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Re-visiting of 5-[(*E*)-2-(aryl)-1-diazenyl]-quinolin-8-ol with tweaking of Sn–Ph groups: Synthesis, spectroscopic characterization and X-ray crystallography

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Abstract

Reactions of sodium 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olates (LH, where the aryl group is an R-substituted phenyl ring such that for L^1H: R = H; L^2H: R = 2′-CH_3; L^3H: R = 3′-CH_3; L^4H: R = 4′-CH_3; L^5H: R = 4′-OCH_3 and L^6H: R = 4′-OC_2H_5) with Ph_3SnCl in a 1:1 molar ratio yielded complexes of composition Ph_3SnL. The complexes have been characterized by ^1H, ^{13}C, ^{119}Sn NMR, IR and ^{119m}Sn Mössbauer spectroscopic techniques in combination with elemental analyses. The crystal structures of $Ph_3SnL^1 \cdot 0.5C_6H_6$ (**1**), Ph_3SnL^2 (**2**), $Ph_3SnL^5 \cdot C_6H_6$ (**5**) and $Ph_3SnL^6 \cdot 0.5C_6H_6$ (**6**) were determined. The results of the X-ray studies indicated that the benzene solvated compounds **1**, **5** and **6** are distorted square pyramid, with one of the phenyl C atoms in the apex while the ligand arrangement around central Sn atom in **2** is distorted trigonal-bipyramidal, with a phenyl C and the oxinato N atoms in axial positions.

Keywords: Triphenyltin; 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olates; NMR; Mössbauer; Crystal structure

1. Introduction

The chemical, biological and pharmaceutical properties of organotin(IV) complexes have been extensively studied and in this perspective, the structure-antitumour activity relations have also been studied for di- and triorganotin(IV) oxinates and thiooxinates [1]. Because of the important applications, the structures of this class of compounds have received considerable attention. The ability of organotin(IV) moieties to react with quinolin-8-ol is well established and classical examples with R_2SnLX (five-coordinate), R_2SnL_2 (six-coordinate) and $RSnL_3$ (seven-coordinate) (R = alkyl or aryl, L = quinolin-8-olate and X = halogen or isothiocyanate) are known [2–5]. Although most of the conventional techniques, namely ^{119}Sn Mössbauer [2,6], IR [2,3], UV [7] and NMR [3,8] spectroscopic techniques, have been employed as aids in structural investigations, the geometry of certain of these organotin(IV) quinolin-8-olate(s) was unclear. Consequently, a few organotin(IV) quinolin-8-olates have been investigated by X-ray crystallography. The diorganotin(IV) bis(quinolin-8-olate) group of compounds has received most attention and an X-ray crystal studies of R_2SnL_2, for e.g., R = Me [9], *p*-ClPh and *p*-MePh [10], ^{n}Bu and Cl [11], ^{n}Bu [12], ^{t}Bu [12] and Ph [13], showed a highly distorted octahedral molecule with bidentate quinolin-8-olate groups and essentially *cis*-organo groups. In addition, structural information on other two types, viz., R_2SnLX (e.g., R = $EtCO_2Me$ and X = Cl) [14] and $RSnL_3$ (R = *p*-ClPh)

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[15] are also available. Recently, we have also reported six diorganotin(IV) complexes of the type R_2SnL_2 (R = Ph or Bz; L = 5-[(*E*)-2-(aryl)-1-diazenyl]-quinolin-8-olate) [16,17] and these complexes also conform to the same distorted *cis*-octahedral geometry as described for diorganotin(IV) bis(quinolin-8-olate). On the other hand, there has been some disagreement concerning the structure of Ph_3SnL, both four- [18] and five-coordinate [19] structures having been assigned on the basis of ^{119}Sn Mössbauer from the magnitude of the quadrupole splitting. Finally it was concluded that Ph_3SnL is five-coordinate where two phenyl groups and a nitrogen atom are in equatorial positions while a phenyl group and an oxygen atom from the quinolin-8-olate ligand takes up the apical positions [19]. Nevertheless, there is no report on structural characterization of Ph_3SnL by X-ray crystallographic technique.

The present paper reports the results of extending the organotin(IV) work, particularly Ph_3Sn, with the stable and bulkier 5-[(*E*)-2-(aryl)-1-diazenyl]-quinolin-8-olate ligand system (Fig. 1) which is aimed at the evaluation of the bonding mode(s) of the triphenyltin(IV) complexes from a detailed analysis of their IR, NMR (^{1}H, ^{13}C, ^{119}Sn) and ^{119m}Sn Mössbauer spectra. Further, in the course of studies in this area, a series of triphenyltin(IV) complexes provided X-ray quality crystals which have been chosen in the quest to determine the complete stereochemical analyses of the triphenyltin(IV) complexes. The crystal and molecular structures of triphenyltin(IV) complexes, viz., $Ph_3SnL^1 \cdot 0.5C_6H_6$ (**1**), Ph_3SnL^2 (**2**), $Ph_3SnL^5 \cdot C_6H_6$ (**5**) and $Ph_3SnL^6 \cdot 0.5C_6H_6$ (**6**) are also reported.

2. Experimental

2.1. Materials

Ph_3SnCl, Oxine (Merck) and the substituted anilines (reagent grade) were used without further purification. The solvents used in the reactions were of AR grade and dried using standard procedures. Benzene was distilled from sodium benzophenone ketyl.

2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin–Elmer 2400 series **II** instrument. IR spectra in the range 4000–400 cm^{-1} were obtained on a Nicolet Impact 410 FT-IR spectrophotometer with samples investigated as KBr discs. The ^{1}H, ^{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, respectively. The ^{1}H, ^{13}C and ^{119}Sn chemical shifts were referenced to Me_4Si set at 0.00 ppm, $CDCl_3$ set at 77.0 ppm and Me_4Sn set at 0.00 ppm, respectively. Mössbauer spectra were recorded on solid samples at liquid nitrogen temperature by using a conventional constant acceleration spectrometer, coupled with a multichannel analyser (a.e.n., Ponteranica (BG), Italy) equipped with a cryostat Cryo (RIAL, Parma, Italy). A $Ca^{119}SnO_3$ Mössbauer source, 10 mCi (from Ritverc, St. Petersburg, Russia) moving at room temperature with constant acceleration in a triangular waveform was used. The velocity calibration was made using a ^{57}Co Mössbauer source, 10 mCi, and an iron foil as absorber (from Ritverc, St Petersburg, Russia).

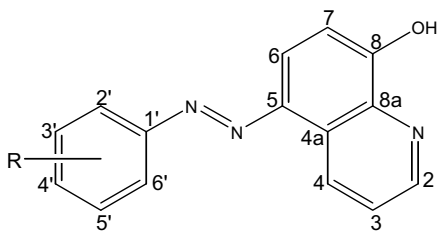


Fig. 1. Generic structure of the ligand (*Abbreviations*. L^1H: R = H; L^2H: R = 2′-CH_3; L^3H: R = 3′-CH_3; L^4H: R = 4′-CH_3; L^5H: R = 4′-OCH_3; L^6H: R = 4′-OC_2H_5, where H represents hydroxyl proton).

2.3. Synthesis of 5-[(*E*)-2-(aryl)-1-(diazenyl)quinolin-8-ols

The 5-[(*E*)-2-(aryl)-1-(diazenyl)]quinolin-8-ols, viz., L^1H to L^6H were prepared by the method described earlier [16,17].

2.4. Synthesis of triphenyltin(IV) complexes

A typical method is described below.

2.4.1. Synthesis of $Ph_3SnL^1 \cdot 0.5C_6H_6$ (*1*)

A methanolic solution of sodium methoxide (generated in situ from 0.046 g, 2.00 mmol of Na in 15 ml anhydrous methanol) was added drop-wise into a stirred hot anhydrous benzene solution (40 ml) containing L^1H (0.5 g, 2.00 mmol). After complete addition, a precipitate appears and the stirring continued for 15 min. To this reaction mixture, an anhydrous benzene solution (15 ml) of Ph_3SnCl (0.77 g, 1.99 mmol) was added drop-wise which resulted in the disappearance of the precipitate. The reaction mixture was refluxed for 3 h and filtered to remove NaCl. The filtrate was collected and the solvent was removed under reduced pressure. The resultant residue was washed several times with hot hexane, dried in vacuo, dissolved in benzene and filtered to remove any suspended particles. The filtrate was concentrated and precipitated with hexane. The crude product was recrystallized from a mixture of benzene and hexane (v/v 1:1), which upon evaporation at room temperature afforded maroon colored crystalline product. Yield: 0.47 g (39.1%), m.p. 115–116 °C. Anal. Calc. for $C_{36}H_{28}N_3OSn$: C, 67.84; H, 4.42; N, 6.59. Found: C, 67.80; H, 4.32; N, 6.51%. IR (cm^{-1}): 1250 ν(C(aryl)O). ^{1}H NMR ($CDCl_3$, 400.13 MHz); δH: ligand skeleton: 9.45 [dd, 1H, H4], 8.26 [dd, 1H, H2], 8.22 [d, 1H, H6], 7.95 [d, 2H, H2′ and H6′], 7.66 [m, 1H, H3], 7.52 [m, 2H, H3′ and H5′], 7.45 [d, 1H, H4′], 7.26 [d, 1H, H7]; Sn–Ph skeleton: 7.59 [m, 6H, H2*], 7.35 [m, 9H, H3* and H4*] ppm. ^{13}C NMR ($CDCl_3$, 100.62 MHz); δC: 160.3 [C8],

153.4 [C1′], 145.1 [C2], 137.5 [C5], 136.9 [C8a], 135.2 [C4], 128.5 [C3′ and C5′], 128.3 [C4′], 127.8 [C4a], 122.5 [C3, C2′ and C6′], 118.2 [C6], 114.1 [C-7]; Sn–Ph skeleton: 144.6 [C1*], 136.2 [C2*], 130.0 [C4*], 129.0 [C3*] ppm. ^{119}Sn NMR ($CDCl_3$, 149.18 MHz) δSn: −183.9 ppm. ^{119}Sn Mössbauer: $\delta = 1.09$, $\Delta = 1.99$, $\Gamma_1 = 0.82$, $\Gamma_2 = 0.82$ mm s^{-1}.

The other triphenyltin(IV) complexes (**2**–**6**) were prepared by reacting Ph_3SnCl with the appropriate ligand (L^2H–L^6H) by following an analogous procedure. The characterization data and spectroscopic data of the complexes are given below.

2.4.2. Synthesis of Ph_3SnL^2 (**2**)

Orange crystals of **2** were obtained from a mixture of benzene and hexane mixture (v/v 1:1). Yield: 0.57 g (49.1%), m.p. 182–183 °C. Anal. Calc. for $C_{37}H_{27}N_3OSn$: C, 66.67; H, 4.44; N, 6.89. Found: C, 66.60; H, 4.34; N, 6.79%. IR (cm^{-1}): 1249 ν(C(aryl)O). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δH: ligand skeleton: 9.45 [dd, 1H, H4], 8.26 [dd, 1H, H2], 8.18 [d, 1H, H6], 7.72 [d, 1H, H6′], 7.55 [m, 2H, H3 and H5′], 7.35 [m, 2H, H3′ and H4′], 7.26 [d, 1H and H7], 2.75 [s, 3H, CH3]; Sn–Ph skeleton: 7.69 [m, 6H, H2*], 7.35 [m, 9H, H3* and H4*] ppm. ^{13}C NMR ($CDCl_3$, 100.62 MHz); δC: 160.0 [C8], 151.4 [C1′], 145.0 [C2], 137.5 [C5], 137.4 [C2′], 135.3 [C8a], 131.2 [C4], 130.0 [C3′], 128.4 [C4′], 127.7 [C4a], 126.3 [C5′], 122.5 [C3], 118.5 [C6′], 115.5 [C6], 114.0 [C7], 17.7 [CH3]: Sn–Ph skeleton: 144.7 [C1*], 136.1 [C2*], 129.0 [C4*], 128.4 [C3*] ppm. ^{119}Sn NMR ($CDCl_3$, 149.18 MHz) δSn: −184.5 ppm. ^{119}Sn Mössbauer: $\delta = 1.11$, $\Delta = 2.12$, $\Gamma_1 = 0.83$, $\Gamma_2 = 0.83$ mm s^{-1}.

2.4.3. Synthesis of Ph_3SnL^3 (**3**)

Orange crystalline product of **3** was obtained from a mixture of benzene and hexane (v/v 1:1). Yield: 0.33 g (28.1%). m.p. 152–153 °C. Anal. Calc. for $C_{34}H_{27}N_3OSn$: C, 66.67; H, 4.44; N, 6.89. Found: C, 66.57; H, 4.34; N, 7.01%. IR (cm^{-1}): 1252 ν(C(aryl)O). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δH: ligand skeleton: 9.47 [dd, 1H, H4], 8.28 [dd, 1H, H2], 8.18 [d, 1H, H6], 7.77 [m, 2H, H2′ and H6′], 7.53 [m, 1H, H3], 7.35 [m, 2H, H4′ and H5′], 7.27 [d, 1H, H7], 2.48 [s, 3H, CH3]; Sn–Ph skeleton: 7.59 [m, 6H, H2*], 7.35 [m, 9H, H3* and H4*] ppm. ^{13}C NMR ($CDCl_3$, 100.62 MHz); δC: 160.1 [C8], 153.5 [C1′], 145.1 [C2], 138.9 [C5], 136.9 [C3′], 135.3 [C8a], 130.9 [C4], 128.8 [C4′], 128.1 [C5′], 127.7 [C4a], 123.0 [C2′], 122.4 [C3], 119.9 [C6′], 118.2 [C6], 114.1 [C-7], 21.4 [CH3]; Sn–Ph skeleton: 144.7 [C1*], 136.2 [C2*], 129.0 [C4*], 128.4 [C3*] ppm. ^{119}Sn NMR ($CDCl_3$, 149.18 MHz) δSn: −184.3 ppm. ^{119}Sn Mössbauer: $\delta = 1.11$, $\Delta = 2.03$, $\Gamma_1 = 0.83$, $\Gamma_2 = 0.83$ mm s^{-1}.

2.4.4. Synthesis of Ph_3SnL^4 (**4**)

Maroon crystals of **4** were obtained from a mixture of benzene and hexane (v/v 2:1). Yield: 0.47 g (40.5%). m.p. 154–155 °C. Anal. Calc. for $C_{34}H_{27}N_3OSn$: C, 66.67; H, 4.44; N, 6.89. Found: C, 66.66; H, 4.34; N, 6.80%. IR (cm^{-1}): 1250 ν(C(aryl)O). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δH: ligand skeleton: 9.43 [dd, 1H, H4], 8.26 [dd, 1H, H2], 8.19 [d, 1H, H6], 7.87 [d, 2H, H2′ and H6′], 7.51 [m, 1H, H3], 7.35 [m, 2H, H3′ and H5′], 7.25 [d, 1H, H7], 2.48 [s, 3H, CH3]; Sn–Ph skeleton: 7.59 [m, 6H, H2*], 7.35 [m, 9H, H3* and H4*] ppm. ^{13}C NMR ($CDCl_3$ 100.62 MHz); δC: 159.9 [C8], 151.5 [C1′], 145.0 [C2], 143.4 [C4′], 140.5 [C5], 135.3 [C8a], 128.4 [C3′ and C5′], 128.3 [C4], 127.7 [C4a], 122.5 [C2′ and C6′], 122.4 [C3], 117.9 [C6], 114.1 [C7], 21.4 [CH3]: Sn–Ph skeleton: 144.7 [C1*], 136.2 [C2*], 129.7 [C4*], 129.0 [C3*] ppm. ^{119}Sn NMR ($CDCl_3$, 149.18 MHz) δSn: −184.1 ppm. ^{119}Sn Mössbauer: $\delta = 1.08$, $\Delta = 1.99$, $\Gamma_1 = 0.80$, $\Gamma_2 = 0.80$ mm s^{-1}.

2.4.5. Synthesis of $Ph_3SnL^5 \cdot C_6H_6$ (**5**)

Orange crystals of **5** were obtained from a mixture of benzene and hexane (v/v 1:1). Yield: 0.35 g (51.4%). m.p. 96–97 °C. Anal. Calc. for $C_{40}H_{33}N_3O_2Sn$: C, 68.01; H, 4.71; N, 5.94. Found: C, 68.10; H, 4.61; N, 5.90%. IR (cm^{-1}): 1247 ν(C(aryl)O). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δH: ligand skeleton: 9.40 [dd, 1H, H4], 8.28 [dd, 1H, H2], 8.17 [d, 1H, H6], 7.85 [m, 2H, H2′ and H6′], 7.55 [m, 2H, H3′ and H5′], 7.51 [m, 1H, H3], 7.10 [m, 1H, H7], 3.95 [s, 3H, OCH3]; Sn–Ph skeleton: 7.58 [m, 6H, H2*], 7.55 [m, 9H, H3* and H4*] ppm. ^{13}C NMR ($CDCl_3$, 100.62 MHz); δC: 160.1 [C8], 160.0 [C1′], 150.0 [C4′], 146.6 [C2], 137.2 [C8a], 130.1 [C4], 129.9 [C4a], 129.6 [C3], 126.2 [C3′ and C5′], 123.9 [C6], 119.6 [C7], 116.0 [C2′ and C6′], 57.2 [OCH3]: Sn–Ph skeleton: 146.6 [C1*], 136.1 [C2*], 130.6 [C4*], 130.3 [C3*] ppm. ^{119}Sn NMR ($CDCl_3$, 149.18 MHz) δSn: −186.1 ppm. ^{119}Sn Mössbauer: $\delta = 1.06$, $\Delta = 1.92$, $\Gamma_1 = 0.89$, $\Gamma_2 = 0.89$ mm s^{-1}.

2.4.6. Synthesis of $Ph_3SnL^6 \cdot 0.5\ C_6H_6$ (**6**)

Orange crystals of **6** were obtained from a mixture of benzene and hexane (1:1 v/v). Yield: 0.45 g (54.1%). m.p. 88–90 °C. Anal. Calc. for $C_{38}H_{32}N_3O_2Sn$: C, 67.00; H, 4.73; N, 6.16. Found: C, 67.10; H, 4.63; N, 6.15%. IR (cm^{-1}): 1254 ν(C(aryl)O). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δH: ligand skeleton: 9.42 [dd, 1H, H4], 9.25 [dd, 1H, H2], 8.18 [d, 1H, H6], 7.92 [m, 2H, H2′ and H6′], 7.51 [m, 1H, H3], 7.33 [m, 1H, H7], 7.10 [m, 2H, H3′ and H5′], 4.10 [q, 2H, OCH_2CH_3], 1.5 [t, 3H, OCH_2CH_3]; Sn–Ph skeleton: 7.55 [m, 6H, H2*], 7.33 [m, 9H, H3* and H4*] ppm. ^{13}C NMR ($CDCl_3$, 100.62 MHz); δC: 160.9 [C8], 159.7 [C1′], 147.7 [C2], 145.0 [C4′], 143.4 [C5], 136.5 [C8a], 135.3 [C4], 128.5 [C3′ and C5′], 127.6 [C4a], 124.3 [C2′ and C6′], 122.3 [C3], 117.6 [C6], 114.8 [C7], 63.8 [OCH_2CH_3], 14.8 [OCH_2CH_3]; Sn–Ph skeleton: 144.8 [C1*], 136.2 [C2*], 129.0 [C4*], 128.5 [C3*] ppm. ^{119}Sn NMR ($CDCl_3$, 149.18 MHz) δSn: −185.4 ppm. ^{119}Sn Mössbauer: $\delta = 1.04$, $\Delta = 1.95$, $\Gamma_1 = 0.86$, $\Gamma_2 = 0.86$ mm s^{-1}.

2.5. X-ray crystallography

Crystals of the triphenyltin(IV) compounds **1**, **2**, **5** and **6** suitable for single crystal X-ray structure determination were obtained from slow evaporation of benzene/hexane (1:1 v/v) solutions. Intensity data were collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), either on a Nonius CAD4 diffractometer (for **1**) or a Bruker D8 goniometer equipped with a SMART APEX CCD detector (for **2**, **5** and **6**). Crystal data, data collection parameters and convergence results are listed in Table 1. Empirical absorption corrections based on a multiscan approach [20] or, for the CAD4 data, on azimuthal scans [21] were applied to the data sets before averaging over symmetry-related reflections. The structures were solved by direct methods with the help of the SHELXS-97 program [22] and refined on reflection intensities F^2 using SHELXL-97 [23]. In the final least-squares refinements, all non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions and included as riding on the corresponding atoms. Compounds **1** and **6** represent hemisolvates, both with a benzene molecule located on a crystallographic inversion center and the complex molecules in general position, whereas **5** contains one benzene per complex molecule. Further details on the structures are available as supplementary material in CIF format, see below.

3. Results and discussion

3.1. Syntheses

The triphenyltin(IV) complexes (**1**–**6**) were prepared by reacting the sodium salts of the ligands ($L^{1-2}Na$, generated in situ from Na and anhydrous methanol) with the Ph_3SnCl in 1:1 molar ratios in anhydrous benzene by following procedure similar to that described by Clark et al. [24]. The work-up details and characterization data for the complexes are described in Section 2.4. The complexes could be isolated by fractional crystallization with high purity in moderate yield (28–54%). The complexes are crystalline in nature, stable in air and soluble in all common organic solvents.

$$LNa + Ph_3SnCl \xrightarrow[\text{Conditions:Stir/reflux, 3 h}]{\text{Benzene}} Ph_3SnL + NaCl$$

3.2. IR spectra

The IR spectra of the ligands, L^1H–L^6H are reported in Refs. [16,17] while their triphenyltin(IV) complexes, **1**–**6** are reported in Section 2.4. The ν(OH) in L^1H–L^6H occurs at around 3380 cm^{-1} as broad band which is assigned due to the presence of intermolecular H-bonding interactions involving the O–H–N bonds which is found to be absent

Table 1
Crystal data, data collection parameters and convergence results for compounds **1**, **2**, **5** and **6**

	1	**2**	**5**	**6**
Empirical formula	$C_{36}H_{28}N_3OSn$	$C_{34}H_{27}N_3OSn$	$C_{40}H_{33}N_3O_2Sn$	$C_{38}H_{32}N_3O_2Sn$
Formula weight	637.30	612.28	706.39	681.36
Crystal size (mm)	0.50 × 0.50 × 0.10	0.31 × 0.14 × 0.12	0.34 × 0.25 × 0.04	0.52 × 0.26 × 0.04
Crystal shape	Plate	Rod	Plate	Plate
Temperature (K)	293(2)	293(2)	110(2)	203(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6623(9)	31.563(5)	8.873(8)	8.5573(8)
b (Å)	11.0909(11)	9.1928(13)	11.296(11)	9.1331(9)
c (Å)	14.3096(8)	22.763(3)	16.636(16)	20.895(2)
α (°)	79.645(6)		97.57(2)	99.741(2)
β (°)	86.971(6)	119.404(2)	99.25(2)	90.912(2)
γ (°)	82.161(8)		96.55(2)	103.737(2)
V (Å^3)	1493.8(2)	5753.9(14)	1616(3)	1560.8(3)
Z	2	8	2	2
D_c (g cm^{-3})	1.417	1.414	1.452	1.450
μ (mm^{-1})	0.888	0.919	0.831	0.857
Transmission factors (min, max)	0.665, 0.916	0.760, 0.900	0.765, 0.967	0.660, 0.970
$2\theta_{max}$ (°)	28.0	30.1	27.3	27.1
Reflections measured	14372	42002	25900	23907
Independent reflections; R_{int}	7189; 0.047	8288; 0.054	7211; 0.063	6792; 0.087
Reflections with $I > 2\sigma(I)$	5050	6766	6392	5145
Number of parameters	370	353	416	398
Number of restraints	0	0	0	1
$R(F)$ [$I > 2\sigma(I)$ reflections]	0.041	0.050	0.036	0.061
$wR(F^2)$ (all data)	0.083	0.114	0.088	0.133
Goodness-of-fit (F^2)	1.01	1.09	1.02	1.10
$\Delta\rho$ max, min (e Å^{-3})	0.39, −0.30	0.88, −0.66	0.93, −0.42	0.74, −1.26

in the triphenyltin complexes, **1**–**6**, confirming bonding through the O-atom of the ligand [16,17]. A strong band at around 1235 cm^{-1} in the ligands is found to be shifted to around 1250 cm^{-1} in the complexes, is assigned to the ν(C(aryl)–O) (i.e. C8–O).

3.3. ^{119}Sn Mössbauer spectra

The ^{119}Sn Mössbauer data, i.e. isomer shift (δ), quadrupole splittings (Δ) and the line widths at half-peak height (Γ) for the triphenyltin complexes (**1**–**6**) are given in Section 2.4. In general, the complexes displayed a doublet with δ and Δ values in the range 1.04–1.11 and 1.92–2.12 mm s^{-1}, respectively. The δ values found (1.04–1.11 mm s^{-1}) are typical of quadrivalent organotin derivatives [25]. The Ph_3SnL_2 (L = electronegative ligands, e.g., O, N and halogen) type compounds may exists in one of the three isomeric forms (**I**–**III**, Fig. 2) and they can be readily distinguished by the Δ values.

On the basis of point charge treatment, the calculated Δ values for five-coordinate trigonal bipyramid Ph_3SnL_2 type compounds were ca. 1.65 mm s^{-1}, 2.85 mm s^{-1} and 3.28 mm s^{-1} and these were assigned for the *facial*- (**I**), *equatorial*- (**III**) and *meridional*-R_3 (**II**) geometries, respectively [26]. The observed Mössbauer Δ values for complexes (**1**–**6**) are in the range 1.92–2.12 mm s^{-1} and the values are greater than for the *facial*-structure (**I**) and smaller for the *equatorial*-structure (**III**). Thus, it may be inferred that the complexes (**1**–**6**) adopt preferably a structure (**I**) and somewhat larger values reflects the possible distortion from the ideal proposed configuration. The Δ value 1.75 mm s^{-1} for Ph_3SnOx (Ox = quinolin-8-olate) [2,19,27] also falls at the limit specified for *facial*-R_3 trigonal-bipyramidal geometry [25]. The larger Δ values observed in the triphenyltin 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olate (**1**–**6**) compared to Ph_3SnOx could be ascribed to the coordination of bulky 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olate ligand and agrees well with the value 1.99 mm s^{-1} reported for tribenzyltin(IV) complex $(C_6H_5CH_2)_3Sn(SPyO)$ (HSPyO: 2-mercaptopyridine) where a square pyramidal structure was reported [25]. The extent of distortion from *facial*-trigonal-bipyramidal geometry is clearly evident from the Mössbauer data and this has been clearly reflected from the results of diffraction studies on the triphenyltin 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olate (**1**, **2**, **5** and **6**) (see Section 3.4).

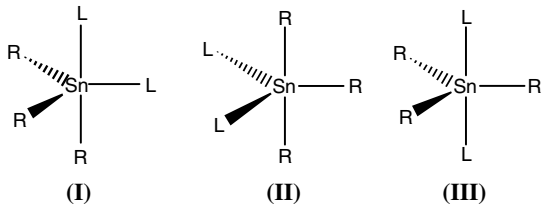


Fig. 2. Possible isomeric forms (**I**–**III**) in Ph_3SnL_2 type compounds.

3.4. Crystal structures

Compounds **1**, **2**, **5** and **6** represent the first examples of structurally characterized triphenyltin(IV) compounds containing the ligand quinolin-8-olate. In all the complexes, a single 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olate ligand chelates the triphenyltin moiety, as illustrated in Figs. 3–6. Selected geometric parameters are collected in Table 2. Compounds **1** and **6** crystallize as benzene hemisolvates while **5** includes one molecule of benzene per complex. Five-coordination of the central Sn atom suggests structural variability which is indeed encountered. The results of the X-ray studies indicate that the benzene solvated compounds **1**, **5** and **6** are closely related with respect to the coordination of the central Sn atom. In these cases, the coordination polyhedron around Sn is best described as a distorted square pyramid, with one of the phenyl C atoms in the apex. In contrast, the ligand arrangement around central Sn atom in **2** is distorted trigonal-bipyramidal, with a phenyl C and the oxinato N in axial positions. A synopsis of the Sn coordination in all four compounds (**1**, **2**, **5** and **6**) is shown in Fig. 7.

The above interpretation is corroborated by the fact that the Sn–N bond in **2**, the only compound with a N-bonded

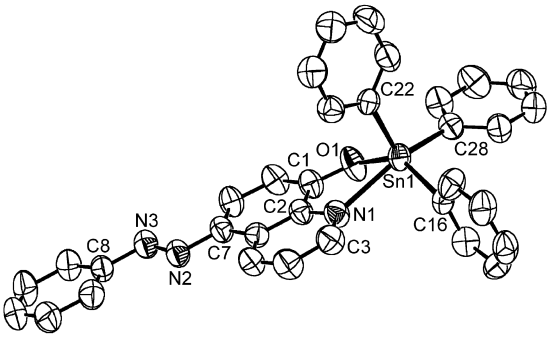


Fig. 3. Displacement ellipsoid plot (50% probability ellipsoids) of the molecular structure of **1** with the atom-labelling scheme. Hydrogen atoms and the solvent molecule have been omitted for clarity.

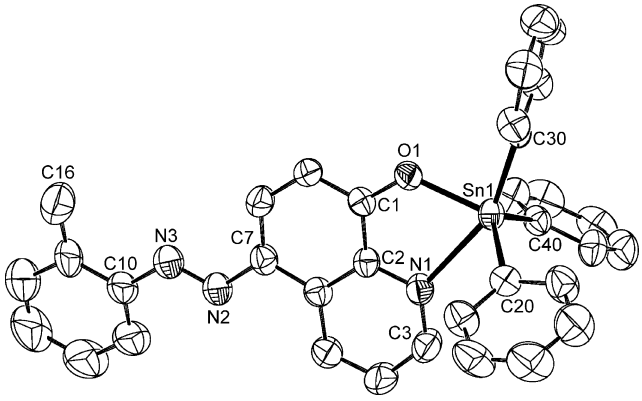


Fig. 4. The molecular structure of **2** with the atom-labelling scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

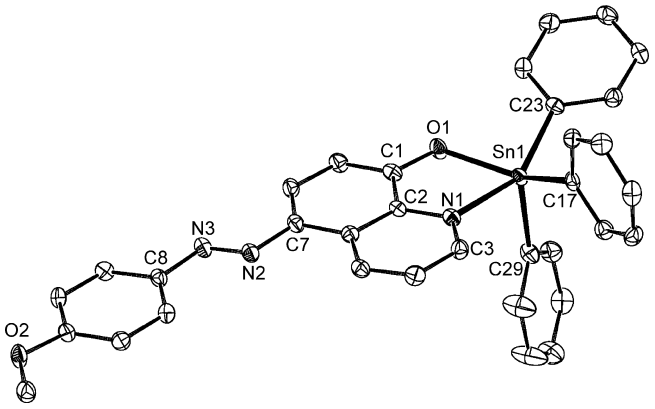


Fig. 5. The molecular structure of **5** with the atom-labelling scheme (50% probability ellipsoids). Hydrogen atoms and the solvent molecule have been omitted for clarity.

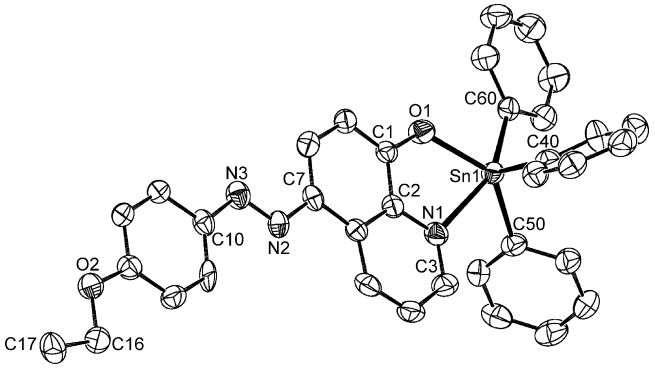


Fig. 6. The molecular structure of **6** with the atom-labelling scheme (50% probability ellipsoids). Hydrogen atoms and the solvent molecule have been omitted for clarity.

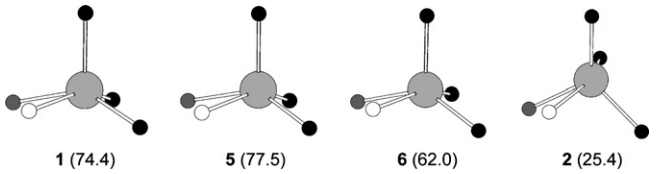


Fig. 7. Square-pyramidal (sp) Sn coordination in triphenyltin(IV) compounds **1**, **5** and **6** and trigonal-bipyramidal (tbp) coordination in **2**; the numbers in parentheses denote the percentage of Berry pseudorotation from tbp to sp. [28,29]. Color code: Sn, light grey; N, white; O, dark grey; C, black.

ligand in an axial position, amounts to 2.528(2) Å and is significantly longer than the Sn–N distances in the other three compounds **1**, **5** and **6** (min 2.409(4), max 2.438(3) Å). In line with this argument, the axial Sn–C bond in **2** (2.170(3) Å) is longer than the equatorial Sn–C bonds (2.130(3) and 2.134(3) Å). Distorted trigonal-bipyramidal coordination geometries have been described by Strutchkov et al. [30] for two symmetrically independent molecules of a thioxinate. In this report, the longest Sn–C bond is also associated with the ligand in axial position. With respect to intermolecular interactions, solid **1**, **2**, **5** and **6** represent typical molecular crystals without exceptionally short contacts. Intermolecular distances significantly shorter than the sum of the van der Waals radii only occur between H and alkoxy O atoms in **5** and **6** and amount to ca. 2.45 Å.

3.5. Solution ^{1}H, ^{13}C, ^{119}Sn NMR spectra

Further characterization was accomplished from the NMR spectra of complexes **1**–**6** in order to obtain structural information in solution. The assignments of ^{1}H and ^{13}C NMR signals of $L^{1}H$–$L^{6}H$ were described earlier

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1**, **2**, **5** and **6**

1		**2**		**5**		**6**	
Sn(1)–O(1)	2.088(2)	Sn(1)–O(1)	2.063(2)	Sn(1)–O(1)	2.101(3)	Sn(1)–O(1)	2.072(4)
Sn(1)–N(1)	2.438(3)	Sn(1)–N(1)	2.528(2)	Sn(1)–N(1)	2.428(3)	Sn(1)–N(1)	2.409(4)
Sn(1)–C(22)	2.137(3)	Sn(1)–C(40)	2.130(3)	Sn(1)–C(23)	2.165(3)	Sn(1)–C(50)	2.159(6)
Sn(1)–C(28)	2.160(3)	Sn(1)–C(20)	2.134(3)	Sn(1)–C(17)	2.153(3)	Sn(1)–C(60)	2.160(6)
Sn(1)–C(16)	2.142(3)	Sn(1)–C(30)	2.170(3)	Sn(1)–C(29)	2.137(3)	Sn(1)–C(40)	2.153(6)
O(1)–C(1)	1.325(3)	O(1)–C(1)	1.329(3)	O(1)–C(1)	1.323(3)	O(1)–C(1)	1.338(6)
N(1)–C(2)	1.354(4)	N(1)–C(2)	1.357(4)	N(1)–C(2)	1.361(3)	N(1)–C(2)	1.360(7)
N(1)–C(3)	1.319(4)	N(1)–C(3)	1.321(4)	N(1)–C(3)	1.322(4)	N(1)–C (3)	1.319(7)
N(2)–N(3)	1.255(3)	N(2)–N(3)	1.251(4)	N(2)–N(3)	1.260(3)	N(2)–N(3)	1.268(6)
C(22)–Sn(1)–C(28)	109.17(12)	C(40)–Sn(1)–C(20)	119.84(11)	C(23)–Sn(1)–C(29)	110.39(12)	C(50)–Sn(1)–C(60)	101.1(2)
C(28)–Sn(1)–C(16)	102.30(12)	C(20)–Sn(1)–C(30)	103.67(11)	C(29)–Sn(1)–C(17)	108.70(12)	C(60)–Sn(1)–C(40)	106.80(2)
C(16)–Sn(1)–C(22)	108.46(11)	C(40)–Sn(1)–C(30)	107.99(11)	C(17)–Sn(1)–C(23)	103.03(12)	C(40)–Sn(1)–C(50)	112.0(2)
C(22)–Sn(1)–O(1)	104.36(10)	C(40)–Sn(1)–O(1)	111.44(10)	C(23)–Sn(1)–O(1)	88.79(10)	C(50)–Sn(1)–O(1)	136.65(19)
C(28)–Sn(1)–O(1)	87.82(10)	C(20)–Sn(1)–O(1)	120.22(10)	C(29)–Sn(1)–O(1)	103.62(11)	C(60)–Sn(1)–O(1)	87.36(18)
C(16)–Sn(1)–O(1)	139.87(12)	C(30)–Sn(1)–O(1)	86.82(9)	C(17)–Sn(1)–O(1)	138.66(9)	C(40)–Sn(1)–O(1)	105.71(18)
N(1)–Sn(1)–O(1)	71.23(8)	N(1)–Sn(1)–O(1)	70.47(8)	N(1)–Sn(1)–O(1)	71.39(8)	N(1)–Sn(1)–O(1)	71.90 (15)
N(1)–Sn(1)–C(22)	92.90(11)	N(1)–Sn(1)–C(40)	84.92(9)	N(1)–Sn(1)–C(23)	151.79(9)	N(1)–Sn(1)–C(50)	85.90(18)
N(1)–Sn(1)–C(28)	152.94(11)	N(1)–Sn(1)–C(20)	85.09(10)	N(1)–Sn(1)–C(29)	94.06(11)	N(1)–Sn(1)–C(60)	155.22(18)
N (1)–Sn(1)–C(16)	84.54(10)	N(1)–Sn(1)–C(30)	156.92(9)	N(1)–Sn(1)–C(17)	81.16(11)	N(1)–Sn(1)–C(40)	92.10(18)
C(7)–N(2)–N(3)–C(8)	179.7(3)	C(7)–N(2)–N(3)–C(10)	175.3(3)	C(7)–N(2)–N(3)–C(8)	179.7(2)	C(7)–N(2)–N(3)–C(10)	179.5(5)

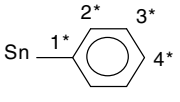
[16,17]. The conclusions drawn from the ligand assignments were then subsequently extrapolated to the complexes **1**–**6** owing to the data similarity.[1] The ^{1}H NMR integration values were completely consistent with the formulation of the products. The ^{1}H and ^{13}C NMR chemical shift assignment of the triphenyltin moiety is straight forward from the multiplicity pattern, resonance intensities and also by examining the $^{n}J(^{13}C–^{119/117}Sn)$ coupling constants [31,32]. In the ^{1}H and ^{13}C NMR spectra of the complexes, **1**–**6**, there is only one set of NMR signals for all the three phenyl groups (Sn–Ph) which provides evidence for the magnetic equivalence of the phenyls on the NMR time scale. This indicates that the predicted positions of the phenyl groups in solid state (see ^{119}Sn Mössbauer and the X-ray crystallography discussion, vide supra) is not retained in solution owing to axial-equatorial exchange. The chemical shifts $\delta(^{13}C)$ of the carbon atoms of the phenyl substituents (Sn–Ph) are not very sensitive to changes in the coordination of central tin atom. Nevertheless, the values $\delta(^{13}C(1^{*}))$, which are shifted mostly around 8–13 ppm downfield, in comparison with those in compounds having four-coordinate tin atom [33].

NMR spectral parameters (^{13}C, ^{15}N and ^{119}Sn (in solution) and ^{119}Sn CP MAS) of Ph_3SnOx have been investigated in great detail [34–37]. The results of ^{119}Sn CP MAS (in absence of X-ray diffraction data of Ph_3SnOx) and ^{119}Sn (solution) NMR spectra indicated that the solid state structure of triphenyltin(IV) quinolin-8-olate, i.e. five-coordinate structure, is retained in solution [37]. In view of this information, the results of ^{13}C and ^{119}Sn NMR have been utilized to provide structural evidence of the complexes (**1**–**6**) in solution. The value of the coupling constants $^{n}J(^{119}Sn–^{13}C(Sn–Ph))$ matches closely with the data for penta-coordinated Ph_3SnOx complex in $CDCl_3$ solution ($^{1}J = 633.1$, $^{2}J = 47.8$, $^{3}J = 62.5$ (Hz)) [34]. The triphenyltin(IV) complexes **1**–**6**, all display a sharp singlet in the range −184 to −186 ppm and the $\delta(^{119}Sn)$ chemical shifts lie inside the range delimited for five-coordinate triphenyltin(IV) compounds [33]. The $\delta(^{119}Sn)$ values are comparable with the shift observed for Ph_3SnOx (−190.1 ppm in $CDCl_3$ solution [33,36]). Thus, ^{119}Sn NMR data indicate that the complexes (**1**–**6**) remain five-coordinated and retain their connectivity (see Mössbauer and X-ray discussion) in solution.

4. Supplementary material

CCDC 664444, 664445, 664446 and 664447 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] Ligand numbering scheme as shown in Fig. 1 and numbering scheme for Sn–Ph skeleton as shown below:



Acknowledgements

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