

Dibenzyltin(IV) complexes of the 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olates: Synthesis and an investigation of structures by X-ray diffraction, solution and solid-state tin NMR, ^{119}Sn Mössbauer and electrospray ionization MS

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Abstract

A series of *cis*-bis{5-[(*E*)-2-(aryl)-1-diazenyl]quinolinolato}dibenzyltin(IV) complexes have been synthesized by reacting sodium salts of 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol (LH) and dibenzyltin dichloride. These complexes have been characterized by ^1H , ^{13}C , ^{119}Sn NMR, ESI-MS in solution and by IR and $^{119\text{m}}\text{Sn}$ Mössbauer, ^{117}Sn CP-MAS NMR spectroscopy in solid state. In addition, the structures of three of the dibenzyltin(IV) complexes, viz., $\text{Bz}_2\text{Sn}(\text{L}^2)_2$ (**2**), $\text{Bz}_2\text{Sn}(\text{L}^3)_2$ (**3**), and $\text{Bz}_2\text{Sn}(\text{L}^5)_2$ (**5**) (L = 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol: aryl = 4'-methylphenyl- (L^2H), 4'-methoxyphenyl- (L^3H) and 4'-bromophenyl- (L^5H)) were determined by single-crystal X-ray diffraction. In general, the complexes were found to adopt a distorted *cis*-octahedral arrangement around the tin atom in both solution and solid state.

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Keywords: 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol; Dibenzyltin(IV) complexes; Solution and solid-state tin NMR; ESI-MS; $^{119\text{m}}\text{Sn}$ Mössbauer; Crystal structures

1. Introduction

Recently, we have elucidated the X-ray structures of $\text{Ph}_2\text{Sn}(\text{Ox})_2$ (Ox = deprotonated quinolin-8-ol) [1] and three

cis-bis{5-[(*E*)-2-(aryl)-1-diazenyl]quinolinolato}diphenyltin(IV), $\text{Ph}_2\text{Sn}(\text{L})_2$ (aryl = phenyl, 4'-methylphenyl and 4'-bromophenyl) complexes [2]. The X-ray results for the complexes indicated a distorted *cis*-octahedral geometry where the phenyl ligands are *cis* to one another and *trans* to the nitrogen atoms of the oxinate ligands. The complexes retain their solid-state structures, in solution, as revealed by the ^{119}Sn NMR spectroscopic results. Based on the multinuclear NMR (^1H , ^{13}C , ^{15}N and ^{119}Sn) chemical shifts and coupling constants, e.g., $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ ($n = 1-5$), $J(^{119}\text{Sn},$

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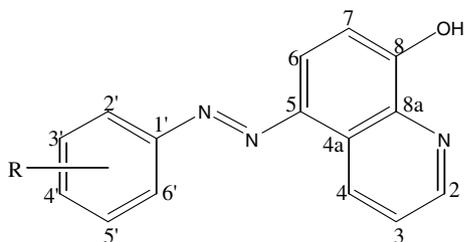


Fig. 1. Generic structure of the ligand (Abbreviations. L¹H, R = 3'-CH₃; L²H, R = 4'-CH₃; L³H, R = 4'-OCH₃; L⁴H, R = 4'-OC₂H₅; L⁵H, R = 4'-Br; L⁶H, R = 4'-Cl, where H represents hydroxyl proton).

¹⁵N) and (²J(¹⁵N, ¹H)), Holeček et al. have shown that in solutions of non-coordinating solvents, the organotin(IV) oxinates and thiooxinates exist as molecular chelates with a medium-to-strong Sn–N donor–acceptor bond [3–7]. The strength of the Sn–N bond depends on the nature and the number of organic substituents (bond strength generally increases with a decrease in the number of substituents and in the series phenyl ~vinyl > benzyl > *n*-butyl) as well as on the ligand composition [5–7]. Although, NMR spectroscopy is an important tool for investigating molecular structure in solution, however, the interpretation of chemical shifts and coupling constants, is generally based on X-ray crystal structure data and is consequently subject to uncertainties ranging from solvation to dynamic effects. Recently, we showed [8] that the solid-state tin NMR measurements on crystalline compounds can be used to deduce their structures. In view of this, a systematic approach was employed to determine the structures of several dibenzyltin(IV) complexes of 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol ligand system (Fig. 1) using ¹H, ¹³C, ¹¹⁹Sn NMR, ESI-MS, IR and ^{119m}Sn Mössbauer spectroscopic techniques in combination with solid-state ¹¹⁷Sn NMR and X-ray diffraction.

2. Experimental

2.1. Materials

Bz₂SnCl₂ (dibenzyltin dichloride) was prepared by the method reported earlier [9]. The solvents used 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 using a Perkin–Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm⁻¹ were obtained on a BOMEM DA-8 FT-IR spectrophotometer as KBr discs. The two-dimensional NMR experiments (see Section 3.4) for the ligands were performed on a Bruker Avance 500 spectrometer equipped with a triple (¹H/¹³C/broad band) 5 mm inverse probe operating at 500.13 and 125.76 MHz, respectively. For the organotin compounds, the ¹H, ¹³C and ¹¹⁹Sn NMR spectra were

recorded on a Bruker AMX 400 spectrometer and measured at 400.13, 100.62 and 149.18 MHz, respectively. The ¹H, ¹³C and ¹¹⁹Sn chemical shifts were referenced to Me₄Si set at 0.00 ppm, CDCl₃ set at 77.0 ppm and Me₄Sn set at 0.00 ppm, respectively. CP-MAS ¹¹⁷Sn spectra were recorded at 89.15 MHz on a Bruker Avance 250 spectrometer, equipped with a 4 or 7 mm MAS broadband probe. ¹¹⁷Sn was chosen instead of the more common ¹¹⁹Sn nucleus, since the latter is interfering with RF radiation from a local radio station. Spinning frequencies are chosen between 5 and 8 kHz. A contact time of 1 ms and a recycle delay of 2 s were employed. The chemical shift reference was set using (cyclo-C₆H₁₁)₄Sn (–97.35 ppm relative to (CH₃)₄Sn). The principle values of the ¹¹⁷Sn chemical shielding tensors were determined by fitting the intensities of the spinning side bands according to the Herzfeld–Berger formalism, using the 'dmfit' program (Massiot D. *dmfit program*; available at <http://crmht-europe.cnrs-orleans.fr>). Positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range *m/z* 50–1500. The samples were dissolved in acetonitrile and analyzed by direct infusion using a flow rate 5 μl/min. The selected precursor ions were further analyzed by MS/MS analyses under the following conditions: the isolation width *m/z* = 8, the collision amplitude in the range 0.7–1.0 V depending on the precursor ion stability, the ion source temperature 300 °C, the tuning parameter compound stability 100%, the flow rate and the pressure of nitrogen 4 l/min and 10 psi, respectively [10,11]. The Mössbauer spectra of the complexes in the solid state were recorded using a Model MS-900 (Ranger Scientific Co., Burleson, TX) spectrometer in the acceleration mode with a moving source geometry. A 10 mCi Ca ^{119m}SnO₃ source was used, and counts of 30,000 or more were accumulated for each spectrum. The spectra were measured at 80 K using a liquid-nitrogen cryostat (CRYO Industries of America, Inc., Salem, NH). The velocity was calibrated at ambient temperature using a composition of BaSnO₃ and tin foil (splitting 2.52 mm s⁻¹). The resultant spectra were analyzed using the Web Research software package (Web Research Co., Minneapolis, MN).

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

The 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ols, viz., L¹H, L²H, L⁴H, L⁵H were prepared by the method described earlier [2]. However, the other quinolinols, viz., L³H, L⁶H, were prepared analogously with the appropriate anilines and their analytical and spectroscopic data are presented below.

2.3.1. Preparation of 5-[(*E*)-2-(4-methoxyphenyl)-1-diazenyl]quinolin-8-ol (L³H)

Recrystallized from methanol to give a brownish yellow precipitate in 44.1% yield; m.p. 170–171 °C. Anal. Calc. for

$C_{16}H_{13}N_3O_2$: C, 68.75; H, 4.60; N, 15.05%. Found: C, 68.70; H, 4.70; N, 15.21%. 1H NMR ($CDCl_3$); δ_H : 9.29 [dd, 1H, H4], 8.87 [dd, 1H, H2], 8.02 [d, 1H, H6], 7.98 [m, 2H, H2' and H6'], 7.60 [m, 1H, H3], 7.27 [d, 1H, H7], 7.05 [m, 2H, H3' and H5'], 3.91 [s, 3H, CH_3] ppm. The signal for the phenol was exchanged due to the presence of water in the solvent. ^{13}C NMR ($CDCl_3$); δ_C : 161.9 [C8], 154.8 [C1'], 148.4 [C2], 147.5 [C4'], 140.2 [C5], 137.8 [C8a], 132.9 [C4], 127.1 [C4a], 124.6 [C3' and C5'], 122.6 [C3], 115.1 [C6], 114.3 [C2' and C6'], 109.9 [C7], 55.6 [CH_3] ppm.

2.3.2. Preparation of 5-[*(E)*-2-(4-chlorophenyl)-1-diazanyl]quinolin-8-ol (L^6H)

Recrystallized from a mixture of ethanol and benzene to give a yellowish brown precipitate in 59.1% yield; m.p. 220–221°C. Anal. Calc. for $C_{15}H_{10}ClN_3O$: C, 63.50; H, 3.50; N, 14.81%. Found: C, 63.40; H, 3.40; N, 14.86%. 1H NMR ($DMSO-d_6$); δ_H : 9.33 [dd, 1H, H4], 9.02 [dd, 1H, H2], 8.04 [d, 1H, H6], 8.04 [m, 2H, H2' and H6'], 7.79 [m, 1H, H3], 7.68 [m, 2H, H3' and H5'], 7.25 [d, 1H, H7] ppm. The signal for the phenol was exchanged due to the presence of water in the solvent. ^{13}C NMR ($DMSO-d_6$); δ_C : 157.8 [C8], 151.3 [C1'], 149.0 [C2], 138.8 [C4'], 138.0 [C5], 135.2 [C8a], 131.8 [C4], 129.5 [C3' and C5'], 127.5 [C4a], 124.1 [C2' and C6'], 123.3 [C3], 115.4 [C6], 111.6 [C7] ppm.

2.4. Synthesis of the dibenzyltin(IV) complexes

A typical method is described below.

2.4.1. Synthesis of $Bz_2Sn(L^1)_2$ (**1**)

A methanolic solution of sodium methoxide (generated in situ from 0.045 g, 1.95 mmol of Na in 15 ml anhydrous methanol) was added drop-wise into a stirred hot anhydrous benzene solution (45 ml) containing L^1H (0.5 g, 1.90 mmol). After complete addition, a precipitate appears and the stirring was continued for 15 min. To this reaction mixture, an anhydrous benzene solution (15 ml) of Bz_2SnCl_2 (0.35 g, 0.94 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 reduce pressure. The resultant residue was extracted into hexane and filtered while hot. The crude product was obtained after evaporation of the hexane. This was then recrystallized from a mixture of benzene–hexane (1:1), which upon slow evaporation afforded dark-red crystalline product. Yield: 0.37 g (33.9 %), m.p. 180–182°C. Anal. Found: C, 66.92; H, 4.64; N, 10.18%. Calc. for $C_{46}H_{38}N_6O_2Sn$: C, 66.99; H, 4.60; N, 10.24%. IR (cm^{-1}): 1248 $\nu(C(aryl)O)$. 1H NMR ($CDCl_3$); δ_H : Ligand skeleton: 9.12 [dd, 2H, H4], 8.10 [m, 4H, H2 and H6], 7.63 [m, 4H, H2' and H6'], 7.31 [m, 2H, H3], 7.20 [m, 4H, H4' and H5'], 7.09 [d, 2H, H7], 2.37 [s, 6H, CH_3]; Sn–Bz skeleton: 2.58 [d, 4H, H1*], 6.73 [m, 4H, H4*], 6.63 [m, 6H, H3* and H5*], ppm. ^{13}C NMR ($CDCl_3$); δ_C : 161.5 [C8], 153.3

[C1'], 142.9 [C2], 138.9 [C5], 136.1 [C3'], 135.7 [C8a], 135.1 [C4], 130.9 [C4' and 5'], 128.5 [C4a], 123.1 [C2'], 122.1 [C3], 119.9 [C6'], 118.3 [C6], 113.8 [C7], 21.4 [CH_3]; Sn–Bz skeleton ($^nJ(^{119}Sn, ^{13}C)$, Hz): 33.5 [C-1* (927)], 140.9 [C-2* (55)], 128.8 [C-3* (17)], 127.6 [C-4* (81)], 122.8 [C-5* (81)] ppm. ESI-MS: MW = 826. Positive-ion MS: m/z 865 [$M + K$] $^+$; m/z 849 [$M + Na$] $^+$; m/z 564 [$M - L^1$] $^+$, 100%. MS/MS of m/z 849: m/z 665 [$M + Na - 2^*toluene$] $^+$; m/z 564 [$M - L^1$] $^+$; m/z 382 [$M - L^1 - toluene - 90$] $^+$. MS/MS of m/z 564: m/z 380 [$M - L^1 - 2^*toluene$] $^+$. Negative-ion MS: m/z 262 [L^1] $^-$, 100%. MS/MS of m/z 262: m/z 234 [$L^1 - N_2$] $^-$; m/z 143 [$L^1 - N_2 - toluene$] $^-$. ^{119}Sn Mössbauer: $\delta = 0.81$, $\Delta = 1.77$, $\Gamma_1 = 1.00$, $\Gamma_2 = 1.00$ mm s^{-1} .

The other dibenzyltin complexes were prepared by reacting quinolinols, viz., L^2H-L^6H with Bz_2SnCl_2 by following the above procedure. The characterization and spectroscopic data of the complexes are presented below.

2.4.2. Synthesis of $Bz_2Sn(L^2)_2$ (**2**)

Orange crystals of **2** were obtained from a mixture of benzene and hexane (v/v 1:1). Yield: 0.58 g (26.5%), m.p. 218–219°C. Anal. Found: C, 67.04; H, 4.50; N, 10.29%. Calc. for $C_{46}H_{38}N_6O_2Sn$: C, 66.92; H, 4.64; N, 10.18%. IR (cm^{-1}): 1248 $\nu(C(aryl)O)$. 1H NMR ($CDCl_3$); δ_H : 9.09 [dd, 2H, H4], 8.09 [d, 2H, H2], 7.97 [d, 2H, H6], 7.65 [d, 4H, H2' and H6'], 7.20 [m, 2H, H-3], 7.13 [m, 4H, H3' and H5'], 7.00 [m, 2H, H7], 2.35 [d, 6H, CH_3]; Sn–Bz skeleton: 2.48 [d, 4H, H1*], 6.67 [m, 4H, H4*], 6.61 [m, 6H, H3* and H5*], ppm. ^{13}C NMR ($CDCl_3$); δ_C : 161.1 [C8], 151.1 [C1'], 142.3 [C2], 139.4 [C4'], 135.5 [C5], 135.4 [C8a], 134.9 [C4], 128.4 [C4a], 127.3 [C3' and C5'], 122.7 [C2' and C6'], 121.4 [C3], 118.1 [C6], 113.5 [C-7], 21.4 [CH_3]; Sn–Bz skeleton ($^nJ(^{119}Sn, ^{13}C)$, Hz): 33.2 [C-1* (927)], 140.7 [C-2* (55)], 129.2 [C-3* (17)], 127.2 [C-4* (81)], 122.4 [C-5* (81)] ppm. ESI-MS: MW = 826. Positive-ion MS: m/z 865 [$M + K$] $^+$; m/z 849 [$M + Na$] $^+$, 100%; m/z 564 [$M - L^2$] $^+$. MS/MS of m/z 865: m/z 683 [$M + K - toluene - 90$] $^+$; m/z 564 [$M - L^2$] $^+$; m/z 382 [L^2Sn] $^+$. MS/MS of m/z 849: m/z 667 [$M + Na - toluene - 90$] $^+$; m/z 564 [$M - L^2$] $^+$; m/z 382 [L^2Sn] $^+$. MS/MS of m/z 564: m/z 382 [L^2Sn] $^+$. Negative-ion MS: m/z 262 [L^2] $^-$, 100%. MS/MS of m/z 262: m/z 234 [$L^2 - N_2$] $^-$; m/z 143 [$L^2 - toluene - N_2$] $^-$. ^{119}Sn Mössbauer: $\delta = 0.91$, $\Delta = 1.69$, $\Gamma_1 = 1.67$, $\Gamma_2 = 1.79$ mm s^{-1} .

2.4.3. $Bz_2Sn(L^3)_2$ (**3**)

Orange crystals of **3** were obtained from a mixture of benzene and hexane (v/v 1:1). Yield: 0.48 g (31.8%), mp: 154–155°C. Anal. Found: C, 64.50; H, 4.70; N, 9.88%. Calc. for $C_{46}H_{38}N_6O_4Sn$: C, 64.43; H, 4.47; N, 9.80%. IR (cm^{-1}): 1251 $\nu(C(aryl)O)$. 1H NMR ($CDCl_3$); δ_H : 9.14 [dd, 2H, H4], 8.12 [d, 4H, H2 and H6], 7.90 [d, 4H, H2' and H6'], 7.25 [m, 2H, H-3], 7.12 [m, 2H, H7], 7.00 [m, 4H, H3' and H5'], 3.90 [d, 6H, OCH_3]; Sn–Bz skeleton: 2.64 [d, 4H, H1*], 6.81 [m, 4H, H4*], 6.73 [m, 6H, H3* and H5*], ppm. ^{13}C NMR ($CDCl_3$); δ_C : 161.5 [C8], 161.1 [C1'],

147.9 [C2], 142.9 [C4'], 136.3 [C5], 135.7 [C8a], 135.4 [C4], 128.3 [C4a], 124.2 [C3' and C5'], 123.1 [C3], 118.2 [C6], 114.3 [C2' and C6'], 113.9 [C-7], 55.6 [OCH₃]; Sn–Bz skeleton ($^nJ(^{119}\text{Sn}, ^{13}\text{C})$, Hz): 33.6 [C-1* (927)], 141.1 [C-2* (55)], 127.8 [C-3* (17)], 127.6 [C-4* (81)], 121.9 [C-5* (81)] ppm. ESI-MS: MW = 858. Positive-ion MS: m/z 897 [M + K]⁺; m/z 881 [M + Na]⁺, 100%; m/z 580 [M – L³]⁺. MS/MS of m/z 897: m/z 715 [M + K – toluene – 90]⁺; m/z 580 [M – L³]⁺; m/z 398 [L³Sn]⁺. MS/MS of m/z 881: m/z 699 [M + Na – toluene – 90]⁺; m/z 580 [M – L³]⁺; m/z 398 [L³Sn]⁺. MS/MS of m/z 564: m/z 398 [L³Sn]⁺. Negative-ion MS: m/z 278 [L³]⁻; m/z 263 [L³ – CH₄]⁻, 100%. MS/MS of m/z 278: m/z 263 [L³ – CH₄]⁻. MS/MS of m/z 263: m/z 234 [L³ – CH₄ – N₂]⁻; m/z 158 [L³ – toluene – N₂]⁻. ¹¹⁹Sn Mössbauer: $\delta = 0.91$, $\Delta = 1.73$, $\Gamma_1 = 2.00$, $\Gamma_2 = 2.00$ mm s⁻¹.

2.4.4. Bz₂Sn(L⁴)₂ (4)

Orange crystals of **4** were obtained from a mixture of carbon tetrachloride and hexane (v/v 1:1). Yield: 0.58 g (37.4%), mp: 175–176 °C. Anal. Found: C, 65.01; H, 4.70; N, 9.60%. Calc. for C₄₈H₄₂N₆O₄Sn: C, 65.10; H, 4.78; N, 9.49%. IR (cm⁻¹): 1248 ν(C(aryl)O). ¹H NMR (CDCl₃) δ_H: 9.05 [dd, 2H, H4], 8.02 [dd, 2H, H2], 7.96 [d, 2H, H6], 7.66 [m, 4H, H2' and H6'], 7.12 [d, 2H, H3], 6.94 [d, 2H, H7], 6.72 [m, 4H, H3' and H5'], 3.89 [q, 4H, OCH₂CH₃], 1.30 [t, 6H, OCH₂CH₃]; Sn–Bz skeleton: 2.45 [d, 4H, H1*], 6.64 [m, 4H, H4*], 6.56 [m, 6H, H3* and H5*], ppm. ¹³C NMR (CDCl₃); δ_C: 160.7 [C8], 160.3 [C1'], 147.2 [C2], 142.3 [C4'], 135.5 [C5], 135.3 [C8a], 134.7 [C4], 128.2 [C4a], 123.9 [C3' and C5'], 121.2 [C3], 117.7 [C2' and C6'], 114.1 [C6], 113.5 [C7], 63.0 [OCH₂CH₃], 14.7 [OCH₂CH₃]; Sn–Bz skeleton ($^nJ(^{119}\text{Sn}, ^{13}\text{C})$, Hz): 33.2 [C-1* (927)], 140.8 [C-2* (55)], 127.5 [C-3* (17)], 127.3 [C-4* (81)], 122.7 [C-5* (81)] ppm. ESI-MS: MW = 886. Positive-ion MS: m/z 925 [M + K]⁺; m/z 909 [M + Na]⁺, 100%; m/z 594 [M – L⁴]⁺. MS/MS of m/z 925: m/z 743 [M + K – toluene – 90]⁺; m/z 594 [M – L⁴]⁺; m/z 412 [L⁴Sn]⁺. MS/MS of m/z 909: m/z 727 [M + Na – toluene – 90]⁺; m/z 594 [M – L⁴]⁺; m/z 412 [L⁴Sn]⁺. MS/MS of m/z 594: m/z 412 [L⁴Sn]⁺. Negative-ion MS: m/z 292 [L⁴]⁻, 100%; m/z 263 [L⁴ – C₂H₆]⁻. MS/MS of m/z 292: m/z 263 [L⁴ – C₂H₆]⁻. MS/MS of m/z 263: m/z 234 [L⁴ – C₂H₆ – N₂]⁻. ¹¹⁹Sn Mössbauer: $\delta = 0.93$, $\Delta = 1.64$, $\Gamma_1 = 1.66$, $\Gamma_2 = 1.69$ mm s⁻¹.

2.4.5. Bz₂Sn(L⁵)₂ (5)

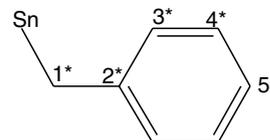
Dark-red crystals of **5** were obtained from a mixture of benzene and hexane (v/v 1:1). Yield: 0.70 g (54.7%), mp: 215–216 °C. Anal. Found: C, 55.38; H, 3.30; N, 8.82%. Calc. for C₄₄H₃₂Br₂N₆O₂Sn: C, 55.32; H, 3.38; N, 8.79%. IR (cm⁻¹): 1248 ν(C(aryl)O). ¹H NMR (CDCl₃) δ_H: 9.08 [dd, 2H, H4], 8.14 [dd, 2H, H2], 8.00 [d, 2H, H6], 7.68 [m, 4H, H2' and H6'], 7.52 [m, 4H, H3' and H5'], 7.17 [m, 2H, H3], 7.07 [m, 2H, H7]; Sn–Bz skeleton: 2.52 [d, 4H, H1*], 6.70 [m, 4H, H4*], 6.62 [m, 6H, H3* and H5*], ppm. ¹³C NMR (CDCl₃); δ_C: 162.0 [C8], 151.7 [C1'],

140.5 [C2], 135.3 [C5], 134.9 [C8a], 135.4 [C4], 131.9 [C3' and C5'], 127.3 [C4a], 123.9 [C4'], 122.9 [C2' and C6'], 121.8 [C3], 116.6 [C6], 113.8 [C7]; Sn–Bz skeleton ($^nJ(^{119}\text{Sn}, ^{13}\text{C})$, Hz): 33.3 [C-1* (927)], 142.6 [C-2* (55)], 127.5 [C-3* (17)], 127.4 [C-4* (81)], 123.8 [C-5* (81)] ppm. ESI-MS: MW = 954. Positive-ion MS: m/z 995 [M + K]⁺; m/z 979 [M + Na]⁺, 100%; m/z 628 [M – L⁵]⁺. MS/MS of m/z 995: m/z 813 [M + K – toluene – 90]⁺; m/z 446 [L⁵Sn]⁺. MS/MS of m/z 979: m/z 797 [M + Na – toluene – 90]⁺; m/z 627 [M – L⁵]⁺; m/z 446 [L⁵Sn]⁺. MS/MS of m/z 628: m/z 446 [L⁵Sn]⁺. Negative-ion MS: m/z 326 [L⁵]⁻, 100%. MS/MS of m/z 326: m/z 143 [L⁵ – brombenzene – N₂]⁻. ¹¹⁹Sn Mössbauer: $\delta = 0.87$, $\Delta = 1.58$, $\Gamma_1 = 2.00$, $\Gamma_2 = 2.00$ mm s⁻¹.

2.4.6. Bz₂Sn(L⁶)₂ (6)

Maroon crystals of **6** were obtained from a mixture of benzene and hexane (v/v 1:1). Yield: 0.50 g (69.4%), mp: 141–142 °C. Anal. Found: C, 61.22; H, 3.50; N, 9.82%. Calc. for C₄₄H₃₂Cl₂N₆O₂Sn: C, 60.99; H, 3.72; N, 9.70%. IR (cm⁻¹): 1248 ν(C(aryl)O). ¹H NMR (CDCl₃) δ_H: 9.06 [dd, 2H, H4], 8.12 [dd, 2H, H2], 8.00 [d, 2H, H6], 7.71 [m, 4H, H2' and H6'], 7.32 [m, 4H, H3' and H5'], 7.15 [m, 2H, H3], 7.04 [m, 2H, H7]; Sn–Bz skeleton: 2.51 [d, 4H, H1*], 6.70 [m, 4H, H4*], 6.61 [m, 6H, H3* and H5*], ppm. ¹³C NMR (CDCl₃); δ_C: 161.9 [C8], 151.4 [C1'], 140.5 [C2'], 135.6 [C4'], 135.4 [C5], 135.3 [C8a], 134.9 [C4], 128.5 [C4a], 127.5 [C3' and C5'], 122.9 [C2' and C6'], 121.7 [C3], 118.7 [C6], 113.7 [C7]; Sn–Bz skeleton ($^nJ(^{119}\text{Sn}, ^{13}\text{C})$, Hz): 33.3 [C-1* (927)], 142.6 [C-2* (55)], 128.9 [C-3* (17)], 127.4 [C-4* (81)], 123.5 [C-5* (81)] ppm. ESI-MS: MW = 866. Positive-ion MS: m/z 905 [M + K]⁺; m/z 889 [M + Na]⁺; m/z 584 [M – L⁶]⁺, 100%. MS/MS of m/z 889: m/z 707 [M + Na – toluene – 90]⁺; m/z 584 [M – L⁶]⁺; m/z 402 [L⁶Sn]⁺. MS/MS of m/z 564: m/z 402 [L⁶Sn]⁺. Negative-ion MS: m/z 282 [L⁶]⁻, 100%. MS/MS of m/z 282: m/z 143 [L⁶ – chlorbenzene – N₂]⁻. ¹¹⁹Sn Mössbauer: $\delta = 0.87$, $\Delta = 1.58$, $\Gamma_1 = 2.00$, $\Gamma_2 = 2.00$ mm s⁻¹.

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



2.5. X-ray crystallography

Crystals of the dibenzyltin(IV) compounds **2**, **3** and **5** suitable for an X-ray crystal structure determination were obtained from benzene–hexane mixture (1:2 v/v), ethanol, chloroform–hexane mixture (1:1 v/v), respectively. Intensity data were collected with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), on Bruker

Table 1
Crystal data, data collection parameters and convergence results for **2**, **3** and **5**

	2	3	5
Empirical formula	C ₄₆ H ₃₈ N ₆ O ₂ Sn	C ₄₆ H ₃₈ N ₆ O ₄ Sn	C ₄₄ H ₃₂ Br ₂ N ₆ O ₂ Sn
Formula weight	825.51	857.51	955.27
Crystal size (mm ³)	0.56 × 0.35 × 0.18	0.80 × 0.55 × 0.35	0.48 × 0.25 × 0.20
Crystal shape	Plate	Prism	Prism
Temperature (K)	93 (2)	93 (2)	296 (2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>n</i>
<i>a</i> (Å)	10.1273 (13)	9.7212 (15)	15.341 (18)
<i>b</i> (Å)	12.6410 (16)	13.714 (2)	15.310 (16)
<i>c</i> (Å)	15.660 (2)	15.809 (3)	17.49 (2)
β (°)	104.711 (2)	105.708 (3)	95.29 (4)
<i>V</i> (Å ³)	1893.7 (4)	1959.6 (5)	4090 (8)
<i>Z</i>	2	2	4
<i>D</i> _x (g cm ⁻³)	1.448	1.453	1.551
μ (mm ⁻¹)	0.723	0.705	2.623
Transmission factors (min, max)	0.792, 1.000	808, 1.000	.0742, 1.000
2 θ _{max} (°)	28.19	28.29	20.81
Reflections measured	14640	15445	15449
Independent reflections (<i>R</i> _{int})	8868 (0.0440)	9206 (0.0376)	4283 (0.0999)
Independent reflections with <i>I</i> > 2 σ (<i>I</i>)	7292	8420	2227
Number of parameters	498	516	472
<i>R</i> (<i>F</i>)/(<i>I</i> > 2 σ (<i>I</i>) reflections)	0.0330	0.0297	0.0749
<i>wR</i> ₂ (<i>F</i> ²) (all data)	0.0450	0.0344	0.1550
GOF(<i>F</i> ²)	0.974	1.038	1.038
Max, min $\Delta\rho$ (e/Å ³)	0.926, -0.702	0.433, -0.602	1.037, -0.977

1 K CCD diffractometer at -180 °C. Crystal data, data collection parameters and convergence results are listed in Table 1.

3. Results and discussion

3.1. Syntheses

The dibenzyltin(IV) complexes of the 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol (LH) could be prepared by reacting stoichiometric amounts of Bz₂SnCl₂ and LNa (generated in situ from Na and anhydrous methanol) in anhydrous benzene. These reactions proceeded smoothly and the pure products were obtained in yields ranging from 26% to 69%. Attempted preparation of dibenzyltin(IV) complexes using Bz₃SnCl via a disproportionation debenzylation reaction (used for the preparation of Ph₂Sn(L)₂) [2] resulted into a complex mixture that could be separated only with great difficulty. In addition, the yield was much lower. The work-up details and characterization data for the complexes are described in Section 2.4.



The complexes are crystalline in nature and stable in air except for compound Bz₂Sn(L⁴)₂ **4** (crystallized from a mixture of carbon tetrachloride and hexane (v/v 1:1)) which loses the solvent of crystallization and becomes amorphous. However, it retains its chemical composition

and properties as evidenced by the spectroscopic results. The complexes are soluble in all common organic solvents.

3.2. IR Spectra

The $\nu(\text{OH})$ bands of the quinolinols L¹H–L⁶H around 3380 cm⁻¹ are absent in the dibenzyltin complexes, **1–6**, confirming bonding through the O-atom of the ligand. In addition, a strong band around 1235 cm⁻¹ due to $\nu(\text{C}(\text{aryl})\text{-O})$ (i.e., C₈-O) in the quinolinols is found to be shifted to around 1250 cm⁻¹ in the complexes which is in agreement with our earlier observation [2]. Attempts were not made to identify the bands due to $\nu(\text{Sn-N})$ and $\nu(\text{Sn-O})$ owing to the complex pattern of the spectra.

3.3. ¹¹⁹Sn Mössbauer data

The Mössbauer data, i.e., isomer shift (δ), quadrupole splittings (Δ) and the line widths at half-peak height (*I*) for the dibenzyltin complexes (**1–6**) are given in Section 2.4. In general, the complexes displayed a doublet with δ and Δ values in the range 0.84–0.93 and 1.58–1.77 mm s⁻¹, respectively. The observed Δ values lie within the range delimited for diorganotin having a *cis*-R₂Sn octahedral geometry [12,13]. The values are in agreement with the data observed for Ph₂SnL₂ complexes with cognate ligands also having a *cis*-R₂Sn octahedral geometry [2]. The magnitude of δ and Δ values in the complexes **1–6** are similar to each other which would

indicate that they are isostructural. Thus, Mössbauer spectroscopic data suggest a *cis*-R₂Sn octahedral geometry for the complexes.

3.4. Solution ¹H, ¹³C, ¹¹⁹Sn NMR and solid-state ¹¹⁷Sn NMR spectra

The ¹H and ¹³C NMR signals for the quinolinols L¹H–L⁶H were assigned by the use of correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HSQC) and heteronuclear multiple-bond connectivities (HMBC) experiments. The conclusions drawn from the ligand assignments were then subsequently extrapolated to the complexes **1–6** owing to the data similarity. The ¹H NMR integration values were completely consistent with the formulation of the products. The ¹H and ¹³C NMR chemical shift assignments for the dibenzyltin moiety are straight-forward using the multiplicity pattern, resonance intensities and also by examining the ⁿJ(¹³C ¹¹⁹/¹¹⁷Sn) coupling constants [9]. In the ¹H and ¹³C NMR spectra of the complexes, **1–6**, there is only one set of NMR signals for both the benzyl groups (Sn–Bz) and for the ligands, which provides evidence for the magnetic equivalence of both the benzyls groups and both ligands on the NMR time scale. This indicates their relative symmetrical arrangement in the coordination sphere of the central tin atom in solution. Further structural conclusions have been extracted from the ¹¹⁹Sn NMR spectra in solution (Table 2). The complexes **1–6**, all display a sharp singlet at -325.7 ± 1.5 ppm and the $\delta(^{119}\text{Sn})$ chemical shifts lie within the range -125 and -515 ppm. These values are in agreement with those reported for other six coordinate diorganotin compounds [14]. The $\delta(^{119}\text{Sn})$ values are comparable with the shift observed for the Bz₂Sn(Ox)₂ complex (-335.2 ppm in CDCl₃ [5]). Thus, the ¹¹⁹Sn NMR data indicate that the complexes in solution, retain their solid-state structures (see Mössbauer discussion, vide supra). ¹¹⁷Sn-CP-MAS NMR spectra were also recorded in the solid state, which is devoid of solvation and dynamic effects to further confirm the structures. The isotropic ¹¹⁷Sn chemical shift and the data of the ten-

sor analysis [15] for compounds **1–6** are reported in Table 2. The isotropic chemical shifts are all in the range -320 – -355 ppm and hardly different from the data in solution, implying that the same octahedral coordination is preserved. The dibenzyltin(IV) compounds, **5** and **6**, bearing a halogen substituent in the *para*-position have axial symmetry ($\eta = 0.00$ or 0.10). Compound **5** has two tin resonances with slightly different isotropic chemical shift suggesting minor differences in the C–Sn–C geometry in the crystals for this compound. This observation is confirmed by crystal structure analysis (see below). The compound is shown to be disordered and adopts two slightly different conformations. Compounds **1** and **2**, with a methyl substituent in the *meta*- and *para*-positions, respectively, display an almost axial symmetry ($\eta = 0.25$) with the same isotropic chemical shift. The difference between the two compounds is reflected in the slightly different chemical shielding anisotropy (182 versus 203 ppm), with corresponding slightly different principal tensor components. The alkoxy-substituted compounds, **3** and **4**, have higher asymmetry parameters ($\eta = 0.35$ and 0.45), which are accompanied by a higher chemical shift anisotropy of ca. 50 ppm.

X-ray data (vide infra) for **2**, **3** and **5** clearly evidence these compounds are essentially isostructural. The differences noted in the asymmetry parameters between these compounds can be traced back to varying deviations from a regular octahedral geometry, being stronger in **2** and **3** than in **5**. Especially the C1SnN1 bond angles are illustrative in this context, as the differences between these angles within one compound and the deviation from a regular octahedral increase in the order **5** < **2** < **3**, exactly the same order as the asymmetry parameter η .

3.5. Mass spectrometry

The typical ions in the first-order positive-ion ESI mass spectra are sodium and potassium ion adducts with the molecule, which is used for the determination of molecular weights of the dibenzyltin(IV) compounds. In addition to these ions, the neutral loss of the ligand [M – L]⁺ are observed as well as in the first-order spectra. The presence of the neutral losses of *m/z* 92 (toluene) or 90 in tandem mass spectra determine the presence of a benzyl group on tin atom. The neutral loss of LH (or LNa) confirms the presence of the corresponding ligand L. The deprotonated molecule of ligand [L][–] is the base peak for all first-order negative-ion mass spectra except for compound **3**. The characteristic neutral losses in tandem mass spectra are 28 (N₂) and losses of ligand substituents (methane, toluene, chlorobenzene and bromobenzene) to form the radical ions.

3.6. Structural results from single-crystal X-ray diffraction

All three structures (**2**, **3**, **5**) are isostructural and contain a central tin atom that is octahedrally coordinated to

Table 2
Solution and solid-state tin NMR data for compounds **1–6**

Compound	$\delta(^{119}\text{Sn})^a$	¹¹⁷ Sn MAS ^b					
		δ_{iso}	ζ	η	σ_{11}	σ_{22}	σ_{33}
1	–325.3	–339	182	0.25	225	271	521
2	–327.2	–338	203	0.25	212	262	541
3	–326.4	–322	249	0.35	154	241	571
4	–326.4	–329	242	0.45	153	262	571
5	–324.3	–336	201	0.10	225	245	537
		–354	201	0.00	253	253	555
6	–324.5	–335	196	0.00	237	237	531

^a In CDCl₃ solution.

^b δ_{iso} (ppm) = $-(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; ζ (ppm) = $\sigma_{33} - \sigma_{\text{iso}}$ and $\eta = |\sigma_{22} - \sigma_{11}|/|\sigma_{33} - \sigma_{\text{iso}}|$ where σ_{11} , σ_{22} and σ_{33} (ppm) are the principal tensor components of the chemical shielding anisotropy, sorted as follows $|\sigma_{33} - \sigma_{\text{iso}}| > |\sigma_{11} - \sigma_{\text{iso}}| > |\sigma_{22} - \sigma_{\text{iso}}|$.

two deprotonated 8-hydroxyquinoline derivatives and two benzyl ligands (see Figs. 2–4). Selected metrical parameters are given in Table 3. The ligands are arranged about

the central Sn such that the oxygen atoms are *trans* to each other while the benzyl carbon atoms and quinoline nitrogen atoms are mutually *cis* to each other. As

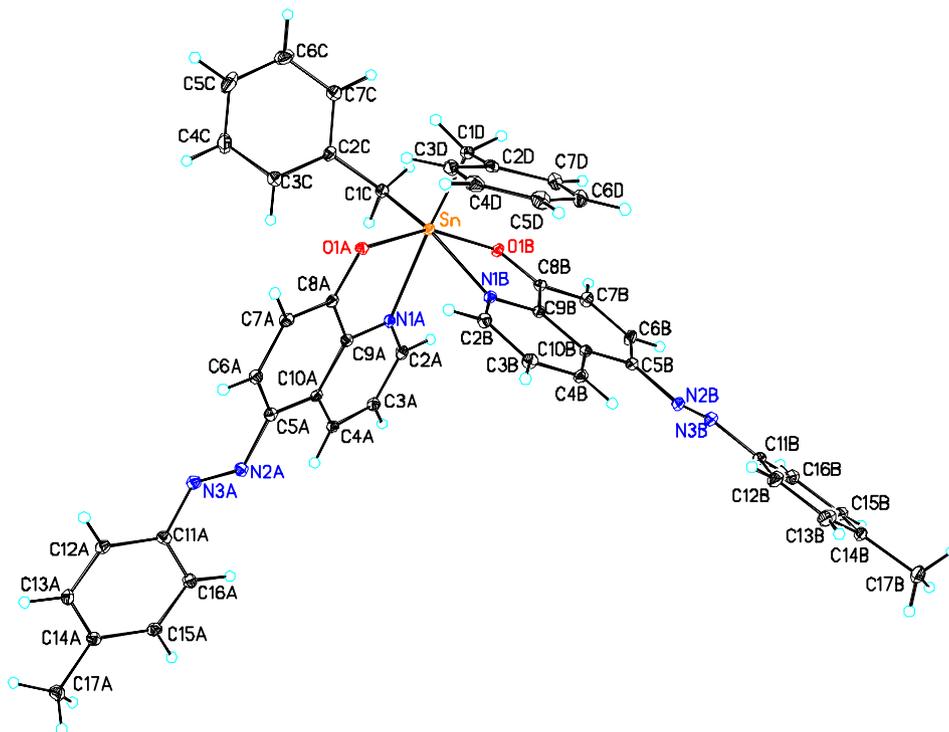


Fig. 2. The molecular structure of $Bz_2Sn(L^2)_2$ (2) with the atom-labelling scheme.

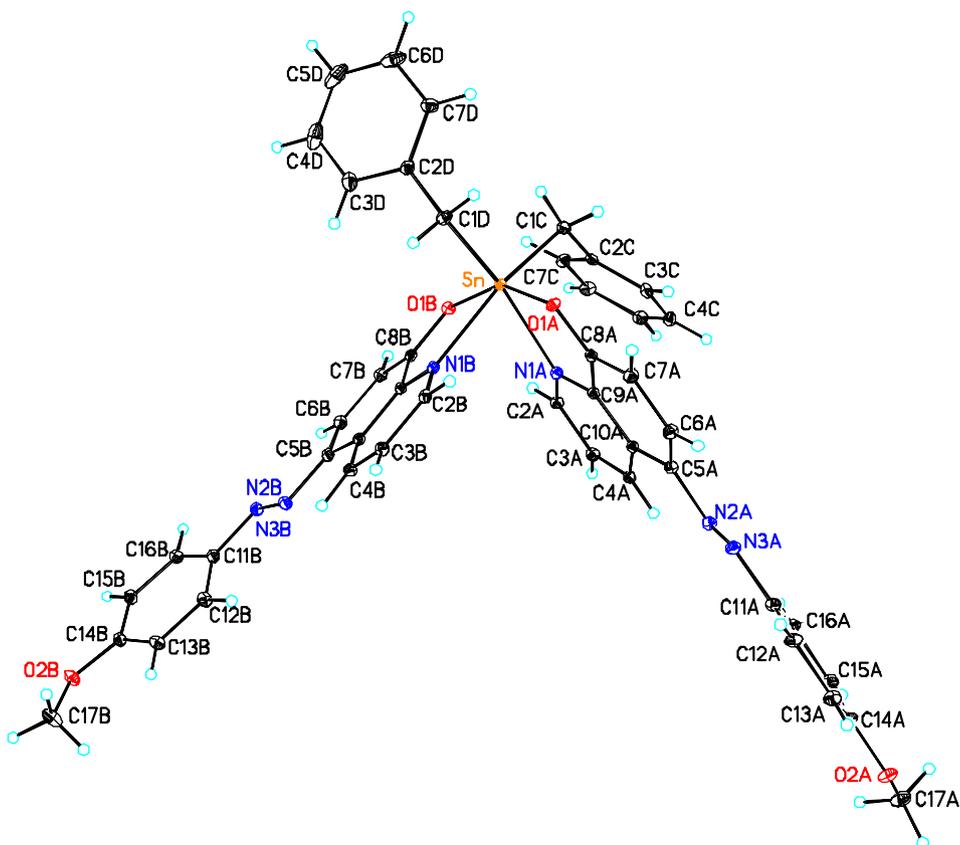


Fig. 3. The molecular structure of $Bz_2Sn(L^3)_2$ (3) with the atom-labelling scheme.

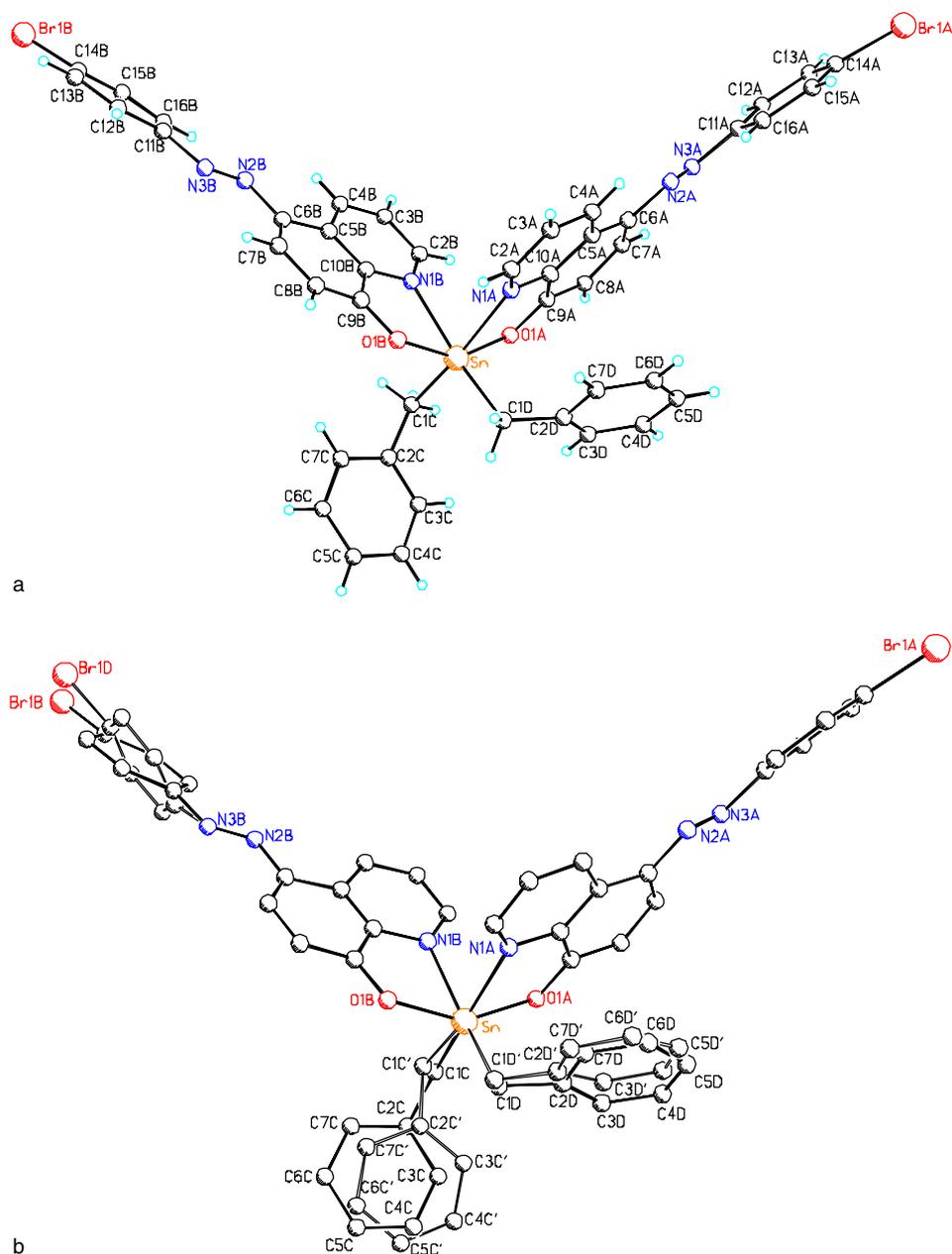


Fig. 4. (a) The molecular structure of $\text{Bz}_2\text{Sn}(\text{L}^3)_2$ (**5**) with the atom-labelling scheme. (b) The molecular structure of $\text{Bz}_2\text{Sn}(\text{L}^3)_2$ (**5**) showing disordered conformation.

indicated in the discussion above, these structures can best be thought of as a distorted octahedron with the two oxygen, nitrogen and benzyl carbon donors forming a plane and the remaining nitrogen and benzyl carbon donors being *trans* to each other. The small bite subtended by the oxygen and nitrogen of the 8-hydroxyquinoline moiety is the main reason for the distortion from a regular octahedral geometry. In summary the metrical values for the three complexes show a remarkable degree of self consistency in the coordination environment about the central tin atom for the three complexes. This, of course,

is to be expected as the variations in the 8-hydroxyquinoline ligands occur at the periphery. A similar set of complexes containing phenyl substituents instead of benzyl substituents has been reported [2]. One point of interest concerns the structure of **5**. As indicated in the discussion of the solid-state ^{117}Sn NMR, there appears to be two slightly different environments for the central Sn atom. This is confirmed in the crystal structure as the two benzyl and one of the 8-hydroxyquinoline ligands are disordered over two conformations. This disorder is shown in Fig. 4b.

Table 3
Selected bond lengths (Å), bond angles (°), and torsion angles (°) for **2**, **3** and **5**

	2	3	5
Sn–C (benzyl)	2.166(2), 2.174(2)	2.176(2), 2.175(2)	2.155(13), 2.179(14)
Sn–O1	2.016(2), 2.114(2)	2.111(1), 2.096(1)	2.075(10), 2.086(10)
Sn–N1	2.306(2), 2.335(2)	2.301(2), 2.357(2)	2.305(11), 2.314(12)
O1–C1	1.320(3), 1.324(3)	1.321(2), 1.321(2)	1.313(15), 1.316(16)
N1–C2	1.320(3), 1.322(3)	1.324(2), 1.322(2)	1.290(15), 1.302(16)
N1–C9	1.361(3), 1.363(3)	1.362(2), 1.363(2)	1.376(15), 1.390(16)
N2–N3	1.265(3), 1.253(3)	1.259(3), 1.268(2)	1.178(15), 1.212(15)
C1C–Sn–C1D	105.87(9)	105.59(8)	103.7(18), 113(2)
O1–Sn–N1	74.16(6), 74.12(6)	74.34(5), 73.80(6)	75.2(4), 74.2(4)
O1A–Sn–O1B	154.68(6)	154.00(5)	152.0(4)
C1–Sn–N1 (<i>trans</i>)	158.57(8), 162.81(8)	156.83(7), 163.18(6)	163.1(12), 165.6(14)
C1–Sn–N1 (<i>cis</i>)	89.23(8), 91.08(8)	89.43(7), 91.86(7)	89.5(14), 88.7(12)
N1A–Sn–N1B	76.40(7)	75.94(6)	79.6(4)
C5–N2–N3–C11	179.04(18), 178.27(19)	–179.01(17), –178.59(16)	–177.7(11), –176.2(17) – 161(5) (minor comp.)

4. Supplementary material

CCDC Nos. 293256–293258 contain the supplementary crystallographic data for complexes **2**, **3** and **5**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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References

- [1] A. Linden, T.S. Basu Baul, A. Mizar, *Acta Crystallogr. Sect. E* 61 (2005) m27.
- [2] T.S. Basu Baul, A. Mizar, A. Lyčka, E. Rivalola, R. Jirásko, M. Holčápek, D. de Vos, U. Englert, *J. Organomet. Chem.*, in press.
- [3] A. Lyčka, J. Holeček, M. Nádvořník, K. Handlír, *J. Organomet. Chem.* 280 (1985) 323.
- [4] J. Holeček, A. Lyčka, R. Wagener, *Collect. Czech., Chem. Commun.* 51 (1986) 2116.
- [5] A. Lyčka, J. Holeček, M. Nádvořník, *Main Group Met. Chem.* 12 (1989) 169.
- [6] A. Lyčka, J. Holeček, K. Handlír, *Collect. Czech., Chem. Commun.* 54 (1989) 2386.
- [7] A. Lyčka, J. Jirman, J. Holeček, I. Tkáč, *J. Organomet. Chem.* 372 (1989) 327.
- [8] T.S. Basu Baul, W. Rynjah, R. Willem, M. Biesemans, I. Verbruggen, M. Holčápek, D. de Vos, A. Linden, *J. Organomet. Chem.* 689 (2004) 4691.
- [9] K. Sisido, T. Takeda, J. Kinigawa, *J. Am. Chem. Soc.* 83 (1961) 538.
- [10] A. Růžička, L. Dostál, R. Jambor, V. Buchta, J. Brus, I. Císařová, M. Holčápek, J. Holeček, *Appl. Organomet. Chem.* 16 (2002) 315.
- [11] A. Růžička, A. Lyčka, R. Jambor, P. Novák, I. Císařová, M. Holčápek, M. Erben, J. Holeček, *Appl. Organomet. Chem.* 17 (2003) 168.
- [12] R.V. Parish, in: L.S. Kothari, J.S. Baijal, S.P. Tewari (Eds.), *Mössbauer Effect: Current Applications to Physical Sciences*, Academic Publications, Delhi, India, 1984, p. 162.
- [13] R. Barbieri, F. Huber, L. Pellerito, G. Ruisi, A. Silvestri, in: P.J. Smith (Ed.), *Chemistry of Tin: ¹¹⁹Sn Mössbauer Studies on Tin Compounds*, Blackie, London, 1998, pp. 496–540.
- [14] J. Otera, *J. Organomet. Chem.* 221 (1981) 57.
- [15] J. Herzfeld, A.E. Berger, *J. Chem. Phys.* 73 (1980) 6021.