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Neutral penta-coordinated diorganotin(IV) complexes derived from *ortho*-aminophenol Schiff bases: Synthesis, characterization and molecular structures

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ABSTRACT

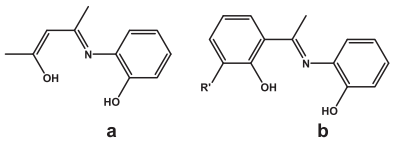
The one pot reactions carried among *ortho*-aminophenol, R_2SnO (R = Me or Ph) and acetyl acetone, 2-hydroxyacetophenone and 2-hydroxy-3-methylacetophenone led to six new diorganotin(IV) compounds Me_2SnL1 (**1**), Ph_2SnL1 (**2**), Me_2SnL2 (**3**) Ph_2SnL2 (**4**), Me_2SnL3 (**5**) and Ph_2SnL3 (**6**) (**H2L1** = 2-(3-hydroxy-1-methyl-but-2-enylideneamino)-phenol, **H2L2** and **H2L3** = 2-[1-(2-hydroxyaryl)alkylideneamino]-phenol) in good yields. Combination of IR, ^1H, ^{13}C and ^{119}Sn NMR and X-ray diffraction techniques along with elemental analyses evidenced the formation of penta-coordinated monomeric species. The crystal structures of ligand **H2L1** and complexes **1**, **3** and **4** were determined by single crystal X-ray diffraction study. In the solid state, the ligand **H2L1** exists as *keto-enamine* tautomeric form. There are N–H…O intra-molecular hydrogen bonds between amine and carbonyl groups. Diorganotin(IV) complexes **1**, **3** and **4** are monomers with TBP (trigonal bipyramidal) geometry surrounding the tin atom. The *O*, *N*, *O*-tridentate ligand places its two oxygen donating atoms in the axial positions, and the nitrogen atom occupies one equatorial position. The two R groups attached to tin occupy the other two equatorial positions. The solution structures were predicted by ^{119}Sn NMR spectroscopy.

1. Introduction

The study of coordination chemistry of tin has received much attention due to its various geometries and coordination numbers known for both inorganic and organometallic complexes [1,2]. Especially, tin(IV) is known to form stable complexes with oxygen, sulfur-, carbon-, and nitrogen containing ligands [3]. Organotin (IV) compounds of oxygen and nitrogen donor ligands are well known for their biological activity [4–7]. This has facilitated the cautious bioinorganic chemist to couple therapeutic agents or systematically substituted molecules and different biomolecules [8–12] with organotin(IV) moieties, in order to track variations and investigate their effects in biological systems [13–16].

Moreover, organotin(IV) complexes show a wide variety of biological applications, such as bactericidal, acaricidal, fungicidal [17,18] and antitumour agents [19–27]. According to Lascourèges et al., the mono- and di-organotin(IV) derivatives are more active than their corresponding triorganotin(IV) analogues against the Sulfate-reducing bacteria (SRB) [28]. Recently, the biocidal usage of triorganotin(IV) molecules has been banned due to its high toxicological effects on marine environment [29]. The present research interest is focus toward the molecular design which can set up a balance between toxicity and biological activity [29–32]. Hence, the reactivity of organotin(IV) cations with aminophenol functionalized Schiff bases has been reported [16,33–35].

In order to obtain more information on the molecular basis of interactions between organotin(IV) cations and biologically important molecules containing {O, N, O} donor atoms, we have synthesized six new penta-coordinated diorganotin(IV) complexes derived from *o*-aminophenol and their complete structural characterization including single crystal X-ray crystallography for ligand **H2L1** and three diorganotin(IV) complexes **1**, **3** and **4**. Ligands used in this study are shown below.



(a) H2L1 (b) H2L2 (R' = H) and H2L3 (R' = CH_3)

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2. Experimental

2.1. Materials

Me_2SnCl_2 (Fluka), Ph_2SnO (Aldrich), *ortho*-aminophenol (Lobachemie), acetyl acetone (Sisco), 2′-hydroxyacetophenone (Aldrich) were used without further purification, while 2-hydroxy-3-methylacetophenone was a gift sample. The solvents used in the reactions were of AR grade and dried using standard procedures. Me_2SnO was synthesized according to literature method [36,37].

2.2. Physical measurements

Elemental analyses were performed with a Perkin Elmer 2400 series instrument. IR spectra in the range 4000–400 cm^{-1} were obtained on a Perkin Elmer Spectrum BX series FT-IR spectrophotometer with samples investigated as KBr discs. The ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AMX 400 spectrometer and measured at 400.13, 100.62 and 149.18 MHz. The ^1H, ^{13}C and ^{119}Sn chemical shifts were referred to Me_4Si set at 0.00 ppm, $CDCl_3$ set at 77.0 ppm and Me_4Sn set at 0.00 ppm, respectively.

2.3. X-ray crystallography

Single crystals of **H2L1** compounds **1**, **3** and **4** suitable for an X-ray crystal structure determination were obtained from hexane (**1**), ethanol (**H2L1** and **3**) and benzene/hexane (**4**) respectively, by slow evaporation of the solutions of the respective compounds. All measurements were made on a Bruker Nonius SMART CCD diffractometer [38] with graphite-monochromated Mo*Kα* radiation (λ = 0.71073 Å) at 296 K. The intensity data were corrected for Lorenz and polarization effects. The structures were solved by direct methods using the program SHELXS-97 [39]. Refinement and all further calculations were carried out using SHELXS-97 [40]. Smart software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using saint software. All the non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The data collection parameters and bond lengths and angles are presented in Tables 1 and 2, respectively. Views of the molecular structures are shown in Figs. 1–4.

2.4. Synthesis of ligand

2.4.1. Preparation of 2-(3-hydroxy-1-methyl-but-2-enylideneamino)-phenol (*H2L1*)

To a warm ethanol solution (20 ml) of *o*-aminophenol (1.63 g, 14.93 mmol), an ethanolic solution (10 ml) of acetyl acetone (1.5 g, 14.98 mmol) was added and refluxed for 4 h. The reaction mixture was filtered while hot, reduced to one-third of its original solvent volume and left to crystallize at room temperature. The block-shaped light yellow crystals of H2L1 were isolated from the mother liquor and dried *in vacuo*. Yield: 2.35 g (82%); m.p.: 182–184 °C. *Anal*. Calc. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.92; H, 6.66; N, 7.23%. IR (KBr pellets, cm^{-1}): 3372 (ν_{NH}), 3007(ν_{OH}), 1586 ($\nu_{C=N}$). ^1H NMR ($CDCl_3$, δ_H): 12.13 (s, 1H, OH-1*); 9.74 (s, 1H, OH-2*), 7.13 (d (8.0 Hz), 1H, H5), 7.00 (t, 1H, H3), 6.89 (d (8.0 Hz), 1H, H2), 6.76 (t, 1H, H4), 5.18 (s, 1H, H8), 2.03 and 1.97 (s, 6H, H7′ and H9′) ppm. ^{13}C NMR ($CDCl_3$, δ_C): 194.56 [C1], 160.84 [C7], 150.73 [C9], 126.25 [C6], 125.70 [C3], 125.20 [C4], 118.75 [C2], 114.90 [C5], 96.75 [C8], 28.52 [C7′], 19.33 [C9′].

The other ligands *viz*., H2L2 and H2L3 were prepared *in situ* and further reacted with appropriate organotin(IV) starting materials to obtain the corresponding complexes.

2.5. Syntheses of diorganotin(IV) complexes

General procedure for the preparation of complexes **1**–**6** are described below.

2.5.1. Synthesis of 6,6, 8, 10-tetramethyl-5, 7-dioxa-11-aza-6-stanna-benzocyclononene [*Me₂SnL1*] (*1*)

Ortho-aminophenol (0.17 g, 1.55 mmol) in absolute ethanol (ca. 10 ml) was added to a stirred ethanolic solution (*ca*. 25 ml) of acetyl acetone (0.16 g, 1.59 mmol). To the above mixture, Me_2SnO (0.26 g,

Table 1
Crystallographic data and structure refinement parameters for **H2L1** and complexes **1**, **3** and **4**.

	H2L1	1	3	4
Empirical formula	$C_{11}H_{13}NO_2$	$C_{26}H_{34}N_2O_4Sn_2$	$C_{16}H_{17}NO_2Sn$	$C_{26}H_{21}NO_2Sn$
Formula weight	191.22	675.9	374	498.13
Crystal size (mm)	0.50 × 0.32 × 0.20	0.45 × 0.26 × 0.16	0.50 × 0.28 × 0.16	0.42 × 0.24 × 0.18
Crystal shape	Block	Prism	Tablet	Block
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclnic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1$	P_1
a (Å)	8.8468(5)	7.6984(2)	12.5680(9)	10.5062(3)
b (Å)	10.5173(5)	15.3905(4)	7.7762(6)	10.5047(3)
c(Å)	11.2200(5)	23.0570(6)	15.6110(11)	12.8084(3)
α (°)	90	90	90	112.9050(10)
β (°)	90	90.6820(10)	101.964(3)	112.8720(10)
γ (°)	90	90	90	101.130(2)
V (Å^3)	1043.96(9)	2731.65(12)	1492.54(19)	1096.59(5)
Z	4	4	4	2
D_x (g cm^{-3})	1.217	1.644	1.712	1.509
μ(mm^{-1})	0.084	1.861	1.881	1.187
Scan range (°)	2.65 < θ < 28.38	1.59 < θ < 28.37	1.90 < θ < 25.99	2.30 < θ < 28.33
Reflections measured	7916	40 127	17 432	9468
Independent reflections; R_{int}	2540; 0.1148	6750; 0.1227	2835; 0.0511	6546; 0.0434
Number of parameters	134	315	184	405
Number of restraints	0	0	0	3
R (*F*) (*I* > 2σ(*I*) reflns)	0.0495, wR_2 0.1194	0.0332, wR_2 0.0890	0.0241, wR_2 0.0631	0.0344, wR_2 0.0809
R indices [I > 2σ(I)]	0.0624, wR_2 0.1258	0.0426, wR_2 0.0952	0.0272, wR_2 0.0669	0.0425, wR_2 0.0850
GOF (F^2)	0.945	1.052	1.059	0.994
Max, min $\Delta\rho$ (e/Å^{-3})	0.157, −0.247	0.929, −0.941	0.755, −0.515	0.489, −0.663

Table 2
Selected bond lengths (Å) and angles (°) for **H2L1**.

Bond lengths		Bond angles	
O(1)–C(2)	1.366(2)	C(7)–N(1)–C(1)	131.50(15)
O(2)–C(9)	1.267(2)	O(1)–C(2)–C(3)	123.60(16)
N(1)–C(7)	1.343(2)	O(1)–C(2)–C(1)	115.94(15)
N(1)–C(1)	1.410(2)	C(6)–C(1)–N(1)	124.72(17)

0.57 mmol) was added at once and the resulting mixture was refluxed for 6 h at ambient temperature. After the completion of the reaction, the volatiles were removed in *vacuo*, washed cautiously with cold hexane, filtered and dried in *vacuo*. The residue was then extracted in hot hexane and filtered. The filtrate was reduced and left for crystallization at room temperature to give bottle green crystalline product of **1** in 56% (0.30 g) yield; m.p.; 98–100 °C. *Anal.* Calc. for $C_{13}H_{17}NO_2Sn$: C, 46.20; H, 5.07; N, 4.14. Found: C, 46.02; H, 4.89; N, 3.99%. IR (KBr pellets, cm^{-1}): 3063, 1573, 1562 ($\nu_{C=N}$), 1512, 1477, 1430, 1386, 1285, 1180, 1112, 941, 746, 732, 606 (ν_{Sn-C}), 558 (ν_{Sn-O}), 457 (ν_{Sn-N}). ^{1}H NMR ($CDCl_3$, δ_H): Ligand skeleton: 7.03 (d (8.0 Hz), 1H, H5); 7.00 (dd (8.0 Hz), 1H, H3); 6.79 (d (8.0 Hz), 1H, H2), 6.60 (dt (8.0 Hz), 1H, H4), 5.27 (s, 1H, H8), 2.32 and 1.96 (s, 6H, H7′ and H9′); Sn-Me (^2J (^{119}Sn-^{1}H) = 37.6 Hz), : 0.66 (s, 6H), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 187.76 [C1], 173.33 [C7], 159.35 [C9], 133.35 [C6], 128.26 [C3], 123.81 [C4], 118.62 [C2], 116.72 [C5], 101.71 [C8], 28.58 [C7′], 25.29 [C9′]; Sn-Me (^1J (^{119}Sn-^{13}C) = 1292 Hz): −0.001, ppm. ^{119}Sn NMR ($CDCl_3$, δ_{Sn}): −129.73, ppm.

2.5.2. Synthesis of 8, 10-dimethyl-6, 6-diphenyl-5, 7-dioxa-11-aza-6-stanna-benzocyclononene [***Ph$_2$SnL1***] (***2***)

An identical method to that of **1** was followed to synthesize **2** using *ortho*-aminophenol, acetyl acetone and Ph_2SnO in equimolar ratios. Bottle green colored crystalline material was obtained from an ethanol-benzene mixture (3:1 v/v). Yield: 51%; m.p.; 124–126 °C. *Anal.* Calc. for $C_{23}H_{21}NO_2Sn$: C, 59.78; H, 4.58; N, 3.03. Found: C, 59.12; H, 4.32; N, 2.87%. IR (KBr pellets, cm^{-1}): 3051, 1602, 1560 ($\nu_{C=N}$), 1514, 1474, 1431, 1383, 1284, 1273, 939, 751, 732, 698 (ν_{Sn-C}), 516 (ν_{Sn-O}), 446 (ν_{Sn-N}). ^{1}H NMR ($CDCl_3$, δ_H): Ligand skeleton: ^{1}H NMR ($CDCl_3$, δ_H): Ligand skeleton: 7.07 (d (8.0 Hz), 1H, H2); 7.07 (d (8.0 Hz), 1H, H2); 6.96 (t (8.0 Hz), 1H, H3), 6.59 (dt, 1H, H4), 5.26 (s, 1H, H8), 2.30 and 2.17 (s, 6H, H7′ and H9′); Sn-Ph (^3J($^{119/117}$Sn-^{1}H) = 44.0 Hz): 7.84 (m, 4H, H-2*), 7.36–7.43 (m, 6H, H-3* and H-4*), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 186.68 [C1], 172.11 [C7], 158.11 [C9], 138.76 [C6], 127.26 [C3], 122.56 [C4], 117.76 [C2], 115.76 [C5], 101.39 [C8], 27.51 [C7′], 24.35 [C9′]; Sn-Ph: 136.40 (C-1*) (J($^{119/117}$Sn-^{13}C) = 956.0 Hz), 132.08 (C-2*) (^2J($^{119/117}$Sn-^{13}C) = 53.7 Hz), 130.30 (C-4*) (^3J($^{119/117}$Sn-^{13}C) = 15.7 Hz), 128.67 (C-3*)(^4J($^{119/117}$Sn-^{13}C) = 84.2 Hz), ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −307.71, ppm.

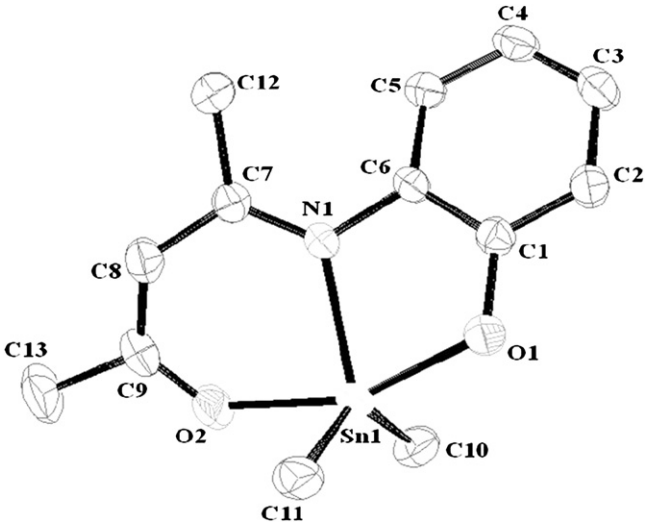


Fig. 2. Molecular structure of Me_2SnL1 (**1**) at 35% probability level. Hydrogen atoms have been omitted for clarity.

2.5.3. Synthesis of 6, 12, 12-trimethyl-11, 13-dioxa-5-aza-12-stanna-dibenzo [a, e]cyclononene [***Me$_2$SnL2***] (***3***)

Greenish yellow colored crystals of **3** were obtained from hexane-benzene mixture (4:1 *v*/*v*). Yield: 45%; m.p.; 132–134 °C. *Anal.* Calc. for $C_{16}H_{17}NO_2Sn$: C, 51.38; H, 4.58; N, 3.74. Found: C, 50.86; H, 4.33; N, 3.19%. IR (KBr pellets, cm^{-1}): 3054, 1599, 1568 ($\nu_{C=N}$), 1525, 1466, 1435, 1326, 1288, 1187, 853 777, 753, 733 (ν_{Sn-C}), 562(ν_{Sn-O}), 522 (ν_{Sn-N}). ^{1}H NMR ($CDCl_3$, δ_H): Ligand skeleton: 7.71 (d (8.0 Hz), 1H, H13); 7.37 (t (7.6 Hz), 1H, H11), 7.17 (dd (7.6 Hz), 1H, H4), 7.08 (d (8.0 Hz), 1H, H2), 6.88 (d (8.0 Hz), 2H, H5 and H10), 6.79 (dd (7.2 Hz), 1H, H3), 6.69 (t (6.4 Hz), 1H, H12), 2.84 (s, 3H, H7′); Sn-Me (^2J (^{119}Sn-^{1}H) = 36.8 Hz): 0.63 (s, 6H), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 176.76 [C9], 169.63 [C7], 160.66 [C1], 137.05 [C11], 133.33 [C13], 132.18 [C6], 130.94 [C3], 125.65 [C10], 124.75 [C2], 121.37 [C8], 119.85 [C12], 118.96 [C4], 117.32 [C5], 22.00 [C7′]; Sn-Me(^1J (^{119}Sn-^{13}C) = 1284.4 Hz): −0.001 ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −139.74, ppm.

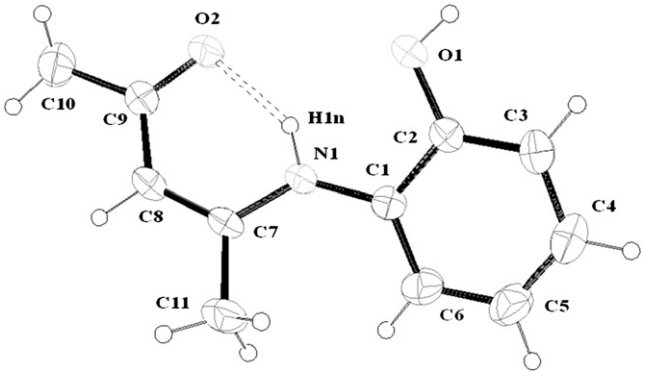


Fig. 1. Molecular structure of **H2L1** showing the atom-labeling scheme at 35% probability level; N–H…O intra-molecular hydrogen bonds are drawn as dashed lines.

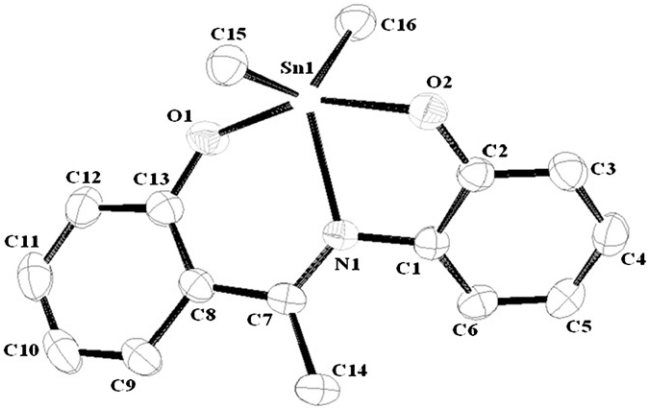


Fig. 3. Molecular structure of Me_2SnL2 (**3**) at 35% probability level. Hydrogen atoms have been omitted for clarity.

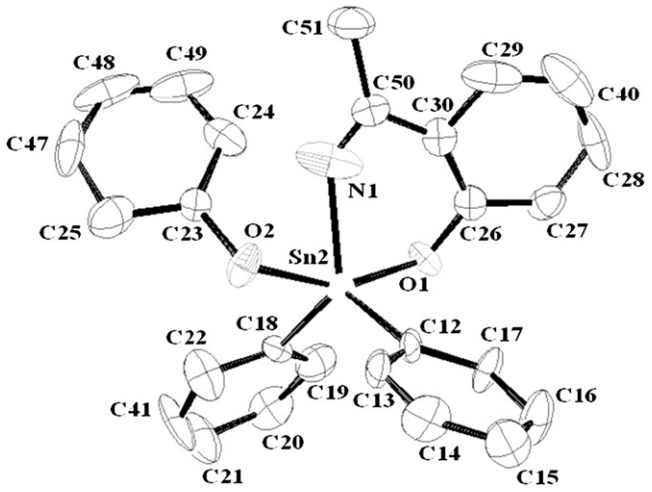
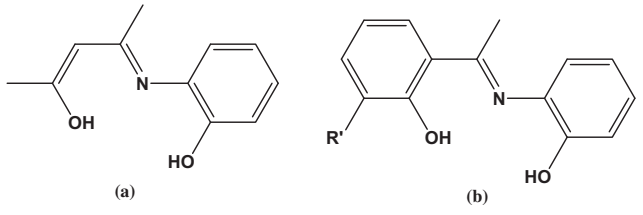


Fig. 4. Molecular structure of Ph_2SnL2 (**4**) at 35% probability level. Hydrogen atoms have been omitted for clarity; the bond between C24–N1 could not be located as the molecule is disordered.

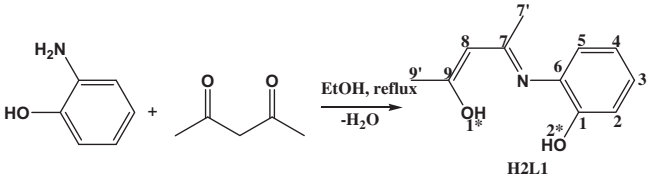
*2.5.4. Synthesis of 6-methyl-12, 12-diphenyl-11, 13-dioxa-5-aza-12-stanna-dibenzo [a, e]cyclononene [**Ph_2SnL2**](**4**)*

An identical method to that of **1** was followed to synthesize **4** using *ortho*-aminophenol, *ortho*-hydroxyacetophenone and Ph_2SnO in equimolar ratios. Green colored crystals was obtained from an ethanol. Yield: 62%; m.p.: 206–208 °C. *Anal.* Calc. for $C_{26}H_{21}NO_2Sn$: C, 62.68; H, 4.24; N, 2.81. Found: C, 62.26; H, 3.76; N, 2.35%. IR (KBr pellets, cm^{-1}): 3054, 1601, 1570 ($\nu_{C=N}$), 1531, 1466, 1430, 1318, 1187, 847, 761, 733, 699, (ν_{Sn-C}), 523 (ν_{Sn-O}), 448 (ν_{Sn-N}). ^1H NMR ($CDCl_3$, δ_H): Ligand skeleton: 7.59 (d (8.0 Hz), 1H, H13); 7.44 (t (7.6 Hz), 1H, H11), 7.17–7.00 (m, 2H, H4 and H2), 6.98 (d (8.0 Hz), 2H, H5 and H10), 6.73 (dd (7.0 Hz), 1H, H3), 6.62 (t (6.4 Hz), 1H, H12), 2.77 (s, 3H, H7′); Sn-Ph: 7.86 (m, 4H, H-2*) ($^3J(^{119/117}Sn\text{-}^1H)$ = 44.8 Hz), 7.40–7.32 (m, 6H, H-3* and H-4*), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 175.79 [C9], 168.78 [C7], 159.08 [C1], 135.76 [C11], 131.97 [C13], 131.30 [C6], 130.66 [C3], 124.52 [C10], 123.54 [C2], 119.94 [C8], 118.71 [C12], 117.52 [C4], 116.07 [C5], 21.00 [C7′]; Sn-Ph: 138.47 (C-1*) ($J(^{119/117}Sn\text{-}^{13}C)$ = 958.0 Hz), 136.67 (C-2*) ($^2J(^{119/117}Sn\text{-}^{13}C)$ = 54.3 Hz), 129.63 (C-4*) ($^3J(^{119/117}Sn\text{-}^{13}C)$ = 16.4 Hz), 128.64 (C-3*) ($^4J(^{119/117}Sn\text{-}^{13}C)$ = 85.9 Hz), ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −320.40, ppm.

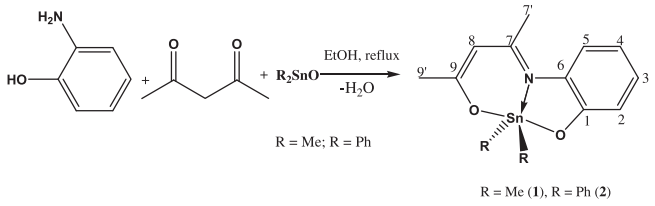


(a) H2L1 (b) H2L2 (R' = H) and H2L3 (R' = CH_3)

Ligands used in this study



Scheme 1.



Scheme 2.

*2.5.5. Synthesis of 6, 10, 12, 12-tetramethyl-11, 13-dioxa-5-aza-12-stanna-dibenzo [a,e] cyclononene [**Me_2SnL3**] (**5**)*

Dark bottle green crystals of **5** were obtained from ethanol. Yield: 55%; m.p.; 94–96 °C. *Anal.* Calc. for $C_{17}H_{19}NO_2Sn$: C, 52.62; H, 4.93; N, 3.60. Found: C, 52.13; H, 4.46; N, 3.29%. IR (KBr pellets, cm^{-1}): 3056, 1597 ($\nu_{C=N}$), 1521, 1462, 1433, 1326, 1284, 1182, 851 776, 750, 731 (ν_{Sn-C}), 565(ν_{Sn-O}), 524 (ν_{Sn-N}). ^1H NMR ($CDCl_3$, δ_H): Ligand skeleton: 7.58 (d (8.0 Hz), 1H, H13); 7.30 (d (8.0 Hz), 1H, H11), 7.16 (dd (7.4 Hz), 1H, H4), 7.08 (d (8.0 Hz), 1H, H2), 6.88 (d (8.0 Hz), 1H, H5), 6.69 (dt, 2H, H3 and H12), 2.79 (s, 3H, H7′), 2.18 (s, 3H, H10′); Sn-Me (^2J ($^{119}Sn\text{-}^1H$) = 38.6 Hz): 0.60 (s, 6H), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 177.20 [C9], 168.36 [C7], 160.71 [C1], 137.31 [C11], 134.01 [C13], 133.64 [C6], 130.90 [C3], 130.02 [C10], 125.00 [C2], 120.73 [C8], 119.95 [C12], 118.43 [C4], 117.49 [C5], 22.25 [C7′] and 17.17 [C-10′); Sn-Me (^1J ($^{119}Sn\text{-}^{13}C$) = 1272.2 Hz): −0.001 ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −137.63, ppm.

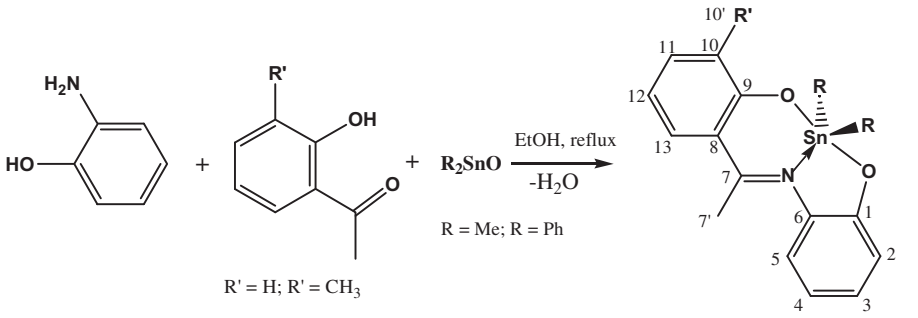
*2.5.6. Synthesis of 6, 10-dimethyl-12, 12-diphenyl-11, 13-dioxa-5-aza-12-stanna-dibenzo [a,e] cyclononene [**Ph_2SnL3**](**6**)*

Bottle green colored crystals of compound **6** was obtained from ethanol. Yield: 70%; m.p.; 138–140 °C. *Anal.* Calc. for $C_{27}H_{23}NO_2Sn$: C, 63.31; H, 4.52; N, 3.60. Found: C, 62.97; H, 4.01; N, 3.22%. IR (KBr pellets, cm^{-1}): 3049, 1587, 1572 ($\nu_{C=N}$), 1529, 1466, 1429, 1286, 1191, 835, 745, 731, 698, (ν_{Sn-C}), 529 (ν_{Sn-O}), 451 (ν_{Sn-N}). ^1H NMR ($CDCl_3$, δ_H): Ligand skeleton: 7.48 (d (8.0 Hz), 1H, H13); 7.17–7.06 (m, 3H, H2, H4 and H11), 6.98 (d (8.0 Hz), 2H and H5), 6.65 (dd (7.2 Hz), 2H, H3 and H12), 2.77 (s, 3H, H7′), 2.47 (s, 3H, H10′); Sn-Ph: 7.83–7.61 (m, 4H, H-2*) ($^3J(^{119/117}Sn\text{-}^1H)$ = 46.8 Hz), 7.41–7.33 (m, 6H, H-3* and H-4*), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 176.13 [C9], 167.10 [C7], 159.10 [C1], 137.27 [C11], 132.12 [C13], 132.00 [C6], 129.50 [C3], 128.92 [C10], 123.47 [C2], 119.08 [C8], 118.63 [C12], 116.96 [C4], 116.06 [C5], 21.31 [C7′] and 17.17 [C-10′); Sn-Ph: 138.65 (C-1*) ($J(^{119/117}Sn\text{-}^{13}C)$ = 959.8.0 Hz), 136.67 (C-2*) ($^2J(^{119/117}Sn\text{-}^{13}C)$ = 56.2 Hz), 130.29 (C-4*) ($^3J(^{119/117}Sn\text{-}^{13}C)$ = 16.7 Hz), 128.67 (C-3*) ($^4J(^{119/117}Sn\text{-}^{13}C)$ = 86.2 Hz), ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −319.46, ppm.

3. Results and discussion

3.1. Synthetic aspect

The 2-(3-hydroxy-1-methyl-but-2-enylideneamino)-phenol (**H2L1**) was prepared by condensing acetyl acetone with *o*-aminophenol in ethanol, whereas ligands H2L2 and H2L3 were obtained *in situ*. The preparation of diorganotin(IV) complexes of type R_2SnL followed the procedure involving 1:1:1 stoichiometric addition of *ortho*-aminophenol, diorganotin(IV) oxide (R_2SnO; R = Me or Ph), and substituted ketones (acetyl acetone, 2′-hydroxyacetophenone or 2-hydroxy-3-methylacetophenone) to ethanol (see Schemes 1–3). The resulting mixture was maintained at reflux for 6 h to give the products **1**–**6** in 50%–70% yield. The obtaining of **1** to **6** compounds in pure crystalline form was accomplished either by slow evaporation of the reaction solvent reaching the precipitation point or by crystallization done using suitable solvents. The compounds were obtained as shiny green, non-hygroscopic, air-stable crystalline solids. They are soluble in all common organic



Scheme 3.

solvents. The structural elucidation of **1**–**6** were accomplished by IR, ^{1}H, ^{13}C, ^{119}Sn NMR, elemental analyses and single crystal X-ray crystallography for the ligand **H2L1** and complexes **1**, **3** and **4**.

3.2. Spectroscopic characterization

The ligand H2L1 can exist in the *keto-enamine* (I) and *enol-imine* (II) tautomeric forms [42], as shown in Scheme 4. The tautomeric form (I) was found to be prominent in the solid state, where the phenolic proton migrates to the near by imine N-atom [see Fig. 1 for crystal structure]. This is also evident in the IR spectrum, where a medium intensity band at around 3372 cm^{-1} was detected due to ν_{NH} vibration along with the IR bands due to ν_{OH} centered at approximately 3007 cm^{-1} of the free ligand which disappears in the complexes **1** and **2**, indicating that the two oxygen atoms are attached to the tin atom. The IR spectra of **1** to **6** showed diagnostically important bands for the C═N fragment between 1562 and 1602 cm^{-1}. Also, the Sn–C, Sn–O and Sn←N bands were observed in the range 606–777, 516–558 [43–45], and 446–457 cm^{-1} correspondingly.

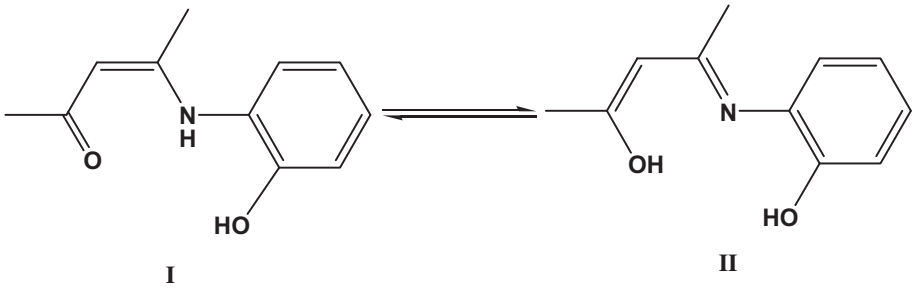
The ^{1}H and ^{13}C NMR data of **H2L1** and complexes **1**–**6** are given in the experimental section. The ^{1}H and ^{13}C NMR signals were assigned by the use of homonuclear correlated spectroscopy (COSY), heteronuclear single–quantum correlation (HSQC), heteronuclear multiple bond connectivity (HMBC) and distortion less enhancement by polarization transfer (DEPT) experiments. The conclusions drawn from the ligand (H2L1) assignments were then subsequently extrapolated to complexes, especially **1** and **2**, owing to their data similarity and it was also possible to detect all protons and carbon signals for compounds **1**–**6**. The ^{1}H NMR integration values (see Experimental) were consistent with the formulation of products. The ^{13}C NMR spectra of the ligand and Sn-R skeletons displayed the expected carbon signals in all cases; also, the assignment of the phenyl tin moiety is straight forward from the multiplicity patterns and resonance intensities. The difference in the chemical shift (*i.e.* Δ) of corresponding protons and carbons between the free ligand and the organotin complexes is evidence of the existence of the formation of complexes in solution. The ^{2}J (^{119}Sn-^{1}H) coupling constant value (36–39 Hz) for the dimethyltin (IV) complexes (**1**, **3** and **5**) were in agreement with the values reported earlier for dimethyltin(IV) complexes containing O_2-donor ligand [46]. For all compounds the determination of almost all the ^{n}J (^{119}Sn-^{13}C), $n = 2$–4 was feasible. The missing of some couplings was related to overlapping of the signals as well as the magnitude of the coupling, in some other cases simply they were not observed in the stated experimental conditions.

The structure of complex **4** is disordered due to which the bond between C24–N1 is not connected. However, the IR, ^{1}H and ^{13}C NMR spectral studies of complex **4** confirms the formulation of the product with complete condensed ligand. In the IR and ^{1}H NMR spectra, no band or signals are obtained due to the presence of NH_2 group, which further confirms complete formation of the condensed ligand.

The ^{119}Sn NMR chemical shifts of the diorganotin(IV) complexes (**1**–**6**) obtained in non-coordinating ($CDCl_3$) solvent are listed in the experimental section. The dimethyltin(IV) complexes (**1**, **3** and **5**) in $CDCl_3$ exhibit a single sharp ^{119}Sn resonance in the range of −129–−139 ppm; whereas, in the diphenyltin(IV) complexes (**2**, **4** and **6**) from −307 to −320 ppm, indicative of penta-coordinated atoms [41,46–49]. These results testify that the monomeric structure with five-coordinate tin atom found in the solid state is retained in solution (Schemes 2 and 3).

3.3. X-ray crystallography

The results of the X-ray crystallographic studies on **H2L1** and compounds **1**, **3** and **4** were fully consistent with the other spectroscopic evidences presented above. Ligand **H2L1** (Fig. 1) and compounds **1**, **3** and **4** were successfully crystallized (Figs. 2–4) and the details of the collection data are presented in Table 1. The ligand



Scheme 4. The tautomeric equilibrium: *Keto-enamine* (I) and *enol-imine* (II) in **H2L1**.

Table 3
Selected bond lengths (Å) and angles (°) for complexes **1**, **3** and **4**.

1		**3**		**4**	
Bond lengths					
O(1)–Sn(1)	2.1027(19)	O(1)–Sn(1)	2.076(2)	O(1)–Sn(2)	2.061(8)
O(2)–Sn(1)	2.180(2)	O(2)–Sn(1)	2.119(18)	O(2)–Sn(2)	2.071(8)
N(1)–Sn(1)	2.168(2)	N(1)–Sn(1)	2.191(2)	N(1)–Sn(2)	2.182(13)
C(11)–Sn(1)	2.107(3)	C(16)–Sn(1)	2.113(3)	C(12)–Sn(2)	2.133(3)
C(10)–Sn(1)	2.111(3)	C(15)–Sn(1)	2.112(3)	C(18)–Sn(2)	2.162(3)
C(9)–O(2)	1.268(4)	C(2)–O(2)	1.336(3)	C(23)–O(2)	1.369(9)
C(1)–O(1)	1.332(3)	C(13)–O(1)	1.316(3)	C(26)–O(1)	1.301(8)
Bond angles					
O(1)–Sn(1)–C(11)	96.12(12)	O(1)–Sn(1)–C(16)	93.08(12)	O(1)–Sn(2)–C(12)	98.4(3)
O(1)–Sn(1)–C(10)	99.44(11)	O(1)–Sn(1)–C(15)	96.48(11)	O(1)–Sn(2)–C(18)	94.3(2)
C(11)–Sn(1)–C(10)	133.81(13)	C(16)–Sn(1)–C(15)	131.07(12)	C(12)–Sn(2)–C(18)	121.65(12)
O(1)–Sn(1)–O(2)	158.80(8)	O(1)–Sn(1)–O(2)	156.26(7)	O(1)–Sn(2)–O(2)	155.7(3)
C(11)–Sn(1)–O(2)	91.83(12)	C(16)–Sn(1)–O(2)	95.24(11)	C(12)–Sn(2)–O(2)	94.2(2)
C(10)–Sn(1)–O(2)	88.97(11)	C(15)–Sn(1)–O(2)	94.71(10)	C(18)–Sn(2)–O(2)	96.7(3)
O(1)–Sn(1)–N(1)	76.77(7)	O(1)–Sn(1)–N(1)	81.04(8)	O(1)–Sn(2)–N(1)	79.6(5)
C(11)–Sn(1)–N(1)	112.73(11)	C(16)–Sn(1)–N(1)	113.73(10)	C(12)–Sn(2)–N(1)	120.1(3)

H2L1′ crystallizes in the orthorhombic $P2_12_12_1$ space group. There are N1–H1…O2 intra-molecular hydrogen bonds between amine and carbonyl groups. The bond lengths and angles are given in Table 2.

Compounds **1**, **3** and **4** crystallized with TBP (trigonal bipyramidal) geometry surrounding tin atoms. The *O*, *N*, *O*- tridentate ligand places its two oxygen donating atoms in the axial positions, and the nitrogen atom occupies one equatorial positions. The two R groups attached to tin occupy the other two equatorial positions. In the crystal structure of compound **1**, there are two symmetry independent molecules in the asymmetric unit. The molecular structure of compound **4** is disordered due to which a bond between C24–N1 could not be located in the crystal structure. However, the formation of complex **4** was confirmed using other spectroscopic techniques (refer to Section 3.2).

The significant geometrical parameters are condensed in Table 3. The N(1)–Sn(1) bond distance for **1** is 2.16 Å, for **3** is 2.19 Å and 2.18 Å for N(1)–Sn(2) for **4**. The Sn(1)–O(1) bond distances for **1** and **3** are 2.10 Å and 2.07 Å, the bond distance for Sn(2)–O(1) for **4** is 2.06 Å respectively. Whereas, Sn(1)–O(2) for **1** and **3** and Sn(2)–O(2) for **4** distances are 2.18 Å, 2.11 Å and 2.07 Å respectively; the three sets of distances are within the range reported for penta-coordinated tin atom bearing two organic substituents [41,47–52]. The bond angles between both carbon and tin atoms (C–Sn–C) are 133.81° for **1**, 131.07° for **3** and 121.65° for **4** indicating TBP geometry surrounding the tin atoms. In general, these structures revealed very similar geometrical parameters as those reported in the literature.

4. Conclusions

Analyses of the molecular structure of complexes **1**, **3** and **4** shows that variation in the nature of the R group binding to tin atom and the ligand can have hardly any effect on the nature of coordination around the tin atom. This testifies that by changing R from methyl to bulkier phenyl group still maintains a penta-coordinated TBP geometry surrounding tin atom. The compounds were fully characterized using different spectroscopic techniques. In solution, the molecules show no tendency to form any kind of aggregate.

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Appendix. A. Supplementary material

CCDC- 765589 (H2L1), 765590 (**1**), 765591 (**3**) and 765592 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif..

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