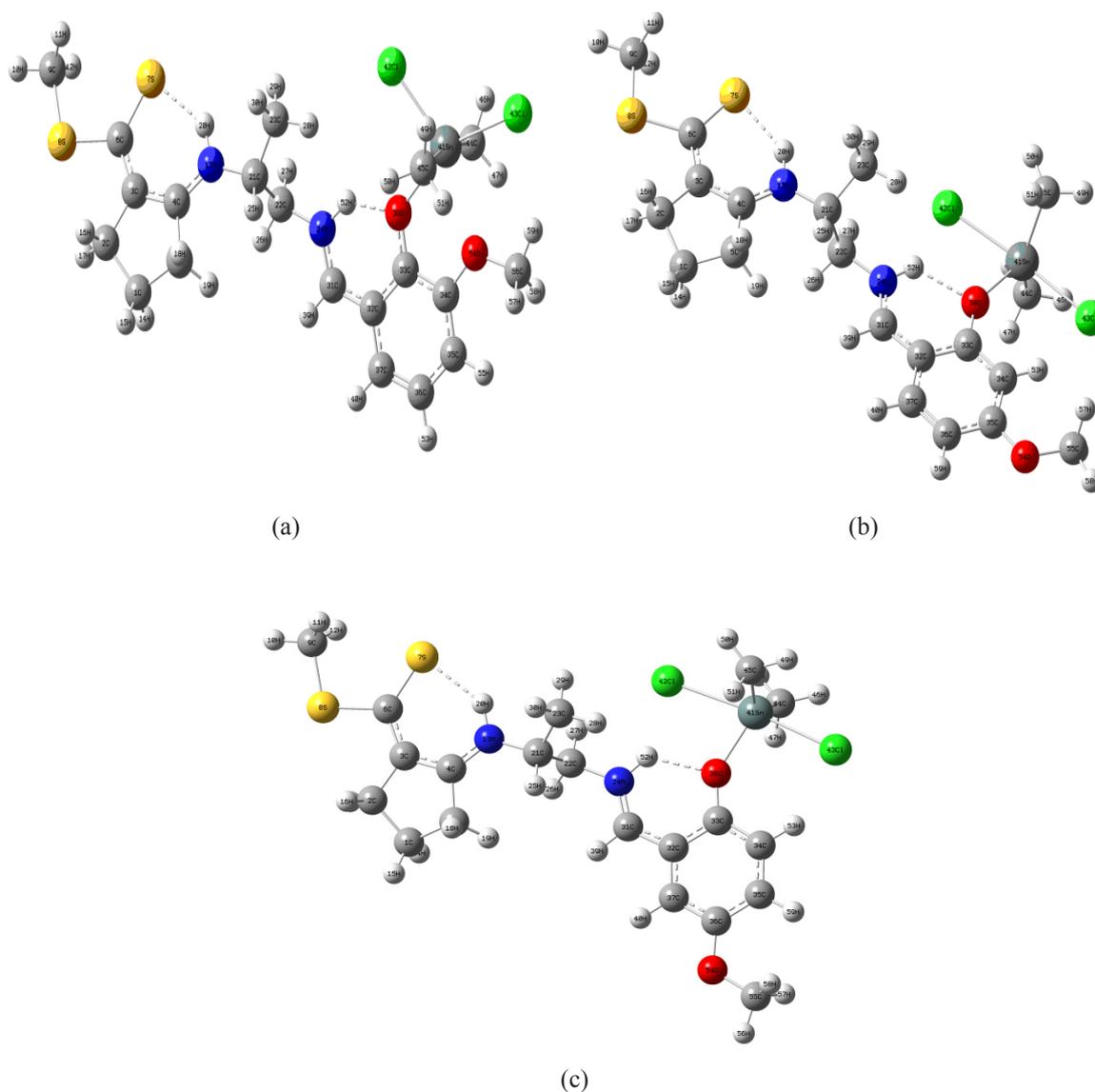
Figure 1. The B3LYP optimized geometry of the (a) [Me$_2$SnCl$_2$.H$_2$L1], (b)[[Me$_2$SnCl$_2$.H$_2$L^2], (c) [Me$_2$SnCl$_2$.H$_2$L^3].

Table 6. Selected structural parameters for Sn(IV) complexes, labels for atoms can be found in Figure 1.

	$[Me_2SnCl_2.H_2L^1]$	$[Me_2SnCl_2.H_2L^2]$	$[Me_2SnCl_2.H_2L^3]$
Bond length (Å)			
Sn-O38	2.257	2.035	2.035
Sn-Cl43	2.563	2.577	2.556
Sn-Cl42	2.512	2.652	2.669
Sn-C44	2.123	2.120	2.120
Sn-C45	2.124	2.119	2.119
C-O54	1.395	1.375	1.397
O38-H52	2.047	2.050	2.019
S7-H20	2.229	2.234	2.233
N24-C31	1.438	1.440	1.434
N13-C4	1.332	1.337	1.335
Bond angle (°)			
Cl42-Sn-Cl43	179.24	179.06	178.73
Cl43-Sn-C44	90.43	91.04	90.86
O38-Sn-Cl43	90.63	90.58	90.75
O38-Sn-Cl42	90.13	90.49	90.99
Cl42-Sn-C45	89.82	89.58	89.06
Cl42-Sn-C44	91.09	89.96	89.40
O38-Sn-C45	119.98	120.11	120.04
O38-Sn-C44	119.67	119.88	120.11
Dihedral angle (°)			
O38-C33-C32-C31	-0.65	-0.14	-0.11
N13-C4-C3-C6	-0.49	-0.08	-0.03

The Sn- Schiff base ligand interaction is not lead to twisting of the ligand compared to the free ligand. In the optimized structure of the complexes cyclopentene and benzene ring are in the same plane. Their planes make approximately a 2° dihedral angle to each other. The calculated O38-C33-C32-C31 and N13-C4-C3-C6 dihedral angles are near to each other. These molecules are not twisted, so that the OMe group is in opposite orientation. The aromatic rings are essentially planar, where the bond lengths of C=C (142.9-143.7 Å) are in the expected range [34]. The two O38-H52 and S7-H20 asymmetrical intramolecular hydrogen bonds with distances 2.019-2.050 and 2.229-2.234 Å [35]. However, the two C-N bond lengths differ significantly of the two types of C-N bonds, the bond length for the imine nitrogen (N24=C31) is 0.11 Å shorter than that for primary amine nitrogen (N13-C4). This C-N bond is not essentially in the same plane and makes a dihedral angle about 40° with the

plane of benzene and cyclopentene ring.

Relative energies

The DFT calculation is performed to predict the interaction between the Schiff base ligands organotin (IV) comparison of the energies show that the $[Me_2SnCl_2.H_2L^2]$ complex is slightly stable than the $[Me_2SnCl_2.H_2L^1]$ and $[Me_2SnCl_2.H_2L^3]$ complexes. The equilibrium geometry of the complex has been determined by the energy minimization with the LANL2DZ basis set. The comparison of the relative energies values shows that the $[Me_2SnCl_2.H_2L^2]$ complex is slightly stable than the $[Me_2SnCl_2.H_2L^1]$ and $[Me_2SnCl_2.H_2L^3]$ complexes. The

energy different between complexes is 2.33 kJ/mol which is larger by about two times of the thermal energy kt (at room temperature where k is Boltzmann constant). As a result, there is no the same possibility of existence of these complexes and have a difference stability at room temperature. This result will be shown by the energy difference between HOMO and LUMO orbital of these complexes.

Molecular orbital analysis

It can be found that the $[Me_2SnCl_2.H_2L^2]$ complex has lower dipole moment and high stable HOMO electronic state is stable than other complexes (See Table 7).

Table 7. The computed electronic properties of Sn(IV) complexes at B3LYP/Lan2DZ level of theory.

| Complexes	HF energies	HOMO/eV	LUMO/eV	gap/eV	Hardness	Dipole/ Debye
$[Me_2SnCl_2.H_2L^1]$	-1093.5961	-0.2149	-0.1214	0.0935	0.0467	15.65
$[Me_2SnCl_2.H_2L^2]$	-1093.6117	-0.2099	-0.1062	0.1036	0.0518	8.42
$[Me_2SnCl_2.H_2L^3]$	-1093.5994	-0.2113	-0.1164	0.0948	0.0474	9.76

The frontier orbital for all complexes are plotted in Figure 2. The LUMO surface mostly delocalized within the non-metallic atoms, and for the HOMO level, The Sn atom is overlapped. HOMO which can be thought the outermost orbital containing electrons tends to give these electrons such as an electron donor. LUMO can be thought the innermost orbital containing free places to acceptor electron, owing to the interaction between HOMO and LUMO orbitals, transition of

$\pi \rightarrow \pi^*$ type was observed with regard to the molecular orbital theory. As shown in figure 2, the HOMO is localized over the azomethine group and cyclopentene ring, while the LUMO is localized over the benzene ring and N13-C4 bond. The energy difference between HOMO and LUMO orbitals so called as energy gap is an important stability for structures [36]. The HOMO-LUMO energy gap of the Sn(IV) complexes are shown in Table 7 and revealed that the energy gap reflect to the chemical

activity of the complexes.

Absolute hardness is half of the HOMO-LUMO gap [37]. On the basis of the data in

Table 7 $[Me_2SnCl_2.H_2L^2]$ complex have a higher hardness and is stable than the other complexes.

(a)

(b)

(c)
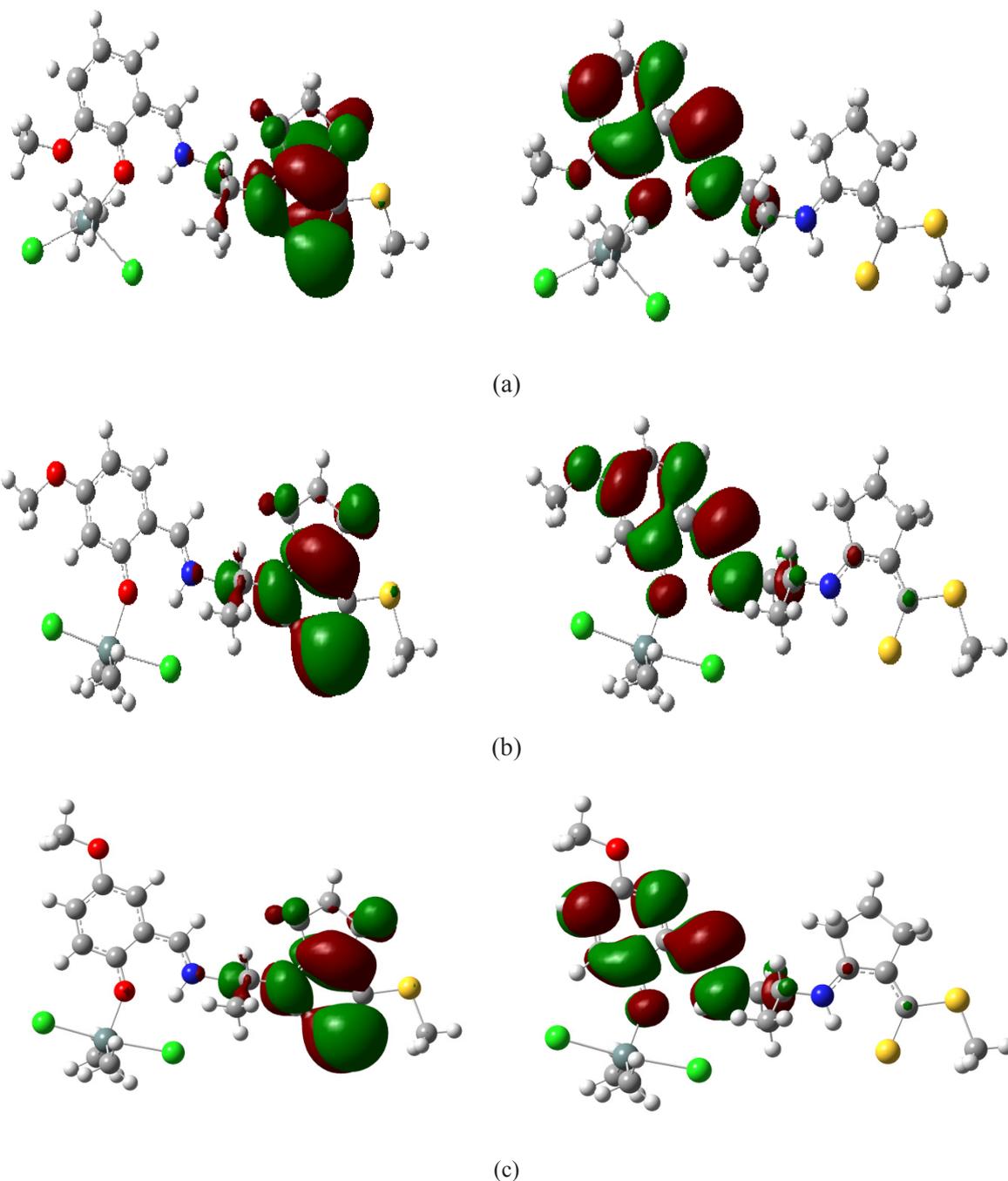
Figure 2. HOMO (left) and LUMO (right) molecular orbital of the (a) [Me2SnCl2.H2L1], (b) [$[Me_2SnCl_2.H_2L^2]$, (c) $[Me_2SnCl_2.H_2L^3]$.

Vibrational Assignment

For the all complexes, the degree of freedom is 171 [(3N-6), where N is the number of atoms N=59]. The conformation obtained from the geometry optimization exhibits no special molecular symmetric, and hence the molecule belongs to the C1 group. Consequently, all the 171 fundamental vibrations of the gas phase molecule belong to the A irreducible representation and are both IR and Ramman active.

Vibrational Frequencies

In order to obtain reliable and stable structures, vibration frequencies were calculated for all optimized complexes. Selected experimental and calculated FTIR vibration frequencies (cm^{-1}) of the complexes were listed in Table 2. The calculated C=C stretching frequency is somewhat different from the experimental data, may be due to the fact that the theoretical data calculated in gas phase.

The predicted stretching modes at 1722-1750, 1560 and 1481-1490 cm^{-1} correspond to C=C bond. C=C bond near the OMe group vibrates at a higher frequency compared to the vibration of C=C bond on the ring in the farrest position to OMe. The C=C stretching mode in cyclopentene rings is 1481-1490 cm^{-1} which occurs at a lower frequency relative to the C=C bond in the ring involving OMe. For C-O, C=N and Sn-O stretching frequencies at 1550-1561, 1650-1663 and 2851-2857 showed

the agreement between the experimental and scale calculated frequencies (Table 2).

Conclusions

A series of three coordinated diorganotin (IV) complexes have been synthesized and characterized by different chemical techniques such as elemental analysis, infrared spectra, ^{1}H and ^{119}Sn NMR, and UV-Vis spectroscopy. Physico- chemical measurements confirm the 1:1 metal to ligand stoichiometry of the complexes. The antibacterial activity of the ligands and corresponding complexes were evaluated against different bacteria and it was found that the complexes exhibit significant antimicrobial activity than the ligands. We have used DFT to compute the equilibrium structure and vibrational frequencies. The calculated results are in good agreement with the experimental evidence, confirming the obtained geometries for them. The FTIR spectra of the complexes were recorded and the important bands were identified and compared. They can use for analysis of complexes, help to explain the behavior of their vibrational modes. The results were showed that the ligand was coordinated through oxygen to Sn(IV).

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