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Synthesis and characterization of diorganotin(IV) complexes of Schiff bases with ONO-type donors and crystal structure of [*N*-(2-hydroxy-4-nitrophenyl)-3-ethoxysalicylideneiminato]diphenyltin(IV)†

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A series of neutral complexes, namely, [*N*-(2-hydroxy-4-nitrophenyl)-3-hydroxysalicylideneiminato]-diphenyltin(IV) (Ia), [*N*-(2-hydroxy-4-nitrophenyl)-3-methoxysalicylideneiminato]diphenyltin(IV) (IIa) and [*N*-(2-hydroxy-4-nitrophenyl)-3-ethoxysalicylideneiminato]diphenyltin(IV) (IIIa) were prepared by the reaction of diphenyltin dichloride on the corresponding Schiff bases. The Schiff bases were the reaction products of 2-hydroxy-4-nitroaniline and appropriate salicylaldehydes. All the compounds were characterized by elemental analysis, ^{1}H-NMR, ^{13}C-NMR, IR and mass spectroscopy. Compound IIIa was also characterized by single crystal X-ray diffraction and shows a C_2NO_2 coordination geometry nearly half-way between a trigonal bipyramidal and square pyramidal arrangement. In the solid state, $\pi - \pi$ interactions exist between the aniline fragments of neighbouring molecules. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: diorganotin(IV) complexes; tridentate Schiff base; spectroscopic studies; crystal structure; $\pi - \pi$ interactions

INTRODUCTION

In recent years, there has been much interest in the synthesis and structure of organotin(IV) complexes of anionic Schiff base ligands.[1–11] Organotin(IV) complexes have found applications in medicinal chemistry[10,12–14] and biotechnology.[15,16] For example, diorganotin(IV) complexes containing nitrogen donor ligands have attracted considerable attention in recent years due to their potential antitumour activity.[17–20] Recently, considerable research activity has been undertaken to generate new supramolecular entities having the desired structural network as a result of the self-assembling capability of metal ions due to their preference for different coordination geometry, choice of suitable ligands and intermolecular interactions such as hydrogen bonding and $\pi - \pi$ interaction.[21–24] Such species are of immense interest due to their physical properties and potential use as metal-based molecules, magnetic materials, optical and thermal switches, and probes for DNA structures.[25–27] Continuing our previous studies[28,29] here we report the synthesis and characterization of three *N*-salicylidene-2-hydroxyaniline-type, potentially tridentate ONO-donor Schiff bases. We also describe the synthesis, properties and solid-state structure of diphenyltin(IV) complexes of these Schiff base ligands. The structural formula for the ligands depicted in their Schiff base form is given in Scheme 1 with positional numbers.

The corresponding diphenyltin(IV) complexes with the formulas $(C_6H_5)_2Sn(OC_6H_3OHCH{=}NC_6H_3NO_2O)$ (**Ia**), (C_6

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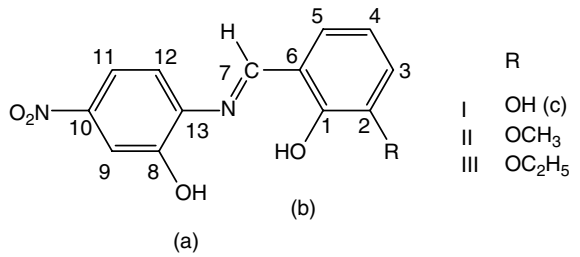

Scheme 1. The general framework of the Schiff bases.

$H_5)_2Sn(OC_6H_3OCH_3CH{=}NC_6H_3NO_2O)$ (**IIa**) and $(C_6H_5)_2Sn(OC_6H_3OC_2H_5CH{=}NC_6H_3NO_2O)$ (**IIIa**) were prepared by treating $(C_6H_5)_2SnCl_2$ with the corresponding ligands.

EXPERIMENTAL

Material and measurements

All chemicals and reagents were of reagent-grade quality. Diphenyltin dichloride, 2-hydroxy-4-nitroaniline, 3-hydroxysalicylaldehyde, 3-methoxysalicylaldehyde, 3-ethoxysalicylaldehyde and solvents were purchased from Aldrich and used without further purification.

The ^{1}H-NMR and ^{13}C-NMR spectra were obtained in deuterated DMSO and chloroform solvents on a Bruker-400 MHz Ultrashield NMR spectrometer with TMS as internal standard. The infrared spectra were recorded on a Mattson-1000 FTIR spectrophotometer using KBr pellets, in the range 4000–400 cm^{-1}. Bands were located by means of a microprocessor. Mass spectra were recorded on an Agilent 5973 MSD spectrometer with an electron impact quadropol analyser. Melting points were determined with in hot-stage Leica DM EP Polarizing Microscope System. Chemical analysis of C, H and N was determined using a LECO CHNS-932 elemental analyser.

Intensity data for **IIIa** were measured at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized MoK_α ($\lambda = 0.73071$ Å) radiation and using the $\omega - 2\theta$ scan technique. The structure was solved by direct-methods and full-matrix least-squares refinement was carried out on F^2 {anisotropic displacement parameters for non-hydrogen atoms, hydrogen atoms in calculated positions and a weighting scheme of form $w = 1/[\sigma^2(F_o^2) + (0.581P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$} using SHELXL-97.[30] Diagrams were drawn with ORTEPIII.[31] *Crystal data* for $C_{27}H_{22}N_2O_5Sn$: $M = 573.2$, monoclinic, $P2_1/a$, $a = 9.7101(14)$, $b = 15.1050(16)$, $c = 16.401(5)$ Å, $\beta = 92.625(16)$, $V = 2403.0(2)$ Å^3, $Z = 4$, R [2443 data with $I \geq 2\sigma(I)$; θ_{max} 26.3°] = 0.054, *wR* (all 4578 data) = 0.142. CCDC deposition number: 642278.

Preparation of the Schiff bases

Methanolic solutions of 2-hydroxy-4-nitroaniline and the appropriate salicylaldehyde (both 1.00 mmol in 20 ml) were mixed. The resulting solution was boiled under reflux for ca. 30 min, then the solution was concentrated on a rotary evaporator and cooled in an ice bath until crystallization was complete. The powdery product was filtered, dried and recrystallized from dichloromethane–methanol (1 : 1, v/v) mixture. The descriptions of the individual products were as follows.

*N-(2-hydroxy-4-nitrophenyl)-3-hydroxysalicylideneimine (**I**)*

Reddish-brown crystals, m.p.: 239–241 °C. Mass spectrum (EI) {*m*/*z* [assignment] (%)}: 274 $[M]^+$ (5.1). Elemental anal.: found C, 56.80; H, 3.59; N, 10.30%. Calcd for $C_{13}H_{10}N_2O_5$: C, 56.93; H, 3.65; N, 10.22%. IR (cm^{-1}): 3473 υ(O–H), ~3000 br, υ(O–H); 1631, υ(C=N). ^{1}H-NMR (DMSO-d6), δ: 6.78 (t, $^3J = 7.8$ Hz, 1H, H-4), 6.96 (dd, $^3J = 7.8$ Hz, $^4J = 1.5$ Hz, 1H, H-5), 7.11 (dd, $^3J = 7.8$ Hz, $^4J = 1.5$ Hz, 1H, H-3), 7.59 (dd, $^3J = 7.6$ Hz, $^4J = 1.5$ Hz, 1H, H-12), 7.75–7.85 (m, 2H, H-9 + H-11), 9.03 (s, 1H, H-7), 9.65 [s, 1H, (OH)c], 10.77 [s, 1H, (OH)a], 13.30 [s, 1H, (OH)b]. ^{13}C-NMR (DMSO-d6), δ: 111.23 (C-11), 115.59 (C-9), 119.12 (C-5), 119.80 (C-4), 120.14 (C-6), 120.75 (C-12), 123.34 (C-3), 142.90 (C-13), 146.03 (C-10), 146.61 (C-2), 150.20 (C-8), 151.51 (C-1), 165.31 (C-7).

*N-(2-hydroxy-4-nitrophenyl)-3-methoxysalicylideneimine (**II**)*

Reddish-black crystals, m.p.: 258–260 °C. Mass spectrum (EI) {*m*/*z* [assignment] (%)}: 288 $[M]^+$ (15.1). Elemental anal.: found C, 58.21; H, 4.03; N, 9.55%. Calcd for $C_{14}H_{12}N_2O_5$: C, 58.33; H, 4.17; N, 9.72%. IR (cm^{-1}): ~3000 br υ(O–H), 1635 s υ(C=N). ^{1}H-NMR (DMSO-d6), δ: 3.83 (s, 3H, OCH_3), 6.92 (t, $^3J = 7.9$ Hz, 1H, H-4), 7.17 (dd, $^3J = 7.9$ Hz, $^4J = 1.1$ Hz, 1H, H-5), 7.27 (dd, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, 1H, H-3), 7.57 (d, $^3J = 8.7$ Hz, 1H, H-12), 7.75–7.85 (m, 2H, H-9 + H-11), 9.03 (s, 1H, H-7), 10.78 [s, 1H, (OH)a], 13.24 [s, 1H, (OH)b]. ^{13}C-NMR (DMSO-d6), δ: 56.39 (OCH_3), 111.24 (C-11), 115.56 (C-9), 116.53 (C-5), 119.01 (C-4), 119.67 (C-6), 120.97 (C-12), 124.42 (C-3), 142.14 (C-13), 146.33 (C-10), 148.61 (C-2), 151.53 (C-8), 151.94 (C-1), 165.29 (C-7).

*N-(2-hydroxy-4-nitrophenyl)-3-ethoxysalicylideneimine (**III**)*

Reddish-black crystals, m.p.: 208–210 °C. Mass spectrum (EI) {*m*/*z* [assignment] (%)}: 302 $[M]^+$ (25.3). Elemental anal.: found C, 59.49; H, 4.58; N, 9.19%. Calcd for $C_{15}H_{14}N_2O_5$: C, 59.49; H, 4.58; N, 9.19%. Calcd for C, 59.60; H, 4.64; N, 9.27%. IR (cm^{-1}): ~3000 br υ(O–H), 1631 υ(C=N). ^{1}H-NMR (DMSO-d6), δ, 4.08 (q, $^3J = 7.0$ Hz, 2H, OCH_2), 1.35 (t, $^3J = 7.0$ Hz, 3H, CH_3), 6.89 (t, $^3J = 7.8$ Hz, 1H, H-4), 7.19 (d, $^3J = 8.0$ Hz, 1H, H-5), 7.25 (d, $^3J = 7.8$ Hz, 1H, H-3), 7.57 (d, $^3J = 9.4$ Hz, 1H, H-12), 7.77–8.00 (m, 2H, H-9 + H-11), 9.02 (s, 1H, H-7), 10.80 [s, 1H, (OH)a], 13.32 [s, 1H, (OH)b]. ^{13}C-NMR (DMSO-d6), δ: 15.23 (CH_3), 64.88 (OCH_2), 111.26 (C-11), 115.54 (C-9), 117.91 (C-5), 119.34 (C-4), 119.80 (C-6), 120.92 (C-12), 124.65 (C-3), 142.01 (C-13), 146.35 (C-10), 147.73 (C-2), 151.59 (C-8), 152.26 (C-1), 165.38 (C-7).

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Synthesis of the complexes

Diphenyltin(IV)dichloride, 1 mmol, dissolved in 2-propanol (25 ml) was added to a solution of the appropriate Schiff base (1.00 mmol, 25 ml) in the same solvent. When heating the reaction mixture under reflux, the colour of the solution changed from reddish black to red. The resulting red solution was left aside at room temperature for overnight. The red, powdery precipitate was filtered off and recrystallized from 2-propanol–dichloromethane (1:1, v/v) mixture. The descriptions of the individual complexes were as follows.

[N-(2-hydroxy-4-nitrophenyl)-3-hydroxysalicyli deneiminato]diphenyltin(IV) (***Ia***)

Red crystals, m.p.: >300 °C (no decomposition). Mass spectrum (EI) {*m/z* [assignment] (%)}: 546 $[M]^+$ (19.8). Elemental anal.: found C, 55.04; H, 3.27; N, 5.27%. Calcd for $C_{25}H_{18}N_2O_5Sn$: C, 55.15; H, 3.31; N, 5.15%. IR (cm^{-1}): ~3000 br υ(O–H), 1610s υ(C=N); ^{1}H-NMR ($CDCl_3$): δ: 6.84 (t, $^3J = 8.0$ Hz, 1H, H-4), 6.97 (dd, $^3J = 7.9$ Hz, $^4J = 1.4$ Hz, 1H, H-5), 7.02 (dd, $^3J = 7.8$ Hz, $^4J = 1.4$ Hz, 1H, H-3), 7.33–7.39 [m, 7H, *meta*-H + *para*-H ($SnPh_2$) + H-9], 7.40–7.80 [m, 6H, *ortho*-H ($SnPh_2$) + H-11 + H-12], 8.81[s, $^3J(^{117/119}Sn-^1H) = 53.0$ Hz, 1H, H-7], 9.69 [s, 1H, (OH)c]. ^{13}C-NMR ($CDCl_3$), δ: 111.47 (C-11), 113.25 (C-12), 116.18 (C-9), 118.00 (C-4), 118.34 (C-6), 120.85 (C-3), 126.69 (C-5), 128.45 [$^3J(^{117/119}Sn-^{13}C) = 89.0$ Hz, *meta*-C ($SnPh_2$)], 130.60 [$^4J(^{117/119}Sn-^{13}C) = 19.1$ Hz, *para*-C ($SnPh_2$)], 136.23 [$^2J(^{117/119}Sn-^{13}C) = 52.5$ Hz, *ortho*-C ($SnPh_2$)], 136.46 [ipso-C ($SnPh_2$)], 139.06 (C-13), 147.28 (C-10), 152.80 (C-2), 158.72 (C-8), 161.02 (C-1), 167.88 (C-7).

[N-(2-hydroxy-4-nitrophenyl)-3-methoxysalicylideneiminato]diphenyltin(IV) (***IIa***)

Red crystals, m.p.: 228–230 °C. Mass spectrum (EI) {*m/z* [assignment] (%)}: 560 $[M]^+$ (58.3). Elemental anal.: found C, 55.80; H, 3.45; N, 5.15%. Calcd for $C_{26}H_{20}N_2O_5Sn$: C, 55.91; H, 3.58; N, 5.02%. IR (cm^{-1}): 1615s υ(C=N). ^{1}H-NMR ($CDCl_3$), δ: 4.03 (s, 3H, OCH_3), 6.78 (t, $^3J = 7.9$ Hz, 1H, H-4), 6.93 (dd, $^3J = 8.0$ Hz, $^4J = 1.3$ Hz, 1H, H-5), 7.12 (dd, $^3J = 7.8$ Hz, $^4J = 1.3$ Hz, 1H, H-3), 7.42–7.47 [m, 7H, *meta*-H + *para*-H ($SnPh_2$) + H-9], 7.62 (dd, $^3J = 8.9$ Hz, $^4J = 2.5$ Hz, 1H, H-11), 7.84–8.04 [m, $^3J(^{117/119}Sn-^1H) = 88.0$ Hz, 5H, *ortho*-H ($SnPh_2$) + H-12], 8.76 [s, $^3J(^{117/119}Sn-^1H) = 49.5$ Hz, 1H, H-7]. ^{13}C-NMR ($CDCl_3$), δ: 56.54 (OCH_3), 111.88 (C-11), 113.79 (C-12), 114.93 (C-9), 117.42 (C-4), 117.64 (C-6), 118.18 (C-3), 126.94 (C-5), 128.91 [$^3J(^{117/119}Sn-^{13}C) = 90.2$ Hz, *meta*-C ($SnPh_2$)], 130.66 [$^4J(^{117/119}Sn-^{13}C) = 19.5$ Hz, *para*-C ($SnPh_2$)], 136.47 [$^2J(^{117/119}Sn-^{13}C) = 53.6$ *Hz*, *ortho*-C ($SnPh_2$)], 136.94 [ipso-C ($SnPh_2$)], 138.61 (C-13), 148.53 (C-10), 152.29 (C-2), 158.97 (C-8), 161.75 (C-1), 164.57 (C-7).

[N-(2-hydroxy-4-nitrophenyl)-3-ethoxysalicylideneiminato]diphenyltin(IV) (***IIIa***)

Red crystals, m.p.: 226–229 °C. Mass spectrum (EI) {*m/z* [assignment] (%)}: 574 $[M]^+$ (98.0). Elemental anal.: found C, 56.41; H, 3.72; N, 4.95%. Calcd for $C_{27}H_{22}N_2O_5Sn$: C, 56.54; H, 3.84; N, 4.89%. IR (cm^{-1}): 1600s υ(C=N). ^{1}H-NMR ($CDCl_3$), δ: 1.59 (t, $^3J = 7.0$ Hz, 3H, CH_3), 4.24 (q, $^3J = 7.0$ Hz, 2H, OCH_2), 6.75 (t, $^3J = 7.9$ Hz, 1H, H-4), 6.92 (dd, $^3J = 8.1$ Hz, $^4J = 1.4$ Hz, 1H, H-5), 7.11 (dd, $^3J = 7.7$ Hz, $^4J = 1.4$ Hz, 1H, H-3), 7.39–7.49 [m, 7H, *meta*-H + *para*-H ($SnPh_2$) + H-9], 7.62 (dd, $^3J = 8.9$ Hz, $^4J = 2.5$ Hz, 1H, H-11), 7.86–8.10 [m, $^3J(^{117/119}Sn-^1H) = 93.0$ Hz, 5H, *ortho*-H ($SnPh_2$) + H-12], 8.74 [s, $^3J(^{117/119}Sn-^1H) = 52.4$ Hz, 1H, H-7]. ^{13}C-NMR ($CDCl_3$), δ: 15.08 (CH_3), 65.06 (OCH_2), 111.93 (C-11), 113.74 (C-12), 114.93 (C-9), 117.48 (C-4), 117.88 (C-6), 120.26 (C-3), 127.15 (C-5), 128.88 [$^3J(^{117/119}Sn-^{13}C) = 86.7$ Hz, *meta*-C ($SnPh_2$)], 130.64 [$^4J(^{117/119}Sn-^{13}C) = 17.4$ Hz, *para*-C ($SnPh_2$)], 136.49 [$^2J(^{117/119}Sn-^{13}C) = 56.2$ Hz, *ortho*-C ($SnPh_2$)], 136.99 [ipso-C ($SnPh_2$)], 138.71 (C-13), 148.49 (C-10), 151.45 (C-2), 158.91 (C-8), 162.11 (C-1), 164.57 (C-7).

RESULTS AND DISCUSSION

Single crystal structure of IIIa

The crystal structure of [*N*-(2-hydroxy-4-nitrophenyl)-3-ethoxysalicylideneiminato] diphenyltin(IV), was elucidated by single crystal X-ray diffraction. The ORTEP diagram including atom-numbering scheme, is illustrated in Fig. 1 and selected bond lengths and angles are given in Table 1.

The coordination around the tin atom is defined by the ipso-carbon atoms of the phenyl groups, two oxygen atoms and an imino-N atom. To quantify the extent of distortion from the ideal trigonal bipyramidal (TBP) geometry towards the square pyramidal, the trigonal index, τ, was computed.[32,33] The τ-value is defined as $\tau = (\beta - \alpha)/60$, α and β being the two largest donor–metal–donor angles in the five coordinated environment. For a perfectly square pyramidal (SP) geometry, τ should be equal to zero, while it becomes unity for a perfect trigonal bipyramidal geometry. For the complex **IIIa,** $\tau = 0.49$, and consequently the coordination topology should be regarded as nearly half-way between TBP and SP geometries.

Table 1. Selected geometric parameters (Å, deg)

Sn–O1	2.072(3)	O3–C14	1.423(4)
Sn–O2	2.082(3)	O4–N2	1.210(5)
Sn–N1	2.202(3)	O5–N2	1.209(5)
Sn–C16	2.105(3)	N1–C7	1.303(4)
Sn–C22	2.129(3)	N1–C13	1.411(4)
O1–C1	1.321(4)	N2–C10	1.466(4)
O2–C8	1.338(4)	C9–C10	1.378(5)
O1–Sn–O2	158.32(19)	N1–Sn–C22	122.7(2)
O1–Sn–N1	82.2(2)	C16–Sn–C22	129.2(3)
O1–Sn–C22	94.9(3)	Sn–O1–C1	128.4(5)
O2–Sn–C16	97.2(2)	Sn–O2–C8	114.1(4)
O2–Sn–C22	92.9(3)	Sn–C16–C17	121.0(6)
N1–Sn–C16	108.1(2)	Sn–C16–C21	121.8(6)

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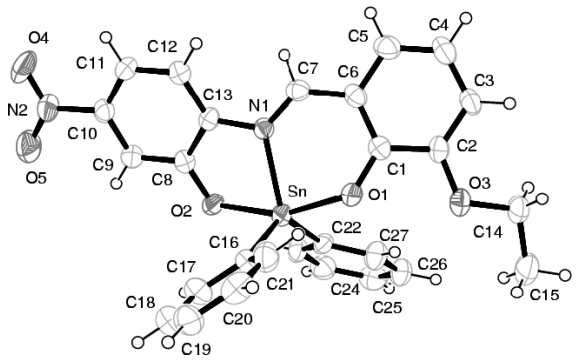

Figure 1. The molecular structure of **IIIa** showing the atom-numbering scheme. The displacement ellipsoids are plotted at the 50% probability level.

Five- and six-membered rings form upon chelation of the Sn atom to the ligands. The organic part of the five-membered ring is nearly planar [the torsion angle, O2–C8–C13–N1: −1.8(3)°], but the tin atom is out of this plane as indicated by the torsion angles, Sn–O2–C8–C13, 19.2(2)° and N1–Sn–O2–C8, −20.3(2)°. The six-membered ring is puckered with the torsion angles reaching up to 37.3(3)°.

The Sn–N, Sn–O, Sn–C bond distances and O–Sn–N bite angles in the coordination environment are comparable to those reported for similar diphenyltin(IV) complexes.[34–37] However, the Sn–N1 and C=N bond lengths reported for the diphenyltin(IV)[2-hydroxy-*N*-(2-hydroxybenzylidene)-aniline] complex, $[(C_6H_5)_2SnSAB]$, which has the same skeletal framework but no substituents on the aromatic rings[3] appear to be remarkably different. In the compound $[(C_6H_5)_2SnSAB]$, Sn–N1 and C13–N1 bond lengths are 2.241(13) and 1.553(19) Å, respectively, longer than the values [2.202(3) and 1.411(4) Å] in **IIIa**. By contrast, the C=N bond is apparently shorter in $[(C_6H_5)_2SnSAB]$ {the value is reported as 1.13(2) Å which is unrealistically short owing to disorder in that region of the molecule but is indicative of a strong C=N bond} compared with 1.303(4) Å in **IIIa**. This indicates that the substitution of the nitro group on C10 forces the aromatic ring to take a partially quinoid structure, with shorter C13–N1 and longer C7–N1 bond distances, respectively. Obviously, this tautomerism imparts different donor character to the nitrogen atom; thereby a shorter Sn–N1 distance appears in the structure of **IIIa**.

The four-atom C6, C7, N1, C13 plane across the imino double bond is planar. Within the ligand, the two phenyl ring planes are twisted in opposite directions from the four-atom imino plane. The dihedral angle between the planes through two phenyl rings is 26.3(3)°.

The partial packing diagram of **IIIa**, Fig. 2, indicates that the two aniline moieties located in successive strata are involved in a $\pi - \pi$ interactions. The interplanar and centroid-to-centroid distances between the aniline rings are 3.527(4) and 3.734(4) Å, respectively and the slip angle is 19.1(2)°. These values are comparable with those reported for similar structures in the literature.[21,38]

Spectroscopic studies

Diphenyltin complexes (**Ia** and **IIa**) were characterized by their elemental analysis and by the comparison of their ^{1}H, ^{13}C NMR, IR and mass spectral data with those of **IIIa**.

Because of the low solubility in $CDCl_3$, the NMR spectra of the Schiff bases were made in deuterated DMSO. The NMR spectra of the organotin(IV) complexes were recorded in $CDCl_3$. Two-dimensional COSY homonuclear, HETCOR and HMBC heteronuclear correlation techniques were made use of for signal assignments. The ^{1}H NMR and ^{13}C NMR data for the ligands and their tin(IV) complexes were summarized in the Experimental section.

In the ^{1}H-NMR spectra of the ligands, the singlet at 9.02–9.03 ppm belongs to the azomethine proton. This is in agreement with the literature values.[28,29,39–41] The Schiff bases are apparently in the phenol–imine tautomeric form as the azomethine proton in a quinoid structure is known to exhibit a three-bond coupling to the NH proton.[39–45] The lack of such coupling in our case indicates that the phenol–imine tautomer predominates.

The ^{1}H-NMR spectra of all the complexes are of similar overall appearance, pointing to the fact that the coordination of the ligands does not change from one to another. That is, the structure of **IIIa** elucidated by X-ray diffraction may also be applied to the other complexes. Some of the general features are summarized below.

The ^{1}H-NMR signal of the azomethine proton of the complexes appears at 8.74–8.81 ppm, which means 0.22–0.28 ppm highfield shift when compared with the corresponding Schiff base. These values are in agreement with the literature[35,46,47] on similar structures. The $^3J(^{117/119}Sn-^1H)$ coupling (53–55 Hz) due to NMR-active Sn isotopes is visible and this is a strong indication to the ligation of azomethine nitrogen to Sn atom. The extent of coupling is comparable with the literature.[6,35,49] The coupling constants of both the NMR-active Sn isotopes, ^{117}Sn (7.61%) and ^{119}Sn (8.58%), seem to be approximately equal, because there is only one doublet situated on the two sides of the central azomethine

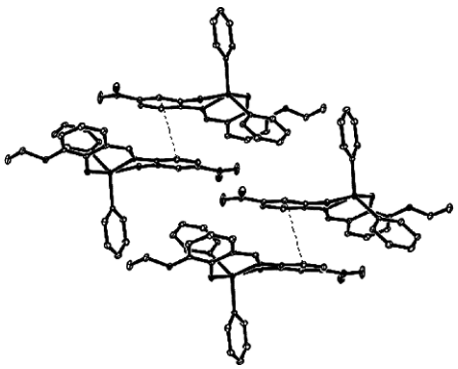

Figure 2. The geometry of $\pi - \pi$ intermolecular interactions.

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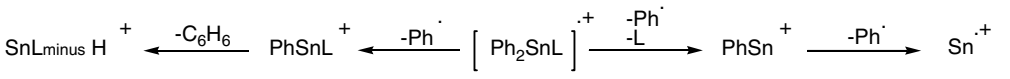

	m/z (%)	m/z (%)	m/z (%)	m/z 197 (%)	m/z 120 (%)
Ia	391 (19.7)	469 (12.9)	546 (19.8)	(34.8)	(15.4)
IIa	405 (15.0)	483 (41.7)	560 (58.3)	(16.7)	(11.3)
IIIa	419 (21.5)	497 (40.0)	574 (98.0)	(100.0)	(31.0)

Scheme 2. Proposed fragmentation pattern for complexes (L: dianionic Schiff base).

singlet. This singlet is obviously due to those isotopomers bearing the NMR-inactive Sn isotopes. Indeed, the integral area of the doublet was measured to be around 15% of the total signal, reflecting the approximate total abundance of the two isotopes, ^{117}Sn and ^{119}Sn. No appreciable difference in the chemical shifts of the CH═N proton signals, due to the existence of various tin isotopes, is observed.

On the ^{1}H-NMR spectra of the ligands, the signal at 10.77–10.80 ppm is assigned to the $(OH)_a$ proton on the aniline moiety. The signals at 13.24–13.32 ppm belong to the OH group of the salicylaldehyde moiety (downfield shift due to intramolecular hydrogen bonding).[43] OH-proton signals disappear in the ^{1}H-NMR spectra of the corresponding Sn(IV) complexes, indicating the engagement of phenolic O atoms in complexations.

For the ligands and complexes, the signals of H-3 and H-5 protons are confirmed by two-dimensional heteronuclear-correlated NMR technique (2D ^{13}C–^{1}H HMBC) in addition to two-dimensional ^{1}H–^{1}H COSY experiments. Other protons in the phenyl rings are found in their normal δ range.[48] The spectra of the complexes display additional signals due to phenyl protons ($(C_6H_5)_2$Sn moiety) that appear in the 7.39–8.10 ppm range.

Discrete ^{13}C signals for all the individual carbons are identified in the ^{13}C-NMR spectra. In the ^{13}C-NMR spectra of Schiff bases and tin(IV) complexes, the signals of the azomethine carbon (C-7) appears in the ranges 165.29–165.38 and 164.57–167.88 ppm, respectively. Comparing the ^{13}C NMR spectra of the free ligands and the tin complexes, the most important difference appears to occur for the C–O carbons numbered C1 and C8 (Scheme 1), namely, a downfield chemical shift ($\Delta\delta \approx 10$ ppm)[49] indicating the formation of covalent Sn–O bonds. The $^1J(^{117/119}\text{Sn}-^{13}\text{C})$ couplings are not observed in the complexes. Probably the satellites are lost in the background noise, for the ipso-carbon gives rise to a weak signal. The $^nJ(^{117/119}\text{Sn}-^{13}\text{C})$ coupling constants ($n = 2, 3, 4$) of the diorganotin(IV) compounds are consistent with those generally observed for five-coordinate tin species.[35,50]

In the solid-state IR spectra of the Schiff bases, the bands due to intra- and inter-molecularly hydrogen bonded O–H stretching vibrations seem to have overlapped with the aromatic C–H region.[51] Therefore these bands do not seem to be diagnostic in deciding whether or not the O–H groups are involved in coordination. The strong ν(CH═N) bands of the ligands at 1631–1635 cm^{-1} shift to lower frequencies (1600–1615 cm^{-1}) in the complexes, indicating the coordination of the imino-nitrogen to the diorganotin(IV) moiety. The FIR region in the spectra of the complexes is difficult to analyse as the same region is not so clear in the spectra of the ligands as to permit to ascribe individual bands to specific vibrations. Therefore the IR data relating to the coordination bonds mainly depend on literature knowledge[6] and therefore are tentative.

The diorganotin compounds were also characterized by mass spectrometry using electron impact ionization technique. The molecular ion peaks are observed at m/z 546, 560 and 574 for **Ia**–**IIIa**, respectively. The molecular ions and Sn-containing fragments display the natural abundance of the major Sn isotopes. The experimental isotopic distributions of all the Sn-containing fragment ions were compared with the theoretically calculated one and found in agreement with the theoretical relative abundances. As an example, the molecular ion peak with the characteristic tin isotopes of **IIIa** was measured (theoretical relative abundances in parentheses): m/z 570, 40.3% (40.7%); 571, 33.6% (33.5%); 572, 75.5% (75.4%); 573, 45.4% (45.5%); 574, 100% (100%); 575, 28.9% (28.8%); 576, 17.7% (17.5%); 577, 4.3% (4.4%); 578, 16.7% (16.1%); 579, 4.3% (4.5%). Other peaks corresponding to fragments of the parent molecular ions due to loss of various groups are given in Scheme 2. The fragmentation pattern is in agreement with the literature reports.[7,18,52]

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