

Experimental and theoretical studies of the triphenyltin(IV) chloride adduct of pyridine-2-ethanol

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ABSTRACT

In this paper, we have reported adduct complex structure of triphenyltin(IV) chloride and pyridine-2-ethanol as a novel triorganotin complex, which was prepared by the reaction of Ph_3SnCl with pyridine-2-ethanol. The complex was characterized by elemental analysis, mass spectrometry, and IR, ^1H , ^{13}C and ^{119}Sn NMR spectroscopies. The molecular structure was determined by single crystal X-ray analysis. Complex adapts trigonal-bipyramidal geometry with trigonality index $\tau = 0.88$; the phenyl substituents on tin occupying the equatorial positions and the oxygen and chlorine atoms taking up the axial positions. DFT calculations of adduct complex compound of triphenyltin(IV) chloride and pyridine-2-ethanol ligand as a monomeric and dimeric forms at the B3LYP/6-31G (d, p) level using effective core potential with consideration of relativistic effects for stannous have been performed. Theoretical investigation of dimeric form of complex, which exists in the crystal structure, shows the stabilization role of intermolecular hydrogen bonding in this system.

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1. Introduction

Hydrogen bond formation is often the key interaction in both intramolecular and intermolecular contacts. Its understanding carries the potential of correlating structure with chemical properties and it may provide opportunity to design molecules with desired characteristics. The presence of hydrogen bonding interactions can play an important role in stabilizing of many biological and chemical systems. Researching into hydrogen-bonded molecular clusters is crucial with a view to understanding a wide variety of chemical and biochemical processes. Hydrogen bonding and in effect, anomalous physical and chemical properties have been extensively studied both theoretically and experimentally [1–4].

Organotin compounds, which are amongst the most widely used organometallic compounds, because of industrial and agricultural applications in general and di- and triorganotin containing Sn–O bonds in particular continues to grow, are very focus of attention [5–7]. Donor ligands such as carboxylate group, water and alkoxide molecules can provide coordinated oxygen to tin center [8–10]. X-ray crystal structure investigations of several aqua complexes of di- and triorganotin(IV) compounds has demonstrated the basic behavior of hydrogen bonding in formation of corresponding complexes. In fact, the pumping of electron density

from the other moieties into oxygen atoms of H_2O by polar hydrogen bonding can increase the basicity of oxygen atom until it can easily coordinate to tin center. This has been observed in the crown-ether complex of $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]18\text{-crown-6}\}_n$ previously [11]. In this paper, similar to above verified evidence, in a new synthesized triphenyltin(IV) complex of pyridine-2-ethanol, $[\text{Ph}_3\text{SnCl}(\text{HOC}_7\text{H}_9\text{N})]$, hydrogen bonding has been investigated in which pyridine-2-ethanol retains the hydrogen atom of alcohol and oxygen of hydroxyl group act as a ligand in complex formation. In fact, the existence of hydrogen atom engaged in the intermolecular hydrogen bonding forms the stable dimer of complex. The role of this hydrogen bonding as an important factor in the stabilization of structure has been considered at the density functional level of theory (DFT). All calculations were performed using the hybrid exchange–correlation functional B3LYP method.

2. Experimental

2.1. Materials and physical measurements

Triphenyltin(IV) chloride and pyridine-2-ethanol were purchased from Merck and used without further purification. Melting point was obtained with Electrothermal 9200 melting point apparatus and was not corrected. Infrared spectrum from 4000 to 400 cm^{-1} was recorded on a Shimadzu 470 FT-IR instrument, using KBr pellets. ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded at room

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Table 1
Crystal data for title compound.

Formula	C ₂₅ H ₂₄ ClNOSn
Formula wt.	508.61
Crystal size	0.50 × 0.40 × 0.18
Crystal system	Monoclinic
Space group	P2 ₁ /c
T (K)	293 (2)
a (Å)	10.0375 (11)
b (Å)	10.6965 (10)
c (Å)	21.608 (3)
β (°)	97.233 (10)
V (Å ³)	2301.5 (4)
Z	4
ρ _{calcd} (g cm ⁻³)	1.468
μ (Mo K _α , mm ⁻¹)	1.241
2θ _{max} (°)	56
# ref. meas., unique	12445, 5375
# of parameters	266
R _{int}	0.0316
R ₁ , wR ₂ [I > 2σ(I)]	0.0314, 0.0648
R ₁ , wR ₂ (all data)	0.0261, 0.0625
Goof	1.057

temperature in CDCl₃ on a Bruker AVANCE 300-MHz operating at 300.3, 75.4 MHz and 111.9 MHz, respectively. The NMR spectra are referenced to Me₄Si (¹H and ¹³C) or Me₄Sn (¹¹⁹Sn) as external standards. The mass spectroscopy was performed on a Varian MAT 44 instrument (electron impact, 20 eV). The calculated isotopic distribution for each ion was in agreement with experimental values.

2.2. Synthesis and characterization

The triphenyltin(IV) chloride (0.385 g, 1 mmol) was treated with pyridine-2-ethanol (0.123 g, 1 mmol) in chloroform (10 ml) and was refluxed for 2 h. Slow evaporation of the resulting solution furnished

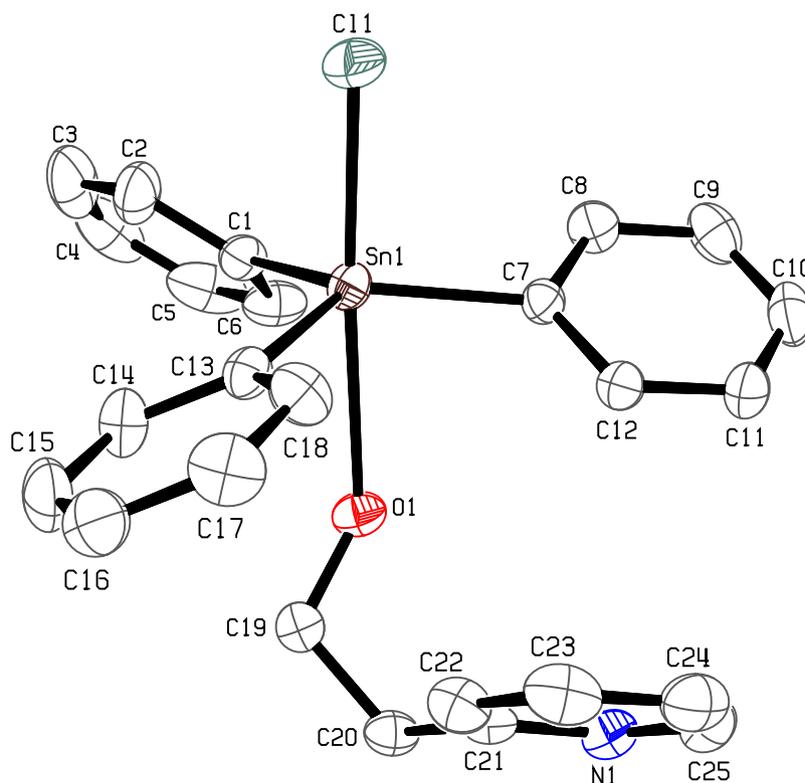
colorless crystals. Anal. Calc. for C₂₅H₂₄ONClSn: C, 59.04; H, 4.76; N, 2.75. Found: C, 58.82; H, 4.83; N, 2.49. IR (KBr, cm⁻¹): 477(m), 504(w), 576(w), 695(s), 732(s), 765(m), 1007(m), 1049(m), 1077(m), 1430(s), 1480(m), 1596(m), 1634(b), 2923(w), 3048(w), 3422(s). ¹H NMR (CDCl₃, ppm): 2.13 (2H, t, CH₂, ³J_{H-H}, 7.5 Hz), 2.3 (2H, t, CH₂, ³J_{H-H}, 7.5), 7.2–7.7 (19H, m, C₆H₅ and C₅H₄N), 8.5 (1, OH). ¹³C NMR (CDCl₃, ppm): 38.7 (CH₂), 61.8 (CH₂), 121.6 (C, C₅H₄N), 123.5 (C, C₅H₄N), 129.2 (C_{meta}, ³J^{117/119}Sn-¹³C, 61 Hz), 130.4 (C_{para}, ⁴J^{117/119}Sn-¹³C, 20 Hz), 136.2 (C_{ortho}, ²J^{117/119}Sn-¹³C, 49 Hz), 136.8 (C_{ipso}, ¹J^{117/119}Sn-¹³C, 460 Hz), 137.5 (C₅H₄N). ¹¹⁹Sn NMR (ppm): -33.3. Mass spectra data, tin-bearing fragment: m/e 351 [(C₆H₅)₃Sn]⁺ (calcd 351), 309 [(C₆H₅)₂SnCl]⁺ (calcd 309), 197 [(C₆H₅)Sn]⁺ (calcd 197), 155 [(SnCl)]⁺ (calcd 155), 120 [Sn]⁺ (calcd 120).

2.3. Crystal structure determination

The X-ray diffraction measurement was made on a STOE IPDS-II diffractometer with graphite monochromated Mo K_α radiation. A crystal of title compound with a dimension of 0.50 × 0.40 × 0.35 mm, was mounted on a glass fiber and used for data collec-

Table 2
Selected bonds length (Å) and angles (°) for title compound.

<i>Bond lengths</i>			
Sn1–C1	2.122 (2)	Sn1–O1	2.6263 (17)
Sn1–C7	2.124 (2)	O1–H1	0.79 (3)
Sn1–C13	2.124 (2)	C19–O1	1.428 (3)
Sn1–Cl1	2.4526 (7)	C25–N1	1.341 (3)
<i>Bond angles</i>			
C1–Sn1–C7	118.10 (8)	O1–Sn1–Cl1	176.01(4)
C1–Sn1–C13	114.04 (8)	C13–Sn1–Cl1	98.88 (6)
C7–Sn1–C13	123.25 (8)	C25–N1–C21	117.8 (2)
C1–Sn1–Cl1	97.38 (6)	C19–O1–H1	106 (2)
C7–Sn1–Cl1	95.27 (6)		

**Fig. 1.** Molecular structure of [Ph₃SnCl(HOC₇H₉N)] compound with ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

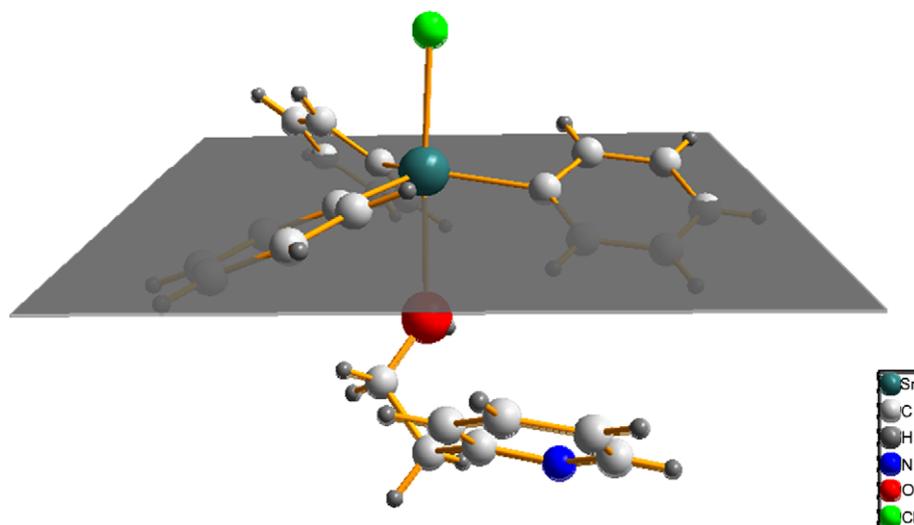


Fig. 2. Representation of trigonal bipyramidal geometry around tin (IV) atom.

tion. Cell constants and an orientation matrix for the data collection were obtained by least-squares refinement of diffraction data from 5563 unique reflections (Table 1). Data were collected at a temperature of 20 °C to a maximum 2θ value of 53.6 and in a series

of ω scans in 1° oscillations and integrated using the Stoe X-Area software package [12]. The numerical absorption coefficient, μ , for Mo K_{α} radiation is 0.918 mm^{-1} . A numerical absorption correction was applied using X-RED [13] and X-SHAPE software's [14]. The

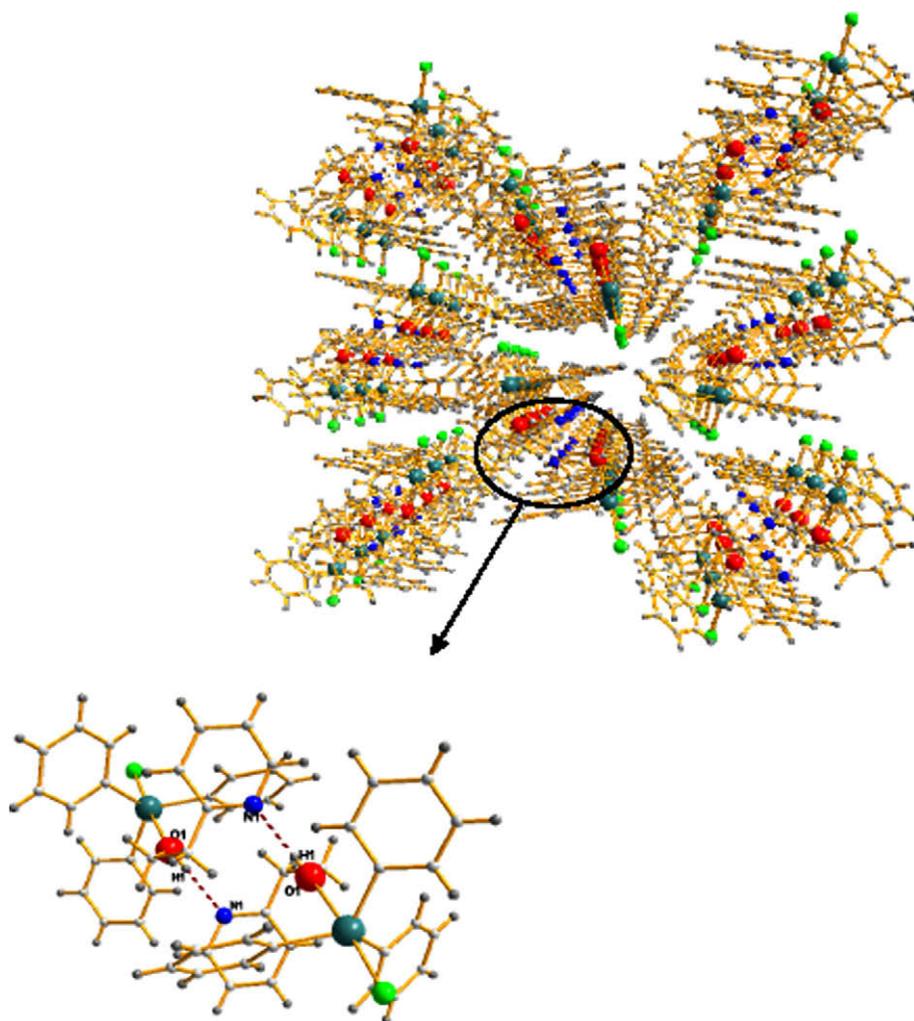


Fig. 3. Representation of symmetrical intermolecular hydrogen bonding between two monomeric complexes.

data was corrected for Lorentz and Polarizing effects. The structures were solved by direct and subsequent difference Fourier map and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters methods [15]. Subsequent refinement then converged with R factors and parameters errors significantly better than for all attempts to model the solvent disorder. Atomic factors are from International Tables for X-ray Crystallography [16]. All refinements were performed using the X-STEP32 crystallographic software package [17].

2.4. Computational approach

All theoretical calculations were performed with the Gaussian 98 program package [18]. Full geometry optimizations of all investigated molecular structures were computed by density functional theory (DFT) using the hybrid density functional B3LYP [19]. The LanL2DZ basis set with quasi-relativistic effective core potentials (LanL2) was used to represent the atomic cores and double-zeta quality (DZ) to describe the valence electrons of tin atom. The standard basis set 6-31G (d, p) was used that use to describe the electrons of carbon, nitrogen oxygen, and hydrogen atoms.

3. Results and discussion

3.1. General characterization

For the determination of structural feature of complex in solution, its ^1H , ^{13}C , and ^{119}Sn has been recorded in CDCl_3 . The ^1H NMR spectrum of complex showed expected aliphatic and aromatic peaks with right multiplicities. Although, the ^{13}C NMR spectrum of the title compound almost was identical with the ^{13}C NMR spectrum of triphenyltin(IV) chloride [20], the ^{119}Sn NMR chemical of it shifted 40 ppm to up field and indicate that the coordination geometry in solution is somewhat different than triphenyltin(IV) chloride [20]. The $^1J^{117/119}\text{Sn}-^{13}\text{C}$ value, 460 Hz, suggest that the tin atom is pentacoordinated in solution [21,22]. The average C–Sn–C angle in solution is estimated to be about 117.10° from the magnitude of $^1J^{117/119}\text{Sn}-^{13}\text{C}$ [21]. The estimated value is in good agreement with the C–Sn–C angles found in solid-state (114.04 – 123.25° , average 118.46°), which indicates that the solid-state structure and hydrogen bonding maintained in solution.

3.2. Crystal structure description

The adopted numbering scheme of the non-hydrogen atoms along with the thermal vibrational ellipsoids is shown in an ORTEP drawing of $[\text{Ph}_3\text{SnCl}(\text{HOC}_7\text{H}_9\text{N})]$ complex (Fig. 1). Selected bond distances and angles are listed in Table 2. In the titled compound, Sn exhibit a slightly distorted trigonal–bipyramidal geometry (hereafter tbp), with trigonality index $\tau = 0.88$ ($\tau = (\beta - \alpha)/60$, where β is the greatest basal angle and α is the second in magnitude; $\tau = 0$ and 1 for perfect square–pyramidal and trigonal–bipyramidal geometries, respectively) [23] (Fig. 2).

Our findings confirm that the three carbon atoms of phenyl rings are in equatorial position, while the chlorine and hydroxyl group of alcohol occupy the apical positions with different bond distances [Sn–Cl: 2.453 (1) Å and Sn–O: 2.626 (2) Å]. Furthermore, the Cl–Sn–O bond angle of 176.01 (4°), which is close to ideal value of 180° in the axial position of tbp geometry, can be a clear evidence for the interaction of hydroxyl group of pyridin–2–ethanol moiety as a ligand with the central tin atom. In addition, the planarity of carbon atoms of phenyl rings with tin atom is resulted as a summation of C–Sn–C angles in the equatorial plane to 355.40° . Moreover, the C–Sn–Cl bond angles of title compound are 97.38° , 95.27° and 98.88° for the C1, C7 and C13 atoms of phe-

nyl rings, respectively. Although, these values are significantly different from ideal value of 90° in tbp geometry, they are far from that of in the tetrahedral Ph_3SnCl (106.40°) [24]. It is of interest to note that the pyridine–2–ethanol with two coordination sites of N-pyridine and O-alcohol coordinated to the central tin atom using hydroxyl group. Since the nitrogen atom of pyridine ring is more basic than oxygen atom, it was expected nitrogen atom coordinated to tin rather than oxygen, however, it seems due to the steric factor coordination of N-pyridine inhibited and instead the

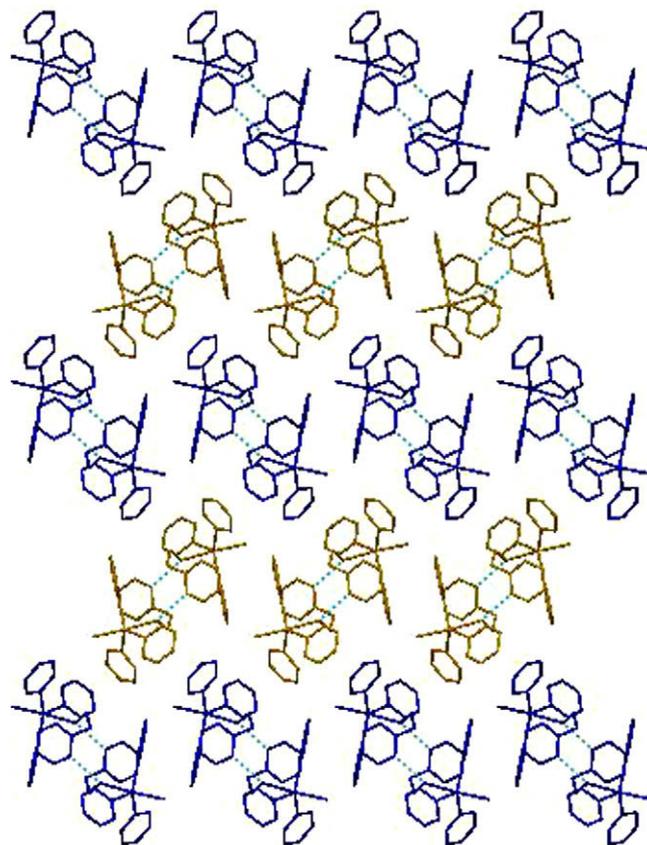


Fig. 4. Representation of crystal packing of titled compound along a -axis. Hydrogen atoms are omitted for clarity.

Table 3

Geometrical parameters of calculated structures at the B3LYP level with experimental data from X-ray analysis (distances in Å, angles in $^\circ$).

	Complex		Ligand		Exp.
	C1.calc	C2.calc	L1.calc	L2.calc	
Sn–O (hydroxyl group)	2.479	2.620			2.626
Sn–C (phenyl group)	2.140	2.132			2.123
Sn–Cl	2.507	2.496			2.453
C–C (phenyl group)	1.400	1.400			1.379
C–O (hydroxyl group)	1.434	1.429	1.412	1.407	1.428
C–N (pyridine ring)	1.343	1.346	1.343	1.342	1.342
O–H	0.995	0.995	0.975	0.984	0.793
O–H...N (intermolecular)					
O...N		2.821		2.851	2.798
H...N		1.837		1.873	2.010
O–H...N		169.58		172.89	172.06
O–H...N (intramolecular)					
O...N	2.656		2.820		
H...N	1.771		2.013		
O–H...N	146.28		138.79		
C–Sn–C (summation)	355.88	355.92			355.40
Cl–Sn–O	176.06	177.98			176.01

oxygen of the hydroxyl group with enhanced basicity due to hydrogen bonding is coordinated to tin. This suggestion is in accordance with the ^{119}Sn NMR chemical shift that shows coordination of pyridine-2-ethanol is maintained in solution. Alternatively, coordination of oxygen of alcohol instead of nitrogen can be explained by steric demand of pyridine ring. The steric control over the molecular structure of organotin compounds has been noticed previously [25].

The crystal structure analysis reveals that the complex consists of $[\text{Ph}_3\text{SnCl}(\text{HOC}_7\text{H}_9\text{N})]$ discrete monomeric molecular units, which are involved the hydrogen bonding between two units (Fig. 3). Two hydrogen bonds ($\text{O1-H}\dots\text{N1}$, 2.010 Å; $\text{O1-H}\dots\text{N1}$, 172.06°) between alcohol hydroxyl group and pyridine ring of two monomers give rise to a base pairing and forming dimer complexes that exhibit crystallographically imposed inversion symmetry. We present a more detailed analysis of these hydrogen bonds and follow this, dimer complexes, in the computational section of this article. Finally, the existence of dimeric units in tandem with electrostatic forces, generate an interesting zig-zag layered structure that is viewed along *a*-axis in Fig. 4.

3.3. Computational studies

To get insight into the hydrogen bonding in the title compound and the pyridine-2-ethanol ligand, DFT calculations of monomer complex $[\text{Ph}_3\text{SnCl}(\text{HOC}_7\text{H}_9\text{N})]$ and the base paired dimer complex at the B3LYP/6-31G (d, p) level using effective core potential

with consideration of relativistic effects for stannous have been performed. Geometrical parameters of optimized structures are listed in Table 3. The optimization of complex in form of a monomer ended up with equilibrium structure that the conformation of pyridine-2-ethanol ligand has changed in the calculated monomeric complex (C1.calc) (Fig. 5). The severe change in the conformation of ligand is the rotation along with aliphatic bonds and the change of dihedral angle of C20-C9-O1-H from -68.19° to 52.16° in initial and optimized structure of C1.calc, respectively, which result in formation of strong intramolecular hydrogen bonding between alcohol hydroxyl group and pyridine ring ($\text{O1-H}\dots\text{N1}$, 1.771 Å; $\text{O1-H}\dots\text{N1}$, 146.28°). In addition, the bond lengths of Sn–O and Sn–Cl have changed to 2.479 and 2.507 Å, respectively. Since, formation of complex is acid–base reaction between tin metal atom and oxygen atom of hydroxyl group, one can found that increases of the basicity of oxygen atom by hydrogen bonding can decrease the Sn–O bond length.

DFT calculation of free ligand (L1.calc) shows that the change of conformation of ligand occurs similarly. The intramolecular hydrogen bond, which forms with 2.013 Å and 138.79° distance and angle respectively, indicate that pyridine-2-ethanol has hydrogen bond in the complex stronger than free form.

The optimization of base paired dimer complex (C2.calc) reveals that the change of conformation of ligand did not occur and the structure of ligand retained without any rotation. In fact, the existence of intermolecular hydrogen bonds between two monomer that exist in the crystal structure can play a key role in the for-

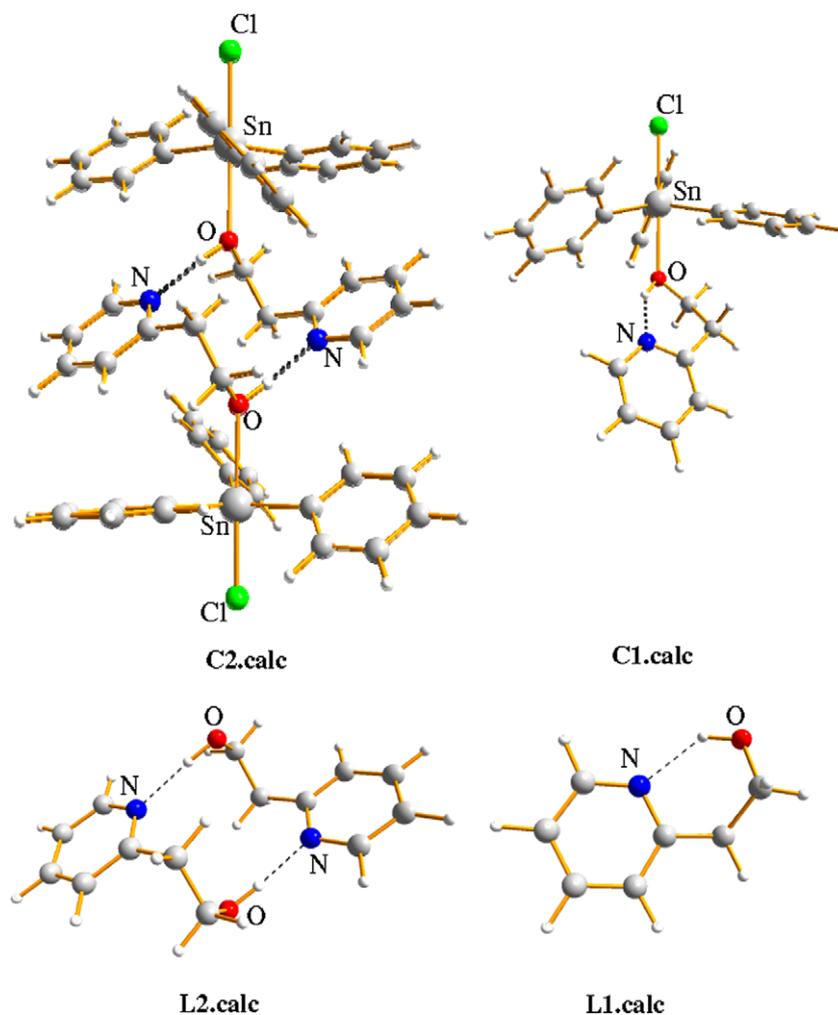


Fig. 5. Calculated structures of monomer and dimer complexes, C1.calc and C2.calc, and monomer and dimer ligands L1.calc and L2.calc, respectively.

mation of dimer complex and stabilization of this structure in the real system. In order to investigate the stabilization effect of intermolecular instead of intramolecular hydrogen bond, calculation of base paired dimer ligands (L2.calc) also has been carried out. Similarly, in the dimer complex, the structure of ligands remained without any change in conformation. The O1–H...N1 distance; angle in C2.calc and L2.calc are 1.837 Å; 169.58° and 1.873 Å; 172.90° respectively. The bond lengths of Sn–O and Sn–Cl and bond angle of Cl–Sn–O in C2.calc structure are 2.620 Å, 2.496 Å and 178.00°, respectively. Overall, the agreement between geometrical parameters of calculated C2.calc and experimental structures is very good.

The strength of hydrogen bonds calculated based on the energies differences of the paired dimer complexes and ligands, C2.calc and L2.calc, with the requisite monomer complex and ligand, respectively. The cleavage of the dimeric complex, which having same hydrogen bond pattern as in L2.calc, to monomeric units costs 83.51 kJ/mol (corrected for the basis set superposition error, BSSE). This exhibits a moderate strength hydrogen bond [1] for the C2.calc with energy of 41.76 kJ/mol. The analogous hydrogen bonds in L2.calc proved to be slightly stronger (41.84 kJ/mol, BSSE corrected) than dimer complex (C2.calc). Comparison of dimeric complex (C2.calc), which it is consistent with the crystal structure, with the monomeric complex of C1.calc that contains intramolecular hydrogen bonding shows that the half energy of dimer is greater than monomer complex (8.63 kJ/mol). These results probably can explain reason for chose of dimeric structure by complex.

4. Conclusion

In this study, a new adduct complex of triphenyltin(IV) chloride and pyridine-2-ethanol has been prepared and characterized by spectroscopic methods. DFT calculations of monomer complex [Ph₃SnCl(HOC₂H₅N)], dimer complex, monomer free pyridine-2-ethanol ligand, and dimeric form of ligands at the B3LYP/6-31G (d, p) level have been carried out. Based on the theoretical results we can conclude that intermolecular hydrogen bonding in the crystal structure can play important role in the stabilization of title compound as a dimeric complex. Theoretical results are in accordance with the experimental data to good extent.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 739025. Copy of this information may be obtained free of

charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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