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Synthesis, Spectroscopic and Theoretical Studies of Organotin(IV) and Organosilicon(IV) Complexes of Schiff bases Derived from Tryptophan and Phenylalanine

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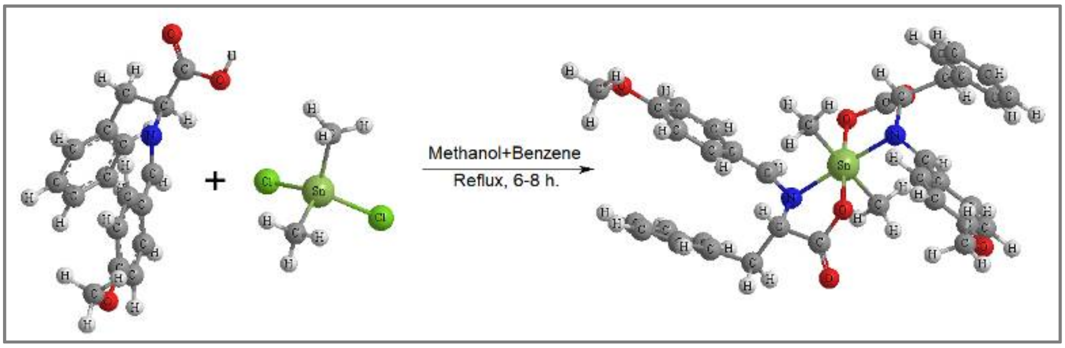
ABSTRACT

New organotin(IV) and organosilicon(IV) complexes have been synthesized with Schiff bases derived from tryptophan, phenylalanine alpha-amino acids. These ligands act as monobasic bidentate species and coordinate with the tin and silicon atom through the nitrogen and oxygen atom. The synthesized complexes have been characterized by various physic-chemical and spectroscopic techniques. The mode of bonding of the ligands and tin and silicon complexes have been confirmed on the basis of infrared, UV-visible, and ^{1}H*, and* ^{13}C *NMR spectroscopic studies and probable structures have been assigned to these complexes. The optimized structural parameters such as bond length, bond angles, HOMO, LUMO orbital, electronegativity, global softness, and electrophilicity index were calculated by the methods based B3LYP on the density functional theory (DFT). The ligands and their corresponding complexes have also been screened for antibacterial activities.*

Graphical Abstract



Keywords: Alpha aminoacids, Organotin(IV), Organosilicon(IV) complexes, Spectroscopic studies, Schiff base, DFT calculations, Antibacterial activities.

INTRODUCTION

Amino acids are organic molecules that contain both a carboxyl and an amino group with a side chain that varies between different α-amino acids. Amino acids and their compounds with different metal ions play an important role in medicinal, pharmaceutical, and industrial chemistry [1-5]. Since amino acid contains these groups, therefore, they contain potential donor sites such as (COOH) and (NH_2) which they could coordinate with metals ions [6-8].

Recently, the chemistry of Schiff base and its metal complexes are undergoing fast progress due to their essential roles in biological systems and chemical industries. Schiff base ligands which generally contain oxygen, sulphur and nitrogen donor atoms have played an important role in coordination chemistry [9-11]. Schiff base ligands have significant importance, especially in the development of coordination chemistry, because Schiff base ligands are potentially capable of forming stable chelates with metal ions [12-15]. Also, Schiff bases have been studied extensively due to their applications in the medicinal, biological, chemical, analytical and pharmacological study [16, 17].

However, studies of new kinds of Schiff bases are now interesting the consideration of researchers for their biological activity and perspective accessibility for pharmaceuticals, only less attention has been given to Schiff bases metal complexes derived from amino acids and 4-methoxybenzaldehyde. As a part of our research work, herein we report, in situ synthesis and spectroscopic characterization of Schiff base organotin(IV) and organosilicon(IV) complexes derived from 4-methoxybenzaldehyde, phenylalanine, and L-tryptophan. In vitro biological activities such as antibacterial and antifungal activities have also been reported.

MATERIALS AND METHODS

All Chemicals were of analytical grade and used as such without any further purification and solvents purified by standard methods and moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes. Melting points were determined in open glass capillaries.

Analytical methods and spectral measurements: Tin and silicon were determined gravimetrically as SnO_2 and SiO_2, respectively. Nitrogen was determined by Kjeldahl's methods. Systronics conductivity bridge model 305 was used to measurements of molar conductivity. Molecular weight determined by the Rast camphor method. The electronic spectra were recorded in on Agilent carry-60, UV-Vis spectrophotometer, in the range of 800–200 nm. The IR spectra of the ligands and metal complexes were recorded in KBr pellets using a Perkin-Elmer Spectrum-2 FTIR spectrometer in the range of 4000–400 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE II (400 MHz) NMR spectrometer using DMSO-d6 as a solvent. TMS was used as an internal reference for ^1H NMR and ^{13}C NMR.

Theoretical calculations: Density functional theory (DFT) calculations were carried out using the Gaussian 03 software package, and Gauss view visualization program [18]. The geometry is optimized at Becke, 3-parameter, hybrid model using the Lee-Yang–Parr basic sets to predict the molecular structures of the newly synthesized compounds.

Antimicrobial Activity: All newly synthesized compounds were checked in vitro for their antimicrobial activity against some bacteria and fungi. The microorganisms involved were *Staphylococcus aureus, Bacillus cereus, Escherichia coli, K. pneumoniae* (bacteria) and *Rhizopus, Aspergillus, Alternaria, Penicillium* (Fungi) at a concentration of 200 ppm by the disc diffusion method [19]. In this method, the different test organisms were processed separately using a previously sterilized culture medium plates. The Petri-plates were kept for incubation for 24 h at 37°C. Antimicrobial activity was checked by measuring the zone of inhibition against the test microorganism.

Synthesis of ligands: The ligands [3-(1H-indol-3-yl)-2-((4-methoxy-benzylidene) amino)- propanoic acid (L^1H), 2-((4-methoxybenzylidene)amino)-3-phenylpropanoic acid (L^2H), were synthesized as described earlier[15].

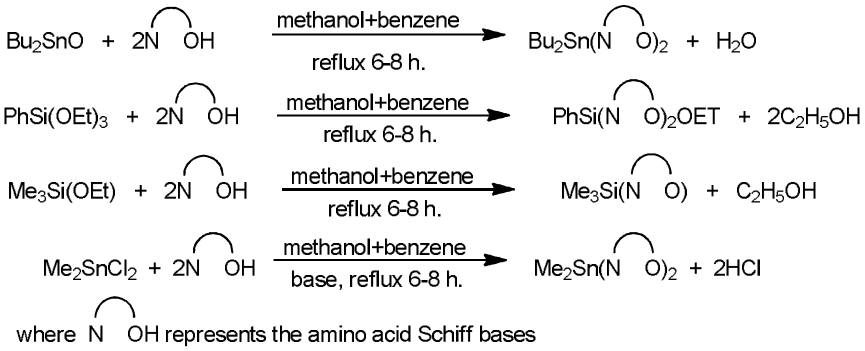
Syntheses of dibutyltin(IV), dimethyltin(IV) and phenylsilicon(IV) Complexes: To a suspension of ligands (L^1H-L^2H) in of dry benzene (80 mL) and dry methanol (30 mL), a solution of Bu_2SnO, $PhSi(OEt)_3$, Me_2SnCl_2 (1.18 mmol) and Me_3SiOEt (2.36 mmol) in 15 mL of the same solvent were added. The mixtures were stirred under reflux on a fractionating column for 6-8 h. The water liberated in the reaction was evacuated azeotropically with solvent. At the end of the reaction, the subsequent compounds were rendered free from solvent and at that point washed over and over with dry cyclohexane. The crystalline solids were isolated out and purified by recrystallization from the same solvent. Analytical information was recorded in table 1.

Table 1. Analytical data of the organotin(IV) and organosilicon(IV) complexes of amino-acid Schiff-bases

Compounds	Products & Colour	M.P. °C (d)	Yield (%)	Elemental Analysis				Mol. Wt. Found (Calcd.)
				%M	%C	%H	%N	
$Bu_2Sn(L^1)_2$	$C_{46}H_{52}N_4O_6Sn$ Dark brown	94	72.5	13.40 (13.56)	63.02 (63.10)	5.95 (5.99)	6.32 (6.40)	867.87 (876.29)
$Bu_2Sn(L^2)_2$	$C_{42}H_{50}N_2O_6Sn$ Cream	146	68.9	14.80 (14.88)	63.02 (63.25)	6.25 (6.32)	3.45 (3.51)	790.65 (798.27)
$Me_2Sn(L^1)_2$	$C_{40}H_{40}N_4O_6Sn$ Dark brown	132	68.7	14.92 (15.00)	60.55 (60.70)	5.07 (5.09)	7.01 (7.08)	785.32 (791.48)
$Me_2Sn(L^2)_2$	$C_{36}H_{38}N_2O_6Sn$ Cream	162	74.6	16.60 (16.64)	60.56 (60.61)	5.34 (5.37)	3.88 (3.93)	701.25 (713.41)
$Me_3Si(L^1)$	$C_{22}H_{26}N_2O_3Si$ Dark brown	172	76.4	7.01 (7.12)	66.78 (66.97)	6.60 (6.64)	7.02 (7.10)	3.88.05 (394.54)
$Me_3Si(L^2)$	$C_{20}H_{25}NO_3Si$ Creamish yellow	156	73.8	7.68 (7.90)	67.50 (67.57)	7.04 (7.09)	3.78 (3.94)	350.21 (355.50)
$PhSi(L^1)_2OEt$	$C_{46}H_{44}N_4O_7Si$ Dark Brown	128	62.7	3.50 (3.54)	69.25 (69.68)	5.50 (5.59)	7.01 (7.07)	785.88 (792.95)
$PhSi(L^2)_2OEt$	$C_{42}H_{42}N_2O_7Si$ Cream	210	72.5	3.88 (3.93)	70.40 (70.56)	5.90 (5.92)	3.87 (3.92)	700.54 (714.88)

RESULTS AND DISCUSSION

The reaction of trimethyl ethoxy silane, triethoxy phenyl silane and dibutyltin oxide with these ligands has been carried out in 1:1 and 1:2 molar ratios utilizing anhydrous benzene and dry methanol (3:1) as reaction medium. These reactions continue with the liberation of ethanol and water molecule, which was azeotropically evacuated. Dimethyltin dichloride was added to the calculated amount of the ligands in 1:2 molar ratios, utilizing anhydrous benzene and dry methanol (3:1) as reaction medium. These reactions carried out and established beneath:



The above reactions were observed to be very easy and could be finished in 6–8 h of refluxing. All these complexes are coloured solids. They are partially dissolvable in common solvents and totally soluble in DMF and DMSO. The molar conductance estimations of the complexes fall in the range 8.40 to 14.64 $\Omega^{-1}cm^2\ mol^{-1}$ demonstrating that these complexes are non-electrolytes. The basic investigation information concurs with the proposed formulae of the ligands and furthermore affirms the composition of organotin(IV) and organosilicon(IV) complexes.

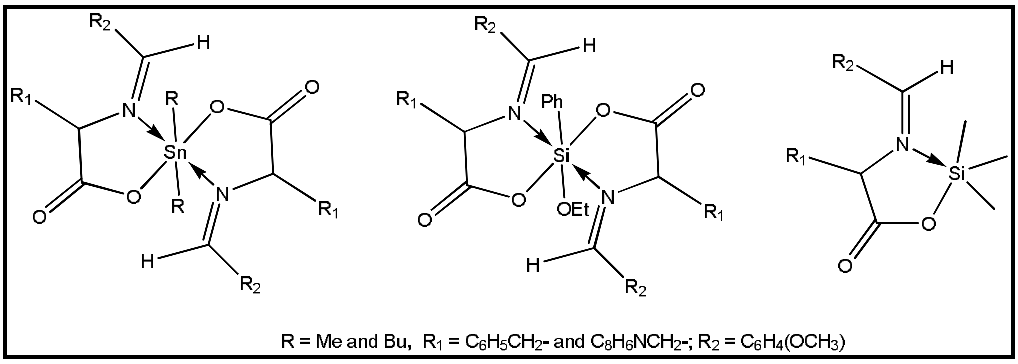
Electronic Spectral Studies: In the electronic spectra, two intense maxima are seen in the complexes at 210-220 and 382-390 nm which might be assigned to n– π* transition of carboxylate group and of the azomethine (>CH=N) chromophore. The huge shifting saw in the n-π* transition (~370 nm) is because of the polarization in the >CH=N– bond caused by the metal-ligand electron association. This plainly demonstrates the coordination of the azomethine nitrogen to the tin atom. A band in the region 350-345 nm in the spectra of the Schiff bases and metal complexes are probably going to be the secondary band of the benzene ring combined with the intramolecular charge transfer transition occurring inside the ligand moiety. Besides, sharp bands were seen in the region 315±20 nm in the spectra of the tin(IV) and silicon(IV) complexes which could be allocated to the charge transfer transition from ligand to metal [20].

Infrared spectral studies: The IR spectra of the complexes were contrasted and that of the ligands to decide the coordination sites that might be engaged with coordination. The IR spectra of the ligands demonstrate the nonappearance of groups at ~3400 and ~1740 cm^{-1}, respectively because of $\nu(NH_2)$ group of amino acids andν(C=O) of aldehydes. Rather, another band at 1625±15 cm^{-1} due to azomethine ν(C=N) linkage showed up in all the ligands [21, 22] demonstrating that condensation between the carbonyl group of aldehydes. In addition, correlation of the IR spectra of the ligands with their organotin(IV) complexes demonstrated a noteworthy move to bring down wave numbers by 10–18 cm^{-1} in azomethine group ν(C=N) at 1615±10 cm^{-1} proposing the involvement of the azomethine nitrogen with the metal ion[23-24]. The new bands showed up in the region 540±5 cm^{-1} in the spectra of the complexes, are assigned to stretching frequencies of $\nu(M \leftarrow N)$ bond formations. In the spectra of the ligands, broadband showed up in the area 3140-2725 cm^{-1} that is assigned to the hydrogen-bonded (OH) group. This band vanishes on complexation, proposing chelation of the carboxylate oxygen to the tin atom. The infrared spectra of complexes revealed that the ν_{asym}(COO) was moved to a lower wavenumber contrasted with the ligands which recommend that the coordination took place via the carboxylate anion. Complexes demonstrated the ν_{asym}(COO) and ν_{sym}(COO) are in the range 1602−1580 and 1330−1320 cm^{-1}, respectively. Moreover, for complexes Δ below 200 cm^{-1} would be normal for bridging or chelating carboxylate [25]. Additional confirmation for the coordination to tin by means of oxygen atom was uncovered by the presence of the ν(M−O) stretching vibrations in the spectra of complexes, in the area of 435±10 cm^{-1}. The new band shows up in the complexes at 630±10 cm^{-1} which is most likely because of ν(M−C) stretching vibration.

NMR spectral studies: The ^1H NMR spectra of complexes, coordination of the ligands through azomethine nitrogen was set up by downfield moving of these signals in the tin(IV) complexes because of the expanded conjugation and coordination. The number of protons calculated from the integration curves and those acquired from the estimations of the normal CHN examinations concurs with each other. The ligands also show the OH proton signal at δ 11.20–12.65 ppm and is not appeared in the spectra of the M(IV) complexes, showing thereby chelation of the ligand through the deprotonated carboxylate oxygen. The ^1H NMR spectra of the ligands, a sharp signal shows up at δ ~ δ 8.50 ppm due to the immine proton. It moved downfield (~ δ 9.10 ppm) in the spectra tin(IV) complexes in comparison with its position in the ligands, because of the coordination of nitrogen to the tin atom. The signal because of aromatic and OCH_3 protons stays unaltered in the tin complexes showing that the aromatic protons and OCH_3 protons are not partaking in the complexation. The complexes, nevertheless, demonstrate extra signals in the region δ 0.72– 1.90 ppm inferable from the protons of the butyl and methyl groups. The CH_3 protons of dibutyltin compounds are huge as a triplet at 0.78¬0.85 ppm with $^3J_{HH}$ = 7.4 Hz, while – CH_2– protons show up as a multiplet.

The ^{13}C NMR spectra of the ligands show signal for the carbon atoms connected to the carboxylate and azomethine groups appear at ~ δ 178.5 ppm and ~ δ 165.2 ppm, respectively. However, in the spectra of the tin complexes, these signals show up at ~ δ 181.6 ppm (carboxylate group) and ~ δ 154 ppm (azomethine group), respectively. The moving in the position of carbon of COOH group proposes the bonding of oxygen to the tin and silicon atom. Further, the moving of the azomethine (>CH=N–) carbon signal in the spectra of the complexes when contrasted with the ligands, plainly demonstrates that the azomethine moiety has been engaged with bond formation. The carbon of the butyl group is seen at (~26.6, 27.8, 26.0, 14.3 ppm) and a methyl group is seen at ~10.6, position comparable to other similar compounds. The alkyl group attached to tin shows resonance for chemically proportional carbon; in any case, the butyl group shows three resonances.

The aforementioned diverse spectral investigations propose that the bonding occur through the azomethine nitrogen and carboxylate oxygen atoms to the tin. On the bases of above spectral evidences, distorted octahedral and trigonal bipyramidal geometries around the tin and silicon atom have been proposed (Figure 1).



R = Me and Bu, $R_1 = C_6H_5CH_2$- and $C_8H_6NCH_2$-; $R_2 = C_6H_4(OCH_3)$

Figure 1. Structure of Organotin(IV) and Organosilicon(IV)Complexes.

Molecular structure and Analysis: The molecular modeling of the representative compounds, in view of its structures and every one of the measurements, are obtained (bond edges, bond lengths). In most of the cases, the actual bond angles and lengths are near the ideal values, and consequently, the proposed structure of the compound is acceptable (Table 2 and 3).

The deprotonated ligand is coordinated through carboxylate oxygen and azomethine nitrogen atoms. The ligands act as bidentate with the NO donors placed on the same side. Since the synthesized compounds are related and differ only in substituted groups, three compounds were theoretically studied. The Sn-O bond distance is close to being identical values. The calculated Sn-O bond distances of 2.051/2.052 Å in $Me_2Sn(L^2)_2$/ $Bu_2Sn(L^2)_2$, are also close to the already reported [26, 27]

Table 2. Optimized selected bond lengths (Å) of organotin(IV) and organosilicon(IV) compounds

Atom Connectivity	bond length (Å)		
	$Me_2Sn(L^2)_2$	$Bu_2Sn(L^2)_2$	$Me_3Si(L^2)$
Sn(22)-C(76)/Sn(22)-C(100)	2.176	2.2187	--
O(34)-Sn(22)/ C(23)-Si(22)	2.0519	2.0529	1.923
N(24)-C(35)/ Si(22)-C(47)	1.2714	1.2756	1.9336
C(23)-O(34)/ Si(22)-C(44)	1.36	1.3574	1.9266
N(2)-Sn(22)/ N(2)-Si(22)	2.0974	2.0948	1.8089
N(24)-Sn(22)	2.0936	2.0966	--
O(12)-Sn(22)/ O(12)-Si(22)	2.0512	2.0523	1.6471
Sn(22)-C(77)/ Sn(22)-C(103)	2.1846	2.2407	--
N(2)-C(13)	1.2775	1.2768	1.2765
C(1)-O(12)	1.361	1.3583	1.3556

Sn-O distances in {$CH_2N(Me)CH(Me)CH(Ph)O$}$_2$Sn (2.048/2.078). The Sn-N distances in compounds $Me_2Sn(L^2)_2$/ $Bu_2Sn(L^2)_2$ are 2.0974/2.0948 Å, which are similar to the already reported [27] structures. In $Me_2Sn(L^2)_2$ complex two methyl groups occupied in axial positions C(77)–Sn(22)–C(76) angle is 179.96 °, showing distortion from linear (Figure 2). The sum of the equatorial angles C(77)-Sn(22)-N(2) (88.15 °), C(77)-Sn(22)-O(34) (91.86 °), C(77)-Sn(22)-N(24) (80.37 °) and C(77)-Sn(22)-O(12) (94.38 °) is 354.73 ° showing in figure 2 and table 2. Thus the atoms Sn18, N2, O12, N24, and O34 are coplanar and are good agreement with the values reported for five coordinated tin complexes [26, 27].

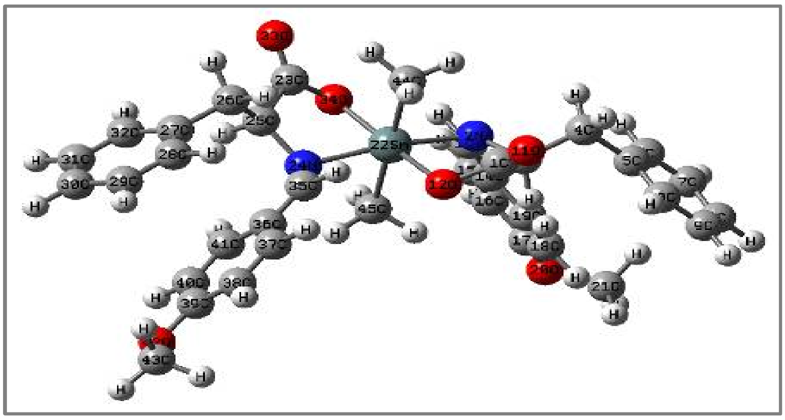


Figure 2. Minimum energy optimized geometry of $Me_2Sn(L^2)_2$ complex and with numbering of atoms.

In $Bu_2Sn(L^2)_2$ complex two carbon atoms of butyl group occupied in axial positions C(103)-Sn(22)-C(100) angle is 169.15 °, showing distortion from linear (Figure 3). The sum of the equatorial angles C(103)-Sn(22)-N(2) (79.07 °), C(103)-Sn(22)-O(34) (87.07 °), C(103)-Sn(22)-N(24) (85.09°) and C(103)-Sn(22)-O(12) (86.27 °) is 337.5 ° showing in Figure 3 and Table 2. Thus the atoms Sn18, N2, O12, N24, and O34 are coplanar and are good agreement with the values reported for six coordinated tin complexes [26, 27]. For the compound $Me_3Si(L^2)$ the optimized values of bond angles C(47)-Si(22)-N(2), between one carbon atom of a methyl group and nitrogen atom occupied in axial positions is 176.89° showing distortion from linear. The sum of the equatorial angles C(44)-Si(22)-C(23) (138.36°), C(44)-Si(22)-O(12) (113.39°) and C(23)-Si(22)-O(12) (108.04°) is 359.79 ° showing in table 2. Thus the atoms Si22, O12, C23, and C44 are coplanar and are good agreement with the values reported for five coordinated silicon complexes [28, 29].

Table 3. Optimized selected bond angles (°) of tin and silicon complexes

Atom Connectivity	bond angles (°)	Atom Connectivity	bond angles (°)	Atom Connectivity	bond angles (°)
$Me_2Sn(L^2)_2$					
$C_{(77)}$-$Sn_{(22)}$-$C_{(76)}$	179.96	$C_{(76)}$-$Sn_{(22)}$-$N_{(2)}$	91.83	$N_{(2)}$-$Sn_{(22)}$-$N_{(24)}$	168.51
$C_{(77)}$-$Sn_{(22)}$-$N_{(2)}$	88.15	$C_{(76)}$-$Sn_{(22)}$-$O_{(34)}$	88.12	$N_{(2)}$-$Sn_{(22)}$-$O_{(12)}$	81.07
$C_{(77)}$-$Sn_{(22)}$-$O_{(34)}$	91.86	$C_{(76)}$-$Sn_{(22)}$-$N_{(24)}$	99.66	$O_{(34)}$-$Sn_{(22)}$-$N_{(24)}$	77.89
$C_{(77)}$-$Sn_{(22)}$-$N_{(24)}$	80.37	$C_{(76)}$-$Sn_{(22)}$-$O_{(12)}$	85.64	$O_{(34)}$-$Sn_{(22)}$-$O_{(12)}$	172.93
$C_{(77)}$-$Sn_{(22)}$-$O_{(12)}$	94.38	$N_{(2)}$-$Sn_{(22)}$-$O_{(34)}$	102.48	$N_{(24)}$-$Sn_{(22)}$-$O_{(12)}$	99.88
$Bu_2Sn(L^2)_2$					
$C_{(103)}$-$Sn_{(22)}$-$C_{(100)}$	169.15	$C_{(100)}$-$Sn_{(22)}$-$N_{(2)}$	106.68	$N_{(2)}$-$Sn_{(22)}$-$N_{(24)}$	163.38
$C_{(103)}$-$Sn_{(22)}$-$N_{(2)}$	79.07	$C_{(100)}$-$Sn_{(22)}$-$O_{(34)}$	101.48	$N_{(2)}$-$Sn_{(22)}$-$O_{(12)}$	81.96
$C_{(103)}$-$Sn_{(22)}$-$O_{(34)}$	87.07	$C_{(100)}$-$Sn_{(22)}$-$N_{(24)}$	89.78	$O_{(34)}$-$Sn_{(22)}$-$N_{(24)}$	80.14
$C_{(103)}$-$Sn_{(22)}$-$N_{(24)}$	85.09	$C_{(100)}$-$Sn_{(22)}$-$O_{(12)}$	85.48	$O_{(34)}$-$Sn_{(22)}$-$O_{(12)}$	172.75
$C_{(103)}$-$Sn_{(22)}$-$O_{(12)}$	86.27	$N_{(2)}$-$Sn_{(22)}$-$O_{(34)}$	93.96	$N_{(24)}$-$Sn_{(22)}$-$O_{(12)}$	102.13
$Me_3Si(L^2)$					
$C_{(44)}$-$Si_{(22)}$-$C_{(47)}$	86.87	$C_{(47)}$-$Si_{(22)}$-$C_{(23)}$	87.90	$C_{(23)}$-$Si_{(22)}$-$N_{(2)}$	92.78
$C_{(44)}$-$Si_{(22)}$-$C_{(23)}$	138.36	$C_{(47)}$-$Si_{(22)}$-$O_{(12)}$	91.67	$O_{(12)}$-$Si_{(22)}$-$N_{(2)}$	91.00
$C_{(44)}$-$Si_{(22)}$-$O_{(12)}$	113.39	$C_{(47)}$-$Si_{(22)}$-$N_{(2)}$	176.89	--	--
$C_{(44)}$-$Si_{(22)}$-$N_{(2)}$	90.61	$C_{(23)}$-$Si_{(22)}$-$O_{(12)}$	108.04	--	--

Frontier Molecular Orbitals: Energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are established quantum mechanical descriptors. It has been shown that these orbitals play a key role in leading many chemical reactions, and are also responsible for charge-transfer complexes. The HOMO's and LUMO's are known as FMO's frontier molecular orbitals, which played an important role in evaluating molecular stability, reactivity, hardness and softness of the molecules.The HOMO and LUMO energy, energy gap (ΔE), chemical potential ($\mu = -\chi$), electronegativity ($\chi = -(E_{LUMO}+E_{HOMO})/2$), chemical hardness ($\eta = (E_{LUMO}-E_{HOMO})/2$), global softness ($S = 1/\eta$) and electrophilicity index ($\omega = \mu^2/2\eta$) of compounds (L^2H, $Me_2Sn(L^2)_2$, $Bu_2Sn(L^2)_2$, $PhSi(L^2)_2OEt$ and Me_3SiL^2 have been calculated theoretically and reported in table 4.

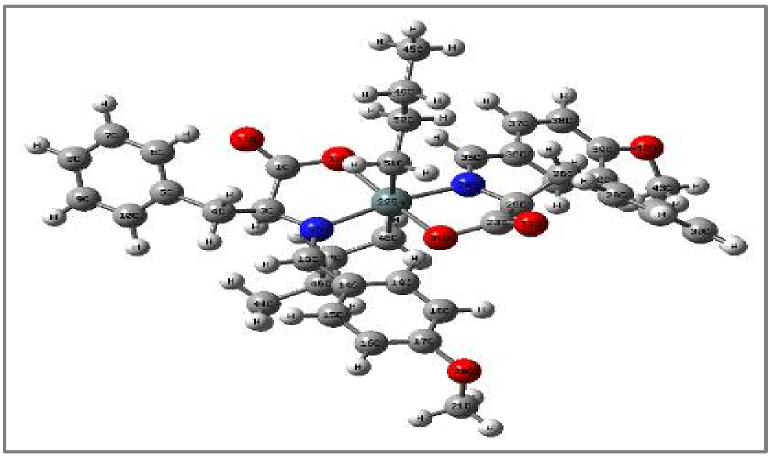


Figure 3. Minimum energy optimized geometry of $Bu_2Sn(L^2)_2$ complex and with numbering of atoms.

Orbital density plots of HOMO and LUMO for the ligand (L^2H), in which the LUMO surface mostly is delocalized on the aromatic ring and HOMO surface delocalized on carboxylate group. In the surface shown for the HOMO level, the azomethine group is overlapped. In the molecular system shows that the 3D plots of the HOMO frontier orbital density are located around the metal atom.

Table 4. Calculated energy parameters of ligand (L^2H) and its metal complexes

Property	Compounds				
	L^2H	$Me_2Sn(L^2)_2$	$Bu_2Sn(L^2)_2$	$PhSi(L^2)_2OEt$	Me_3SiL^2
E_{HOMO} (eV)	-8.986	-7.930	-7.713	-5.159	-6.099
E_{LUMO} (eV)	-2.307	-4.435	-3.377	-3.725	-2.534
Energy Gap (ΔE, eV)	6.679	3.495	4.336	1.434	3.565
Chemical potential (μ)	-5.6465	-6.1825	-5.545	-4.442	-4.3165
Electronegativity (χ)	-5.6465	-6.1825	-5.545	-4.442	-4.3165
Chemical hardness (η)	6.679	3.495	4.336	1.434	3.565
Global softness (S)	0.1497	0.2861	0.2306	0.6974	0.2805
Electrophilicity index (ω)	2.3868	5.4683	3.5456	6.8798	2.6132

eV: energy unit (electron volt); au: energy unit (atomic unit); HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital.

Energies of the HOMO and LUMO orbitals have been directly related to the concept of hard and soft nucleophiles and electrophiles. Hard molecules (nucleophile) have a low energy of HOMO, soft molecules (nucleophile) have high energy of HOMO, hard electrophiles have high energy of LUMO and soft electrophiles have a low energy of LUMO. As depicted in Table 4, L^2H has a larger energy gap than its metal complexes. The energy gap, ΔE, is directly concerned with the chemical hardness and softness of molecules. Furthermore, softness is proportional to the polarizability of the system, whereas the hardness of a system implies resistance to charge transfer. Calculated negative heat of formation for the tin compounds indicated that molecules were thermodynamically more stable than the ligands. Another electrophilicity index is directly related to the electron-accepting ability of the molecules and high values of the electrophilicity index increase the electron-accepting abilities of the molecules. Thus, the electron-accepting abilities of tin complexes (Table 4) are arranged in the following order: $PhSi(L^2)_2OEt > Me_2Sn(L^2)_2 > Bu_2Sn(L^2)_2 > Me_3Si(L^2) > (L^2H)$.

Antimicrobial Activity: The results of antimicrobial activities of the newly synthesized complexes and their parent ligand against different Gram positive and Gram negative bacteria and four fungi have been listed in table 5.

Table 5. Antimicrobial Activity of some representative ligand and its metal complexes

Compounds	**Inhibition zone (mm)**							
	E. coli	***K. pneumoniae***	***B. cereus***	***S. aureus***	***Rhizopus***	***Aspergillus***	***Alternaria***	***Penicillium***
L^1H	-	-	-	-	6.2	7.6	4.2	3.5
$Me_2Sn(L^1)_2$	8.2	10.1	11.9	10.2	8.1	11.4	6.4	6.1
$Bu_2Sn(L^1)_2$	9.9	10.2	12.0	14.2	10.2	12.8	8.4	8.7
$Me_3Si(L^1)$	6.8	5.7	8.1	7.2	8.4	10.1	7.3	6.5
$PhSi(L^1)_2OEt$	8.9	10.4	18.1	16.4	8.2	8.7	7.8	7.1

The observation indicates that the metal complexes are much more active than the free ligands due to the chelation. According to the nature of structure and affinity to target sites within the bacterial cells, different antibiotics have different modes of action. Drugs which have targets cell wall can inhibit the bacterial organisms because bacterial cells have cell wall while human and animal cell not have a cell wall. All living organisms replicate by RNA and DNA including bacteria, some antibiotics inhibit the process of DNA and RNA synthesis in bacteria so the multiplication and survival of bacteria are stops [**30, 31**]. For the survival of bacterial cell protein synthesis is essential to the process. Some antibiotics target the process of protein synthesis in bacterial cells by binding the subunits of ribosomes and disrupt the normal cellular metabolism of bacteria and leads to death or inhibition of growth and multiplication of bacteria for example tetracycline. The result of antimicrobial screening shows that organotin complexes show good antimicrobial activity. Complexes of tin, silicon, and lead inhibit the growth of organisms greater than parent ligands. The higher solubility of metal complexes also increases the activity of them against bacteria. Metal complexes show high activity against fungi even at lower concentrations. Metal ions are absorbed by the cell wall of microorganisms than these ions disturbed the respiration process of the fungal cell and blocked the process of protein synthesis which is essential for the growth of the organisms. This shows that the metal ions act as growth inhibitory ions. Lipid bilayer membrane of cells provides a permeable barrier for nutrient transport and energy production. These membranes are necessary for cell life. Only lipid-soluble materials passage through this membrane so this is the most important factor, which controls the antifungal activity [**31**]. Metal complexes have better antifungal activity than ligands but the exact antifungal mechanism is not known, various antimicrobials may include various targets of the mode of action.

APPLICATION

The synthesized organotin and organosilicon compounds exhibited a lot of applications in the biological field. The results evaluated for the synthesized Schiff bases and their complexes show that the compounds are good antifungal and antibacterial agents and act as hopeful drugs in the treatment of attacks caused by microbes with least harmful effects in patients' body. The results of antimicrobial action reveal that the tin and silicon complexes were more biologically active than Schiff bases and could be capable of antimicrobial drug contenders.

CONCLUSION

Organotin(IV) and organosilicon(IV) complexes of 3-(1H-indol-3-yl)-2-((4-methoxy-benzylidene) amino)-propanoic acid, and 2-((4-methoxybenzylidene)amino)-3-phenyl-propanoic acid, are insoluble in common organic solvents but soluble in DMF and DMSO. The proposed structures of all metal complexes are based on elemental analysis, IR, NMR, electronic and DFT calculations. Metal complexes are more reactive than free ligands. Also, Metal complexes were found to be more active against microbial strains than the parent ligand. Further, efforts are under progress to synthesize, characterize, evaluate biological properties of different tin and silicon complexes of Schiff bases derived from the condensation of amino acids with aromatic aldehydes containing heteroatom moieties and finding their applicability into various analytical and spectroscopic processes.

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