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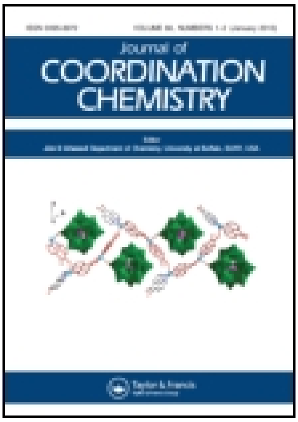

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Synthesis and structural studies of dimethyltin(IV) 5-[(E)-2-(aryl)-1-diazenyl)quinolin-8-olates

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Synthesis and structural studies of dimethyltin(IV) 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olates

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A series of *cis*-bis{5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olato}dimethyltin(IV), $Me_2Sn(L)_2$, and chloro-{5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olato}dimethyltin(IV), $Me_2SnCl(L)$, complexes have been synthesized by reacting the sodium salts of 5-[(*E*)-2-(aryl)-1-diazenyl)quinolin-8-ol (LH) and dimethyltin dichloride in 2:1 and 1:1 molar ratios, respectively. These complexes have been characterized by ^1H, ^{13}C, ^{119}Sn NMR in solution and by IR and ^{119}Sn Mössbauer spectroscopy in the solid state. The structures of two of the dimethyltin(IV) complexes, *viz*., $Me_2Sn(L^2)_2$ (**2**) and $Me_2SnCl(L^3)$. C_7H_8 (**6**) (L^2 = 5-[(*E*)-2-(4′-methoxyphenyl)-1-diazenyl)quinolin-8-olate, L^3 = 5-[(*E*)-2-(4′-ethoxyphenyl)-1-diazenyl)quinolin-8-olate), were determined by single crystal X-ray diffraction. In general, the $Me_2Sn(L)_2$ complexes were found to adopt a distorted *cis*-octahedral arrangement, while $Me_2SnCl(L)$ complexes have a distorted trigonal bipyramidal coordination geometry around the tin atom in solution and in the solid state.

Keywords: 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol; Dimethyltin(IV) complexes; NMR; ^{119}Sn Mössbauer; Crystal Structures

1. Introduction

We have been concentrating on the coordination chemistry of organotin(IV) 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olato because of their potential cytotoxic properties and structural diversities [1–5]. This includes detailed studies of diorganotin(IV) *bis*{5-[(*E*)-2-(aryl)-1-diazenyl] quinolin-8-olato}, with the crystal structure determinations of R_2SnL_2 complexes, where $R = {}^nBu$ [3], Ph [2,4], and Bz [1], revealing molecules with a highly distorted octahedral coordination of tin by bidentate quinolin-8-olate groups and essentially *cis*-R groups [scheme 1 (i)]. Structural information on $R_2SnX(L)$ complexes is also available, e.g. $R = {}^nBu$; X = Cl, L = 5-[(*E*)-2-(4-methoxyphenyl)-1-diazenyl]quinolin-8-ol [6]. The chemistry and structural properties of organotin(IV) 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olato have also been explored for mixed ligand complexes, which provided some elegant structural architectures

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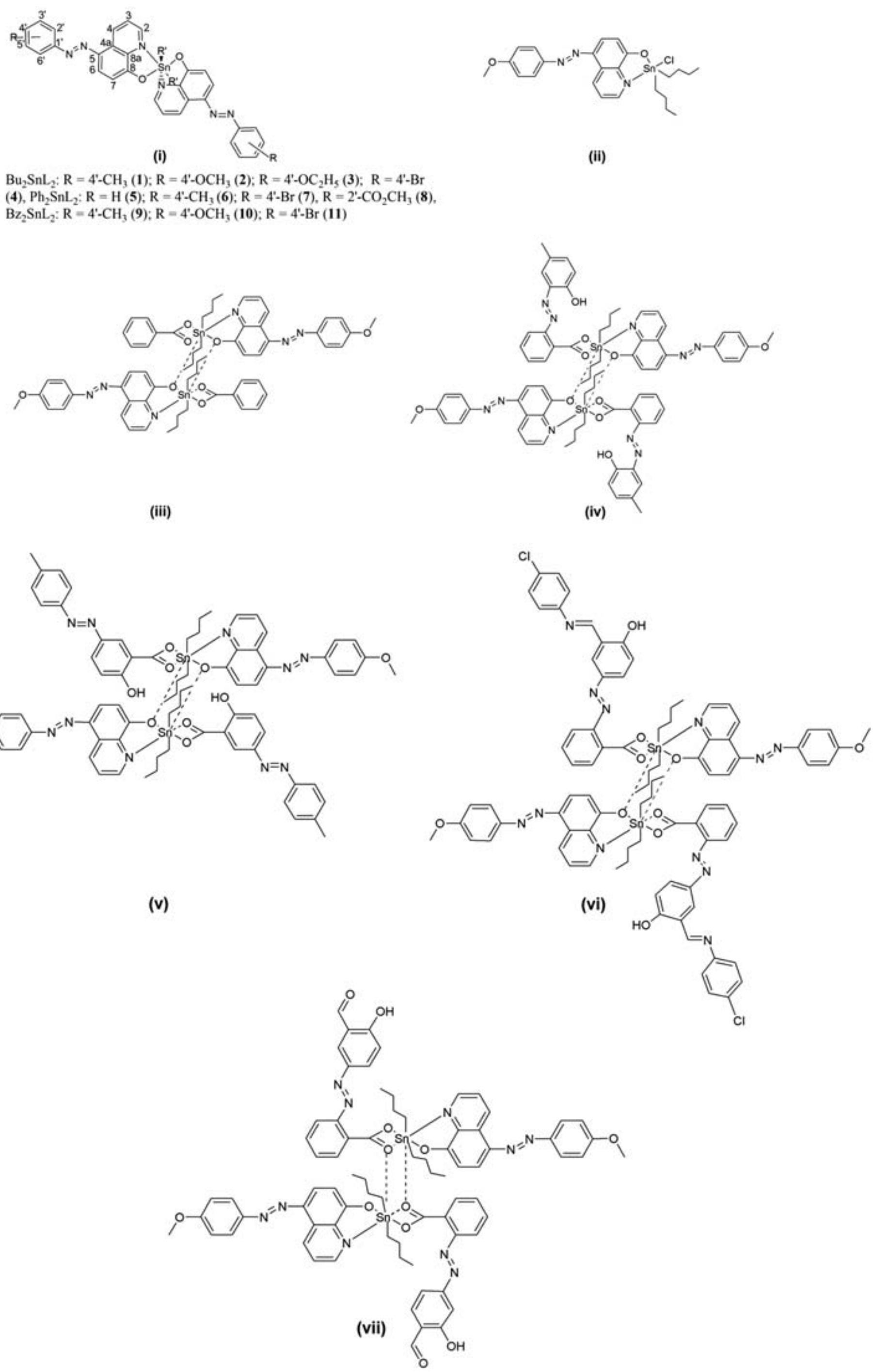

Bu_2SnL_2: R = 4'-CH_3 (**1**); R = 4'-OCH_3 (**2**); R = 4'-OC_2H_5 (**3**); R = 4'-Br (**4**), Ph_2SnL_2: R = H (**5**); R = 4'-CH_3 (**6**); R = 4'-Br (**7**), R = 2'-CO_2CH_3 (**8**), Bz_2SnL_2: R = 4'-CH_3 (**9**); R = 4'-OCH_3 (**10**); R = 4'-Br (**11**)

Scheme 1. Coordination modes of 5-[(*E*)-2-(aryl)-1-diazenyl]quinolinolate(s) towards diorganotin(IV) and investigated structural architectures with a range of carboxylate ligands.

[6] [see scheme 1(ii–viii)]. The literature contains no reports of structural characterization by X-ray crystallography of dimethyltin(IV) compounds with 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olato, except for a very old report involving the ligand precursor quinolin-8-ol (Ox), i.e. Me_2SnOx_2 [7], which had been characterized because of conflicting structural conclusions (octahedral coordination with the possibility of either a *cis*- or *trans*- methyl group) obtained from both NMR, IR, and ^{119}Sn Mössbauer results.

The present paper reports the results of extending the organotin(IV) work, particularly the combination of Me_2Sn with bulkier 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ols [aryl = 4′-methylphenyl- (L^1H), 4′-methoxyphenyl- (L^2H), 4′-ethoxyphenyl- (L^3H), and 4′-bromophenyl- (L^4H); refer to scheme 1(i) for ligand description]. The aim of this study was to evaluate the bonding mode(s) and to judge the disposition of Sn-Me groups in $Me_2Sn(L)_2$ and $Me_2SnCl(L)$ complexes from a detailed analysis of their IR, NMR (^{1}H, ^{13}C, ^{119}Sn), and ^{119}Sn Mössbauer spectroscopic studies. Further, in the course of the studies in this area, the dimethyltin (IV) complex $Me_2Sn(L^2)_2$ (**2**) and a chloro derivative, $Me_2SnCl(L^3)$ (**6**), (as its toluene solvate) provided X-ray quality crystals enabling a detailed analysis of the coordination geometry and the supramolecular structures of these materials.

2. Experimental

2.1. *Materials*

Me_2SnCl_2 (Aldrich), Oxine (Merck), and the substituted anilines (reagent grade) were used without purification. The solvents used in the reactions were AR grade and dried using standard procedures. Benzene was distilled from sodium benzophenone ketyl. The ligands, *viz*. 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]quinolin-8-ol (L^1H), 5-[(*E*)-2-(4-methoxyphenyl)-1-diazenyl]quinolin-8-ol (L^2H), 5-[(*E*)-2-(4-ethoxyphenyl)-1-diazenyl]quinolin-8-ol (L^3H), and 5-[(*E*)-2-(4-bromophenyl)-1-diazenyl]quinolin-8-ol (L^4H) were synthesized by following previously described procedures [1, 2].

2.2. *Physical measurements*

Carbon, hydrogen, and nitrogen analyses were performed with a Perkin-Elmer 2400 series II instrument. IR spectra (4000–400 cm^{-1}) were obtained on a BOMEM DA-8 FT-IR spectrophotometer as KBr disks. ^{1}H, ^{13}C, and ^{119}Sn-NMR spectra of the complexes 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 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. Mössbauer spectra of the complexes in the solid-state were recorded using a Ranger Model MS-900 spectrometer in the acceleration mode with a moving source geometry. A 5 mCi $Ca^{119}SnO_3$ source was used and counts of 30,000 or more accumulated for each spectrum. The spectra were measured at 80 K using a liquid–nitrogen cryostat. The velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tin foil (splitting 2.52 mm s^{-1}). The resultant spectra were analyzed using the software package from Web Research Corporation.

2.3. *Synthesis of dimethyltin(IV) complexes*

2.3.1. Synthesis of $Me_2Sn(L^1)_2$ (1). A methanolic solution of sodium methoxide (generated *in situ* from 0.044 g, 1.90 mmol of Na in anhydrous methanol) was added dropwise 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 Me_2SnCl_2 (0.20 g, 0.91 mmol) was added dropwise 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 residue was washed with hexane and dried *in vacuo*. The dried residue was dissolved in benzene, precipitated with hexane, filtered and finally dried. The crude product was then crystallized from a mixture of benzene and hexane (v/v, 1:1) to afford orange crystals. Yield: 0.35 g (57%), m.p.: 200–201 °C. Anal. Calcd for $C_{34}H_{30}N_6O_2Sn$ (%): C, 60.65; H, 4.49; N, 12.48. Found: C, 61.05; H, 4.29; N, 12.32. IR (cm^{-1}): 1248 ν(C(aryl)O). ^1H NMR ($CDCl_3$); δ_H: 9.28 [dd, 2H, H4], 8.56 [dd, 2H, H2], 8.21 [d, 2H, H6], 7.82 [m, 4H, H2′ & H6′], 7.20–7.42 [m, 8H, H3, H7, H3′ & H5′], 2.44 [s, 6H, CH_3], and 0.55 [s, 6H, Sn-CH_3, $^2J(^{119}Sn, ^1H = 69\,Hz)$], ppm. ^{13}C NMR ($CDCl_3$); δ_C: 161.3 [C8], 151.5 [C1′], 142.8 [C2], 140.5 [C4′], 136.4 [C5], 135.7 [C4], 135.3 [C8a], 129.7 [C3′ & C5′], 128.7 [C4a], 122.5 [C2′ & C6′], 122.4 [C3], 118.5 [C6], 114.1 [C7], 21.4 [CH_3], and 7.30 [Sn-CH_3, $^1J(^{119}Sn, ^{13}C = 625\,Hz)$], ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: –224.0 ppm. ^{119}Sn Mössbauer: $\delta = 0.86$, $\Delta = 2.06$, $\Gamma_1 = 1.09$, $\Gamma_2 = 1.14\,mm\,s^{-1}$.

The other dimethyltin(IV) complexes were prepared by reacting appropriate ligands, L^2H-L^4H with Me_2SnCl_2 according to the above procedure. The characterization and spectroscopic data of the complexes are presented below.

2.3.2. Synthesis of $Me_2Sn(L^2)_2$ (2). Red crystals of **2** were obtained from a mixture of benzene and hexane (v/v, 1:1) after recrystallization. Yield: 65%, m.p.: 218–219 °C. Anal. Calcd for $C_{34}H_{30}N_6O_4Sn$ (%): C, 57.90; H, 4.29; N, 11.91. Found: C, 57.78; H, 4.53; N, 11.88. IR (cm^{-1}): 1255 ν(C(aryl)O). ^1H NMR ($CDCl_3$); δ_H: 9.27 [dd, 2H, H4], 8.56 [dd, 2H, H2], 8.18 [d, 2H, H6], 7.89 [m, 4H, H2′ & H6′], 7.20–7.40 [m, 4H, H3 & H7], 7.01 [m, 4H, H3′ & H5′], 3.85 [s, 6H, OCH_3], and 0.50 [s, 6H, Sn-CH_3, $^2J(^{119}Sn, ^1H = 70\,Hz)$], ppm. ^{13}C NMR ($CDCl_3$); δ_C: 161.4 [C8], 160.8 [C1′], 147.8 [C4′], 142.8 [C2], 136.4 [C5], 135.6 [C4], 135.3 [C8a], 128.5 [C4a], 124.2 [C3′ & C5′], 122.2 [C3], 118.1 [C6], 114.2 [C2′ & C6′], 114.1 [C7], 55.5 [OCH_3], and 7.30 [Sn-CH_3, $^1J(^{119}Sn, ^{13}C = 625\,Hz)$], ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: –224.6 ppm. ^{119}Sn Mössbauer: $\delta = 0.86$, $\Delta = 2.05$, $\Gamma_1 = 1.14$, $\Gamma_2 = 1.21\,mm\,s^{-1}$.

2.3.3. $Me_2Sn(L^3)_2$ (3). Orange crystals of **3** were obtained from a mixture of benzene and hexane (v/v, 1:1) after recrystallization. Yield: 68%, m.p.: 196–197 °C. Anal. Calcd for $C_{36}H_{34}N_6O_4Sn$ (%): C, 58.96; H, 4.67; N, 11.46. Found: C, 58.63; H, 4.66; N, 11.54. IR (cm^{-1}): 1255 ν(C(aryl)O). ^1H NMR ($CDCl_3$); δ_H: 9.25 [dd, 2H, H4], 8.55 [dd, 2H, H2], 8.17 [d, 2H, H6], 7.90 [m, 4H, H2′ & H6′], 7.22–7.40 [m, 4H, H3 & H7], 7.0 [d, 4H, H3′ & H5′], 4.13 [q, 4H, $OC\mathbf{H_2}CH_3$], 1.45 [t, 6H, $OCH_2C\mathbf{H_3}$], and 0.54 [s, 6H, Sn-CH_3, $^2J(^{119}Sn, ^1H = 70\,Hz)$], ppm. ^{13}C NMR ($CDCl_3$); δ_C: 160.8 [C8 & C1′], 147.6 [C4′], 142.8 [C2], 136.4 [C5], 135.6 [C4], 135.3 [C8a], 128.5 [C4a], 124.2 [C3′ & C5′], 122.1 [C3], 118.1 [C6], 114.7 [C2′ & C6′], 114.0 [C7], 63.8 [$O\mathbf{C}H_2CH_3$], 14.8 [$OCH_2\mathbf{C}H_3$], and

7.20 [Sn-CH$_3$, $^1J(^{119}Sn, ^{13}C = 625$ Hz)], ppm. ^{119}Sn NMR (CDCl$_3$) δ_{Sn}: −224.7 ppm. ^{119}Sn Mössbauer: $\delta = 0.88$, $\Delta = 2.22$, $\Gamma_1 = 1.01$, $\Gamma_2 = 1.06$ mm s^{-1}.

2.3.4. Me$_2$Sn(L^4)$_2$ (4). Orange crystals of **4** were obtained from a mixture of benzene and hexane (v/v, 1:1) after recrystallization. Yield: 73%, m.p.: 208–209 °C. Anal. Calcd for $C_{32}H_{24}N_6O_2Br_2Sn$ (%): C, 47.85; H, 3.01; N, 10.46. Found: C, 47.70; H, 2.89; N, 10.66. IR (cm^{-1}): 1248 ν(C(aryl)O). ^{1}H NMR (CDCl$_3$); δ_H: 9.27 [dd, 2H, H4], 8.55 [dd, 2H, H2], 8.27 [d, 2H, H6], 7.78 [m, 4H, H2′ & H6′], 7.63 [m, 4H, H3′ & H5′], 7.38 [m, 4H, H3 & H7], and 0.57 [s, 6H, Sn-CH$_3$, $^2J(^{119}Sn, ^1H = 69$ Hz)], ppm. ^{13}C NMR (CDCl$_3$); δ_C: 161.9 [C8], 152.1 [C1′], 142.9 [C2], 136.2 [C4], 135.6 [C5], 135.3 [C8a], 132.3 [C3′ & C5′], 128.9 [C4a], 123.9 [C2′ & C6′], 122.6 [C3], 119.1 [C6], and 114.2 [C7], ppm. C4′ could not be detected, possibly overlapped with other signals. ^{119}Sn NMR (CDCl$_3$) δ_{Sn}: −222.0 ppm. ^{119}Sn Mössbauer: δ = 0.87, $\Delta = 2.17$, $\Gamma_1 = 1.16$, $\Gamma_2 = 1.39$ mm s^{-1}.

2.3.5. Me$_2$SnCl(L^2) (5). A methanolic solution of sodium methoxide (generated *in situ* from 0.04 g, 1.74 mmol of Na in anhydrous methanol) was added dropwise into a stirred hot anhydrous benzene solution (45 mL) containing L^{2}H (0.5 g, 1.79 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 Me$_2$SnCl$_2$ (0.39 g, 1.79 mmol) was added dropwise which resulted in the disappearance of the precipitate. The reaction mixture was then 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 then washed with hexane and dried *in vacuo*. The dried residue was dissolved in benzene, precipitated with hexane, filtered and finally dried. Orange crystals of **5** were obtained from a mixture of benzene and hexane (v/v, 1:1) after recrystallization. Yield: 0.38 g (46%), m.p.: 160–161 °C. Anal. Calcd for $C_{18}H_{18}N_3O_2SnCl$ (%): C, 46.74; H, 3.92; N, 9.08. Found: C, 46.72; H, 3.91; N, 9.35. IR (cm^{-1}): 1259 ν(C(aryl)O). ^{1}H NMR (CDCl$_3$); δ_H: 9.65 [dd, 1H, H4], 8.20 [dd, 1H, H2], 7.95 [m, 2H, H2′ & H6′], 7.80 [m, 1H, H6], 7.20–7.40 [m, 2H, H3 & H7], 7.00 [m, 2H, H3′ & H5′], 3.90 [s, 3H, OCH$_3$], and 1.11 [s, 6H, Sn-CH$_3$], ppm. ^{13}C NMR (CDCl$_3$); δ_C: 161.8 [C8], 160.0 [C1′], 147.6 [C4′], 145.3 [C2], 142.8 [C5], 138.2 [C4], 135.6 [C8a], 128.3 [C4a], 124.5 [C3′ & C5′], 122.4 [C3], 118.3 [C6], 115.1 [C7], 114.3 [C2′ & C6′], 55.6 [OCH$_3$], and 7.90 [Sn-CH$_3$, $^1J(^{119}Sn, ^{13}C = 640$ Hz)], ppm. ^{119}Sn NMR (CDCl$_3$) δ_{Sn}: –83.5 ppm. ^{119}Sn Mössbauer: δ = 1.12, $\Delta = 2.80$, $\Gamma_1 = 1.36$, $\Gamma_2 = 1.52$ mm s^{-1}.

2.3.6. Me$_2$SnCl(L^3)·C$_7$H$_8$ (6). Orange crystals of **6** were obtained from a mixture of toluene and chloroform (v/v, 1:1) after recrystallization. Yield: 49%, m.p.: 135–136 °C. Anal. Calcd for $C_{26}H_{28}ClN_3O_2Sn$ (%): C, 54.89; H, 4.96; N, 7.39. Found: C, 55.10; H, 4.90; N, 7.62. IR (cm^{-1}): 1257 ν(C(aryl)O). ^{1}H NMR (CDCl$_3$); δ_H: 9.65 [dd, 1H, H4], 9.10 [dd, 1H, H2], 8.20 [d, 1H, H6], 8.0 [m, 2H, H2′ & H6′], 7.80 [m, 1H, H3], 7.30 [d, 1H, H7], 7.05 [d, 2H, H3′ & H5′], 4.14 [q, 2H, OC$\mathbf{H_2}$CH$_3$], 1.49 [t, 3H, OCH$_2$C$\mathbf{H_3}$], and 1.11 [s, 6H, Sn-CH$_3$], ppm. ^{13}C NMR (CDCl$_3$); δ_C: 161.2 [C8], 159.9 [C1′], 147.5 [C4′], 145.3 [C2], 138.2 [C5], 136.6 [C4], 136.2 [C8a], 128.3 [C4a], 124.5 [C3′ & C5′], 122.3 [C3], 118.2 [C6], 115.1 [C7], 114.8 [C2′ & C6′], 63.8 [O**C**H$_2$CH$_3$], 14.7 [OCH$_2$**C**H$_3$], and 7.90

Table 1. Crystal data, data collection and refinement parameters for **2** and **6**.

	2	**6**
Empirical formula	$C_{34}H_{30}N_6O_4Sn$	$C_{26}H_{28}ClN_3O_2Sn$
Formula weight	705.25	568.58
Crystal size (mm)	0.08 × 0.15 × 0.30	0.25 × 0.25 × 0.28
Crystal shape	Prism	Prism
Temperature (K)	160(1)	160(1)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	8.8379(2)	7.3050(1)
b (Å)	13.5486(4)	10.2826(2)
c (Å)	14.0739(4)	33.2846(6)
α (°)	73.047(1)	90
β (°)	74.184(2)	91.2367(6)
γ (°)	76.580(2)	90
V (Å^3)	1529.49(7)	2499.57(7)
Z	2	4
D_x (g cm^{-3})	1.531	1.511
μ (mm^{-1})	0.884	1.156
Transmission factors (min, max)	0.858, 0.943	0.672, 0.756
$2\theta_{max}$ (°)	55	60
Reflections measured	34,008	50,914
Indep. reflections (R_{int})	7034 (0.064)	7282 (0.058)
Indep. reflections with $I > 2\sigma(I)$	5791	5968
Number of parameters; restraints	411; 0	368; 273
$R(F)$ ($I > 2\sigma(I)$ reflns.)	0.0385	0.0319
$wR(F^2)$ (all data)	0.0884	0.0752
$GOF(F^2)$	1.107	1.081
Max, min $\delta\rho$ (e/Å^3)	1.03, −0.87	1.13, −0.80

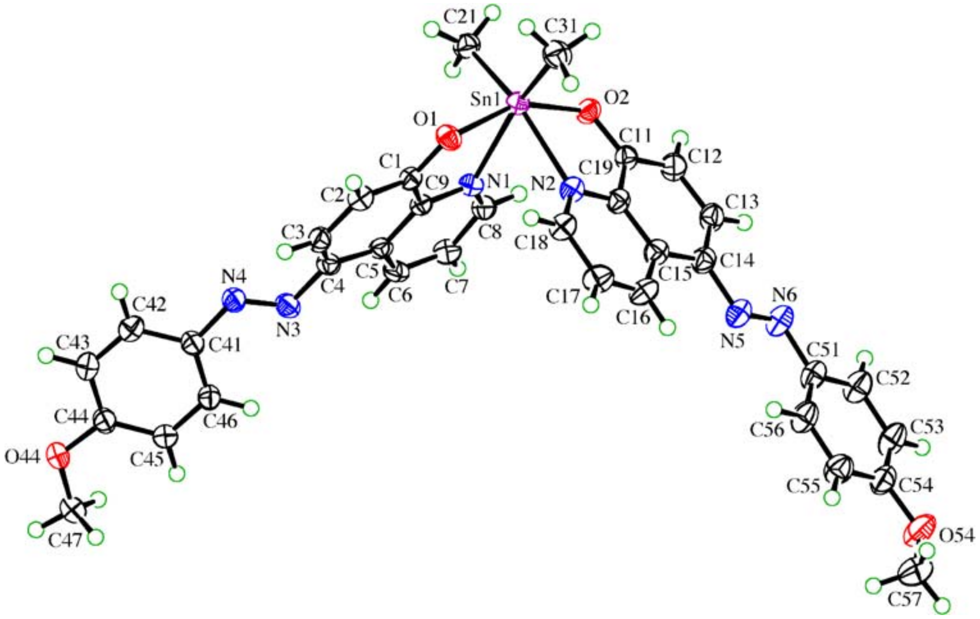

Figure 1. The molecular structure of $Me_2Sn(L^2)_2$ (**2**). Displacement ellipsoids are shown at the 50% probability level.

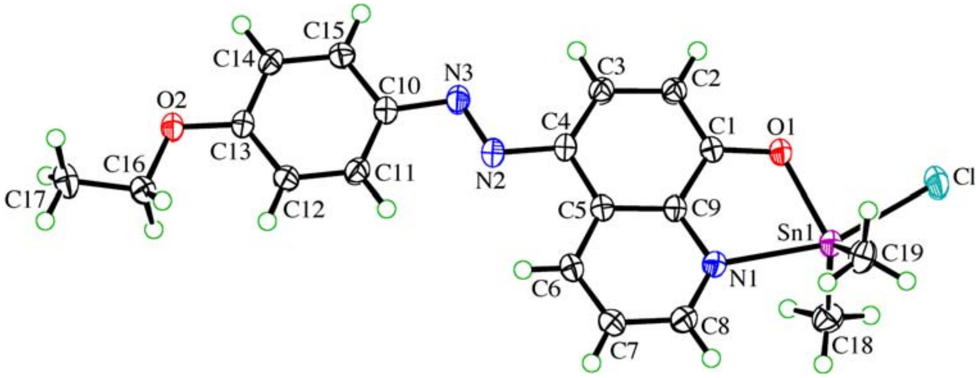

Figure 2. The molecular structure of $Me_2SnCl(L^3){\cdot}C_7H_8$ (**6**). Displacement ellipsoids are shown at the 50% probability level.

[Sn-CH$_3$, $^1J(^{119}Sn,\ ^{13}C = 620\,Hz)$], ppm. ^{119}Sn NMR (CDCl$_3$) δ_{Sn}: −84.5 ppm. ^{119}Sn Mössbauer: $\delta = 1.11$, $\Delta = 2.84$, $\Gamma_1 = 1.33$, $\Gamma_2 = 1.56\,mm\ s^{-1}$.

2.4. *X-ray crystallography*

Crystals of **2** and **6** suitable for an X-ray crystal-structure determination were obtained from slow evaporation of benzene/hexane and toluene/chloroform (v/v 1:1) solutions of the respective compounds. All the measurements were made at 160 K on a Nonius KappaCCD diffractometer [8] with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [9]. The intensities were corrected for *Lorentz* and polarization effects and empirical absorption corrections based on the multi-scan method [10] were applied. Equivalent reflections were merged. The data collection and refinement parameters are given in table 1, and views of **2** and **6** are shown in figures 1 and 2. The structures for **2** and **6** were solved by direct methods using SIR92 [11].

In **6**, the asymmetric unit contains one molecule of the Sn complex plus one disordered molecule of toluene. Two sets of slightly different positions were defined for the atoms of the toluene molecule and the site occupation factor of the major orientation of the molecule refined to 0.597(5). Similarity restraints were applied to all chemically equivalent bond lengths and angles involving the disordered carbon atoms, while neighboring atoms within and between each orientation of the disordered toluene molecule were restrained to have similar atomic displacement parameters.

The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions and refined by using a riding model where each hydrogen atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent carbon atom (1.5U_{eq} for methyl groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimize the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied. Four reflections in **6**, whose intensities were considered to be extreme outliers, were omitted from the final refinement. All calculations were performed using the SHELXL97 program [12].

3. Results and discussion

3.1. *Synthesis*

Dimethyltin(IV) complexes of the 5-[(*E*)-2-(aryl)-1-diazenyl)quinolin-8-ols (LH) could be prepared by reacting stoichiometric amounts of Me_2SnCl_2 and LNa (generated *in situ* from Na and anhydrous methanol) in anhydrous benzene (equations 1 and 2).

$$2LH + 2NaOMe + Me_2SnCl_2 \xrightarrow[\text{Reflux, 3h}]{\text{Benzene}} Me_2Sn(L)_2 + 2MeOH + 2NaCl \qquad (1)$$

$$LH + NaOMe + Me_2SnCl_2 \xrightarrow[\text{Reflux, 3h}]{\text{Benzene}} Me_2SnCl(L)_2 + MeOH + NaCl \qquad (2)$$

These reactions proceeded smoothly and pure products were obtained in yields >45%. The work-up details and characterization data for the complexes are described in section 2.3. The complexes are air stable and soluble in all common organic solvents.

3.2. *IR and NMR (^{1}H, ^{13}C and ^{119}Sn) data*

The ν(OH) of L^1H-L^4H at ~3380 cm^{-1} is absent in the dimethyltin(IV) complexes, **1–6**, confirming deprotonation of the ligand consistent with coordination through the oxygen atom of the ligand. A strong band around 1235 cm^{-1} due to ν(C(aryl)-O) (*i.e.* C_8-O) in the ligands shifts to ~1250 cm^{-1} in the complexes, which is in agreement with our earlier observation of an O→Sn connection [1–5]. There are many absorptions in the 500–600 cm^{-1} region, so no assignments to the ν(Sn-C) modes are possible for **1–6**.

The ^1H and ^{13}C NMR signals for L^1H-L^4H were assigned by the use of correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HSQC), and heteronuclear multiple-bond connectivities (HMBC) experiments [1, 2]. The conclusions drawn from the ligand assignments were then extrapolated to **1–6** owing to the data similarity. The ^1H NMR integration values were consistent with the formulation of the products. The ^1H and ^{13}C NMR chemical shift assignments for the methyl groups attached to tin are straightforward using the multiplicity pattern and also by examining the ^1J (^{13}C-$^{119/117}Sn$) coupling constants [13, 14]. In the ^1H and ^{13}C NMR spectra of **1–6**, there is only one set of NMR signals for both the methyl groups (Sn-Me), which provides evidence for magnetic equivalence of both methyls on the NMR time scale, indicating their symmetrical arrangement in the coordination sphere of tin in solution. The chemical shifts $\delta(^1H)$ and $\delta(^{13}C)$ of Sn-R are not very sensitive to changes in coordination of the tin atom. The coupling constants due to Sn-R: $^2J(^{119}Sn,^1H)$ = 70 Hz and $^1J(^{119}Sn,^{13}C)$ = 630 Hz of **1–4** match (see experimental section) closely with the data for six-coordinate $[Me_2Sn(Ox)_2]$ [13, 15] in $CDCl_3$ solution. Similarly, $^1J(^{119}Sn,^{13}C)$ = 645 Hz of **5** and **6** match that observed for [Me_2SnCl (Ox)] [16]. Further structural conclusions have been extracted from ^{119}Sn solution NMR spectra. Complexes **1–4** display a sharp singlet at −224 ppm, suggesting that Sn complexes are isostructural in solution and the values match well with those reported for six-coordinate $[Me_2Sn(Ox)_2]$ = −237 ppm [17] and cognate *cis*-bis{5-[(*E*)-2-(2-carbomethoxyphenyl)-1-diazenyl]quinolinolato}dimethyltin(IV) [4] in $CDCl_3$ solution. Complexes **5** and **6** display a sharp singlet at −84 ppm and the values correlate well with those reported for five-coordinate $[Me_2SnCl(Ox)] = -92$ ppm in $CHCl_3$ solution [17].

3.3. ^{119}*Sn Mössbauer data*

^{119}Sn Mössbauer data can usually give information on the covalency of bonds formed by tin through determination of the isomer shift values, δ, and also insight into the probable structures of the complexes, in solid state or frozen solution, by determination of experimental nuclear quadrupole splittings, $|\Delta_{exp}|$. The dimethyltin(IV) complexes **1–4** display δ values of 0.86–0.88 $mm\,s^{-1}$, which are typical of diorganotin(IV) derivatives [18] and fall within the limits of δ values observed for related diorganotin(IV) quinolinolates: $[Me_2Sn(Ox)_2] = 0.88\ mm\,s^{-1}$ [19]; *cis*-bis{5-[(*E*)-2-(phenyl)-1-diazenyl]quinolin-8-olato}dimethyltin(IV) = 0.93 $mm\,s^{-1}$ [20] and *cis*-bis{5-[(*E*)-2-(2-carbomethoxyphenyl)-1-diazenyl]quinolin-8-olato}dimethyltin(IV) = 0.84 $mm\,s^{-1}$ [4]. The measured quadrupole splitting values $|\Delta_{exp}|$ of 2.05–2.22 $mm\ s^{-1}$ are consistent with *cis*-R_2 octahedral structures which characterize **1–4**, albeit as severely distorted octahedral [21, 22]. Further, $|\Delta_{exp}|$ values for **1–4** compare well with data for related $[Me_2Sn(Ox)_2] = 1.98\ mm\,s^{-1}$ [19], which has a *cis*-Me_2Sn octahedral geometry as confirmed by single crystal X-ray crystallography [7], and also match with data reported for *cis*-bis{5-[(*E*)-2-(phenyl)-1-diazenyl]quinolin-8-olato}dimethyltin(IV) = 2.18 $mm\,s^{-1}$ [20] and *cis*-bis{5-[(*E*)-2-(2-carbomethoxyphenyl)-1-diazenyl]quinolin-8-olato}dimethyltin(IV) = 2.04 $mm\,s^{-1}$ [4]. The similar magnitudes of δ and $|\Delta_{exp}|$ values in **1–4** further indicate that the complexes are isostructural. On the other hand, **5** and **6** exhibit $|\Delta_{exp}|$ values of approximately 2.80 $mm\,s^{-1}$ and the values are higher than that for the dibutyltin(IV) analog $^{n}Bu_2SnCl(L) = 2.51\ mm\,s^{-1}$ (L = 5-[(*E*)-2-(4-methoxyphenyl)-1-diazenyl]quinolin-8-olato) [3] which has a *cis*-trigonal bipyramidal geometry as characterized by crystallography [6]. Moreover, $|\Delta_{exp}|$ values of **5** and **6** are lower compared to $[Me_2SnCl(Ox)] = 3.12\ mm\,s^{-1}$ [19] which has the same formulation and a *cis*-trigonal bipyramidal geometry was proposed [19] with tentative placement of atoms in axial and equatorial positions in the absence of diffraction data. Thus, Mössbauer spectroscopic data suggest a *cis*-R_2Sn octahedral geometry for **1–4**, where the four positions in one plane are defined by two oxygen atoms, a nitrogen atom, and an organo group, while the two sites perpendicular to that are occupied by an organo group and a nitrogen atom. A distorted *cis*-trigonal bipyramidal geometry is indicated for **5** and **6**, where the bidentate

Table 2. Selected bond lengths (Å) and angles (°) for $Me_2Sn(L^2)_2$ (**2**).

Sn(1)–C(21)	2.149(3)	O(2)–Sn(1)–N(1)	85.88(7)
Sn(1)–C(31)	2.139(3)	O(2)–Sn(1)–N(2)	74.32(7)
Sn(1)–O(1)	2.108(2)	O(1)–Sn(1)–O(2)	153.95(7)
Sn(1)–O(2)	2.093(2)	C(21)–Sn(1)–N(1)	84.99(9)
Sn(1)–N(1)	2.388(2)	C(21)–Sn(1)–N(2)	156.13(9)
Sn(1)–N(2)	2.334(2)	C(31)–Sn(1)–N(1)	158.5(1)
N(1)–C(9)	1.358(3)	C(31)–Sn(1)–N(2)	89.8(1)
N(2)–C(19)	1.365(3)	C(21)–Sn(1)–C(31)	112.8(1)
N(3)–N(4)	1.263(3)	O(1)–Sn(1)–C(21)	100.92(9)
N(5)–N(6)	1.254(3)	O(1)–Sn(1)–C(31)	91.3(1)
		O(2)–Sn(1)–C(21)	91.86(9)
O(1)–Sn(1)–N(1)	72.89(7)	O(2)–Sn(1)–C(31)	104.7(1)
O(1)–Sn(1)–N(2)	85.46(8)	N(1)–Sn(1)–N(2)	74.86(7)

Table 3. Selected bond lengths (Å) and angles (°) for $Me_2SnCl(L^3)\cdot C_7H_8$ (**6**).

Sn(1)–O(1)	2.053(2)	C(18)–Sn(1)–C(19)	128.8(1)
Sn(1)–N(1)	2.343(2)	O(1)–Sn(1)–N(1)	74.66(6)
Sn(1)–Cl	2.4724(6)	C(18)–Sn(1)–N(1)	91.00(8)
Sn(1)–C(18)	2.113(2)	C(19)–Sn(1)–N(1)	93.04(8)
Sn(1)–C(19)	2.113(2)	O(1)–Sn(1)–Cl	85.69(4)
O(1)–C(1)	1.336(2)	C(18)–Sn(1)–Cl	97.15(7)
N(1)–C(8)	1.323(3)	C(19)–Sn(1)–Cl	95.68(7)
N(1)–C(9)	1.363(3)	N(1)–Sn(1)–Cl	160.35(5)
		C(1)–O(1)–Sn(1)	119.4(1)
O(1)–Sn(1)–C(18)	115.17(8)	C(8)–N(1)–Sn(1)	130.6(2)
O(1)–Sn(1)–C(19)	115.11(8)	C(9)–N(1)–Sn(1)	110.3(1)

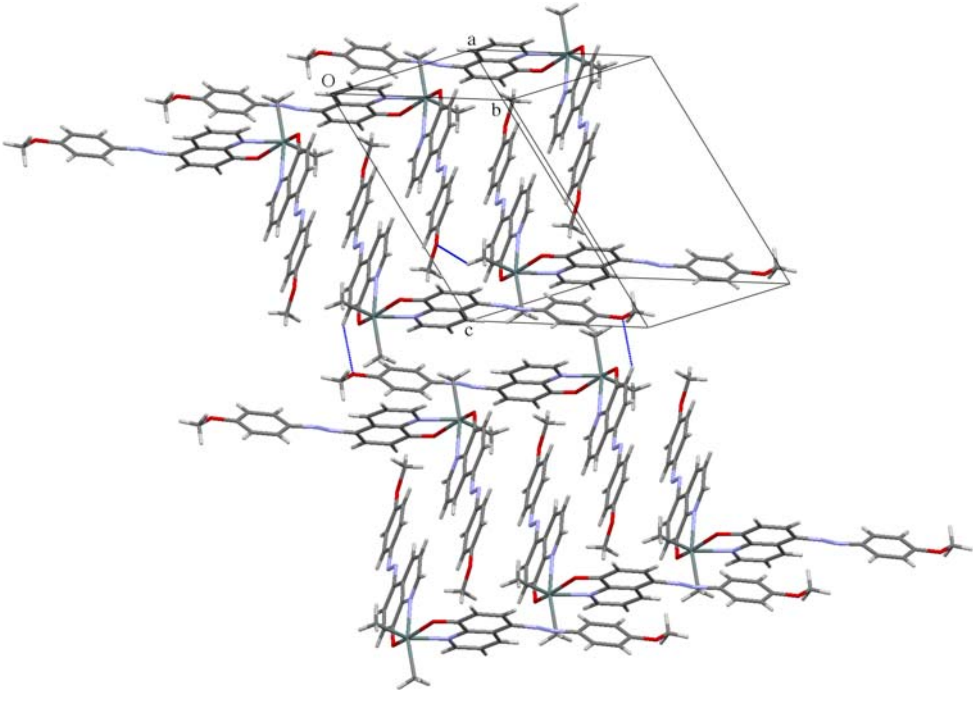

Figure 3. The crystal packing of $Me_2Sn(L^2)_2$ (**2**) showing stacks formed by the planar ligands and the C–H···O interactions (blue lines) cross-linking the stacks.

quinolin-8-olate ligand coordinates such that the nitrogen and oxygen atoms are in axial and equatorial positions, respectively. The other axial position is occupied by Cl^- and the methyl groups complete the equatorial plane. The structures of two representative complexes, **2** and **6**, have been confirmed from the diffraction study (see below).

3.4. ***Structural results from single crystal X-ray diffraction***

The results of the X-ray crystallographic study on **2** and **6** (figures 1 and 2) are consistent with the spectroscopic evidence described in Sections 3.2–3.3. The selected geometric parameters of **2** and **6** are given in tables 2 and 3, respectively.

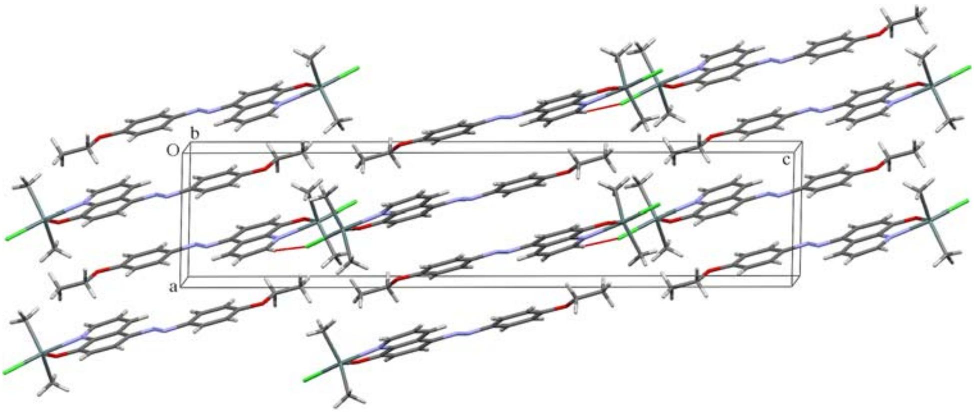

Figure 4. The crystal packing of $Me_2SnCl(L^3)\cdot C_7H_8$ (**6**) showing stacks formed by the planar ligands and the C–H···Cl interactions (red lines) cross-linking the stacks parallel to the *b* axis. The solvent molecules have been omitted for clarity.

The Sn atom in **2** has a distorted octahedral coordination geometry in which the oxygen atoms from the two bidentate ligands are approximately *trans*, while the quinolin-8-olate nitrogen atoms are *trans* to the methyl ligands. The small bite angle subtended by the donor atoms of the quinolin-8-olate moiety is the main reason for the distortion from a regular octahedral geometry, as observed for the dibutyltin(IV), diphenyltin(IV) and dibenzyltin(IV) analogs [1–4]. The metric parameters of **2** compare well with those of their diorganotin(IV) analogs and the Sn-coordination geometry is also very similar [1–4]. There are 10 diorganotin bis(quinolin-8-olate) structures bearing similar azo functionality available in the literature for comparison [1–3], e.g. Bu_2SnL_2: R = 4′-CH_3; R = 4′-OCH_3; R = 4′-OC_2H_5; R = 4′-Br [3], Ph_2SnL_2: R = H; R = 4′-CH_3; R = 4′-Br [2], Bz_2SnL_2: R = 4′-CH_3; R = 4′-OCH_3; R = 4′-Br [1] [see scheme 1(i) for details]. One of the quinolin-8-olate ligands in **2** is quite planar, while the other has a significant twist of the plane of the terminal methoxyphenyl segment out of the plane of the fused rings of the ligand. The dihedral angle between these planes is about 47°. This difference in planarity is correlated with the observed packing of the molecules. The molecules are arranged so that the planar quinolin-8-olates align face-to-face to give columns of parallel ligands interpenetrating from molecules lying on the opposite sides of the column (figure 3). The columns run parallel to the *a* axis with the ligand planes slanted slightly to this direction. Within the column, pairs of quinolin-8-olate ligands from two adjacent molecules align antiparallel across a center of inversion with the distance between the planes being approximately 3.6 Å. The methoxyphenyl ring overlaps almost perfectly the 8-quinolyloxy ring of the neighboring ligand, which suggests the presence of a significant π···π interaction; the centroid···centroid distance is 3.713(2) Å, the perpendicular distance from the centroid of one ring to the plane of the other is 3.616(1) Å and the ring planes are inclined at only 4.5(1)°. However, the next pair of quinolin-8-olate ligands in the column is sufficiently offset from the previous pair to preclude significant π···π interactions between them. The other quinolin-8-olate ligand does not have any close face-to-face contacts, but its methoxy oxygen atom is involved in a weak C–H···O interaction with the planar quinolin-8-olate ligand of a neighboring molecule, namely with the C–H group *ortho* to the oxygen atom coordinating to the tin atom (O···H = 2.68 Å and O···H–C = 140°). This interaction links pairs of molecules across centers of inversion and thereby cross-links the stacks of molecules to give two-dimensional supramolecular sheets which lie parallel to the ($\bar{1}01$) plane. The C–H···O interaction and the absence of $\pi\cdots\pi$ interactions involving the second quinolin-8-olate may contribute to this ligand being twisted.

In **6**, the asymmetric unit contains one molecule of the mononuclear Sn-complex plus one disordered molecule of toluene. The tin atom is five-coordinate (figure 2) and the compound assumes a similar geometry to that observed for its dibutyltin(IV) analog; the geometric parameters are also very similar [6]. The coordination geometry is best described as distorted *cis*-trigonal bipyramidal. The bidentate quinolin-8-olate coordinates such that nitrogen and oxygen atoms are in axial and equatorial positions, respectively. The other axial position is occupied by Cl^- and the methyl ligands complete the equatorial plane. Except for the methyl ligands, **6** is essentially planar. The molecules are stacked parallel to the *a* axis in an alternating antiparallel arrangement and adjacent molecules in the stack are almost perfectly overlapping across centers of inversion with a distance between the planes of approximately 3.3 Å. Despite this, the six-membered rings in adjacent molecules lie mostly offset from one another, reducing the strength of any $\pi\cdots\pi$ interactions. The toluene molecules fill spaces between neighboring stacks. Cl···H–C interactions, which involve the quinolin-8-olate C–H group *ortho* to the nitrogen atom that coordinates to the tin atom (Cl···H = 2.70 Å and Cl···H–C = 163°), link the metal ends of the molecules head-to-head into chains which run parallel to the *b* axis. In conjunction with the stacks, these interactions complete a three-dimensional supramolecular network (figure 4).

4. Conclusion

We have demonstrated that 5-[(*E*)-2-(aryl)-1-diazenyl)quinolin-8-olates readily combine with dimethyltin to form new coordination complexes of the types $Me_2Sn(L)_2$ and $Me_2SnCl(L)$. Both spectroscopic and crystal structure results show that $Me_2Sn(L)_2$ has a distorted *cis*-octahedral arrangement while $Me_2SnCl(L)$ has a distorted trigonal bipyramidal coordination geometry around the tin atom in both solution and solid state. Notably, the reactivity of the related dibutyltin(IV) chloro analog $Bu_2SnCl(L)$ demonstrated elegant structural architectures with a range of carboxylate ligands and now $Me_2SnCl(L)$ is structurally accessible which may provide a route for synthesizing new complexes with various architectures.

Supplementary material

CCDC–889287–889288 contains the supplementary crystallographic data for **2** and **6**. These data can be obtained free of charge from Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

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