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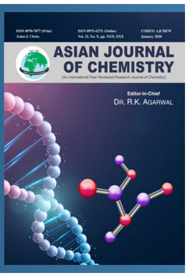

Design, Spectroscopic Characterization and Theoretical Studies of Organotin(IV) and Organosilicon(IV) Complexes with Schiff Base Ligands Derived from Amino Acids

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A new series of organotin(IV) and organosilicon(IV) complexes were synthesized using the Schiff base ligands [2-((3,4-dimethoxybenzylidene)amino)-3-(1*H*-indol-3-yl)propanoic acid (L^1H) and 2-((3,4-dimethoxybenzylidene)amino)-3-methylbutanoic acid (L^2H)]. The synthesized compounds were characterized by IR, NMR (^1H and ^{13}C), elemental analysis and theoretical studies. The molar conductivity values of the complexes in DMF implied the presence of non-electrolyte species. Spectral data showed that in these complexes the metal atoms are coordinated with the Schiff base ligand acts as a bidentate ON moiety, coordinating to the metal through its carboxylate oxygen and imine nitrogen. The IR spectra of the complexes showed large differences between ν_{asy}(COO) and ν_{sy}(COO), $\Delta\nu$ (ν_{asy}(COO)–ν_{sy}(COO)) of 260-276 cm^{-1}, indicating monodentate nature of the carboxylate group. Furthermore, the density functional theory (DFT) calculations were executed at the B3LYP/6-31G(d,p)/LanL2DZ basis set of theory for the optimized geometry of Schiff base complexes. The structural parameters, bond length, bond angles, chemical potential, electronegativity, hardness, softness, global electrophilicity index have been studied theoretically by density functional theory (DFT) to support the experimental results.

Keywords: Amino acids, Schiff base, Complexes, Spectral studies, Theoretical studies.

INTRODUCTION

Schiff bases are considered as valuable compounds in coordination chemistry due to their potentiality for stable complex formation with metal ions [1,2]. Structural presence of donor atoms such as nitrogen, oxygen and sulfur are helpful in chelating properties which makes foundation for the stable complex formation with metal ions [3,4]. Biological activities are enhanced drastically when Schiff bases coordinate with metal ions [5]. Easy and facile synthesis and wide spread applications of these metal complexes make them very interesting and significant in various industries. Remarkable contribution of Schiff base metal complexes is used for development of catalysis and enzymatic reactions, molecular architectures, materials and pharmaceutical chemistry [6-8].

Metal complexes of Schiff base ligands have gained importance in synthetic biology and industrial chemistry fields due to their vital role as antibacterial, antiviral and antifungal agents [9,10]. Anticancer activities of Schiff bases metal complexes drastically enhanced when they are in complex form which make them useful as potential anticancer drugs [11,12]. These are extensively investigated because of their interesting structural design and functional framework [13]. Various organic syntheses which involve oxidation and reduction reactions and number of electrochemical reduction processes are studied with the help of catalytic uses of transition metal complexes with imine ligands [14,15].

In this category of metal ligand Schiff base complexes organotin(IV) and organosilicon(IV) possess versatile applications in the industrial, environmental and pharmaceutical sectors [16,17]. Both of these organosilicon(IV) and organotin(IV) complexes because of their stability, various geometries and coordination numbers becomes significant and remarkable [18,19]. Two main properties structural diversity and coordination geometries of organotin(IV) complexes make them useful as anticarcinogenic, antibacterial, antifungal, tuberculostatic, insecticidal and antitumor agents in various environmental industries [20,21]. Likewise organosilicon compounds of Schiff base ligands possesses important applications such as anticarcinogenic, antibacterial, antitumor, antifungal and insecticidal agents [22,23].

In continuation to our ongoing research herein, the synthesis and characterization of new series of metal complexes containing bidentate Schiff base ligands are reported. Moreover, density functional theory (DFT) calculations for the newly synthesized organotin(IV) and organosilicon(IV) complexes were also performed for confirmation of the experimental observations. Both of these parameters are studied and compared which also make a basis for structural identification of the complexes.

EXPERIMENTAL

All the chemicals such as dimethyltin dichloride, dibutyltin oxide, ethoxytrimethylsilane and triethoxyphenylsilane were purchased from Sigma-Aldrich, Fluka and were used as without purification. All the reactions were carried out under moisture and oxygen-free atmosphere. The solvents were dried and purified before use according to the standard method. The melting points were measured on a Digital melting point apparatus. IR spectra were obtained in KBr using a Perkin Elmer FTIR–Spectrum-2 spectrophotometer. The NMR (^{1}H and ^{13}C) spectra were recorded on a 400 MHz Bruker Avance NMR spectrometer using TMS as an internal standard.

Theoretical calculations: Theoretical calculations (DFT) were carried out by Gaussian 03 software package and Gauss view visualization program [24]. The geometry was optimized at B3LYP basic sets to predict the molecular structure of the newly synthesized compounds.

Synthesis of ligands: The ligands 2-((3,4-dimethoxybenzylidene)amino)-3-(1*H*-indol-3-yl)propanoic acid (L^1H) and 2-((3,4-dimethoxybenzylidene)amino)-3-methylbutanoic acid (L^2H) were synthesized as described earlier [25].

Compound (L^1H): Dark brown; yield, 65%; m.p. 198 °C; elemental analysis (%), found for $C_{20}H_{20}N_2O_4$: C 68.01, H 5.70, N 5.90; calcd. C 68.17, N 7.95, H 5.72; molecular weight: found, 349.52, calcd. 352.38. ^{1}H NMR (δ ppm): 11.50 (s, OH), 9.82 (s, NH), 8.50 (s, CH=N), 4.72 (t, CH), 3.81 (s, OCH_3), 6.94-7.65 (m, Ar. protons). ^{13}C NMR (δ ppm): 176.5 (COOH), 38.2 ($–CH_2–$), 159.6 (C=N), 74.5 (CH), 58.7 (OCH_3), 152.1, 149.7, 138.0, 136.4, 127.8, 123.9, 122.1, 121.5, 120.1, 119.2, 112.8, 112.4, 110.0, 109.6 (Ar. carbons); infrared (cm^{-1}): ν(C=N) 1635, (NH) 3416, (COOH), 3165-2790.

Compound (L^2H): brown; yield, 78%; m.p. 150 °C; elemental analysis (%), found for $C_{14}H_{19}NO_4$: C 63.25, N 5.20, H 7.20; calcd. C 63.38, H 7.22, N 5.28; molecular weight: found 263.95 calcd. 265.30. ^{1}H NMR (δ ppm): 11.40 (s, OH); 8.45 (s, CH=N); 4.39 (t, CH); 3.80 (s, OCH_3); 2.12 (m, $CH_3\text{-}C\underline{H}\text{-}CH_3$); 6.95-7.58 (m, aromatic protons). ^{13}C NMR (δ ppm): 174.6 (COOH), 72.2 (–CH–), 160.8 (C=N), 31.4 (CH), 55.8 (OCH_3), 151.9, 149.4, 133.7, 122.8, 112.8, 109.5 (aromatic carbons); infrared (cm^{-1}): ν(C=N), 1625; ν(COOH), 3145-2888.

Syntheses of dibutyltin(IV), dimethyltin(IV) and phenylsilicon(IV) complexes: To a suspension of ligands (L^1H–L^2H) in of dry benzene (70 mL) and dry methanol (30 mL), a solution of Bu_2SnO, $PhSi(OEt)_3$, Me_2SnCl_2 and Me_3SiOEt in 30 mL of the same solvent were added. The mixtures were stirred under reflux on water bath for 6-8 h. The water liberated in the reaction was evacuated azeotropically with solvent. At the end of the reaction, compounds were dried and free from solvent and compounds washed with cyclohexane. The solid compounds were isolated out and purified by recrystallization from the same solvent. Analytical information was given below:

Compound 1: $Bu_2Sn(L^1)_2$ was synthesized by reacting dibutyltin oxide with 2-((3,4-dimethoxybenzylidene)amino)-3-(1*H*-indol-3-yl)propanoic acid (L^1H); yield, 70.6%; colour, Dark-brown; m.p. 105 °C (d); elemental analysis (%), calcd. for $C_{48}H_{56}N_4O_8Sn$: C, 61.61; H, 6.03; N, 5.99; Sn, 12.69; found, C 61.55; N 5.90, H 6.00; Sn 12.60; molecular weight: found, 928.77, calcd. 935.69. Molar conductance (10^{-3} M, Ω^{-1}, moL^{-1}, cm^2): 13.7. ^{1}H NMR (δ ppm): 9.80 (s, NH); 9.12 (s, CH=N); 4.70 (t, CH); 3.83 (s, OCH_3); 6.92-7.70 (m, Ar. protons); 0.92-1.96 (m, Sn-Bu). ^{13}C NMR (δ ppm): 185.2 (COO), 39.8 ($–CH_2–$), 165.5 (C=N), 75.4 (CH), 58.6 (OCH_3), 150.1, 148.9, 137.5, 136.7, 126.7, 124.1, 122.2, 121.3, 120.5, 119.5, 113.2, 112.8, 110.8, 109.7 (Ar. carbons); 29.6, 27.8, 21.1, 13.7 (Sn-Bu). Infrared (cm^{-1}): (NH), 3405; ν(C=N), 1615; ν_{asy}(COO), 1602; ν_{sy}(COO), 1330; ν(Sn←N), 535; ν(Sn–O), 446; ν(Sn-C), 625.

Compound 2: $Bu_2Sn(L^2)_2$ was synthesized by reacting dibutyltin oxide with 2-((3,4-dimethoxybenzylidene)amino)-3-methylbutanoic acid (L^2H); yield, 72.1%; colour, Cream; m.p. 178 °C; elemental analysis (%), calcd. for $C_{36}H_{54}N_2O_8Sn$: C, 56.78; H, 7.15; N, 3.68; Sn, 15.59; found C 56.70; H 7.12; N 3.62; Sn 15.51; molecular weight: found, 756.22, calcd. 761.53. Molar conductance (10^{-3} M, Ω^{-1}, moL^{-1}, cm^2): 10.4. ^{1}H NMR (δ ppm): 9.28(s, CH=N); 4.40 (t, CH); 3.81 (s, OCH_3); 2.14 (m, $CH_3\text{-}C\underline{H}\text{-}CH_3$); 6.90-7.65 (m, Ar. protons); 0.90-1.98 (m, Sn-Bu). ^{13}C NMR (δ ppm): 184.5 (COO), 71.8 (–CH–), 166.0 (C=N), 32.1 (CH), 56.5 (OCH_3), 150.9, 149.1, 134.3, 123.5, 113.2, 108.1 (Ar. carbons); 28.9, 26.4, 18.4, 14.4 (Sn-Bu). Infrared (cm^{-1}): ν_{asy}(COO), 1598; ν_{sy}(COO), 1325; ν(C=N), 1610; ν(Sn←N), 542; ν(Sn–O), 438; ν(Sn-C), 622.

Compound 3: $Me_2Sn(L^1)_2$ was synthesized by reacting dimethyltin dichloride with 2-((3,4-dimethoxybenzylidene)-amino)-3-(1*H*-indol-3-yl)propanoic acid (L^1H); yield, 78.4%; colour, Light brown; m.p. 180 °C; elemental analysis (%), calcd. for $C_{42}H_{44}N_4O_8Sn$: C 59.24, H 5.21, N 6.58; Sn 13.94; found, C 59.20, H 5.18, N 6.48; Sn 13.90; molecular weight: found, 845.96, calcd. 851.53. Molar conductance (10^{-3}M, Ω^{-1}, moL^{-1}, cm^2): 12.7. ^{1}H NMR (δ ppm): 9.80 (s, NH); 9.08 (s, CH=N); 4.72 (t, CH); 3.81 (s, OCH_3); 6.98-7.68 (m, Ar. protons); 0.94 (s, Sn-Me). ^{13}C NMR (δ ppm): 181.5 (COO), 39.8 ($–CH_2–$), 165.5 (C=N), 75.4 (CH), 58.6 (OCH_3), 150.2, 149.9, 136.7, 136.2, 127.2, 124.6, 122.5, 120.8, 120.3, 119.1, 114.3, 112.6, 110.6, 109.2 (Ar. carbons); 9.8 (Sn-Me). Infrared (cm^{-1}): 1612; (NH), 3425; ν(C=N), ν_{asy}(COO), 1595; ν_{sy}(COO), 1326; ν(Sn←N), 540; ν(Sn–O), 448; ν(Sn-C), 634.

Compound 4: $Me_2Sn(L^2)_2$ was synthesized by reacting dimethyltin dichloride with 2-((3,4-dimethoxybenzylidene)-amino)-3-methylbutanoic acid (L^2H); yield, 68.6%; colour, Brown; m.p. 248 °C (d); elemental analysis (%), calcd. for $C_{32}H_{38}N_6O_8Sn$: C 51.02, H 5.08, N 11.15; Sn 15.76; found, C 51.00, H 5.00, N 11.02; Sn 15.71; molecular weight: found, 750.11, calcd. 753.39. Molar conductance (10^{-3}M, Ω^{-1}, moL^{-1}, cm^2): 10.8. ^{1}H NMR (δ ppm): 9.15(s, CH=N); 4.42 (t, CH); 3.80 (s, OCH_3); 2.10 (m, $CH_3\text{-}C\underline{H}\text{-}CH_3$); 6.92-7.68 (m, Ar. protons); 0.90 (s, Sn-Me). ^{13}C NMR (δ ppm): 182.4 (COO), 72.6 (CH), 164.6 (C=N), 34.2 (CH), 58.5 (OCH_3), 150.2, 149.6, 135.1, 124.3, 113.6, 108.8 (Ar. carbons); 10.5 (Sn-Me). Infrared (cm^{-1}): ν_{asy}(COO), 1596; ν_{sy}(COO), 1320; ν(C=N), 1614; ν(Sn←N), 534; ν(Sn–O), 458; ν(Sn-C), 630.

Compound 5: Me_3SiL^1 was synthesized by reacting ethoxytrimethylsilane with 2-((3,4-dimethoxybenzylidene)-amino)-3-(1*H*-indol-3-yl)propanoic acid (L^1H); yield, 65.8%; colour, Light brown; m.p. 168 °C; elemental analysis (%), calcd. for $C_{23}H_{28}N_2O_4Si$: C 65.07, H 6.65, N 6.60: Si 6.62; found, C 65.00, H 6.62, N 6.55; Si 6.60; molecular weight: found, 418.68, calcd. 424.56. Molar conductance (10^{-3}M, Ω^{-1}, moL^{-1}, cm^2): 10.2. ^{1}H NMR (δ ppm): 9.82 (s, NH); 9.10 (s, CH=N); 3.72 (t, CH); 3.82 (s, OCH_3); 6.96-7.74 (m, Ar. protons). ^{13}C NMR (δ ppm): 184.1 (COO), 61.6 (–CH–), 164.4 (C=N), 110.4, 116.8, 121.2, 122.6, 122.8, 124.6, 128.2, 131.0, 136.7, 149.2 (Ar. carbons); infrared (cm^{-1}): ν_{asy}(COO), 1594; ν_{sy}(COO), 1328; ν(C=N), 1615; Δν, 272; ν(NH), 3415; ν(Si←N), 555; ν(Si–O), 432.

Compound 6: Me_3SiL^2 was synthesized by reacting ethoxytrimethylsilane with 2-((3,4-dimethoxybenzylidene)amino)-3-methylbutanoic acid (L^2H); yield, 68.2%; colour, Light brown; m.p. 194 °C; elemental analysis (%), calcd. for $C_{17}H_{27}NO_4Si$: C 60.50, H 8.06, N 4.15; Si 8.32; found, C 60.38, H 8.02, N 4.04; Si 8.30; molecular weight: found, 327.98, calcd. 337.49. Molar conductance (10^{-3} M, Ω^{-1}, moL^{-1}, cm^2): 10.1. ^{1}H NMR (δ ppm): 9.12 (s, CH=N); 3.44(t, CH); 3.80 (s, OCH_3); 6.99-7.82 (m, Ar. protons). ^{13}C NMR (δ ppm): 182.2 (COO), 72.6 (CH), 164.6 (C=N), 34.2 (CH), 58.5 (OCH_3), 149.4, 148.8, 135.4, 124.6, 114.5, 109.1 (Ar. carbons). Infrared (cm^{-1}): ν_{asy}(COO), 1594; ν_{sy}(COO), 1332; Δν, 264; ν(C=N), 1614; ν(Si←N), 554; ν(Si–O), 438.

Compound 7: $PhSi(L^1)_2OEt$ was synthesized by reacting triethoxyphenylsilane with 2-((3,4-dimethoxybenzylidene)-amino)-3-(1*H*-indol-3-yl)propanoic acid (L^1H); yield, 65.4%; colour, Light brown; m.p. 148 °C; elemental analysis (%), calcd. for $C_{48}H_{48}N_4O_9Si$: C 67.59, H 5.67, N 6.57; Si 3.29; found, C 67.45, H 5.65, N 6.50; Si 3.20; molecular weight: found, 845.98, calcd. 853.00. Molar conductance (DMF, 10^{-3}, Ω^{-1}, moL^{-1}, cm^2): 16.7; ^{1}H NMR (δ ppm): 9.80 (s, NH); 9.16 (s, CH=N); 3.74 (t, CH); 3.80 (s, OCH_3); 6.94-7.68 (m, Ar. protons). ^{13}C NMR (δ ppm): 182.1 (COO), 58.8 (–CH–), 165.2 (C=N), 111.6, 118., 121.4, 121.6, 122.4, 124.4, 127.8, 131.6, 137.1, 148.5 (Ar. carbons); infrared (cm^{-1}): ν(NH), 3414; ν(C=N), 1612; ν_{asy}(COO), 1590; ν_{sy}(COO), 1330; Δν, 260; ν(Si←N), 544; ν(Si–O), 440.

Compound 8: $PhSi(L^1)_2OEt$ was synthesized by reacting triethoxyphenylsilane with 2-((3,4-dimethoxybenzylidene)-amino)-3-methylbutanoic acid (L^2H); colour, Brownish yellow; yield, 66.2%; m.p. 248-250 °C; elemental analysis (%), calcd. for $C_{36}H_{46}N_2O_9Si$: C 63.69, H 6.83, N 4.13; Si 4.14; found, C 63.62, H 6.80, N 4.07; Si 4.03; molecular weight: found, 669.56, calcd. 678.84. Molar conductance (DMF, 10^{-3}, Ω^{-1}, moL^{-1}, cm^2): 12.1. ^{1}H NMR (δ ppm): 9.08 (s, CH=N); 3.36 (t, CH); 3.80 (s, OCH_3); 6.98-7.82 (m, Ar. protons). ^{13}C NMR (δ ppm): 180.4 (COO), 72.6 (CH), 164.8 (C=N), 34.2 (CH), 58.5 (OCH_3), 149.5, 148.9, 135.7, 124.6, 114.3, 109.2 (Ar. carbons). Infrared (cm^{-1}): ν_{asy}(COO), 1592; ν_{sy}(COO), 1326; Δν, 266; ν(C=N), 1610; ν(Si←N), 562; ν(Si–O), 445.

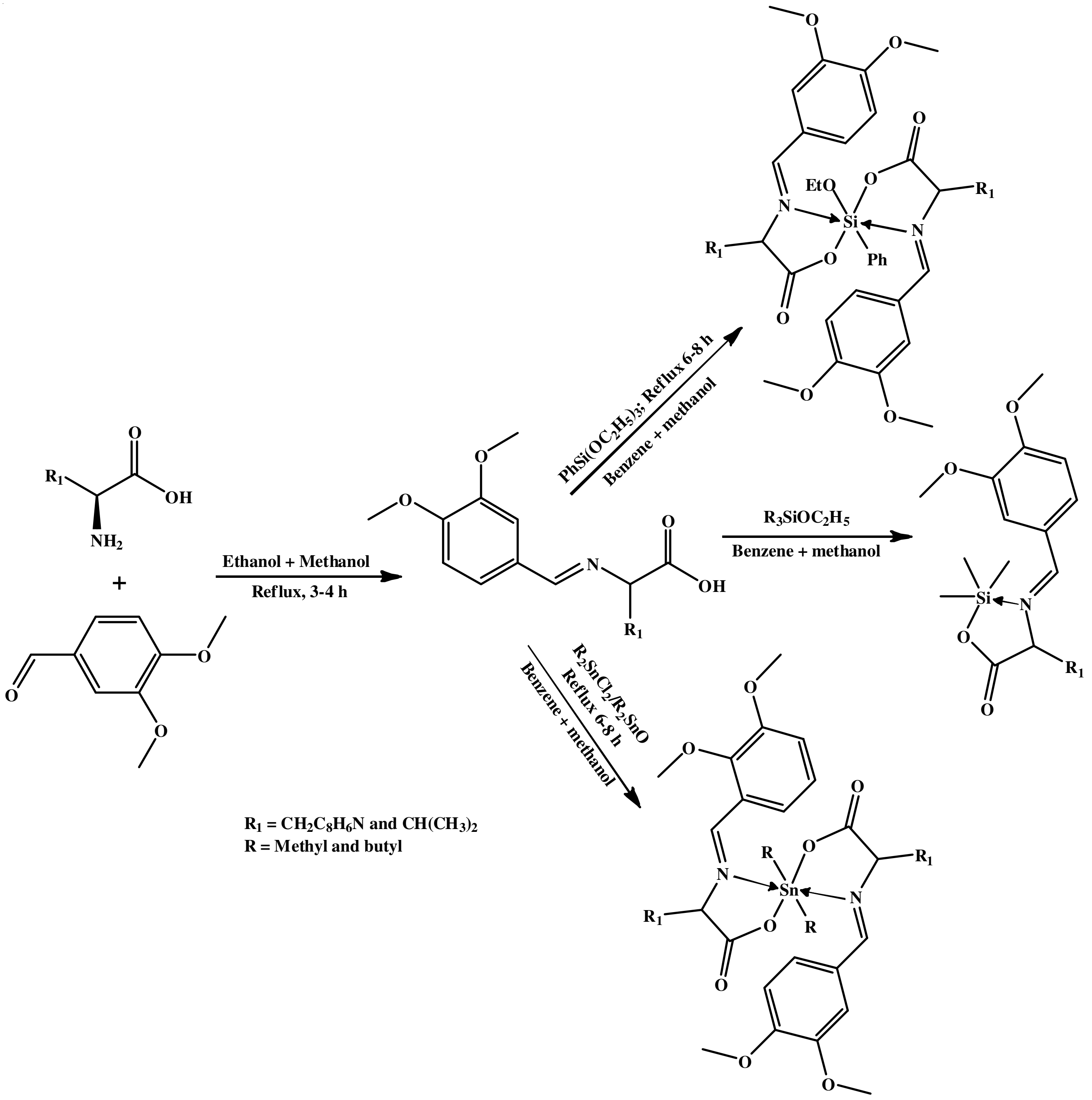
RESULTS AND DISCUSSION

The reaction of Schiff base ligands such as (2-((3,4-dimethoxybenzylidene)amino)-3-(1*H*-indol-3-yl)propanoic acid (L^1H) and 2-((3,4-dimethoxybenzylidene)amino)-3-methylbutanoic acid (L^2H)) with triethoxyphenylsilane, dibutyltin oxide and dimethyltin dichloride has been carried out in a 2:1 molar ratio, utilizing anhydrous benzene (90 mL) and dry methanol (30 mL) as reaction medium. The reactions continue with the liberation of ethanol and water molecule, which was azeotropically evacuated. Trimethylethoxysilane was added to the calculated quantity of the ligands in a 1:1 molar ratio, using anhydrous benzene and dry methanol (3:1) as reaction medium. These reactions carried out and established beneath (**Scheme-I**).

The above reactions were completed in 6-8 h of refluxing of the reaction mixture. All these precipitated compounds are coloured. They are partially solvable in common solvents and completely solvable in DMF and DMSO. The molar conductance of the compounds lies between the range 10.1 to 16.7 Ω^{-1} cm^2 mol^{-1} therefore; indicates that the nature of the complexes are non-electrolytic. The basic investigation information concurs with the proposed formulae of the Schiff bases and furthermore supports the composition of organotin(IV) and organosilicon(IV) complexes.

Infrared spectral studies: The IR spectra are an key tool for identifying the chelating behaviour of the ligand with the metal ions. Newly synthesized compounds were characterized by the absorption bands of the following groups such as C=N (azomethine), carboxylate, metal-oxygen and metal-nitrogen absorption bands. The assignments of characteristic infrared bands are represented in experimental section. The IR spectra of the ligands show the absence of groups at ~3400 and ~1740 cm^{-1}, respectively because of ν(NH_2) group of amino acids and ν(C=O) of aldehydes. A new band at 1630 ± 15 cm^{-1} appears due to azomethine ν(C=N) linkage showed up in all the ligands [26] demonstrating that condensation between the carbonyl group of aldehydes.

The strong absorption band appeared in 1615-1610 cm^{-1} region can be assigned to the coordination through azomethine group with metal ions [27,28]. The appearance of an absorption band at ~1325 and ~1332 cm^{-1} for organotin(IV) and organosilicon(IV) complexes, respectively, are assignable to the symmetric stretching vibrations of the carboxylate group [29]. The asymmetric stretching (ν_{as}COO-) was observed at ~1600 and ~1595 cm^{-1} for organotin(IV) and organosilicon(IV) complexes, respectively. The separation between asymmetric and symmetric stretching frequencies [Δν = ($\nu_{as}COO^-$ – ν_sCOO^-)] was found to be more than that of free carboxylate



Scheme-I: Synthesis of Schiff bases and its organotin(IV) and organosilicon(IV) complexes

anion (175 cm^{-1}). This confirmed that the carboxylate group coordinated to metal ions in a monodentate nature [30].

In the spectra of the ligands, broad band showed up in the area 3165-2790 cm^{-1} that is assigned to the hydrogen-bonded (OH) group. This absorption band is completely absent in the metal complexes due to the chelation through the carboxylate oxygen to the metal atoms. The new bands appeared in the range 432 and 458 cm^{-1} for organotin(IV) and organosilicon(IV), respectively, confirm the formation of metal-oxygen coordination in complexes [31,32]. Also, the new bands observed at 534 and 562 cm^{-1} for organotin(IV) and organosilicon(IV) complexes, respectively, are assignable to metal-nitrogen coordination [31,32]. Infrared data revealed that the Schiff base acts as a bidentate ligands and coordinated through carboxylate oxygen and imine nitrogen present in the ligand moiety. The new band shows up in the complexes at 625 ± 8 cm^{-1} which is most likely because of ν(M–C) stretching vibration [33].

NMR spectral studies: In tin and silicon complexes, ligands coordinate with imine, due to this coordination and extensive conjugation proton magnetic resonance spectra moved downfield. Calculated proton numbers and estimated values (C, H and N analysis) both are in good agreement to each other. Disappearance of proton signal in metal complexes at δ 11.50-11.40 ppm which is due to OH in ligands confirms that oxygen of group carboxylate is involved in chelation process of ligand. In ligands, proton of imine gives a sharp signal at δ 8.45-8.50 ppm, when compared with metal complexes showed downfield (δ 9.18 ± 0.10 ppm) movement. This is another confirmation that ligand is not free now and coordinated with metal ion. Nitrogen of imine is involved in this coordination. There is no change in positions of aromatic and OCH_3 protons showed that they are not involved in complexation. Some extra signal in complexes at δ 0.72-1.90 ppm range indicated towards butyl and methyl group protons.

Carboxylate connected carbon and the imine group connected carbon signals appear at ~ δ 175 ppm and ~ δ 160 ppm, respectively in ^{13}C NMR spectra obtained for ligands. ^{13}C NMR spectra obtained for metal complexes, these signals show up at ~ δ 183 ppm (carboxylate group) and ~ δ 165 ppm (imine group), respectively. This shift in values gives an account for association of oxygen with tin and silicon metal. Involvement of imine moiety in formation of bond has been confirmed by comparison of ligands and the complexes spectra which involve moving carbon signal of the imine group. Confirmation of butyl group carbon which appears at (~ 26.4, 27.6, 26.0, 15.4 ppm) and a methyl group is seen at ~9.6 position done by comparing them with resemblant compounds. The alkyl group attached to metal shows resonance for chemically proportional carbon; in any case, butyl group shows three resonances.

The aforementioned diverse spectral investigations propose that the bonding occurs through the imine nitrogen and carboxylate oxygen atoms to the silicon and tin. On the bases of above spectral evidence, distorted octahedral and trigonal bipyramidal geometries around the tin and silicon atoms, respectively have been suggested (**Scheme-I**).

Frontier molecular orbitals: One of the well-known descriptor in quantum mechanics is evaluating Frontier orbital energy by HOMO/LUMO gap. They play an important character in leading various reactions of chemistry and gives account for electron donor accepter complexes (CT complexes). Evaluation of hardness, softness, reactivity and stability of the molecule is performed by calculation of frontier molecular orbitals (HOMO and LUMO). The HOMO and LUMO energy, energy gap (ΔE), chemical potential ($\mu = -\chi$), electronegativity ($\chi = -1/2(E_{LUMO} + E_{HOMO})$), hardness ($2\eta = 1/2(E_{HOMO}-E_{LUMO})$, softness ($S = 1/2\eta$) and global 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 by DFT/B3LYP level of theory and reported in Table-1. HOMO and LUMO orbital density plots for the ligand (L^2H) are obtained, in which the delocalization of LUMO orbitals surface takes place on the aromatic ring and carboxylate group is delocalized by HOMO orbitals surface and there is overlapping of imine group in HOMO level surface. Location of HOMO orbital density 3D plots is nearby the metal atom shown in molecular system (Fig. 1).

Furthermore, system gains polarizability from softness, whereas system hardness implies resistance to charge transfer. Calculated negative heat of formation for the tin compounds indicated that the molecules were thermodynamically more stable than the ligands. Another electrophilicity index is directly related to the tendency of electron-acceptance of the molecules and increase in these values of the global electrophilicity index is responsible for enhancing the abilities of electron-acceptance of the molecules. Thus, the power of electron-acceptance of tin and silicon complexes (Table-1) are organized as: $Me_3Si(L^2)$ > $Bu_2Sn(L^2)_2$ > $PhSi(L^2)_2OEt$ > $Me_2Sn(L^2)_2$ > (L^2H).

Optimized geometrical structures: The optimized molecular geometries of the complexes were calculated at the DFT/B3LYP level with the LanL2DZ basis set. The deprotonated ligand is coordinated to the metal ions through carboxylate oxygen and imine nitrogen atoms. The optimized parameters such as bond lengths and bond angles of compounds $Me_2Sn(L^2)_2$ and Me_3SiL^2 are listed in Tables 2 and 3.

The optimized molecular geometries along with the numbering atom of the $Me_2Sn(L^2)_2$ complex is shown in Fig. 2. The geometry of the tin complex is best described as a distorted octahedral structure. The equatorial positions are occupied by two nitrogen (N10, N30), two oxygen (O12, O32) atoms and two carbon atom of methyl group are axial, while nitrogen (N10) is *trans* to nitrogen (N30). Nitrogen (N10) and (N30) show slightly longer bond lengths [(Sn20–N10) 2.097 Å] than [(Sn20–O12) 2.051 Å]. The Sn20–N10 and Sn20–N30 bond distances are 2.097 and 2.096 Å, significantly different, probably resulting from the geometry, indicating strong tin–nitrogen interaction (Table-2). The Sn20–O12 bond distance is 2.051 Å, close to the sum of the covalent radii of Sn–O (2.05 Å), but much smaller than the sum of the van der Waals radii (3.7 Å).

TABLE-1
CALCULATED ENERGY PARAMETERS OF 2-((3,4-DIMETHOXYBENZYLIDENE)AMINO)-3-METHYLBUTANOIC ACID AND THEIR METAL COMPLEXES

Property	L^2H	$Me_2Sn(L^2)_2$	$Bu_2Sn(L^2)_2$	$PhSi(L^2)_2OEt$	Me_3SiL^2
Total energy (Kcal/mol)	25.543	135.496	139.626	173.156	76.444
E_{HOMO} (eV)	-10.318	-8.761	-7.751	-6.989	-7.548
E_{LUMO} (eV)	-2.113	-3.302	-3.870	-3.219	-4.003
Energy gap (ΔE, eV)	8.205	5.459	3.881	3.770	3.545
Chemical potential (μ)	-6.216	-6.042	-5.811	-5.104	-5.776
Electronegativity (χ)	6.216	6.042	5.811	5.104	5.776
Chemical hardness (η)	4.103	2.730	1.941	1.885	1.773
Global softness (S)	0.122	0.183	0.258	0.265	0.282
Electrophilicity index (ω)	4.709	5.458	8.698	6.910	9.408

eV: energy unit (electron volt); au: energy unit (atomic unit); HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital; L^2H: 2-((3,4-dimethoxybenzylidene)amino)-3-methylbutanoic acid.

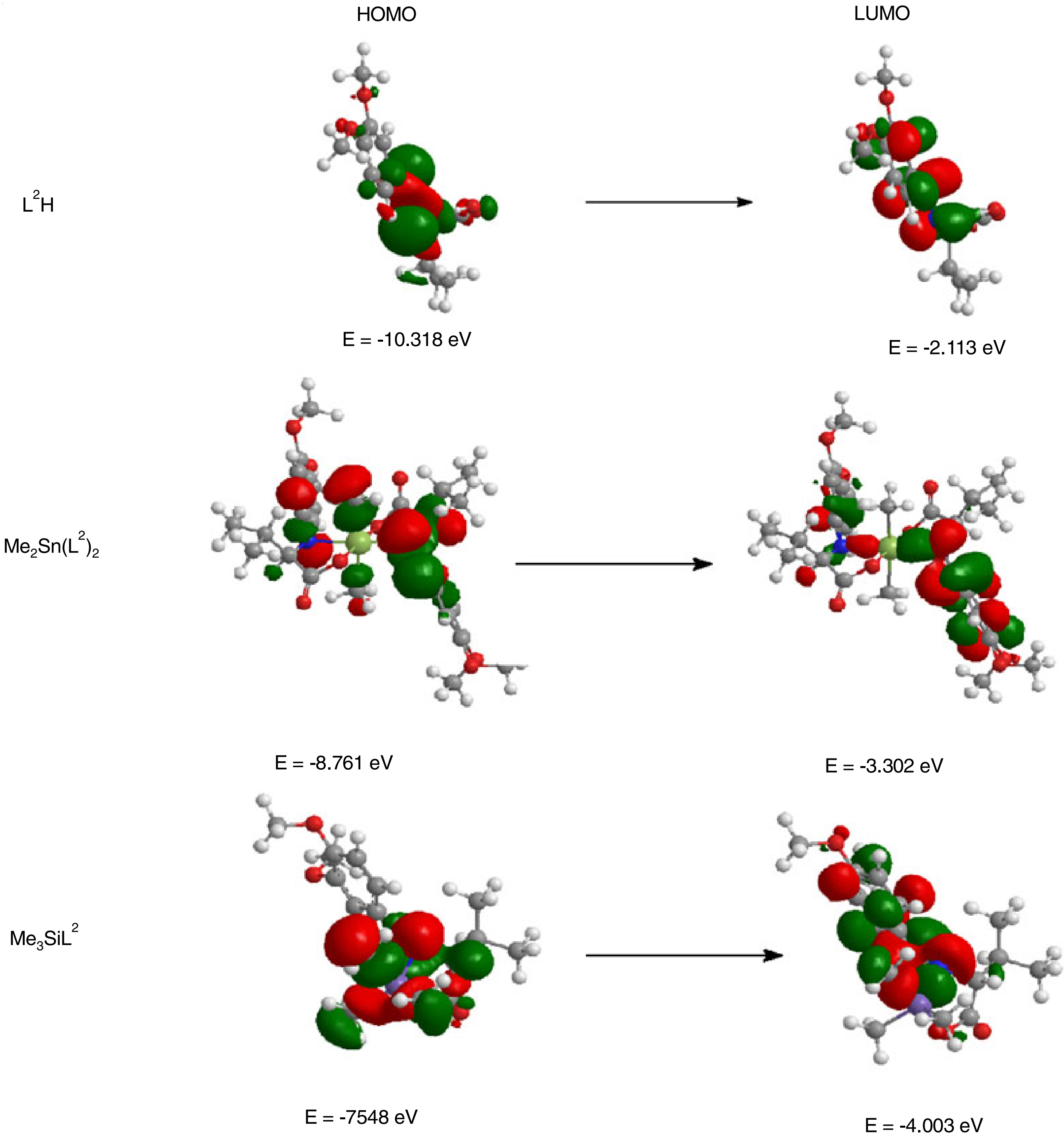


Fig. 1. Various highest occupied molecular orbitals and lowest unoccupied molecular orbitals localization with their energy values for 2-((3,4-dimethoxybenzylidene)amino)-3-methylbutanoic acid and their metal complexes

The N10–C1 and N30–C21 bond distances are 1.272 Å and 1.275 Å, respectively, in conformity with a formal C=N double bond (1.28 Å). The coordination geometry about the tin(IV) is distorted octahedral with two methyl groups in axial positions with a C40–Sn20–C41 angle is 172°, deviating from linearity (Fig. 2), is in good agreement with the values reported for dimethyltin(IV) complexes [34,35].

The optimized structural data for [$Me_3Si(L^2)$] is shown in Table-3. The value of bond angles C(23)–Si(20)–O(12) of 179.7° slightly deviating from linearity, is in good agreement with the values reported for silicon complexes [36]. The sum of the equatorial angles C(22)-Si(20)-C(12) (116.19°), C(22)-Si(20)-N(10) (117.47°) and C(21)-Si(20)-N(10) (126.19°) is 359.85 °. Thus the atoms Si20, C21, N10 and C22 are coplanar (Table-2). The calculated Si–N bond distance of 1.811 Å is also close to the already reported Si–N distance in silicon(IV) complex. The Si–O distance is 1.660 Å, which is similar to the already reported in the structures of silicon complexes [37].

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) OF 2-((3,4-DIMETHOXYBENZ-YLIDENE)AMINO)-3-METHYL-BUTANOIC ACID AND ITS DIMETHYLTIN(IV) COMPLEX

Atom connectivity	Bond length (Å)	Atom connectivity	Bond length (Å)
C(1)-N(10)	1.272	N(30)-Sn(20)	2.096
C(11)-O(12)	1.355	C(31)-O(32)	1.355
Sn(20)-C(41)	2.181	C(21)-N(30)	1.275
Sn(20)-C(40)	2.179	N(10)-Sn(20)	2.097
O(32)-Sn(20)	2.051	O(12)-Sn(20)	2.051
C(40)-Sn(20)-C(41)	171.35	C(41)-Sn(20)-O(12)	82.57
C(40)-Sn(20)-N(10)	84.01	N(10)-Sn(20)-O(32)	96.99
C(40)-Sn(20)-O(32)	87.42	N(10)-Sn(20)-N(30)	173.75
C(40)-Sn(20)-N(30)	100.08	N(10)-Sn(20)-O(12)	83.78
C(40)-Sn(20)-O(12)	88.81	O(32)-Sn(20)-N(30)	78.59
C(41)-Sn(20)-N(10)	94.37	O(32)-Sn(20)-O(12)	176.06
C(41)-Sn(20)-O(32)	101.21	N(30)-Sn(20)-O(12)	100.95
C(41)-Sn(20)-N(30)	82.29	–	–

TABLE-3
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) OF 2-((3,4-DIMETHOXYBENZYLIDENE)AMINO)-3-METHYLBUTANOIC ACID AND ITS TRIMETHYLSILICON(IV) COMPLEX

Atom connectivity	Bond length/ angles	Atom connectivity	Bond length/ angles
C(1)-N(10)	1.275	N(10)-Si(20)	1.811
C(11)-O(12)	1.350	Si(20)-C(23)	1.935
C(21)-Si(20)	1.919	Si(20)-C(22)	1.922
O(12)-Si(20)	1.660	–	–
C(22)-Si(20)-C(23)	87.99	C(23)-Si(20)-O(12)	179.79
C(22)-Si(20)-C(21)	116.19	C(23)-Si(20)-N(10)	87.83
C(22)-Si(20)-O(12)	91.79	C(21)-Si(20)-O(12)	89.86
C(22)-Si(20)-N(10)	117.47	C(21)-Si(20)-N(10)	126.19
C(23)-Si(20)-C(21)	90.24	O(12)-Si(20)-N(10)	92.26

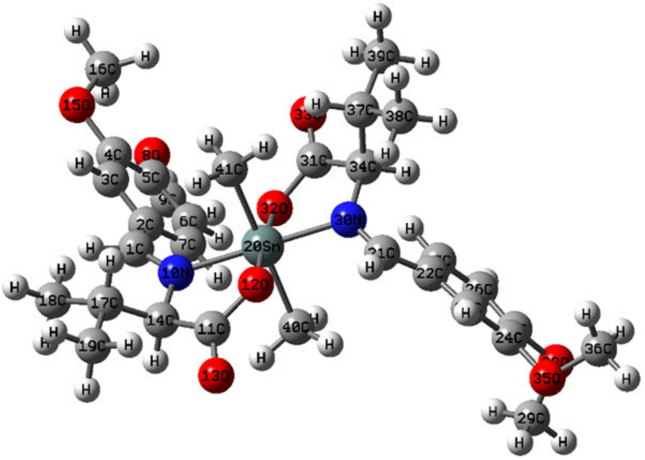


Fig. 2. Optimized geometry of $Me_2Sn(L^2)_2$ Complex

Conclusion

A new series of diorganotin(IV) and organosilicon(IV) complexes with Schiff base ligands were successfully synthesized and characterized by the physico-chemical and spectroscopic investigations, it was established that the ligands act as bidentate and coordinated through imine nitrogen and carboxylate oxygen to the tin and silicon atoms. Geometry of complexes is also supported by DFT calculations. The HOMO-LUMO orbitals energy gap value of the tin and silicon complexes are less than that of the free ligands. This means that in any excitation process, the metal compounds need less energy than that for free ligands and metal complexes are high chemical reactivity.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. S.M. Wilkinson, T.M. Sheedy and E.J. New, *J. Chem. Educ.*, **93**, 351 (2016); https://doi.org/10.1021/acs.jchemed.5b00555
2. E. Yousif, A. Majeed, K. Al-Sammarrae, N. Salih, J. Salimon and B. Abdullah, *Arab. J. Chem.*, **10**, S1639 (2017); https://doi.org/10.1016/j.arabjc.2013.06.006
3. H.L. Singh, M. Sharma and A.K. Varshney, *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 445 (2000); https://doi.org/10.1080/00945710009351773
4. R.A. Shiekh, I. Ab-Rahman, M.A. Malik, N. Luddin, S.M. Masudi and S.A. Al-Thabaiti, *Int. J. Electrochem. Sci.*, **8**, 6972 (2013).
5. H.L. Singh and A.K. Varshney, *Main Group Met. Chem.*, **22**, 529 (1999); https://doi.org/10.1515/MGMC.1999.22.9.529
6. J.M. Savéant, *Chem. Rev.*, **108**, 2348 (2008); https://doi.org/10.1021/cr068079z
7. Q. Zhang, X. Yang and J. Guan, *ACS Appl. Nano Mater.*, **2**, 4681 (2019); https://doi.org/10.1021/acsanm.9b00976
8. S. Kumar, D.N. Dhar and P.N. Saxena, *J. Sci. Ind. Res. (India)*, **68**, 181 (2009).
9. C. Bonaccorso, T. Marzo and D. La Mendola, *Pharmaceuticals*, **13**, 4 (2020); https://doi.org/10.3390/ph13010004
10. A.Z. El-Sonbati, W.H. Mahmoud, G.G. Mohamed, M.A. Diab, S.M. Morgan and S.Y. Abbas, *Appl. Organomet. Chem.*, **33**, e5048 (2019); https://doi.org/10.1002/aoc.5048
11. M.A. Malik, O.A. Dar, P. Gull, M.Y. Wani and A.A. Hashmi, *MedChemComm*, **9**, 409 (2018); https://doi.org/10.1039/C7MD00526A
12. U. Ndagi, N. Mhlongo and M.E. Soliman, *Drug Des. Devel. Ther.*, **11**, 599 (2017); https://doi.org/10.2147/DDDT.S119488
13. K.T. Tadele and T.W. Tsega, *Anticancer. Agents Med. Chem.*, **19**, 1786 (2019); https://doi.org/10.2174/1871520619666190227171716
14. L. Kafi-Ahmadi and L. Shirmohammadzadeh, *J. Nanostruct Chem.*, **7**, 179 (2017); https://doi.org/10.1007/s40097-017-0221-x
15. N. Sathya, G. Raja, N.P. Priya and C. Jayabalakrishnan, *Appl. Organomet. Chem.*, **24**, 366 (2010); https://doi.org/10.1002/aoc.1621
16. I.F. da Silva, L.C. Freitas-Lima, J.B. Graceli and L.C.M. Rodrigues, *Front. Endocrinol.*, **8**, 366 (2018); https://doi.org/10.3389/fendo.2017.00366
17. S. Gaur, N. Fahmi and R.V. Singh, *Phosphorus Sulfur Silicon Rel. Elem.*, **182**, 853 (2007); https://doi.org/10.1080/10426500601087384

18. K. Singh, P. Puri, Y. Kumar and C. Sharma, *ISRN Inorg. Chem.*, **2013**, 356802 (2013); https://doi.org/10.1155/2013/356802.
19. J. Devi and S. Devi, *Asian J. Res. Chem*, **9**, 419 (2016); https://doi.org/10.5958/0974-4150.2016.00063.8
20. E.N.M. Yusof, M.A.M. Latif, M.I.M. Tahir, J.A. Sakoff, M.I. Simone, A.J. Page, A. Veerakumarasivam, E.R.T. Tiekink and T.B.S.A. Ravoof, *Int. J. Mol. Sci.*, **20**, 854 (2019); https://doi.org/10.3390/ijms20040854
21. M. Jain, S. Gaur, S.C. Diwedi, S.C. Joshi, R.V. Singh and A. Bansal, *Phosphorus Sulfur Silicon Rel. Elem.*, **179**, 1517 (2004); https://doi.org/10.1080/10426500490464050
22. H.L. Singh, J. Singh and A. Mukherjee, *Bioinorg. Chem. Appl.*, **2013**, 425832 (2013); https://doi.org/10.1155/2013/425832
23. J. Devi, S. Devi and A. Kumar, *Monatsh. Chem.*, **147**, 2195 (2016); https://doi.org/10.1007/s00706-016-1720-z
24. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian 03, Revision C.02, Inc., Wallingford CT (2004).
25. S. Bhanuka and H.L. Singh, *Rasayan J. Chem.*, **10**, 673 (2017); https://doi.org/10.7324/RJC.2017.1021668
26. B.H. Al-Zaidi, M.M. Hasson and A.H. Ismail, *J. Appl. Pharm. Sci.*, **9**, 45 (2019); https://doi.org/10.7324/JAPS.2019.90406
27. K.A. Maher and S.R. Mohammed, *Int. J. Curr. Res. Rev.*, **7**, 6 (2015).
28. D. Maity, S. Chattopadhyay, A. Ghosh, M.G.B. Drew and G. Mukhopadhyay, *Inorg. Chim. Acta*, **365**, 25 (2011); https://doi.org/10.1016/j.ica.2010.07.029
29. Q. Xie, Z. Yang and L. Jiang, *Main Group Met. Chem.*, **19**, 509 (1996); https://doi.org/10.1515/MGMC.1996.19.8.509
30. Y.F. Win, T.S.T. Muhammad, S.T. Ha, Y. Sivasothy and S.G. Teoh, *Aust. J. Basic Appl. Sci.*, **4**, 1383 (2010).
31. H.L. Singh, J.B. Singh and S. Bhanuka, *J. Assoc. Arab Univ. Basic Appl. Sci.*, **23**, 1 (2017); https://doi.org/10.1016/j.jaubas.2016.05.003
32. M.A. Choudhary, M. Mazhar, S. Ali, U. Salma, S. Ashraf and A. Malik, *Turk. J. Chem.*, **26**, 125 (2002).
33. H.L. Singh, *Phosphorus Sulfur Silicon Rel. Elem.*, **184**, 1768 (2009); https://doi.org/10.1080/10426500802340236
34. N. Ancin, S.G. Öztas and S. Ide, *Struct. Chem.*, **18**, 667 (2007); https://doi.org/10.1007/s11224-007-9199-1
35. N.A. Öztas, G. Yenisehirli, N.A. Ancin, S.G. Öztas, Y. Özcan and S. Ide, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **72**, 929 (2009); https://doi.org/10.1016/j.saa.2008.12.023
36. O. Seiler, C. Burschka, T. Fenske, D. Troegel and R.D. Tacke, *Inorg. Chem.*, **46**, 5419 (2007); https://doi.org/10.1021/ic700389r
37. B. Theis, S. Metz, F. Back, C. Burschka and R. Tacke, *Z. Anorg. Allg. Chem.*, **635**, 1306 (2009); https://doi.org/10.1002/zaac.200900108