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# Synthesis, spectroscopic characterization and computational studies of Schiff base complexes of tin(IV) chloride

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**Abstract:** Reaction of anhydrous tin(IV) chloride with mono functional bidentate Schiff bases ($sb^nH$), in 1:2 molar ratios, gives complexes of the type, $[(sb^n)_2SnCl_2]$ (1-4) (where, n=1-4; sb=2-(((4-chlorophenyl)imino)methyl)phenol, $sb^1$**H, I;** 2-(((4-bromophenyl)imino)methyl) phenol, $sb^2$**H, II;** 2-(((4-chlorophenyl)imino)methyl)-6-methoxyphenol, $sb^3$**H, III** and 2-(((4-bromo phenyl)imino)methyl)-6-methoxyphenol, $sb^4$**H, IV.** All the tin(IV) complexes **(1-4)** were colored solid and soluble in organic solvents. The synthesized complexes were characterized by elemental analysis (C, H, N and Sn), IR, UV-Vis, NMR ($^1H$, $^{13}C$ and $^{119}Sn$) spectroscopy and mass spectrometry. On the basis of spectroscopic studies, six coordination around tin atom has been proposed tentatively. The computational calculations using density functional theory (DFT) of ligands and complexes were also performed to obtained optimized molecular geometry, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and other parameter.

**Keywords:** tin(IV) complexes; Schiff base; synthesis; DFT

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## 1 Introduction

The research area of bio-inorganic and medicinal chemistry, for tackling disease like cancer, grew abruptly after the fortuitous discovery of cisplatin (Che and Siu, 2010; Guo and Sadler, 1999). The amalgamation of biologically active ligands or Schiff bases with metal enhances some properties of metal complexes. Schiff base can be proved to be an ideal functional pharmacophore for tin-based drug design (Hazra et al., 2016; Wang et al., 2014). Tin(IV) complexes have received significant attention due to their biocidal activities (Kumar and Nath, 2018; Nath and Saini, 2011) including high antitumor activity than cisplatin against human cell line *in vitro* tests (Kaluđerović et al., 2010).

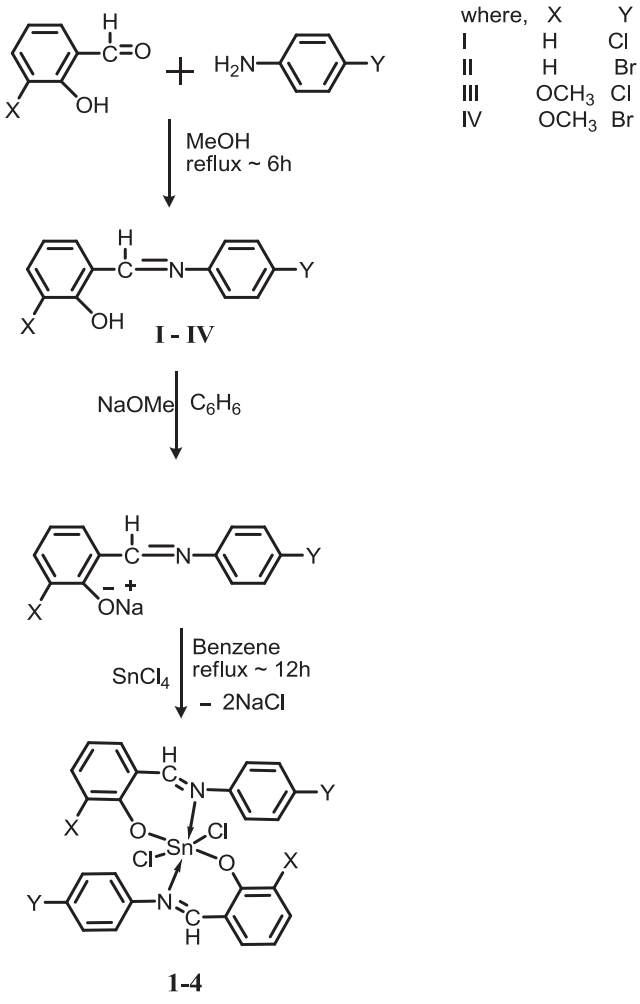
In the last decades, considerable amount of organotin(IV) compounds which focused on cancer chemotherapeutics have been synthesized and studied (Hadjikakou and Hadjiliadis, 2009). The relatively less investigated inorganic tin(IV) complexes may offer remarkable activities along with bio active ligands (Chen et al., 2013). Several tin(IV) complexes of salicyaldehydes derivative Schiff base have been screened for antitumor activities (Al-Allaf et al., 2003; Xu et al., 2016; Yang et al., 2016). Tin(IV) chloride and its complexes act as strong Lewis acid and help in catalyzing organic reactions like cycloaddition (Matsuo et al., 2009) ring-opening polymerization reaction (Darensbourg et al., 2005), polyene cyclization (Kumazawa et al., 2004) and other organic transformation (Jing et al., 2004; Yang et al., 2015).

During the past decades, a number of molecular addition complexes of $SnCl_4$ with N O donor ligands have been reported (Chen et al., 2013; Teoh et al., 1997) while its reaction with sodium salt of bidantate salicylidiminte derivative ligand has been investigated to a very limited extent (Dubey and Singh, 2013). Keeping all the mention fact in mind and our persistent interest in Schiff base derived from salicylaldehyde (Dubey et al., 2011a; Dubey et al., 2012a) with their main group metal complexes (Dubey and Singh, 2015; Dubey et al., 2011b; Dubey et al.,

2012b; Dubey et al., 2014; Kushwaha et al., 2017), we report herein synthesis and spectroscopic characterization of some tin(IV) complexes with salicyaldehyde and o-vanillin derived Schiff base ligands. Density functional theory (DFT) calculation of ligand and complexes were also carried out to obtain optimized molecular geometry and other quantum mechanical parameters.

## 2 Result and discussion

The Schiff base pro ligands were prepared by the condensation reaction of salicylaldehyde/o-vanillin with 4-chloro/bromo-aniline. The reaction of synthesized ligands with $SnCl_4$ in 2:1 molar ratio lead to the formation of colored (light to dark brown) complexes of the type $[(sb)_2SnCl_2]$ (1-4) (Scheme 1). All complexes were found to be soluble in organic polar solvents like chloroform, DMF and DMSO.




**Scheme 1:** Synthetic route for preparation of ligand and tin(IV) complexes.

### 2.1 IR spectroscopy

The comparison of infrared spectra (Figures S1 and S2) of the free ligands as well as of the tin(IV) complexes provides significant information about the coordination mode of ligand and the structures of the complexes. The characteristic band $\nu$(O-H) of free ligands were observed in the region of 3429-3422 $cm^{-1}$. The disappearance of this characteristic band in metal complexes due to deprotontaion of phenolic O-**H** of the ligands results in complex formation through bonding between tin and phenolic oxygen (Dubey et al., 2012a). This coordination mode was further supported by the appearance of band in the region 561-545 $cm^{-1}$ (Kumar and Nath, 2018). The ligands show a sharp and strong band in the region 1616-1611 $cm^{-1}$ assign to characteristic $\nu$(C=N) stretching. The metal complexes exhibited significant shift in this band to lower wave numbers viz; 1610-1595 $cm^{-1}$ indicating the coordination of azomethine nitrogen to tin atom (Dubey and Singh, 2013; Pettinari et al., 2001). This Sn←N mode of coordination in complexes was further supported by the appearance of new band in region 470-450 $cm^{-1}$ (Kumar and Nath, 2018).

### 2.2 NMR spectroscopy

The comparison of NMR Spectra of ligands and complexes reveal significant inference about the coordination mode of tin in complexes. The $^1$H NMR spectra (Figures S3 and S4) of ligands show an important signal in the region 13.41-12.99 ppm due to phenolic –O-**H** and this signal disappears in complexes because of deprotonation and subsequent participation of phenolic oxygen in bonding through tin during the complex formation (Dubey and Singh, 2014). The signal observed in the range 8.60-8.59 ppm was attributed to the characteristic azomethine group of the ligand (-HC=N) shows upfield chemical shift to 8.42–8.27 ppm suggestive of involvement of imine nitrogen in coordination with central tin atom (Xu et al., 2016). The chemical shifts of aromatic hydrogens appear in the region 7.50-6.75 ppm for free ligands which depict slight shift to 7.85-6.58 ppm in complexes.

The $^{13}$C NMR spectra (Figures S5 and S6) of ligands show signals in the region 163.0-148.5 ppm were assigned to phenolic carbon shifted downfield in the complexes in the region 164.5-152.3 ppm which established the coordination of phenolic oxygen to tin. Similarly, a signal for imine carbon appears in the region 163.1-161.0 ppm

shows upfield chemical shift in the region 159.6-155.3 ppm which is indicative of involvement of azomethine nitrogen in coordination with tin. The signals in region 149.59-113.56 ppm were attributed to aromatic carbons of ligand and in metal complexes it appears in the region 148.4-114.7 ppm (Dubey et al., 2011b).

In order to provide further evidence of coordination mode to establish the structure of the complexes, $^{119}$Sn NMR spectra were recorded (Figure S7) in $CDCl_3$. The $^{119}$Sn NMR chemical shifts are very sensitive to changes in the coordination number of tin and to the nature as well as electronegativity of groups or atom directly attached to the tin atom. As the electronegativity of atom increases, $^{119}$Sn NMR chemical shifts increases. The $^{119}$Sn NMR chemical shift for similar type of tin(IV) chloride complexes reported in the wide range of -600 ± 50 ppm, showing a six coordinated octahedral environment around tin(IV) (Dubey et al., 2011b; Pettinari et al., 2006; Wrackmeyer, 1985). The tin(IV) complexes (**1-4**) exhibit a single sharp $^{119}$Sn resonance in the range -629.8 to -625.3 ppm region supports a six coordinate octahedral geometry around tin atom (Chauhan and Arjmand, 2007; Tabassum et al., 2011).

## 2.3 UV-Visible spectroscopy

UV-Vis spectra (Figures S8 and S9) of ligands and corresponding complexes were recorded in methanol. The ligands exhibited intense bands in 200-400 nm region. The π-π* transitions of the aromatic rings were observed in the region 220-240 nm. The bands in the region 270-294 nm and 345-360 nm were assigned to π-π* and n-π* transitions of the C=N group, respectively. The absorption spectra of complexes show a longer wavelength shift (red-shift) compare to free ligand is due to coordination of ligand to tin center (Hong et al., 2013).

## 2.4 Mass spectrometry

The mass spectra of the complexes (**1-4**) exhibits molecular ion peaks *m/z* which is correspond to the molecular composition of the complexes. Since the tin metal have several stable isotopes, the mass spectra of tin complexes show group of peaks at an individual molecular ion peak. In the mass spectrum (Figure 1) of the complex **1**, molecular peak observed at *m/z* 650.12 [Calculated= 650.96]. The observed isotopic distribution for molecular ion peak at m/z 650.129 and others were compared to the calculated (bars) isotopic distribution for molecular ion peak and other important peaks with the mass spectrum of the complex **1** confirm the molecular composition of the complex **1**. Similarly, the mass spectra of other complexes shows molecular ion peak at *m/z* 739.10 [calculated= 739.86] **2**; 710.83 [calculated= 711.01] **3** and 798.87 [calculated= 799.91] **4.**

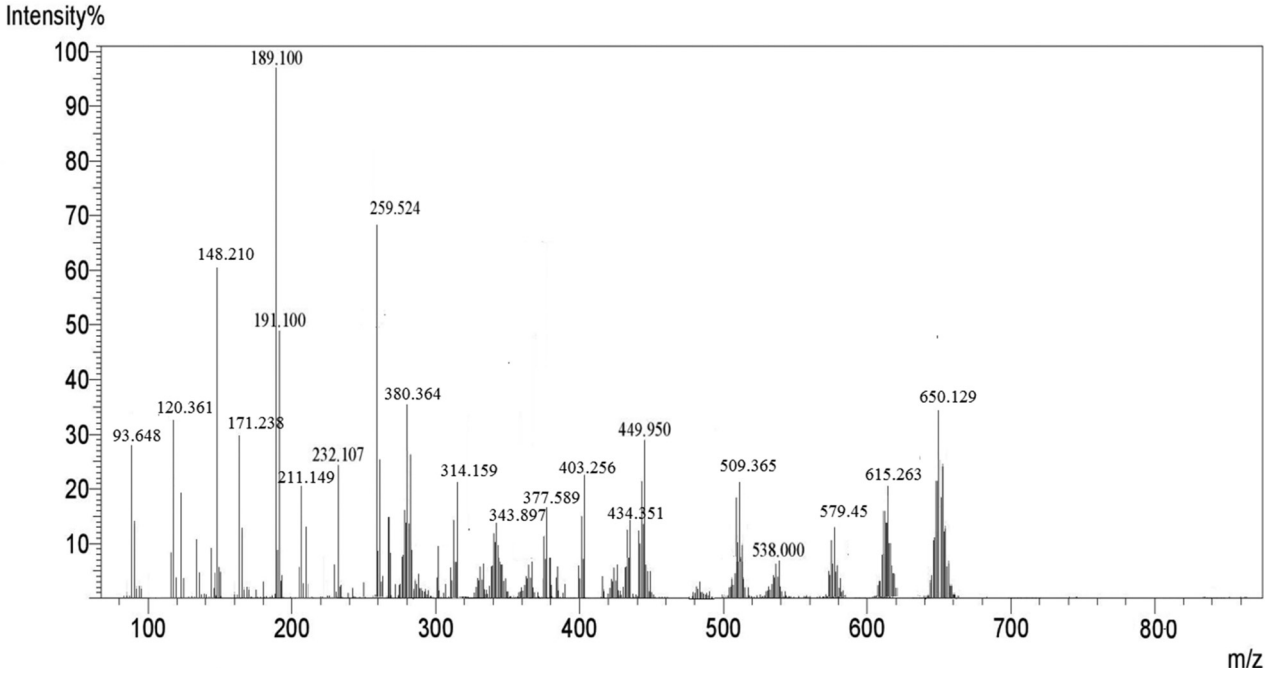



**Figure 1:** Mass spectrum of Complex, $[(sb^1)_2SnCl_2]$ (**1**).

## 2.5 Computational studies

Since several attempts have failed to grow the suitable crystal for X-rays studies so computation calculation have been performed to get a further authentication for synthesized tin(IV) complexes. All computational calculations have been carried out using density functional theory (DFT). DFT calculations were carried out for the ligands and its complexes to fully optimize the ground state structure. The fundamental vibrational frequencies were also calculated using the same program.

The optimized energy, dipole moment and energy band gap values are summarized in Table 1. The molecular structure of ligand and its tin(IV) complex with atom labeling scheme is shown in Figure 2 and selected bond lengths and angles are summarized in Table 2.

The theoretically calculated values of different bond lengths in complexes viz. Sn-O, Sn←N, Sn-Cl and others

**Table 1:** Computed electronic properties for ligands (**I-IV**) and complexes (**1-4**).

| Compounds | | Total Energy (in au) | Dipole Moment | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $\Delta E = E_{HOMO} - E_{LUMO}$ |
|---|---|---|---|---|---|---|
| $sb^1H$ | **I** | −1085.88 | 5.40 | −5.94 | −1.69 | 4.25 |
| $sb^2H$ | **II** | −3202.77 | 4.81 | −5.79 | −1.64 | 4.15 |
| $sb^3H$ | **III** | −1199.78 | 7.21 | −5.78 | −1.57 | 4.21 |
| $sb^4H$ | **IV** | −3317.25 | 6.70 | −5.68 | −1.55 | 4.13 |
| $[(sb^1)_2SnCl_2]$ | **1** | −1324.70 | 0.02 | −6.33 | −2.70 | 3.63 |
| $[(sb^2)_2SnCl_2]$ | **2** | −1321.09 | 0.14 | −6.32 | −2.62 | 3.70 |
| $[(sb^3)_2SnCl_2]$ | **3** | −1553.70 | 1.72 | −5.93 | −2.55 | 3.38 |
| $[(sb^4)_2SnCl_2]$ | **4** | −1550.13 | 2.87 | −5.93 | −2.58 | 3.35 |

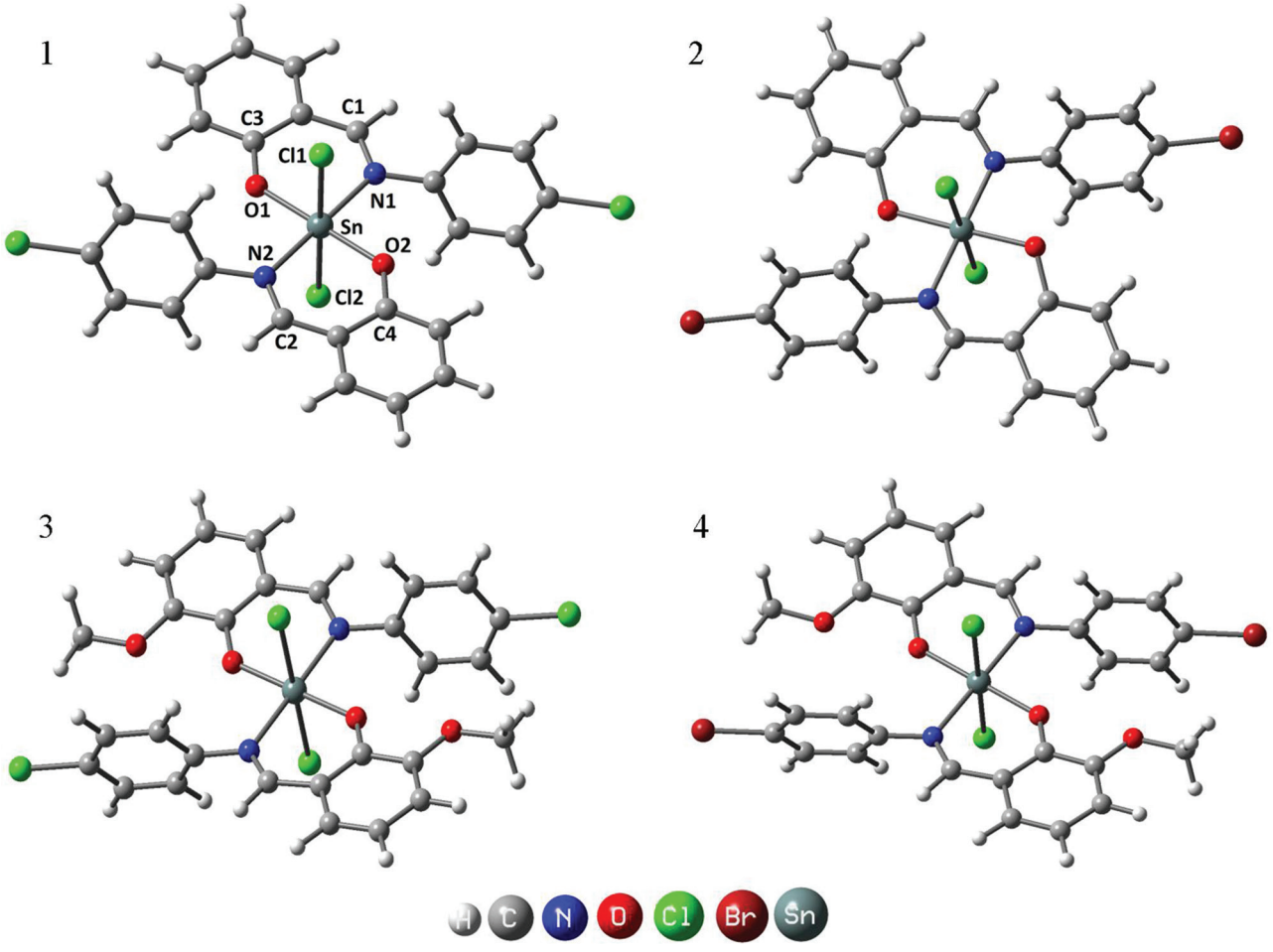



**Figure 2:** The ground state optimized geometry for Complexes (**1-4**) at B3LYP/LANL2DZ level.

**Table 2:** Selected structural (bond length and bond angle) parameters for $[(sb^1)_2SnCl_2]$, **1** and $[(sb^3)_2SnCl_2]$, **3** at B3LYP/LanL2DZ level of theory.

| Bond length (Å) | | | Bond angle (⁰) | | |
|---|---|---|---|---|---|
| | $[(sb^1)_2SnCl_2]$ | $[(sb^3)_2SnCl_2]$ | | $[(sb^1)_2SnCl_2]$ | $[(sb^3)_2SnCl_2]$ |
| Sn-N1 | 2.15902 | 2.16014 | O1-Sn-N1 | 88.34544 | 87.89386 |
| Sn-N2 | 2.15940 | 2.16017 | O2-Sn-N2 | 88.34834 | 87.89285 |
| Sn-O1 | 1.99136 | 1.99203 | O2-Sn-N1 | 91.63616 | 92.11026 |
| Sn-O2 | 1.99124 | 1.99201 | O1-Sn-N2 | 91.67007 | 92.10686 |
| Sn-Cl1 | 2.48764 | 2.49183 | O1-Sn-Cl1 | 89.80520 | 90.06188 |
| Sn-Cl2 | 2.48761 | 2.48280 | O1-Sn-Cl2 | 90.20268 | 89.94145 |
| C3-O1 | 1.34239 | 1.33693 | O2-Sn-Cl1 | 90.18601 | 90.05678 |
| C4-O2 | 1.34233 | 1.33691 | O2-Sn-Cl2 | 89.80611 | 89.93989 |
| C1=N1 | 1.32531 | 1.32535 | N1-Sn-Cl1 | 89.29038 | 89.06814 |
| C2=N2 | 1.32547 | 1.32535 | N1-Sn-Cl2 | 90.69316 | 90.92800 |
| | | | N2-Sn-Cl1 | 90.72464 | 89.07864 |
| | | | N2-Sn-Cl2 | 89.29182 | 90.92522 |

are in close agreement to the values reported form X-rays crystallography studies of tin(IV) complexes of N, O donor ligands in octahedral system. In all complexes axial position to the Sn atom are occupied by two chlorine atom while the four equatorial positions to the Sn atom are engaged with N and O atom of ligand (Takano et al., 2012). The value of the Sn–O distance, in the range 1.99-2.10 Å and Sn–N in the range 2.14-2.18 Å as well as the other bond distances and angle are in good agreement, for complex **1–4**, with the values reported for Sn–complexes using X-ray diffraction (Mridula and Nath, 2016). The deviations in the values of bond angles from perfect octahedral geometry suggest distorted octahedral geometry around tin atom.

The stability of complexes with respect to ligand can also be predicted by observing the energy gap of HOMO and LUMO. The stability of the complexes is proportional to the energy band gap. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of ligand (**I** & **III**) and respective complex (**1** & **3)** are also shown in Figure 3. The comparison of total energy(E) and energy gap (ΔE) of ligands and complexes also suggest stability of complexes The obtained energy gap (ΔE) values of optimized complexes suggest the following order of stability i.e. 2>1>4>3.

# 3 Conclusion

In this work, we have synthesized four N O donor Schiff base ligand and their corresponding tin(IV) chloride complexes. These ligand and complexes have been characterized by elemental analyses (C, H, N and Sn) and spectroscopic FT-IR, NMR ($^1$H, $^{13}$C and $^{119}$Sn) technique as well as mass spectrometry. The DFT calculation for ligands and complexes has been performed in order to get optimized geometry of complexes and other quantum mechanical properties. Hexa-coordinated geometry around tin atom proposed on the basis of spectroscopic observation.

# Experimental

## Materials

All reagents were commercial products and were purchased from Aldrich, Alfa Aesar, Loba and used as received. Solvents were of analytical grade and purified through literature method before use (Armarego and Perrin, 1997). Salicyldehyde, 4-chloroaniline, 4-bromoaniline (CDH, New Delhi, India) and *o*-vanillin (Alfa-aesar) were obtained commercially and used without further purification. Tin tetrachloride (Sigma Aldrich, Bangalore, India) purified before use through distillation under vacuum. All the syntheses were carried out under strict anhydrous condition.

## Methods and instrumentation

Stringent precautions were taken to exclude the atmospheric moisture throughout the reaction process. Silica gel guard tubes were used during the reaction. All glass apparatus fitted with standard interchangeable

ground joints were used during the investigation. The tin content in the synthesized complexes was determined gravimetrically as $SnO_2$ (Vogel, 2008). The melting points of synthesized complexes were determined using capillary melting point apparatus. The elemental analyses were carried out on a Euro E 3000. FT-IR spectra were recorded

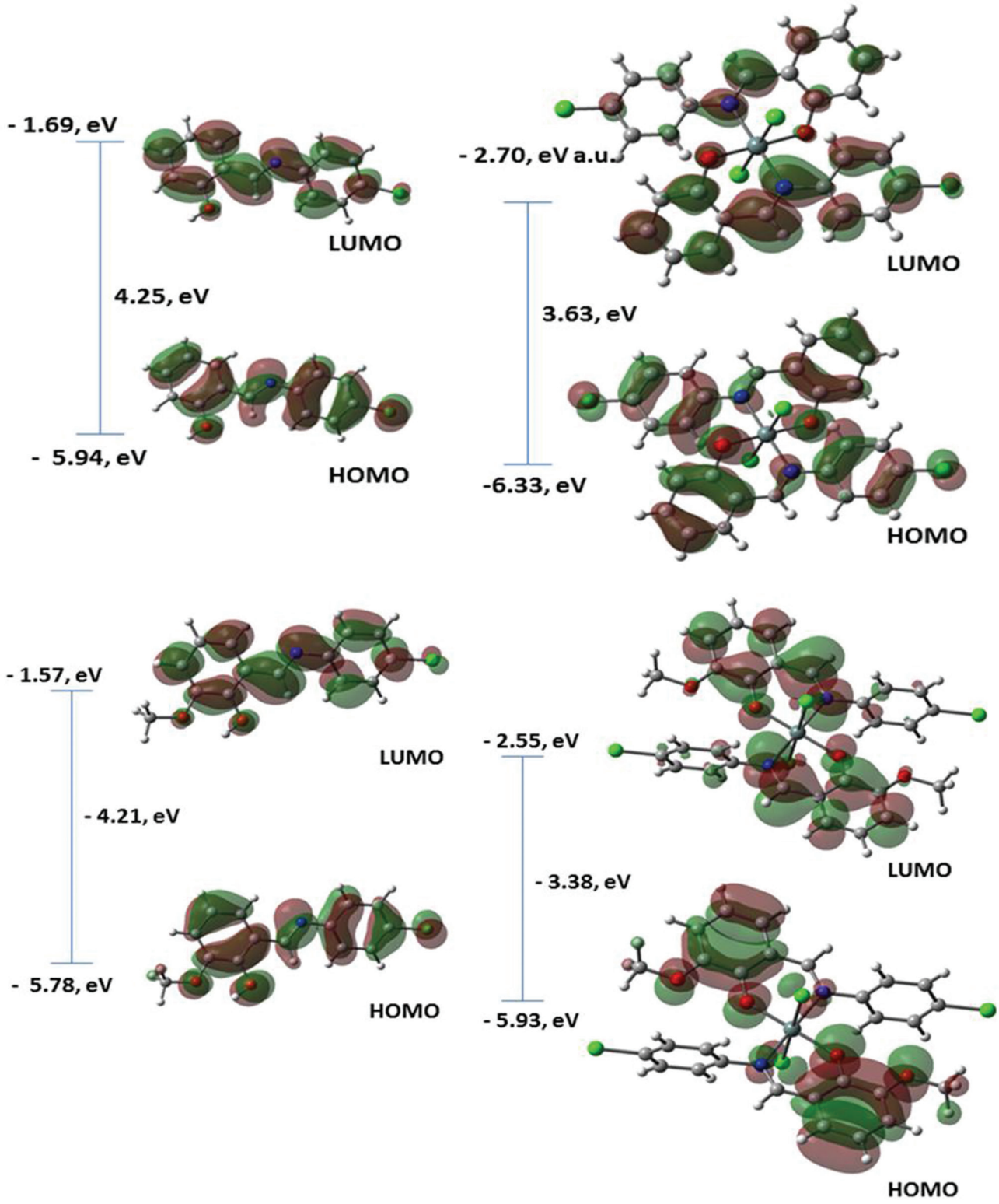



**Figure 3:** Energy diagram of frontier molecular orbitals HOMO and LUMO of ligand, **I & III** and complex, **1** & **3** derived from DFT calculations using B3LYP/LANL2DZ level of theory.

on 510Perkin Elmer infrared spectrophotometer. $^{1}H$, $^{13}C$ NMR and $^{119}Sn$ spectra were recorded in chloroform-D on a JEOL 500 spectrometer. The $^{1}H$ and $^{13}C$ NMR chemical shifts (in ppm) are reported from tetramethylsilan (TMS) as standard and $^{119}Sn$ NMR spectra were measured relative to tetramethyltin. Electronic spectra were recorded at room temperature with an UV-1800 Shimadzu UV-Vis Spectrophotometer between 200 and 600 nm in methanol. The mass spectra were obtained on a Shimadzu LCMS 2020 instrument in acetonitrile solvent.

Computational calculations were carried out for the ligands and its complexes in the gas phase to fully optimize the ground state structure by using Gaussian 09 program package (Frisch et al., 2009). The computations were carried out with the B3LYP functional level (Becke, 1993) using LANL2DZ basis set (Lee et al., 1988) to describe tin atom while for all other atoms 6-31G. The fundamental vibrational frequencies were also calculated and compared using the same program.

## Synthesis of Schiff bases

Synthesis of Schiff base pro-ligands (**I-IV**) were done according to our earlier published procedure (Dubey et al., 2012a). 2-(((4-chlorophenyl)imino)methyl)phenol, (sb$^{1}$H) **I**; salicyaldehyde (2.621 g, 21.46 mmol) and 4-chlroaniline (2.737 g, 21.46 mmol) were added to methanol with constant strring for ~2 h. The reaction mixture was refluxed on a water bath for ~4 h and then allowed to cool at room temperature for overnight. The crystalline yellow product (**I**) was obtained and recrystallized from methanol. Similar procedure was followed for synthesis of other ligands (**II-IV**).

2-(((4-chlorophenyl)imino)methyl)phenol, sb$^{1}$**H, I**: Yield: 71%; Yellow crystals; mp: 108°C; Mol. Weight, 231.68; Elem. Anal. for $C_{13}H_{10}ClNO$, Calc.: C, 67.39; H, 4.35; N, 6.05, Found: C, 67.21; H, 4.12; N, 5.95; IR (KBr pellets, $cm^{-1}$): 3429 m ($\nu$O-H), 1614 s ($\nu$C=N), 1256 s ($\nu$C-O); $^{1}H$ NMR ($CDCl_3$) ($\delta_H$, ppm): 13.07 (s, 1H, Ph-OH), 8.59 (s, 1H, HC=N), 7.39-6.93 (m, 8H, Ar-H); $^{13}C$ NMR ($CDCl_3$) ($\delta_C$, ppm): 163.0 (Ar-C-O), 161.1 (C=N), 147.1, 133.5, 132.5, 132.4, 129.6, 122.5, 119.2, 119.1, 117.4 (Ar-C). UV-Vis ($CH_3OH$) [$\lambda_{max}$, nm (ε, $M^{-1}cm^{-1}$)]: 340 (19500), 318 (18700), 271 (20600), 230 (29500).

2-(((4-bromophenyl)imino)methyl)phenol sb$^{2}$**H II**: Yield: 74%; Dark green; mp: 114°C; Mol. Weight: 276.13; Elem. Anal. for $C_{13}H_{10}BrNO$, Calc.: C, 56.55; H, 3.65; N, 5.07, Found: C, 56.26; H, 3.45; N, 5.01; IR (KBr pellets, $cm^{-1}$): 3424 m ($\nu$O-H), 1616 s ($\nu$C= N), 1282 ($\nu$C-O); $^{1}H$ NMR ($CDCl_3$) ($\delta_H$, ppm): 12.99 (s, 1H, Ph-OH), 8.59 (s, 1H, CH=N), 7.54-6.93 (m, 8H, Ar-H); $^{13}C$ NMR($CDCl_3$) ($\delta_C$, ppm): 163.0 (Ar-C-O), 161.0 (C=N), 147.5, 133.4, 132.4, 132.3, 122.8, 120.3, 119.2, 119.0, 117.3 (Ar-C-); UV-Vis ($CH_3OH$) [$\lambda_{max}$, nm(ε, $M^{-1}cm^{-1}$)]: 341 (6200), 320 (6100), 272 (6900), 230 (9500).

2-(((4-chlorophenyl)imino)methyl)-6-methoxyphenol, sb$^{3}$**H, III**: Yield: 76%; Orange crystals, mp: 110°C, Mol. Weight: 261.70; Elem. Anal. for $C_{14}H_{12}ClNO_2$, Calc.: C, 64.25; H, 4.62; N, 5.35, Found: C, 63.96; H, 4.52; N, 5.28; IR (KBr pellets, $cm^{-1}$): 3425 m ($\nu$O-H), 1611 s ($\nu$C=N), 1272 s ($\nu$C-O); $^{1}H$ NMR ($CDCl_3$) ($\delta_H$, ppm): 13.41 (s, 1H, Ph-OH), 8.60 (s, 1H, CH=N), 7.39-6.88 (m, 8H, Ar-H), 3.93 (s, 3H, O-$CH_3$); $^{13}C$ NMR ($CDCl_3$) ($\delta_C$, ppm): 163.0 (C=N), 151.4, 148.5 (Ar-C-O), 146.8 (Ar-C-N), 132.6, 129.6, 123.9, 122.5, 119.0, 118.8, 115.0 (Ar-C), 56.2 (O-$CH_3$); UV-Vis ($CH_3OH$) [$\lambda_{max}$, nm (ε, $M^{-1}cm^{-1}$)]: 318 (7000), 280 (5700), 228 (9800).

2-(((4-bromophenyl)imino)methyl)-6-methoxyphenol sb$^{4}$**H, IV**: Yield: 73%; Light orange crystals; mp: 116°C; Mol. Weight: 306.15; Elem. Anal. for $C_{14}H_{12}BrNO_2$, Calc.: C, 54.92; H, 3.95; N, 4.58, Found: C, 54.52; H, 3.69; N, 4.41; IR (KBr pellets, $cm^{-1}$): 3422 m ($\nu$O-H), 1614 s ($\nu$C= N), 1258 s ($\nu$C-O); $^{1}H$ NMR ($CDCl_3$) ($\delta_H$, ppm): 13.38 (s, 1H, Ph-OH), 8.60 (s, 1H, CH=N), 7.54-6.88 (m, 8H, Ar-H), 3.93 (s, 3H, O-$CH_3$); $^{13}C$ NMR ($CDCl_3$) ($\delta_C$, ppm): 163.1 (Ar-C=N), 151.4, 148.5 (Ar-C-O), 147.3 (Ar-C-N), 132.5, 123.9, 122.9, 120.5, 119.0, 118.8, 115.1 (s, Ar-C) 56.2 (s, O-$CH_3$, C-18); UV-Vis ($CH_3OH$) [$\lambda_{max}$, nm (ε, $M^{-1}cm^{-1}$)]: 316 (8400), 275 (7100), 224 (11500).

## Synthesis of complexes

To a benzene solution of $SnCl_4$ (1.30 g, 4.99 mmol) a methanolic solution of an appropriate sodium salt of sb$^{1}$H (2.31 g, 9.98 mmol) [prepared by dissolving equimolar amount of sodium metal and a Schiff base (sb$^{1}$H), in ~30 ml methanol] was added dropwise in 1:2 molar ratio with constant stirring. The reaction mixture was allowed to reflux for ~8 h. The precipitated NaCl was removed by filtration. The solvent was removed by distillation. The solid product was dried under reduced pressure and washed from the n-hexane solvent. The solid powder product obtained. Similar procedure was adopted for the preparation of other complexes (**2-4**) with optimum refluxing time.

Bis-2-(((4-chlorophenyl)imino)methyl) phenolatodichlorotin(IV), [(sb$^{1}$)$_2$SnCl$_2$] **1** Yield: 70%, Brown solid, mp: 145-147°C; Mol. Weight: 650.96; Elem. Anal. for $C_{26}H_{18}Cl_4N_2O_2Sn$, Calc.: C, 47.97; H, 2.79; N, 4.30; Sn, 18.24 Found: C, 47.38; H, 2.55; N, 4.02; Sn, 18.01%; IR (KBr pellets, $cm^{-1}$): 1609 s ($\nu_{C=N}$), 1260 s ($\nu_{C-O}$), 560 w ($\nu_{Sn-O}$), 452 w ($\nu_{Sn-N}$); $^{1}H$ NMR ($CDCl_3$) ($\delta_H$, ppm): 8.42 (s, 2H, CH = N), 7.40-6.75, (m, 16H, Ar-H); $^{13}C$ NMR ($CDCl_3$) ($\delta_C$, ppm): 164.2

(Ar-C-O), 156.3 (C=N), 148.2, 134.4, 132.4, 132.3, 122.8, 122.3, 121.7, 119.0, 116.9, 114.7 (Ar-C); $^{119}$Sn NMR ($CDCl_3$) (ppm): -629.8; UV-Vis ($CH_3OH$) [$\lambda_{max}$, nm (ε, $M^{-1}cm^{-1}$)]: 370 (6100), 280 (6300), 240 (11200); ESI-MS (m/z): 650.12.

Bis-2-(((4-bromophenyl)imino)methyl) phenolatodichlorotin(IV), [$(sb^2)_2SnCl_2$] **2** Yield: 68%, Brown solid, mp: 140-142°C; Mol. Weight: 739.86; Elem. Anal. for $C_{26}H_{18}Br_2Cl_2N_2O_2Sn$, Calc.: C, 42.21; H, 2.45; N, 3.79; Sn, 16.04 Found: C, 41.85; H, 2.35; N, 3.65; Sn, 15.84%; IR (KBr pellets, $cm^{-1}$): 1605 s ($\nu_{C=N}$), 1243 s ($\nu_{C-O}$), 561 w ($\nu_{Sn-O}$), 467 w ($\nu_{Sn-N}$); $^1$H NMR ($CDCl_3$) ($\delta_H$, ppm): 8.36 (s, 2H, CH = N), 7.45 – 6.95 (16H, m, Ar-H); $^{13}$C NMR ($CDCl_3$) ($\delta_C$, ppm): 164.5 (Ar-C-O), 155.3 (C=N), 148.4, 142.3, 135.8, 133.0, 132.1, 127.2, 123.0, 118.2, 117.9, 116.1 (Ar-C); $^{119}$Sn NMR ($CDCl_3$) (ppm): -626.2; UV-Vis ($CH_3OH$) [$\lambda_{max}$, nm (ε, $M^{-1}cm^{-1}$)]: 350 (7900), 290 (8200), 239 (13100); ESI-MS (m/z): 739.10.

Bis-2-(((4-chlorophenyl)imino)methyl)-6-methoxyph enolatodichlorotin(IV), [$(sb^3)_2SnCl_2$] **3** Yield: 62%, Brown solid, mp: 148-150°C; Mol. Weight: 711.01; Elem. Anal. for $C_{28}H_{22}Cl_4N_2O_4Sn$, Calc.: C, 47.30; H, 3.12; Cl, 19.95; N, 3.94; Sn, 16.70, Found: C, 47.95; H, 3.23; N, 3.59; Sn, 15.96%; IR (KBr pellets $cm^{-1}$): 1602 s ($\nu_{C=N}$), 1288 s ($\nu_{C-O}$), 545 m ($\nu_{Sn-O}$), 447 w ($\nu_{Sn-N}$); $^1$H NMR ($CDCl_3$) ($\delta_H$, ppm): 8.34 (s, 2H, CH = N), 7.50-6.78 (16H, m, Ar-H), 3.89 (s, 6H, $CH_3$); $^{13}$C NMR ($CDCl_3$) ($\delta_C$, ppm): 154.32 (Ar-C-O), 158.63 (-C=N), 148.2, 147.3, 132.5, 123.9, 122.5, 120.8, 119.4, 118.3, 115.2 (Ar-C), 56.8 (O-$CH_3$); $^{119}$Sn NMR ($CDCl_3$) (ppm): -626.1, UV-Vis ($CH_3OH$) [$\lambda_{max}$, nm (ε, $M^{-1}cm^{-1}$)]: 320 (10400), 292 (7400), 240 (14000); ESI-MS (m/z): 710.83.

Bis-2-(((4-bromophenyl)imino)methyl)-6-methoxyp henolatodichlorotin(IV), [$(sb^4)_2SnCl_2$] **4** Yield: 64%, Dark brown solid, mp: 158-160°C; Mol. Weight: 799.91; Elem. Anal. for $C_{28}H_{22}Br_2Cl_2N_2O_4Sn$, Calc C, 42.04; H, 2.77; N, 3.50; Sn, 14.84, Found: C, 43.09; H, 2.87; N, 3.65; Sn, 14.51%; IR (KBr pellets, $cm^{-1}$): 1605 s ($\nu_{C=N}$), 1290 s ($\nu_{C-O}$), 549 m ($\nu_{Sn-O}$), 461 w ($\nu_{Sn-N}$); $^1$H NMR ($CDCl_3$) ($\delta_H$, ppm): 8.27 (s, 2H, CH=N), 7.45-6.81 (m, 16H, Ar-H), 3.84 (s, 6H, $CH_3$); $^{13}$C NMR ($CDCl_3$) ($\delta_C$, ppm): 152.3 (Ar-C-O), 159.6 (C=N), 148.2, 146.3, 139.1, 134.9, 132.6, 130.2, 129.7, 126.9, 122.7, 118.1, 115.2 (Ar-C), $^{119}$Sn NMR ($CDCl_3$) (ppm): -627.3, UV-Vis ($CH_3OH$) [$\lambda_{max}$, nm (ε, $M^{-1}cm^{-1}$)]: 330 (7800), 290 (6800), 233 (12600); ESI-MS (m/z): 798.87.

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