Original Research Article

Experimental and theoretical evaluation of the structure and properties of new stannyl complexes of pyridine amide ligands

ABSTRACT

Aims: Penta and tetra coordinated stannyl derivatives of N, N'-Bis(2-pyridyl)pyridine-2,6-dicarboxamide (H_2L) and N-(pyridine-2-yl)picolinamide (HL^1) have been synthesized. The structure of the complexes has been well established by Sn^{119} NMR and computational studies (GAUSSIAN 03 suit of programs). MESP and NBO studies are carried out to understand different binding modes and properties of the complexes as well as ligands. The relative bond strengths have been estimated using the Wiberg bond index analysis.
Study design: Experimental and computational
Place and Duration of Study: Department of Chemistry, University of Rajasthan, Jaipur, 2014.
Methodology: The structure of the complexes has been analyzed by IR and NMR. Computational studies (GAUSSIAN 03 suit of programs) have been used to elucidate the structure of the newly synthesized complexes.
Results: ^{119}Sn NMR showed a pentacoordinate range for diamide complexes indicating a coordination through the nitrogen of central pyridine ring in addition to amide nitrogens and tetracoordinate range for monoamide complexes confirming the formation of the products. The same have been confirmed by the computational calculations.
Conclusion: A series of dialkyl/diphenyl and trialkyl/triphenyl derivatives of organo tin complexes containing amide functionality have been synthesized and their structural characterizations performed by different spectral techniques and computational analysis.

Keywords: Amide ligands, tin complexes, MESP and NBO

1. INTRODUCTION

Amides are a class of important molecules because they are the major functional group and also of their biological application in various fields [1, 2]. Coordinating efficiency of amides to metal atom have significant role in biology. Various medicinal applications of amide complexes include anticancer, antibacterial, antioxidant, [3, 4] antimicrobial activity etc.[5-8]. Pyridine carboxamide ligand has attracted considerable attention because of their ability for the formation of transannular bonding and also due to biological significance [9].

Organotin complexes has been attracted more researchers due to its various industrial and biological applications [10, 11]. Stannylene complexes with Sn(II) coordination states are most common, however studies in Sn(IV) complexes involving Sn-N bonds and their structural study are scanty and merited detailed investigation.

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In the context mentioned above and in continuation to our work on metallic complexes of group 14 [12-15], U-shaped N, N'-Bis(2-pyridyl)pyridine-2,6-dicarboxamide (H_2L) and N-(pyridine-2-yl)picolinamide (HL^1) are prepared as ligands for the preparation of tin complexes. All the structural aspects and electronic properties of the newly synthesized complexes have been studied by density functional theory (DFT) with mixed valence basis set [15].

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY

2.1 General information and material

In this work 2-aminopyridine, picolinic acid, and 2, 6-pyridine dicarbonyldichloride are purchased from Sigma-Aldrich and used as received. Some reagents in ligand preparation, such as thionyl chloride, and all solvents were dried to remove water [16]. All the reactions were carried out in presence of nitrogen atmosphere. The melting points are recorded on a Perfit apparatus and are uncorrected. The IR spectra from 4000-400cm^{-1} were recorded on Nicolet Shimandzu Spectrometer in KBr pellets and CCl_4 solution 1H-, 13C-, and 119Sn-NMR Spectra: Jeol-300AL-FT-NMR spectrometer; at 300, 75.5, and 111.9 Hz, resp.; in CDCl3 and (D6)DMSO (1H- and 13C) and in C6D6 (119Sn), with Me4Si as internal standard and Me4Sn as external standard, resp. Elemental analyses: estimation of the Sn-content as tin oxide, and of the N-content as reported in [17].

2.2 Computational details

Gaussian 03 suit of programs have been used to understand the structure and properties of ligands and complexes. Optimizations were done by the DFT-B3LYP method. This method is combined with a mixed valence basis set of 631-g(d) for nonmetallic atoms and LanL2DZ for metallic atoms. The nature of bonding and hyperconjugative interactions were well evaluated by NBO 3.0 version incorporated in Gaussian 03 software. Atomic charges in all the structures were obtained using the natural population analysis (NPA) method within the natural bond orbital approach. At the optimized geometries, MESP topological analyses are carried out employing the DFT/6-31G(d) wave functions and using the UNIPROP package.

2.3 Syntheses

2.3.1 N,N'-Bis(2-pyridyl)pyridine-2,6-dicarboxamide(H_2L)

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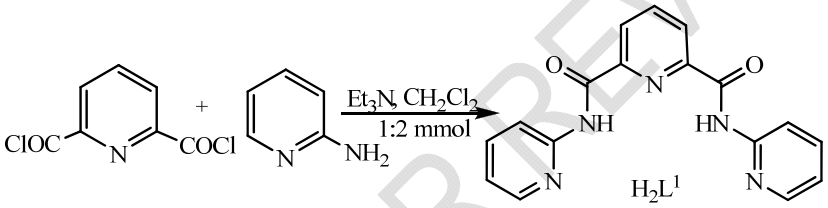
To a solution of 2, 6-pyridine dicarbonyldichloride (0.408g, 2mmol) in dichloromethane (10 ml) at 0^0 C, a solution of 2-aminopyridine (0.430g, 4.53 mmol) in the same solvent was added. The colour of the solution changed from light green to yellow. After 15 minutes stirring, triethylamine is added dropwise to the stirring mixture. Then white precipitate is formed to begin and mixture was stirred for 6hr to ensure completion of reaction. Filtered, dried and the precipitate was washed with saturated solution of sodium bicarbonate, water and acetone. Dried under vaccum and ligand obtained as white powder (60%). White solid, Yield = 60%, M.P = 215 ^{0}C, IR (KBr, cm^{-1})$\nu_{(C=O)}$(1691), $\nu_{(N-H)}$(3354). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.55 (s, NH), 8.63-7.31(m, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.68(C=O), 150.88(C=N), 149.08-123.54(C=C). Anal. Calc. for $C_{17}H_{13}N_5O_2$: C, 63.94; H, 4.10; N, 21.93. Found: C, 63.11; H, 4.03; N, 21.98%.



Scheme 1: synthesis H_2L

2.3.2 N-(pyridine-2-yl) picolinamide (HL^1)

Pyridine carbonyl chloride prepared from picolinic acid (0.492, 4mmol) dissolved in chloroform (15 ml) and cooled to 0^0C. To this 2-aminopyridine (0.364g, 4mmol) is added and stirred. The colour of solution changes from green to blue. After 30 min stirring, solution refluxed for 5 hr. Colour changes to dark blue. Following a brief period of cooling filtered and the filterate washed thrice with water. Chloroform layer evaporated under vaccum and the product was purified by column chromatography on silica gel with petroleum ether/ ethyl acetate (8/1 v/v) as eluent to afford the ligand as white crystals (75%). White crystal, Yield = 75%, M.P = 102 ^{0}C, IR (KBr, cm^{-1})$\nu_{(C=O)}$(1698), $\nu_{(N-H)}$(3350). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.59 (s, NH), 8.57-7.36(m, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.11(C=O), 150.24(C=N), 149.83-123.94(C=C). Anal. Calc. for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.21; H, 4.73; N, 20.98%.

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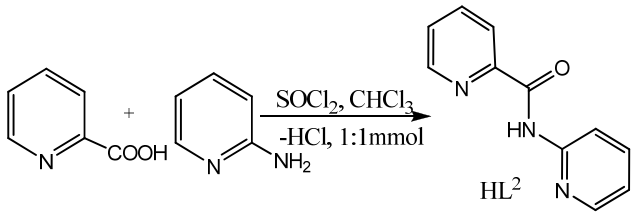
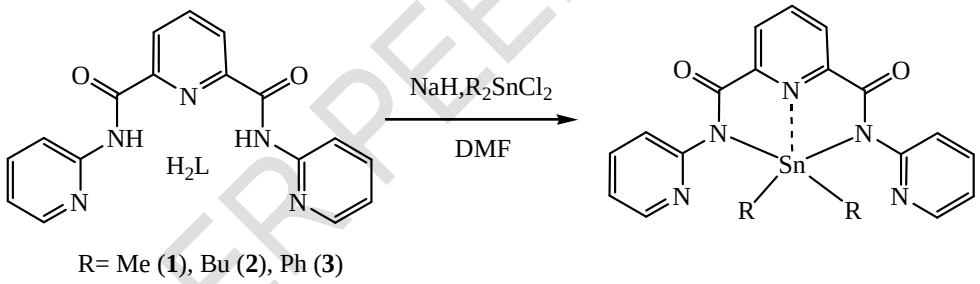


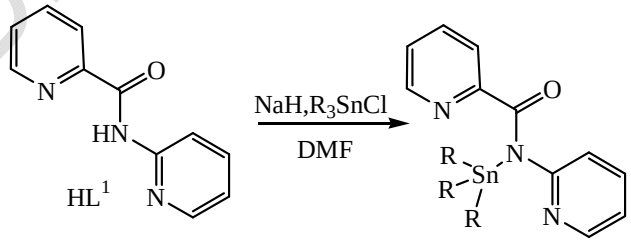
Scheme 2: synthesis HL^1

2.3.3 Complex syntheses

*Reaction of H_2L with dimethyl stannyl dichloride (**1**)*

Sodium hydride (0.025 g, 1.168 mmol) was washed with hexane under dinitrogen and then added to a solution of N, N'-bis(2-pyridyl)pyridine-2, 6-dicarboxamide (H_2L^1) (0.186 g, 0.584 mmol) in DMF. Subsequently dimethyltin dichloride (0.128 g, 0.584 mmol) in DMF (5 ml) was added to the above solution. A precipitate of NaCl was formed, washed with hexane and dried under vacuum to afford a cream product (71%); m.p. 167^0C. All other complexes are produced in the same manner in 1:1 molar ratio with H_2L and HL^1 reacting with different R_2SnCl_2 and R_3SnCl respectively. All complexes are soluble in organic solvents like benzene, hexane, chloroform etc.





R= Me (**4**), Bu (**5**), Ph (**6**)

Scheme 3: synthesis complexes 1-6

Physical and spectral characterization of ligands and complexes

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Complex	*IR*	*NMR* δ		
		H^1	C^{13}	Sn^{119}
dimethylstannyl(IV) N,N'-bis(2-pyridyl)pyridine-2,6-dicarboxamidate (**1**) Found: C, 48.96; H, 3.68; N, 15.03; Sn, 25.47 % Calcd. for $C_{19}H_{17}SnN_5O_2$: C, 48.13; H, 3.11; N, 15.53; Sn, 25.81 %	1694 (C=O), 1604 ($C=C_{arom}$), 1568 (C=N), 570 (Sn-C), 550 (Sn-N) cm^{-1}.	8.43-7.44 (m, 11H, ArH), 2.31 (s, 6H, Sn-Me)	162.61 (C=O), 155.61 (C=N), 139.11-125.55 (ArC)	-124.41 ppm.
dibutylstannyl(IV) N,N'-bis(2-pyridyl)pyridine-2,6-dicarboxamidate (**2**) Found: C, 54.57; H, 5.31; N, 12.73; Sn, 21.57 % Calcd. for $C_{25}H_{29}SnN_5O_2$: C, 54.27; H, 5.80; N, 12.53; Sn, 21.49 %	1691 (C=O), 1602 ($C=C_{arom}$), 1562 (C=N), 568 (Sn-C), 556 (Sn-N) cm^{-1}.	δ 8.59-7.25 (m, 11H, Ar H), 1.19-0.78 (m, 18H, Sn-Bu) ppm.	δ 162.48 (C=O), 156.77 (C=N), 137.11-125.55 (ArC)	-142.27 ppm.
diphenylstannyl(IV) N,N'-bis(2-pyridyl)pyridine-2,6-dicarboxamidate (**3**) Found: C, 59.01; H, 3.59; N, 11.87; Sn, 20.11 % Calcd. for $C_{29}H_{21}SnN_5O_2$: C, 59.07; H, 3.43; N, 11.86; Sn, 20.76%	1690 (C=O), 1601 ($C=C_{arom}$), 1569 (C=N), 572 (Sn-C) 541 (Sn-N)	8.77-7.32 (m, 18H, 8ArH+10PhH)	δ 162.39 (C=O), 154.21 (C=N), 138.29-125.74 (ArC) ppm.	-197.68 ppm.
trimethylstannyl(IV)-N-(pyridine-2-yl)picolinamidate (**4**) Found: C, 46.45; H, 4.73; N, 11.61; Sn, 32.79% Calcd. for $C_{14}H_{17}SnN_3O$: C, 46.53; H, 4.81; N, 11.66; Sn, 32.14%	1696 (C=O), 1595 ($C=C_{arom}$), 562 (Sn-C), 555 (Sn-N)	8.48-7.54 (m, 8H, ArH), 1.31 (s, 9H, Sn-Me)	162.14 (C=O), 151.21 (C=N), 134.45-124.87 (ArC)	+104.73

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tributylstannyl (IV)-N-(pyridine-2-yl)picolinamidate (**5**) Found: C, 56.58; H, 7.23; N, 8.61; Sn, 24.31 % Calcd. for $C_{23}H_{35}SnN_3O$: C, 56.50; H, 7.19; N, 8.19; Sn, 24.19 %	1693 (C=O), 1598 (C=C_{arom}) 565 (Sn-C) 531 (Sn-N)	8.95-7.47 (m, 8ArH), 1.33-0.87 (m, 15H, Sn-Et)	162.19 (C=O), 150.55 (C=N), 139.11-127.31 (ArC)	+62.19 ppm
triphenylstannyl(IV)-N-(pyridine-2 yl) picolinamidate (**6**) Found: C, 63.53; H, 4.23; N, 7.66; Sn, 21.65 % Calcd. for $C_{29}H_{23}SnN_3O$: C, 63.19; H, 4.83; N, 7.19; Sn, 21.43 %	1694 (C=O), 1594 (C=C_{arom}), 563 (Sn-C), 532 (Sn-N)	8.87-7.36 (m, 8ArH+15PhH)	162.57 (C=O), 150.34 (C=N), 136.33-129.94 (ArC)	-90.27

3. RESULTS AND DISCUSSION

A peak at 3354 cm^{-1} was assigned to N-H group whereas another peak at 1691 cm^{-1} corresponded to C=O stretching. In ^{1}H NMR, the signal at 10.55 was assigned to N-H proton and confirmed the formation of the ligand. In ^{13}C NMR carbonyl carbon resonated at 162.68 ppm and C=N carbon at 150.88 ppm respectively.

There was hardly any difference in the characteristic peaks in the spectral data of HL^2 as compared to H_2L^1. N-H and C=O stretching in IR being observed at 3350 and 1698 cm^{-1} respectively, a signal at 10.59 ppm in ^{1}H NMR corresponded to N-H proton of amide linkage and finally C=O and C=N carbons resonated at δ 162.11 and 150.24 ppm respectively in ^{13}C NMR.

Some physical parameters of the ligands were studied by Gaussian 03 software using 6-31G (d) basis set. In the ligand (H_2L^1), there is a parallel displaced π-π stacking interaction between two pyridyl rings with a distance of 4.02 A^0 between the centeres and an angle of 22.5°. In **Figure 1**, H_2L^1 shows the attractive electrostatic interaction between the σ framework and the π electron density in the ligand. In both the ligands the C=O bond lengths (1.22 A^0) are shorter than C-N bond length (1.34 A^0) indicating that in gas phase no charge separated resonance takes place.

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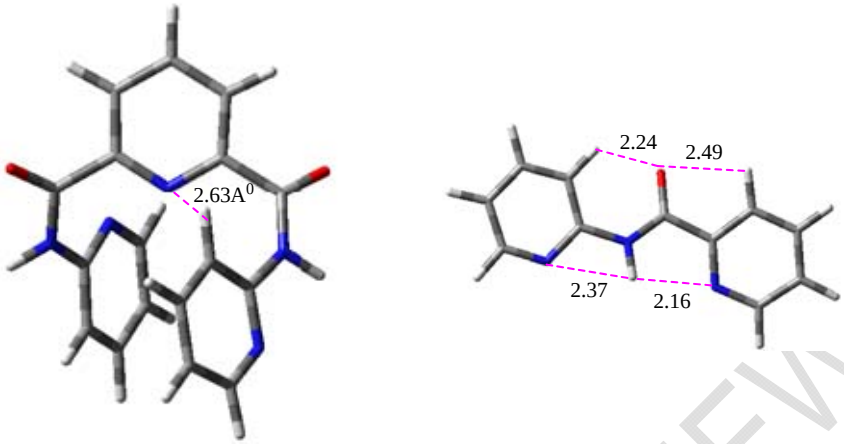

Figure 1: Optimized structure of H_2L^1 and HL^2

This is mainly due to the presence of nitrogen in the ring which has an electron withdrawing effect that reduces the π electron density and thus increases π–π interactions. In HL, *anti-anti* conformation is the most stable because in *cis* form there is lone pair repulsion between N and O. In addition *anti* form acquires intramolecular hydrogen bonding leading to more stable structure.

The disappearance of N-H vibrations in IR spectra of complexes in the range 3354-3350 cm^{-1} suggested the deprotonation and succeeding formation of Sn-N. Vibrations due to carbonyl group remained almost unchanged, discarding the possibility of coordination through oxygen. In ^1H NMR spectra, deuterium exchangeable amide protons disappeared suggesting the product formation. Characteristic signals for R-Sn were observed in ^{13}C NMR. ^{119}Sn NMR showed a pentacoordinate range (-124.41 ppm, -142.27 ppm and -197.68 ppm) for diamide complexes indicating a coordination through the nitrogen of central pyridine ring in addition to amide nitrogens and tetracoordinate range (+104.73 ppm, +62.19 ppm and -90.27 ppm) for monoamide complexes confirming the formation of the products.
For the disclosure of the structural parameters, all the complexes were analyzed by Gaussian 03 software using LanL2DZ basis set with DFT-B3LYP method.

The intermolecular hydrogen bonds between carbonyl oxygen and pyridine nitrogens in trimethyl derivative were in the range 2.49 and 2.18A^0. This is stronger than that of parent ligand by decreasing the distance between the two atoms.

Wiberg Bond index analysis gave bond order of 0.318 (bond length 2.229 A^0) between amide nitrogens and tin metal, 0.300 (bond length 2.249 A^0) between central pyridine nitrogen and tin and 0.094 (bond length 2.843 A^0) each between two side chain pyridine nitrogens and tin for dimethyl derivative. This indicates that both sides of the tin

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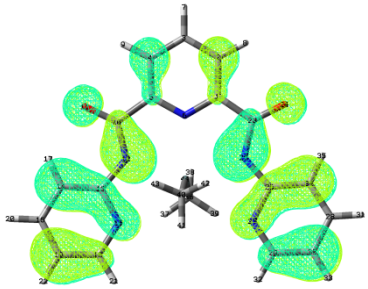
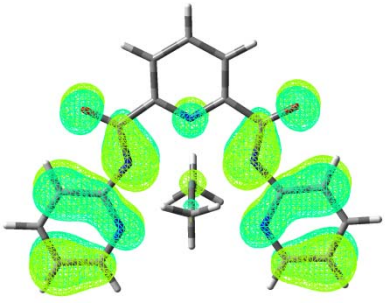
atom are symmetrically oriented and there is no coordination from the side chain pyridine ring. NBO analysis gave an insight into the delocalization of the nitrogen lone pairs to the central metal. Delocalization energy of central pyridine nitrogen to tin is 62.45 kcal/mol, amide nitrogens is 46.77 kcal/mol for each amide linkage and that of side chain pyridine ring is 2.14 kcal/mol. These delocalization effects impart an extra stability to the complex.

In the case of trimethyl derivative bond order between two pyridine nitrogens and tin atom are 0.06 (adjacent to C=O) and 0.046 respectively. That between amide nitrogen and tin is 0.511 (bond length 2.138A^0). In such type of derivatives, coordination is only from amide nitrogen and surroundings of the tin atom are unsymmetrically oriented. This is confirmed from NBO analysis, lone pair of pyridine nitrogen adjacent to carbonyl group has higher delocalization (6.30 kcal/mol) to tin than other pyridine nitrogen (3.30 kcal/mol) and that between amide nitrogen and tin is 88.21 kcal/mol.

Molecular orbital analysis gave an insight into the contribution of atomic orbitals to HOMO and LUMO and respective plots of the dimethyl and trimethyl amides are shown in **Figure 2**. HOMO of dimethyl derivative is composed of nitrogens and oxygens from amide functional group. An extra contribution from pyridine nitrogen and tin atom is attributed to LUMO. The energy gap between HOMO and LUMO is 0.027 eV. Unlike dimethyl derivative, HOMO of trimethyl derivative has a major contribution from tin and its substituent. LUMO is composed mainly from amide functional group and pyridine ring adjacent to amide nitrogen. $E_{HOMO\text{-}LUMO}$ is 0.353 eV**.** That means trimethyl derivative derived from mono amide is kinetically more stable than dimethyl derivative derived from diamide. . The optimized geometries of the complexes are given in **Figure 3**.

1		
Energy	HOMO = -9.251 eV	LUMO = -9.224 eV

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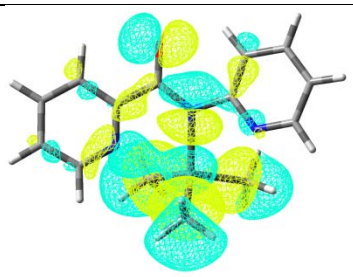
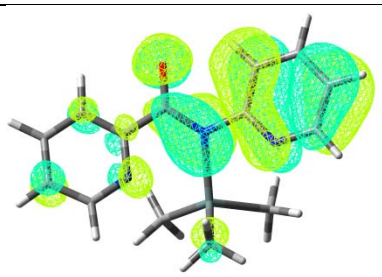
4		
Energy	HOMO = -9.659 eV	LUMO = -9.305 eV

Figure 2: HOMO and LUMO plots for (1) and (4)

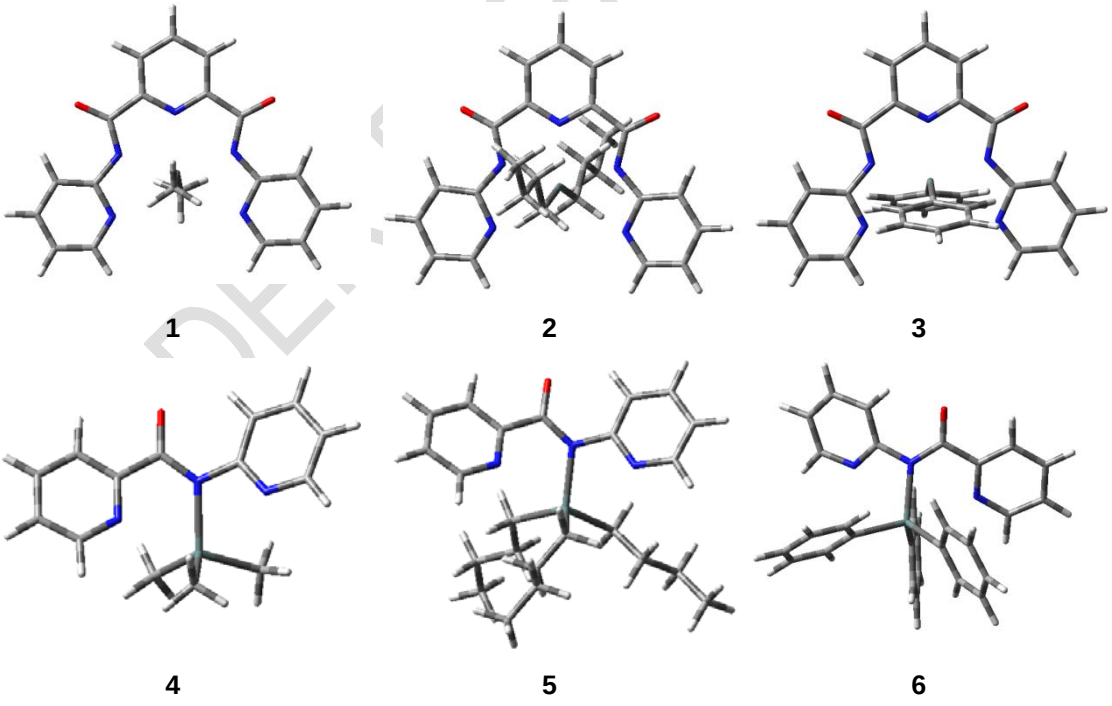


Figure 3: Optimized geometries for stannyl pyridine carboxamide derivatives

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4. CONCLUSION

A series of dialkyl/diphenyl and trialkyl/triphenyl derivatives of organo tin complexes containing amide functionality have been synthesized and their structural characterizations performed by different spectral techniques and computational analysis.

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