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SPECTRAL, DFT AND ANTIBACTERIAL STUDIES OF TIN(II) COMPLEXES OF SCHIFF BASES DERIVED FROM AROMATIC ALDEHYDE AND AMINO ACIDS

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ABSTRACT

New tin(II) complexes of α-amino acid Schiff bases (HL) derived from condensation of various α-amino acids (tryptophan, phenylalanine, valine, isolecine, methionine, alanine, cysteine, serine, aspartic acid) and aromatic aldehyde were synthesized. The molar conductance low vales reveal that all the tin(II) complexes were non-electrolytes. The structure of complexes were proposed in light of analytical techniques, infra-red, multinuclear magnetic resonance (^{1}H, ^{13}C, ^{119}Sn), UV-Vis spectral data and theoretical studies. On the basis of these studies, complexes have distorted tetrahedral geometry. 3D structure of the newly synthesized compounds were studied by DFT/B3LYP method, also the theoretical parameters, HOMO, LUMO and dipole moments were calculated to confirm the geometry of the ligands and its tin(II) complexes. Few representative Schiff bases and its tin(II) complexes were screened for antibacterial activities. The tin(II) complexes have higher antibacterial activity than the free ligands.

Keywords: tin(II) compounds, 4-methoxybenzaldhyde, amino acids, Schiff base, spectral studies, theoretical calculations, antibacterial activities.

INTRODUCTION

Extensive research of Schiff bases derived from α-amino acids have been carried out due to their encouraging and significant properties, such as coordination ability, medicinal and pharmacological activities[1-6]. Recently, amino acid derivatives have been getting increased interest due to their remarkable applications in the field of industrial, medicinal and pharmaceutical fields[7-12]. Metal complexes of nitrogen and oxygen donor Schiff bases have been investigated because they play an important role not only in the development in coordination chemistry, but also in industrial chemistry, enzymatic reaction and molecular architectures[13,14] and show evidence of wide range of biological activities and industrial applications, they have been found to posses the medicinal and pharmacological activities such as antibacterial[15], antifungal[16], anti-malarial[17], anticancer[18], anti-tubercular[19] and anti-inflammatory[20].

In view of the above facts, we have synthesized and characterized some new tin(II) compounds with Schiff bases derived from 4-methoxybenzaldhyde and α-amino acids (tryptophan, phenylalanine, valine, isolecine, methionine, alanine, cysteine, serine, aspartic acid). These compounds have been screened for antibacterial activities. The antibacterial activities of these tin compounds have been compared with the corresponding free Schiff bases.

EXPERIMENITAL

Material and Methods

Chemicals were obtained from Aldrich, sigma, Merck and used without purification. Solvents were dried and purified by standard methods. Melting points were determined on MPA 100 automatic melting point apparatus. The Schiff bases were synthesized by the condensation of 4-methoxybenzaldehyde with α-amino acids as described earlier publication[21].

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Tin was determined gravimetrically as SnO_2. Nitrogen and sulfur were as estimated by Kjeldahl's and Messenger's methods, respectively. Molar conductance of tin derivatives was measured on Systronics conductivity bride model 305 at room temperature. Molecular weight determinations were carried out by the Rast camphor method. The electronic spectra of the ligand and tin derivatives recorded on Agilent Carry-60 UV-Vis spectrophotometer at room temperature. The infrared spectral data of the compounds were recorded on Perkin-Elmer SP-2 spectrophotometer using KBr optics. ^{1}H and ^{13}C NMR spectral data were recorded on Bruker Avance-II NMR spectrometer, DMSO-d_6 and DMSO as solvent at 400 MHz and 100 MHz, respectively and tetramethylsilane as an internal reference. The ^{119}Sn NMR spectra were recorded on Bruker Avance-II spectrometer using dry DMSO as the solvent at 149.21 MHz and tetramethyltin (TMT) as an external reference. 3D molecular structures of the complexes were studied using the Gaussian 03 program with B3LYP/LanL2DZ basic sets[22,23].

Preparation of the tin(II) Complexes

These complexes were synthesized by dissolving ligands (2.40 mmol) in a mixture of benzene and methanol and then adding methanolic solution of tin acetate (1.20 mmol) to this solution in 2:1 molar ratios. The reaction mixture was stirred for 1 hour on magnetic stirrer and then refluxed over a water bath for 6-8 hours. After cooling, the solid compounds separated out. Excess solvent was removed, washed with small amounts of cyclohexane, diethylether. The products were re-crystallized from the same solvent and dried in vacuum.

Table-1: Analytical and physical data of the tin(II) complexes with Schiff bases

Compds	Products & Colour	M.P. °C (d)	Yield (%)	Elemental Analysis					Mol. Cond. ohm^{-1} cm^2 mol^{-1}
				%Sn	%C	%H	%N	%S	
$Sn(L^1)_2$	$C_{38}H_{34}N_4O_6Sn$ Brown	112	70	15.44 (15.59)	59.83 (59.94)	4.48 (4.50)	7.30 (7.36)	-	14.65
$Sn(L^2)_2$	$C_{34}H_{32}N_2O_6Sn$ Cream	195	82	17.30 (17.37)	59.68 (59.76)	4.71 (4.72)	4.00 (4.10)	-	11.38
$Sn(L^3)_2$	$C_{28}H_{28}N_6O_6Sn$ Brown	255	68	17.86 (17.90)	50.55 (50.70)	4.22 (4.26)	12.60 (12.67)	-	10.98
$Sn(L^4)_2$	$C_{26}H_{32}N_2O_6Sn$ Off white	250	62	20.15 (20.21)	53.11 (53.18)	5.45 (5.49)	4.72 (4.77)	-	7.78
$Sn(L^5)_2$	$C_{28}H_{36}N_2O_6Sn$ Off white	240	84	19.18 (19.29)	54.60 (54.66)	5.88 (5.90)	4.48 (4.55)	-	6.64
$Sn(L^6)_2$	$C_{26}H_{32}N_2O_6S_2Sn$ Cream	174	67	18.12 (18.22)	47.87 (47.94)	4.90 (4.95)	4.23 (4.30)	9.78 (9.85)	10.66
$Sn(L^7)_2$	$C_{22}H_{24}N_2O_6Sn$ Cream	230	80	22.30 (22.35)	49.70 (49.75)	4.52 (4.55)	5.20 (5.27)	-	8.95
$Sn(L^8)_2$	$C_{22}H_{24}N_2O_6S_2Sn$ Light brown	340	69	19.90 (19.94)	44.33 (44.39)	4.02 (4.06)	4.65 (4.71)	10.68 (10.77)	14.44
$Sn(L^9)_2$	$C_{22}H_{24}N_2O_8Sn$ Dark green	208	85	21.01 (21.08)	46.90 (46.92)	4.22 (4.30)	4.95 (4.97)	-	16.45
$Sn(L^{10})_2$	$C_{24}H_{24}N_2O_{10}Sn$ Cream	290	63	19.12 (19.17)	46.50 (46.56)	3.86 (3.91)	4.50 (4.52)	-	19.01

Antibacterial Activity: Agar-well diffusion method

The antibacterial activity was determined by agar well diffusion method[24]. Pure cultures of the micro-organism were dissolved in peptone-water and uniformly seeded on nutrient agar Petri plates having the composition (Peptone 5g, Beaf extract 5g, NaCl 5g, Agar-Agar 20g, and distilled water 1000 ml). All the compounds were dissolved in DMSO in 100 ppm concentrations and poured onto properly labeled holes using a pipette in aseptic conditions. The plates were then incubated at 30±2 °C for 24 h and the inhibition zones were observed. Streptomycin (concentration 100 ppm) used as positive reference. Inhibition zone was calculated from triplicate reading. The results are presented in Fig.-1.

RESULTS AND DISCUSSION

The tin complexes of Schiff bases under investigation are assigned to possess the compositions and molecular formulae [Sn(L)$_2$] listed in Table-1. The analytical data of the synthesized compounds are in good agreement with the proposed structures. The reactions of ligands with tin acetate have been carried out in 2:1 molar ratios.

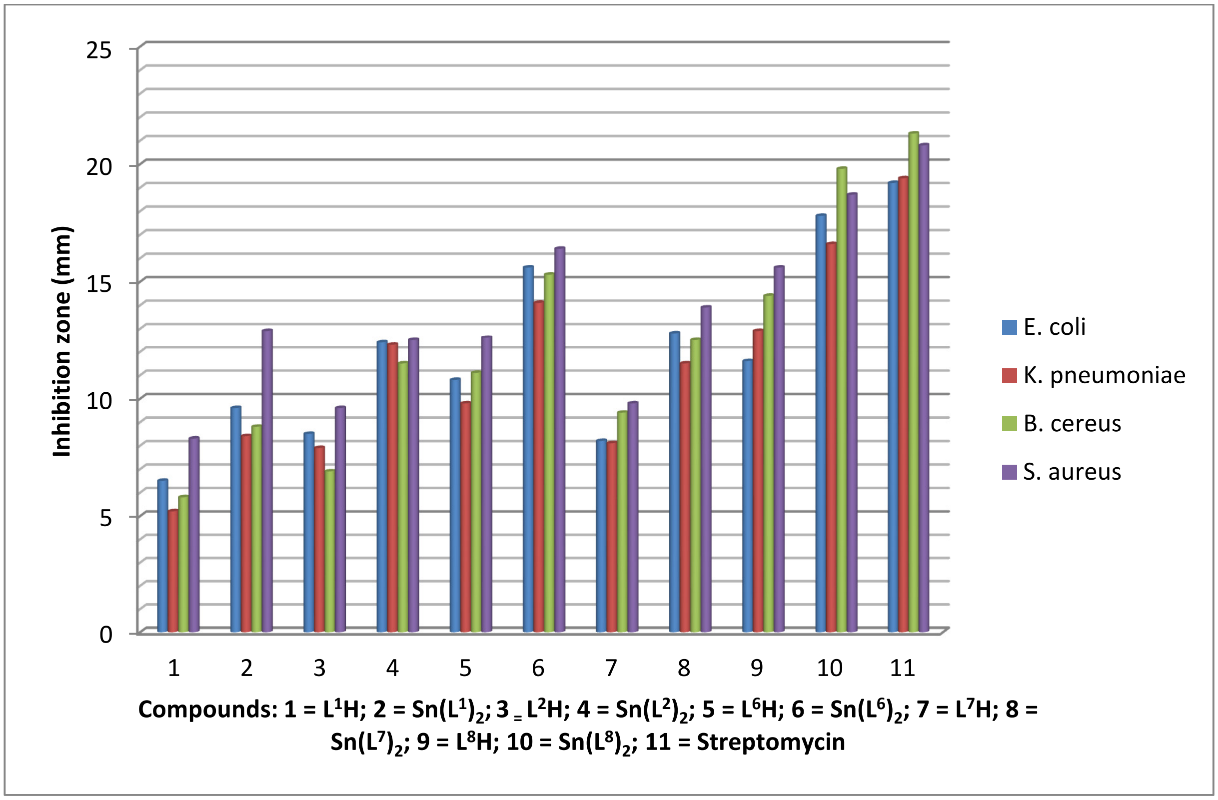
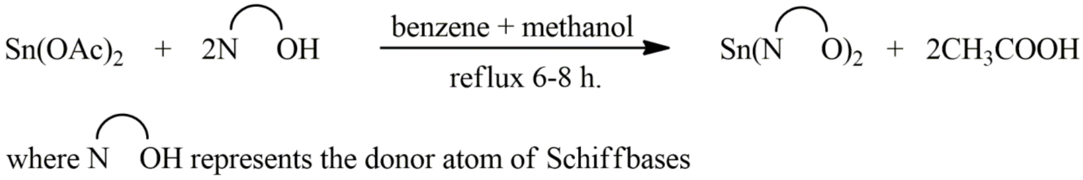


Fig.-1: Antibacterial results of ligands and their tin(II) complexes

The tin complexes are monomers as revealed by molecular weight determinations. The molar conductance values of the tin(II) complexes are given in Table-1. Tin complexes have low molar conductance values lie in the range 6.64–19.01 Ω^{-1} cm^2 mol^{-1} in DMF indicating their non-electrolytic in nature. These reactions proceed with the liberation of acetic acid, which was removed azeotropically. (Scheme 1).



Scheme-1

Electronic spectra

The UV-Vis spectra of the Schiff bases and tin(II) complexes are recorded in dry DMF. Tin(II) complexes exhibit two bands at ~345 and ~380 nm. These bands are due to the π–π* and n–π* transitions of the azomethine chromophore. The considerable shifting observed in the n–π* transition (~370 nm) is due to the polarization of azomethine bond caused by tin-ligand electron interaction. This clearly indicates the coordination of the azomethine nitrogen to the tin atom. The spectra of the tin complexes also have sharp bands in the region 240–260 nm, with one more band at 365 nm; these may be assigned as charge transfer bands. It has been reported that the tin is capable of forming dπ–pπ bonds with ligands containing nitrogen as the donor atom. The tin atom has its 5d orbital completely vacant and hence Sn←N bonding can take place by the acceptance of the lone pair of electrons from the azomethine nitrogen of the ligands.

Infrared Spectra

The infrared spectra of ligand shows band at 3140-2725 cm^{-1} assigned to OH vibrations of the functional (-COOH) group[25], which disappear in the tin(II) derivatives, indicating that deprotonation of the functional group upon chelation. A new band appear in tin complexes at 562-540 cm^{-1} due to formation of ν(Sn-O) bond[26.]. The ligands show a band at 1636-1622 cm^{-1} assigned to azomethine group[27] is shifted to lower wave numbers 10-20 cm^{-1} in the spectra of tin(II) complexes, indicating that the coordination through the azomethine nitrogen atom to the tin atom, which is supported by the existence of new band at 432-456 cm^{-1} in the spectra of tin(II) compounds, due to the formation of ν(Sn←N) bond[28].

^{1}H-NMR Spectra

^{1}H NMR spectral data of Schiff bases and tin(II) complexes were recorded in DMSO-d$_6$. The free Schiff bases exhibit singlet at ~δ 8.50 ppm, due to azomethine proton (-N=CH-). This signal is shifted downfield (~δ 8.85), in the spectra of tin(II) complexes, suggests that the coordination through azomethime nitrogen of the to the tin atom. The COOH group gives signals at δ 12.65-11.20 ppm in free Schiff bases. These signals disappeared in the spectra of tin(II) complexes indicating the deprotonation of the –COOH group. The appearance of a signals at δ 3.82 (s, H, OCH_3) ppm could be assigned to OCH_3 group, in both the ligands and its tin(II) complexes, respectively. It shows that the OCH_3 group is not taking part in bond formation. The Schiff bases show a complex multiplet signal in the region δ 6.95–8.05 ppm for the aromatic protons and its remains at the same position in the spectra of the tin(II) complexes.

^{13}C NMR spectra

The ^{13}C NMR spectra data of few representatives Schiff base and its tin complexes were recorded in dry DMSO. The signals appeared at ~δ 182.5 ppm and ~δ 165.2 ppm, respectively for the carbon atoms of carboxylate and azomethine groups in the Schiff bases. However, in the spectra of the tin(II) complexes, these signal appears at ~δ 172.0 ppm, due to the carboxylate group and ~ δ 158.5 ppm, due to the azomethine group, respectively. The upfield shifting in the position of carbon signal of COOH group, suggest that the carboxylate oxygen of the ligands take part in the complexation. Further, the shifting of the azomethine (–CH=N–) carbon signal in the spectra of the tin(II) compounds as compared to the free ligands, clearly indicates that the coordination through azomethine nitrogen to the tin atom.

Table-2: IR spectral data (cm^{-1}) of Schiff bases and their corresponding tin(II) complexes

Compounds	ν(COOH)	ν(C=N–)	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	Δν	ν(Sn–O)	ν(Sn←N)
L^1H	3125-2780 br	1632 s	-	-	-	-	-
$Sn(L^1)_2$	-	1615 s	1598 s	1322 m	276	555 m	456 m
L^2H	3110-2757 br	1628 s	-	-	-	-	-
$Sn(L^2)_2$	-	1610 s	1600 s	1325 s	275	540 w	440 m
L^3H	3095-2878 br	1634 s	-	-	-	-	-
$Sn(L^3)_2$	-	1618 s	1590 s	1320 m	270	560 m	448 w
L^4H	3085-2776 br	1622 s	-	-	-	-	-
$Sn(L^4)_2$	-	1610 s	1588 vs	1328 s	260	552 m	444 w
L^5H	3115-2786 br	1628 s	-	-	-	-	-

$Sn(L^5)_2$	-	1612 s	1588 vs	1322 s	266	560 w	435 w
L^6H	3105-2808 br	1636 s	-	-	-	-	-
$Sn(L^6)_2$	-	1618 s	1590 vs	1326 s	264	544 w	432 m
L^7H	3102-2775 br	1634 s	-	-	-	-	-
$Sn(L^7)_2$	-	1614 s	1598 s	1320 m	278	554 w	438 w
L^8H	3085-2765 br	1622 s	-	-	-	-	-
$Sn(L^8)_2$	-	1612 s	1596 vs	1326 m	270	548 w	450 m
L^9H	3092-2810 br	1630 s	-	-	-	-	-
$Sn(L^9)_2$	-	1611 s	1598 s	1324 m	274	562 m	446 w
$L^{10}H$	3140-2725 br	1626 s	-	-	-	-	-
$Sn(L^{10})_2$	-	1616 s	1590 vs	1322 m	268	556 m	438 m

br = broad, vs = very sharp, v = sharp, m = medium, w = weak

^{119}Sn NMR Spectra

The ^{119}Sn NMR spectra of $Sn(L^1)_2$ and $Sn(L^3)_2$ give sharp signals at δ -578 ppm and δ -580 ppm[29-31] which is below the reported values for tri-coordinated hydrated tin(II) chloride. Therefore, a four-coordinate distorted tetrahedral geometry have been proposed for resulting tin(II) complexes (Fig.-2).

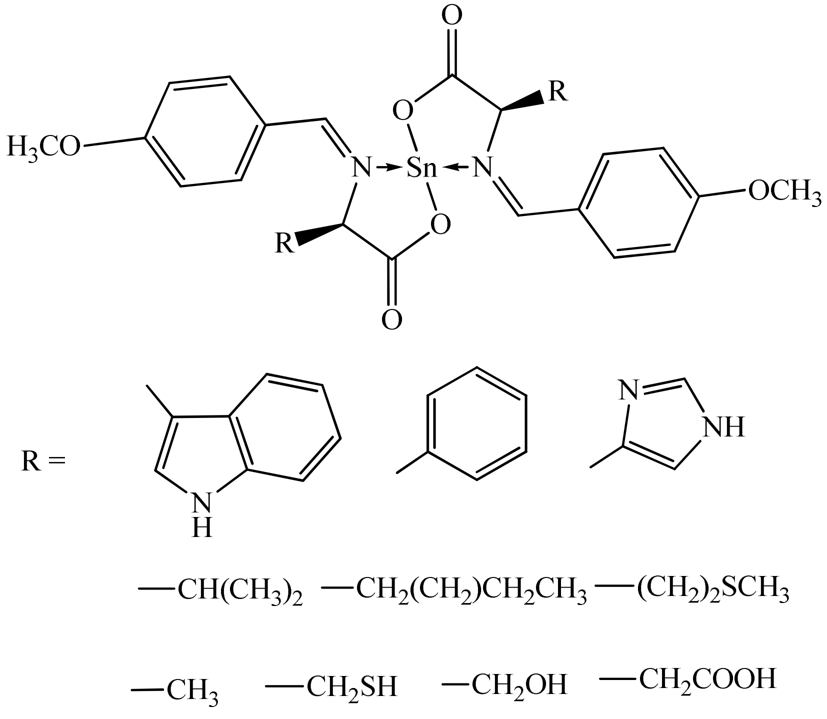


Fig.-2: Proposed structure of tin(II) Complexes

Theoretical Calculations

The theoretical parameters, total energy, dipole moment, energy of HOMO and LUMO orbitals were calculated. Additional parameters, such as separation energy, band gap energy, electronegativity (χ), electrophilicity index (ω), chemical hardness (η), and global softness (S) were calculated for L^4H, L^8H, $Sn(L^4)_2$ and $Sn(L^8)_2$ and represented Table-3. Chemical hardness and softness are significant properties to measure the molecular reactivity and stability of the molecules. A less reactive molecule has large band gap energy and a more reactive molecule has small band gap energy. In a complex formation system, the tin ion act as Lewis acid while ligands acts as Lewis base. Tin ion is soft acids and thus soft base ligands are most effective for complex formation. Accordingly, it is concluded that the ligands with proper softness values has a good tendency to from complexes with metal ions effectively.

The reactivity index measures the stabilization in energy when a complex formation system obtains an additional charge from the ligands. The energy difference between LUMO and HOMO orbitals decreases, interactions between the reacting species become stronger and as a result the stability of metal complexes increases and reactivity decreases. The calculated total energy of the tin complexes have lower values indicated a large stabilization of the complexes compared to the free ligands. The metal complexes have higher values of the dipole moment than that of the free ligands.

Bond Lengths and bond angles Calculations

Selected bond lengths of >C=N- and –COOH groups of the ligands and tin(II) complexes are given in Table 4. From the data obtained we observed that there is an elongation in the bonds of the active group of the ligands taking part in complexation, which correlates with the experimental infrared frequencies. The bond lengths and bond angles generated from the optimized structure of the tin(II) complexes, using Gaussian 03 software are given in the Table 4. Geometry optimization of the complexes $Sn(L^4)_2$ and $Sn(L^8)_2$ at the B3LYP/LanL2DZ level also suggests the distorted tetrahedral geometry for $Sn(L^4)_2$ and $Sn(L^8)_2$. The optimized structure for the compounds $Sn(L^4)_2$ and $Sn(L^8)_2$ are shown in Figure 3 and 4. The computed bond lengths, such as, Sn(1)–O(5), Sn(1)–N(2), Sn(1)–O(17) and Sn(1)–N(20) in the present complex [$Sn(L^4)_2$/ $Sn(L^8)_2$] are 2.044/2.045, 2.089, 2.044/2.045 and 2.088/2.089 Å respectively. The significant computed bond angles in the complex [$Sn(L^4)_2$/$Sn(L^8)_2$], such as, N(20)-Sn(1)-N(2), (114.57/115.74°), N(20)-Sn(1)-O(5), (118.34/118.41°), N(20)-Sn(1)-O(17), (92.90/92.92°), N(2)-Sn(1)-O(5), (92.97/92.92°), N(2)-Sn(1)-O(17), (118.83/118.45°) and O(5)-Sn(1)-O(17), (120.32/120.60°) suggest the distorted tetrahedral structure of the tin complexes. The calculated Sn-O and Sn-N bond distances are also close to the already reported x-ray structures of tin complexes.[32,33]

Table-3: Computed molecular descriptions of Ligands L^4H, L^8H and their tin(II) complexes

Atoms	Compounds				
	L^4H	$Sn(L^4)_2$	L^8H	$Sn(L^8)_2$	$Sn(OAc)_2$
Total Energy (a.u.)	-785.825	-1573.828	-717.301	-1436.771	-460.291
HOMO (eV)	-8.722	-3.858	-8.947	-4.015	-7.697
LUMO (eV)	-2.323	-3.179	-2.313	-2.949	-4.558
Energy Gap (eV)	6.399	0.679	6.634	1.066	3.139
Electronegativity (χ) $\chi = (E_{HOMO} + E_{LUMO})/2$	-5.522	-3.518	-5.630	-3.482	-6.127
Chemical potential (μ, eV) ($\mu = E_{LUMO}+E_{HOMO}/2$)	-3.199	-0.339	-3.317	-0.533	-1.569
Chemical hardness (η, eV)	6.399	0.679	6.634	1.066	3.139
Global softness ($S = 1/\eta$)	0.156	1.473	0.151	0.938	0.319
Electrophilicity index ($\omega = \mu^2/ 2\eta$)	0.799	0.085	0.829	0.133	0.392
Dipole moment (Debye)	4.036	10.285	4.297	11.207	2.687

Antibacterial studies

The antibacterial activity of a few representative ligands and tin(II) complexes have been tested against *Escherichia coli* (-), *Klebsiella pneumonia* (-) and *Staphylococcus aureus* (+), *Bacillus cereus* (+), by the agar well diffusion method[21] at 100 μg ml^{-1} concentration in DMSO. The antibacterial results were shown in figure 4. The effect against *S. aureus* of complexes was found to be close to that of Streptomycin. But there was less inhibitory activity by the Schiff base ligands. It is possible that ligands may be activated by the tin(II) ion. The 2-((4-methoxybenzyli-dene) amino)-4-(methyl-thio) butanoic acid and 3-mercapto-2-((4-methoxy-benzylidene) amino)propanoic acid ligand complex show more antibacterial activity than others. The coordination of metal ion with bulky Schiff base ligand, decreases the polarity of the metal ion. This is due to the overlap of ligand orbitals and metal orbitals, this leads to a delocalization of positive charge. Thus the lipophilic character of the tin complexes increases and this allows its penetration through the bacterial lipoid layer. Further, the greater activity of the complexes can also be explained on the basis of their higher solubility, particle size and the size of the metal ion. This may be the reason why tin complexes have more inhibition than the free ligands against all micro-organisms tested. In the present work 2-((4-methoxybenzyli-dene) amino)-4-(methyl-thio) butanoic acid and 3-mercapto-2-((4-methoxy-benzylidene) amino)propanoic acid-tin complex show an enhanced antibacterial activity. This could make these complexes find application in medicinal chemistry.

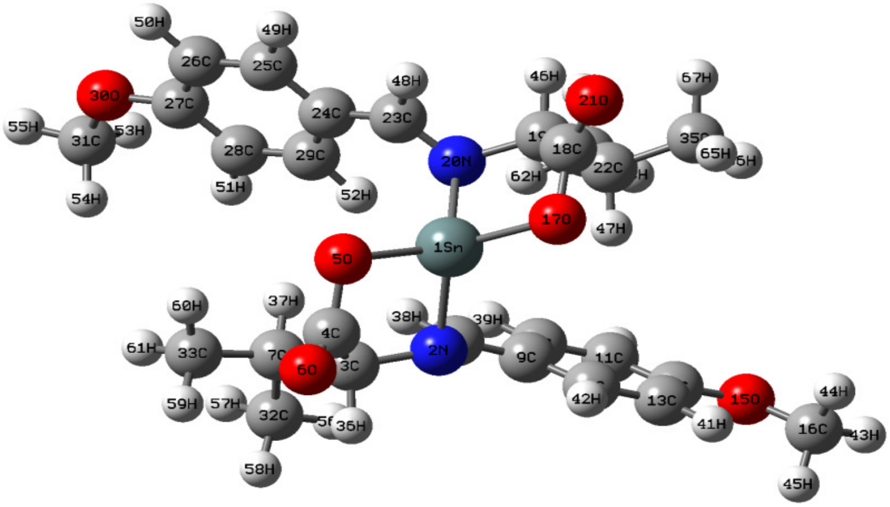


Fig.-3: Molecular structure of $Sn(L^4)_2$ complex along with atom numbering scheme

Table-4: Selected bond parameters of $Sn(L^4)_2$ and $Sn(L^8)_2$ complexes.

Atoms	Compounds			
	L^4H	$Sn(L^4)_2$	L^8H	$Sn(L^8)_2$
bond lengths (Å)				
O(17)-C(18)	1.348	1.373	1.348	1.372
N(2)-C(3)	1.483	1.534	1.484	1.530
N(2)-C(8)	1.267	1.272	1.267	1.272
C(8)-H(38)	1.110	1.103	1.110	1.107
Sn(1)-O(5)	-	2.044	-	2.045
Sn(1)-N(2)	-	2.089	-	2.089
Sn(1)-O(17)	-	2.044	-	2.045
N(20)-Sn(1)	-	2.088	-	2.089
C(4)-O(5)	-	1.372	-	1.372
C(19)-N(20)	-	1.528	-	1.530
N(20)-C(23)	-	1.272	-	1.272
C(3)-C(4)	-	1.558	-	1.554

bond angles of (°)				
O(5)-C(4)-C(3)	111.952	113.70	112.391	113.79
C(8)-N(2)-C(3)	124.413	120.95	124.486	117.53
N(20)-Sn(1)-N(2)	-	114.57	-	115.74
N(20)-Sn(1)-O(5)	-	118.34	-	118.41
N(20)-Sn(1)-O(17)	-	92.90	-	92.92
N(2)-Sn(1)-O(5)	-	92.97	-	92.92
N(2)-Sn(1)-O(17)	-	118.83	-	118.45
O(5)-Sn(1)-O(17)	-	121.32	-	120.60

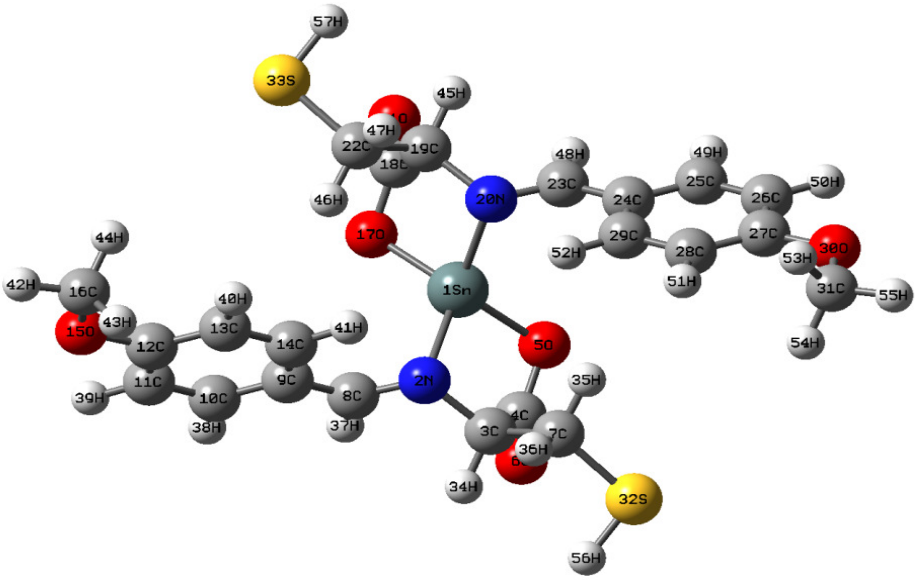


Fig.-4: Molecular structure of Sn(L^8)$_2$ complex along with atom numbering scheme.

CONCLUSION

Tin(II) compounds have a great interest recently due to unique physical and chemical properties, which have great applications as antimicrobial materials. The synthesized amino acid Schiff bases acted as monofunctional bidentate ligands. The tin atom was coordinated through the carboxylate oxygen and azomethine nitrogen atom. Based on the physiochemical, spectral and DFT calculations distorted tetrahedral structures have been assigned to all the tin(II) complexes. The antibacterial screening of the tin(II) complexes showed varied activities but they are more inhibition than the free ligands.

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