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New triorganotin(IV) complexes of polyfunctional S,N,O-ligands: Supramolecular structures based on π···π and/or C–H···π interactions

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Abstract

A series of new triorganotin(IV) complexes with 4-hydroxy-2-mercapto-6-methylpyrimidine (L^1H_2), 4-hydroxy-2-mercapto-pyrimidine (L^2H_2), 2,4(1H,3H)-pyrimidinedithione (L^3H_2) (Scheme 1) of the type $R_3SnLSnR_3$ (R = Me **1**, **4**, **7**; R = Ph **2**, **5**, **8**; R = $PhCH_2$ **3**, **6**, **9**) have been synthesized by reactions of triorganotin(IV) chloride and corresponding ligands. All complexes are characterized by elemental analyses, IR spectra and NMR spectra analyses. Among them, complexes **2**, **5** and **8** are also characterized by X-ray crystallography diffraction analyses. Significant π···π stacking, C–H···π interactions and intramolecular hydrogen bonds stabilize these structures.

Keywords: Triorganotin(IV); 4-Hydroxy-2-mercapto-6-methylpyrimidine; π···π stacking; Crystal structure

1. Introduction

The construction of sophisticated inorganic–organic hybrid [1,2] supramolecular networks [3] based on organized strong covalent interactions [4] and extensive lateral weak non-covalent forces like hydrogen bonding [5], π···π stacking [6] is an area of great activity due to fabrication of functional materials [7] utilizing the wide variety in properties associated with each suitably tailored component. An analysis of complexes with aromatic nitrogen heterocycles as ligands reveals that such a π···π stacking is usually an offset or slipped facial arrangement of the rings, i.e., edge- or point-to-face C–H···π interactions [8,9]. A near face-to-face alignment of the rings is extremely rare. In recent years many organotin(IV) compounds have been the topic of interest for their potential practical applications [10]. In addition to the aforesaid applications, organotin(IV) compounds are also of interest in view of the considerable structural diversity they possess. This aspect has been attracting the attention of a number of researchers and a multitude of structural types have been discovered [11].

We have reported some organotin(IV) complexes with pyrimidine ligands before, such as 2-mercaptopyrimidine, 4-amino-2-mercaptopyrimidine [12a,12b] and 2-mercapto-4-methylpyrimidine [12c]. As an extension of this aspect, here, we report the syntheses and crystal structures of new polymeric triorganotin(IV) complexes of polyfunctional S,N,O-ligands involving π···π and/or C–H···π interactions. We obtained nine new complexes by reaction of triorganotin(IV) chloride and corresponding substituted pyrimidine ligands in the presence of sodium ethoxide. Determinations by elemental analyses, IR and NMR spectra analyses of all the complexes are given. Among them, complexes **2**, **5** and **8** are also characterized by X-ray crystallography diffraction analyses.

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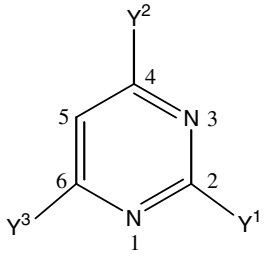


	Y^1	Y^2	Y^3
L^1H_2	SH	OH	CH_3
L^2H_2	SH	OH	H
L^3H_2	SH	SH	H

Scheme 1.

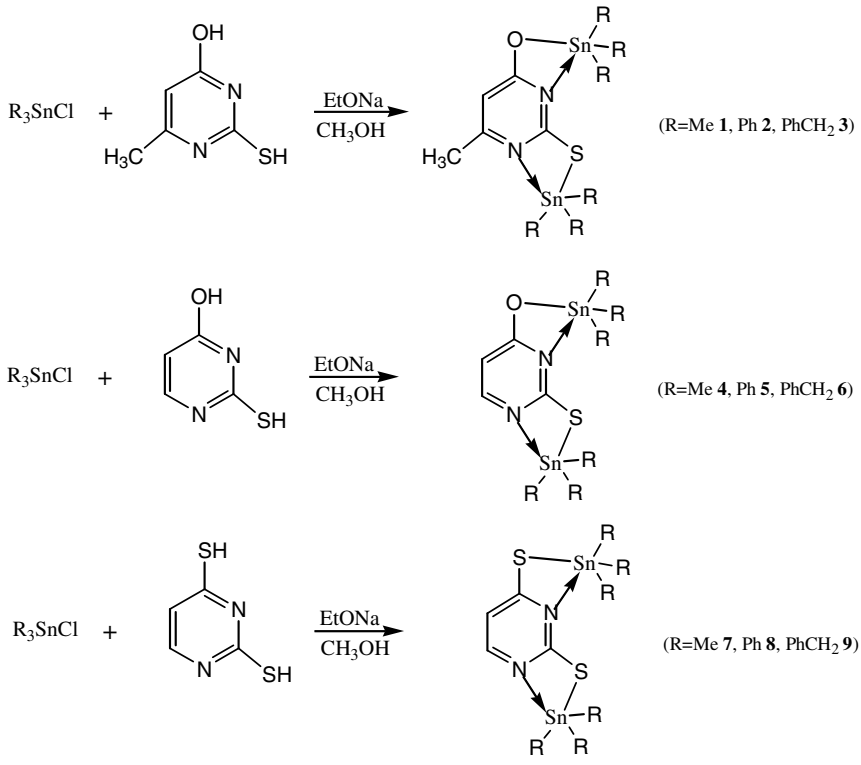
2. Experimental section

2.1. Materials and measurements

Trimethyltin chloride, triphenyltin chloride and 4-hydroxy-2-mercapto-6-methylpyrimidine, 4-hydroxy-2-mercapto-pyrimidine, 2,4(1H,3H)-pyrimidinedithione were commercially available, and they were used without further purification. Tribenzyltin chloride was prepared by a standard method reported in the literature [13]. The melting points were obtained with Kofler micro melting point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet–460 spectrophotometer using KBr discs and sodium chloride optics. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C NMR spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ^1H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR. Elemental analyses (C, H, N) were performed with a PE-2400II apparatus. Mass spectral data were measured on a MAT 8500 Finnigan 70 eV mass spectrometer (Germany) and m/z values were calculated assuming H = 1, C = 12, Sn = 120, O = 16, N = 14 and S = 32.

2.2. Synthesis

The general route of synthesis is shown in the following. The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. Pyrimidine (4-hydroxy-2-mercapto-6-methylpyrimidine, 4-hydroxy-2-mer- capto-pyrimidine, 2,4(1H,3H)-pyrimidinedithione) ligands and the sodium ethoxide were added to the solution of methanol, the mixture was stirred for 30 min, and then added triorganotin(IV) chlorides to the mixture, continuing the reaction about 12 h at 40 °C. After cooling down to room temperature, the mixture was filtered. The solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from methanol. The synthetic experiments of complexes **1**–**9** were shown in Scheme 2.



Scheme 2.

2.2.1. $Me_3Sn(C_5H_4N_2OS)SnMe_3$ (1)

Complex **1** was synthesized by adding 4-hydroxy-2-mercapto-6-methylpyrimidine (0.142 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and trimethyltin chloride (0.398 g, 2 mmol) to the solution of methanol.

m.p. 116–118 °C. Yield, 0.374 g, 80%. Anal. Calc. for $C_{11}H_{22}N_2OSSn_2$: C, 28.24; H, 4.74; N, 5.99. Found: C, 28.27; H, 4.71; N, 6.01%. IR (KBr, cm^{-1}): 1583 (C=N), 560 (Sn–C), 458 (Sn–N), 307 (Sn–S), 467 (Sn–O). ^1H NMR ($CDCl_3$): δ 0.90 (s, $^2J_{Sn,H} = 68.6$ Hz, 18H), 1.34 (s, ring-CH_3, 3H), 7.44 (s, ring-C^5-H, 1H). ^{13}C NMR ($CDCl_3$): δ 8.2, 10.6 (Sn–CH_3), 24.7 (ring-CH_3), 172.4 (C^2), 179.1 (C^4), 132.1 (C^5), 164.4 (C^6). ^{119}Sn NMR ($CDCl_3$): −135, −95 ppm. MS (*m*/*z*, ion, intensity): (470) $[Me_3Sn(C_5H_4N_2OS)SnMe_3]^+$ M^+ (2), (455) $[Me_3Sn(C_5H_4N_2OS)SnMe_2]^+$ (45), (305) $[Me_3Sn(C_5H_4N_2OS)]^+$ (100), (165) $[Me_3Sn]^+$ (80), (120) $[Sn]^+$ (5).

2.2.2. $Ph_3Sn(C_5H_4N_2OS)SnPh_3$ (2)

Complex **2** was synthesized by the same procedure as **1** with 4-hydroxy-2-mercapto-6-methylpyrimidine (0.142 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and triphenyltin chloride (0.770 g, 2 mmol).

m.p. 185–187 °C. Yield, 0.672 g, 76%. Anal. Calc. for $C_{41}H_{34}N_2OSSn_2$: C, 58.61; H, 4.08; N, 3.33. Found: C, 58.56; H, 4.11; N, 3.35%. IR (KBr, cm^{-1}): 1576 (C=N), 560 (Sn–C), 467 (Sn–N), 311 (Sn–S), 469 (Sn–O). ^1H NMR ($CDCl_3$): δ 7.36–7.81 (m, Sn–C_6H_5, 30H), 1.33 (s, ring-CH_3, 3H), 7.45 (s, ring-C^5–H, 1H). ^{13}C NMR ($CDCl_3$): δ 24.7 (ring-CH_3), 172.5 (C^2), 179.2 (C^4), 132.5 (C^5), 164.4 (C^6), 137.5 (*o*-C), 128.8 (*m*-C), 129.3 (*p*-C), 142.6 (*i*-C). ^{119}Sn NMR ($CDCl_3$): −173, −135 ppm. MS (*m*/*z*, ion, intensity): (842) $[Ph_3Sn(C_5H_4N_2OS)SnPh_3]^+$ M^+ (2), (765) $[Ph_3Sn(C_5H_4N_2OS)SnPh_2]^+$ (45), (491) $[Ph_3Sn(C_5H_4N_2OS)]^+$ (100), (351) $[Ph_3Sn]^+$ (80), (120) $[Sn]^+$ (5).

2.2.3. $(PhCH_2)_3Sn(C_5H_4N_2OS)Sn(CH_2Ph)_3$ (3)

Complex **3** was synthesized by the same procedure as **1** with 4-hydroxy-2-mercapto-6-methylpyrimidine (0.142 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and tribenzyltin chloride (0.854 g, 2 mmol).

m.p. 125–127 °C. Yield, 0.703 g, 76%. Anal. Calc. for $C_{47}H_{46}N_2OSSn_2$: C, 61.07; H, 5.02; N, 3.03. Found: C, 61.04; H, 4.98; N, 3.07%. IR (KBr, cm^{-1}): 1581 (C=N), 557 (Sn–C), 456 (Sn–N), 309 (Sn–S), 467 (Sn–O). ^1H NMR ($CDCl_3$): δ 7.46–7.79 (m, Sn–CH_2–C_6H_5, 30H), 3.26 (s, CH_2, 12H), 1.35 (s, ring-CH_3, 3H), 7.43 (s, ring-C^5–H, 1H). ^{13}C NMR ($CDCl_3$): δ 24.7 (ring-CH_3), 172.4 (C^2), 179.1 (C^4), 132.1 (C^5), 163.4 (C^6), 23.6, 21.9 (s, CH_2), 127.3 (*o*-C), 127.4 (*m*-C), 128.2 (*p*-C), 124.2 (*i*-C). ^{119}Sn NMR ($CDCl_3$): −151, −101 ppm. MS (*m*/*z*, ion, intensity): (926) $[(PhCH_2)_3Sn(C_5H_4N_2OS)Sn(CH_2Ph)_3]^+$ M^+ (2), (835) $[(PhCH_2)_3Sn(C_5H_4N_2OS)Sn(CH_2Ph)_2]^+$ (45), (533) $[(PhCH_2)_3Sn(C_5H_4N_2OS)]^+$ (100), (393) $[(PhCH_2)_3Sn]^+$ (80), (120) $[Sn]^+$ (5).

2.2.4. $Me_3Sn(C_4H_2N_2OS)SnMe_3$ (4)

Complex **4** was synthesized by the same procedure as **1** with 4-hydroxy-2-mercapto-pyrimidine (0.128 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and trimethyltin chloride (0.398 g, 2 mmol).

m.p. 119–122 °C. Yield, 0.354 g, 78%. Anal. Calc. for $C_{10}H_{20}N_2OSSn_2$: C, 26.47; H, 4.44; N, 6.17. Found: C, 26.49; H, 4.41; N, 6.18%. IR (KBr, cm^{-1}): 1582 (C=N), 565 (Sn–C), 459 (Sn–N), 306 (Sn–S), 469 (Sn–O). ^1H NMR ($CDCl_3$): δ 0.90 (s, $^2J_{Sn,H} = 68.8$ Hz, 18H), 7.48 (s, ring-C^5–H, 1H), 8.80 (s, ring-C^6–H, 1H). ^{13}C NMR ($CDCl_3$): δ 8.12, 10.5 (Sn–CH_3), 172.4 (C^2), 179.1 (C^4), 132.1 (C^5), 157.2 (C^6). ^{119}Sn NMR ($CDCl_3$): −137, −95 ppm. MS (*m*/*z*, ion, intensity): (456) $[Me_3Sn(C_4H_2N_2OS)SnMe_3]^+$ M^+ (2), (441) $[Me_3Sn(C_4H_2N_2OS)SnMe_2]^+$ (45), (291) $[Me_3Sn(C_4H_2N_2OS)]^+$ (100), (165) $[Me_3Sn]^+$ (80), (120) $[Sn]^+$ (5).

2.2.5. $Ph_3Sn(C_4H_2N_2OS)SnPh_3$ (5)

Complex **5** was synthesized by the same procedure as **1** with 4-hydroxy-2-mercapto-pyrimidine (0.128 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and triphenyltin chloride (0.770 g, 2 mmol).

m.p. 183–185 °C. Yield, 0.644 g, 78%. Anal. Calc. for $C_{40}H_{32}N_2OSSn_2$: C, 58.15; H, 3.90; N, 3.39. Found: C, 58.10; H, 3.91; N, 3.35%. IR (KBr, cm^{-1}): 1578 (C=N), 556 (Sn–C), 469 (Sn–N), 309 (Sn–S), 468 (Sn–O). ^1H NMR ($CDCl_3$): δ 7.36–7.79 (m, Sn–C_6H_5, 30H), 7.49 (s, ring-C^5-H, 1H), 8.81 (s, ring-C^6–H, 1H). ^{13}C NMR ($CDCl_3$): δ 172.5 (C^2), 179.2 (C^4), 132.5 (C^5), 157.3 (C^6), 137.5 (*o*-C), 128.8 (*m*-C), 129.3 (*p*-C), 142.6 (*i*-C). ^{119}Sn NMR ($CDCl_3$): −171, −133 ppm. MS (*m*/*z*, ion, intensity): (828) $[Ph_3Sn(C_4H_2N_2OS)SnPh_3]^+$ M^+ (2), (757) $[Ph_3Sn(C_4H_2N_2OS)SnPh_2]^+$ (45), (477) $[Ph_3Sn(C_4H_2N_2OS)]^+$ (100), (351) $[Ph_3Sn]^+$ (80), (120) $[Sn]^+$ (5).

2.2.6. $(PhCH_2)_3Sn(C_4H_2N_2OS)Sn(CH_2Ph)_3$ (6)

Complex **6** was synthesized by the same procedure as **1** with 4-hydroxy-2-mercapto-pyrimidine (0.128 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and tribenzyltin chloride (0.854 g, 2 mmol).

m.p. 123–125 °C. Yield, 0.692 g, 76%. Anal. Calc. for $C_{46}H_{44}N_2OSSn_2$: C, 60.69; H, 4.87; N, 3.08. Found: C, 60.72; H, 4.88; N, 3.07%. IR (KBr, cm^{-1}): 1581 (C=N), 559 (Sn–C), 458 (Sn–N), 306 (Sn–S), 464 (Sn–O). ^1H NMR ($CDCl_3$): δ 7.46–7.79 (m, Sn–CH_2–C_6H_5, 30H), 3.25 (s, CH_2, 12H), 7.47 (s, ring-C^5–H, 1H), 8.82 (s, ring-C^6–H, 1H). ^{13}C NMR ($CDCl_3$): δ 172.4 (C^2), 179.1 (C^4), 132.1 (C^5), 157.3 (C^6), 23.6, 21.9 (s, CH_2), 127.3 (*o*-C), 127.4 (*m*-C), 128.2 (*p*-C), 124.2 (*i*-C). ^{119}Sn NMR ($CDCl_3$): −158, −102 ppm. MS (*m*/*z*, ion, intensity): (912) $[(PhCH_2)_3Sn(C_4H_2N_2OS)Sn(CH_2Ph)_3]^+$ M^+ (2), (821) $[(PhCH_2)_3Sn(C_4H_2N_2OS)Sn(CH_2Ph)_2]^+$ (45), (519) $[(PhCH_2)_3Sn(C_4H_2N_2OS)]^+$ (100), (393) $[(PhCH_2)_3Sn]^+$ (80), (120) $[Sn]^+$ (5).

2.2.7. $Me_3Sn(C_4H_2N_2S_2)SnMe_3$ (7)

Complex **7** was synthesized by the same procedure as **1** with 2,4(1H,3H)-pyrimidinedithione (0.144 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and trimethyltin chloride (0.398 g, 2 mmol).

m.p. 116–119 °C. Yield, 0.366 g, 78%. Anal. Calc. for $C_{10}H_{20}N_2S_2Sn_2$: C, 25.56; H, 4.29; N, 5.96. Found: C, 25.51; H, 4.31; N, 6.01%. IR (KBr, cm^{-1}): 1581 (C=N), 564 (Sn–C), 459 (Sn–N), 307 (Sn–S). ^1H NMR ($CDCl_3$): δ 0.90 (s, $^2J_{Sn,H} = 69.2$ Hz, 18H), 7.39 (s, ring-C^5–H, 1H), 8.80 (s, ring-C^6–H, 1H). ^{13}C NMR ($CDCl_3$): δ 10.5 (Sn–CH_3), 172.4 (C^2), 181.1 (C^4), 134.1 (C^5), 157.2 (C^6). ^{119}Sn NMR ($CDCl_3$): −131 ppm. MS (*m*/*z*, ion, intensity): (472) $[Me_3Sn(C_4H_2N_2S_2)SnMe_3]^+$ M^+ (2), (457) $[Me_3Sn(C_4H_2N_2S_2)SnMe_2]^+$ (55), (142) $[(C_4H_2N_2S_2)]^+$ (80), (165) $[Me_3Sn]^+$ (100), (120) $[Sn]^+$ (5).

2.2.8. $Ph_3\ Sn(C_4H_2N_2S_2)SnPh_3$ (8)

Complex **8** was synthesized by the same procedure as **1** with 2,4(1H,3H)-pyrimidinedithione (0.144 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and triphenyltin chloride (0.770 g, 2 mmol).

m.p. 176–180 °C. Yield, 0.657 g, 78%. Anal. Calc. for $C_{40}H_{32}N_2S_2Sn_2$: C, 57.04 H, 3.83; N, 3.33. Found: C, 57.01; H, 3.85; N, 3.35%. IR (KBr, cm^{-1}): 1583 (C=N), 557 (Sn–C), 467 (Sn–N), 307 (Sn–S). ^1H NMR ($CDCl_3$): δ 7.36–7.79 (m, Sn–C_6H_5, 30H), 7.38 (s, ring-C^5–H, 1H), 8.81 (s, ring-C^6–H, 1H). ^{13}C NMR ($CDCl_3$): δ 172.5 (C^2), 181.2 (C^4), 134.5 (C^5), 157.3 (C^6), 137.5 (*o*-C), 128.8 (*m*-C), 129.3 (*p*-C), 142.6 (*i*-C). ^{119}Sn NMR ($CDCl_3$): −175 ppm. MS (*m*/*z*, ion, intensity): (844) $[Ph_3Sn(C_4H_2N_2S_2)\text{- }SnPh_3]^+$ M^+ (2), (773) $[Ph_3Sn(C_4H_2N_2S_2)SnPh_2]^+$ (54), (142) $[(C_4H_2N_2S_2)]^+$ (80), (351) $[Ph_3Sn]^+$ (100), (120) $[Sn]^+$ (5).

2.2.9. $(PhCH_2)_3Sn(C_4H_2N_2S_2)Sn(CH_2Ph)_3$ (9)

Complex **9** was synthesized by the same procedure as **1** with 2,4(1H,3H)-pyrimidinedithione (0.144 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and tribenzyltin chloride (0.854 g, 2 mmol).

m.p. 119–122 °C. Yield, 0.704 g, 76%. Anal. Calc. for $C_{46}H_{44}N_2S_2Sn_2$: C, 59.64; H, 4.79; N, 3.02. Found: C, 59.68; H, 4.82; N, 3.03%. IR (KBr, cm^{-1}): 1582 (C=N), 556 (Sn–C), 455 (Sn–N), 303 (Sn–S). ^1H NMR ($CDCl_3$): δ 7.46–7.79 (m, Sn–CH_2–C_6H_5, 30H), 3.12 (s, CH_2, 12H), 7.39 (s, ring-C^5–H, 1H), 8.82 (s, ring-C^6–H, 1H). ^{13}C NMR ($CDCl_3$): δ 172.6 (C^2), 181.3 (C^4), 134.3 (C^5), 157.1 (C^6), 21.6 (s, CH_2), 127.3 (*o*-C), 127.4 (*m*-C), 128.2 (*p*-C), 124.2 (*i*-C). ^{119}Sn NMR ($CDCl_3$): −153 ppm. MS (*m*/*z*, ion, intensity): (928) $[(PhCH_2)_3Sn(C_4H_2N_2S_2)Sn(CH_2\ Ph)_3]^+$ M^+ (2), (837) $[(PhCH_2)_3Sn(C_4H_2N_2S_2)Sn(CH_2\ Ph)_2]^+$ (55), (142) $[(C_4H_2N_2S_2)]^+$ (80), (393) $[(PhCH_2)_3Sn]^+$ (100), (120) $[Sn]^+$ (5).

2.3. X-ray structure analyses of 2, 5 and 8

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart–1000 CCD area-detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full matrix least-squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations of **2**, **5** and **8** are listed in Table 1.

Table 1
Crystal data and structure refinement parameters for **2**, **5** and **8**

Complex	**2**	**5**	**8**
Empirical formula	$C_{41}H_{34}N_2OSSn_2$	$C_{40}H_{32}N_2OSSn_2$	$C_{40}H_{32}N_2S_2Sn_2$
M	840.14	826.12	842.24
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/a$
a (Å)	9.4989(18)	9.3603(14)	15.0738(12)
b (Å)	18.920(4)	39.169(3)	12.6305(10)
c (Å)	21.781(4)	10.0495(16)	19.1210(15)
α (°)	97.502(3)	90.00	90.00
β (°)	96.252(3)	102.596(2)	92.6450(10)
γ (°)	103.193(3)	90.00	90.00
V (Å^3)	3739.2(12)	3595.8(8)	3636.6(5)
Z	4	4	4
μ (mm^{-1})	1.425	1.480	1.518
Reflections collected	19872	18532	30718
Independent reflections	13069	6316	8284
R_{int}	0.0284	0.0326	0.0364
Goodness-of-fit on F^2	0.998	1.002	0.991
R_1, wR_2 [$I > 2\sigma(I)$]	0.0441, 0.0784	0.0543, 0.1543	0.0309, 0.0652
R_1, wR_2 (all data)	0.0969, 0.0980	0.0674, 0.1630	0.0461, 0.0711

3. Results and discussion

3.1. Spectra

Comparing the IR spectra of the free ligand with complexes **1**–**9**, the bands at 2560–2430 and about 2300 cm^{-1}, which appear in the spectra of the free ligand as the *v*(S–H) and *v*(O–H) vibration, are absent in those of complexes **1**–**9**, thus indicating metal–ligand bond formation through these sites. In the far-IR spectra, the absorption about 310 cm^{-1} region for all complexes **1**–**9**, which is absent in the spectrum of the ligand, is assigned to the Sn–S stretching mode of vibration and all the values are located within the range for Sn–S vibration observed in common organotin derivatives of thiolate (300–400 cm^{-1}) [14,15]. The strong absorption appears at about 460–470 cm^{-1} in the respective spectra of complexes **1**–**6**, which is absent in the free ligand, is assigned to the Sn–O stretching mode of vibration. The *v*(C=N) band, occurring at about 1576–1583 cm^{-1} in the spectra of all complexes have been assignable to *v*(C=N) according to the literatures [16], is considerably shifted towards lower frequencies with respect to that of the free ligand 1640–1650 cm^{-1}, confirming the coordination of the heterocyclic N to the tin, which indicated the coordination of free ligand to these complexes

is through sulfur atoms via thiol form and oxygen atoms via phenol form. The stretching frequency is lowered owing to the displacement of electron density from N to Sn atom, thus resulting in the weakening of the C=N bond as reported in the literature [17]. The weak- or medium-intensity band in the region 455–469 cm^{-1} can be assigned to Sn–N stretching vibrations. All these values are consistent with that detected in a number of organotin(IV) derivatives [18,19].

^{1}H NMR data showed that the signal of the –SH proton in the spectrum of the ligand is absent in all of the complexes, indicating the removal of the –SH proton and the formation of Sn–S bonds. The absence of the OH proton signals in the complexes **1**–**6** further supports the binding of the tin center to ligand oxygen atoms through the replacement of phenolic hydrogens. The $^2J_{Sn,H}$ values of trimethyltin derivatives **1**, **4** and **7** (68.6, 68.8 and 69.2 Hz respectively) are similar to those previously reported for five-coordinated trigonal bipyramidal tin(IV) adducts [20]. The structural changes occurring in ligand upon deprotonation and coordination to the Sn atom should be reflected by the changes in the ^{13}C NMR spectra of our complexes. The ^{13}C NMR spectra of all complexes show a significant downfield shift of all carbon resonance, compared with the free ligand. The shift is a consequence of an electron cloud transfer from the ligand to the acceptor.

As reported in the literature [21], values of δ (^{119}Sn) in the ranges −210 to −400, −90 to −190 and 200 to −60 ppm have been associated with six-, five- and four-coordinate tin centers, respectively. The ^{119}Sn NMR data of complexes **1**–**6** (from −95 to −173 ppm) show two signals and complexes **7**–**9** (from −131 to −175 ppm) show only one signal, typical of five-coordinated tin complexes.

The major mass spectral data of complexes **1**–**9** are given along their synthesis in the experimental section. A molecular ion peak of very low intensity was observed in complexes **1**–**9**, while the base peak of complexes **7**–**9** appeared at $m/z = 165$, 351 and 393, respectively, due to the loss of the ligand. Fragments due to the loss of the R groups from the molecular ion were observed in all complexes. The base peak of complexes **1**–**3** appeared at $m/z = 305$, 491 and 533, respectively, due to the loss of the group R_3Sn. Similarly, the base peak of complexes **4**–**6** appeared at $m/z = 291$, 477 and 519, respectively, due to the loss of the group R_3Sn. All the above analyses are confirmed by X-ray diffraction.

3.2. Description of crystal structures

3.2.1. $Ph_3Sn(C_5H_4N_2OS)SnPh_3$ (**2**) and $Ph_3Sn(C_4H_2N_2OS)SnPh_3$ (**5**)

Selected bond lengths (Å) and bond angles (°) for **2** and **5** are given in Tables 2 and 3, and its molecular structure and network are shown in Figs. 1–4, respectively.

As shown in Figs. 1 and 3, complex **2** and **5** are both monomers with one ligand coordinated to two triphenyltin moiety. The central tin atoms are five-coordinated with distorted trigonal bipyramidal geometry. The ligands adopt its thiol sulfur atom and hydroxyl oxygen atom as well as heterocyclic nitrogen atoms to coordinate to the central tin atoms. For complex **2**, the asymmetric unit contains two monomers A and B (see Fig. 1), which are crystallographically non-equivalent. The conformations of the two independent molecules A and B are almost the same, with only small differences in bond lengths and bond angles(see Table 2). The primary bond lengths in **2** and **5** are: Sn(1)–S(1) 2.4263(17) Å, Sn(1)–N(1) 2.841(5) Å,

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

Sn(1)–C(12)	2.103(8)	Sn(1)–C(6)	2.125(6)
Sn(1)–C(18)	2.146(6)	Sn(1)–S(1)	2.4263(17)
Sn(1)–N(1)	2.841(5)	Sn(2)–O(1)	2.071(4)
Sn(2)–C(36)	2.119(6)	Sn(2)–C(24)	2.124(6)
Sn(2)–C(30)	2.131(6)	Sn(2)–N(2)	2.721(5)
Sn(3)–C(53)	2.114(7)	Sn(3)–C(47)	2.120(7)
Sn(3)–C(59)	2.138(6)	Sn(3)–S(2)	2.4280(17)
Sn(3)–N(3)	2.853(5)	Sn(4)–O(2)	2.076(4)
Sn(4)–C(77)	2.123(6)	Sn(4)–C(71)	2.124(6)
Sn(4)–C(65)	2.127(6)	Sn(4)–N(4)	2.756(5)
S(1)–C(1)	1.752(6)	S(2)–C(42)	1.749(6)
C(12)–Sn(1)–C(6)	117.1(3)	C(12)–Sn(1)–C(18)	105.0(2)
C(6)–Sn(1)–C(18)	106.4(3)	C(12)–Sn(1)–S(1)	110.4(2)
C(6)–Sn(1)–S(1)	115.47(17)	C(18)–Sn(1)–S(1)	100.40(18)
C(12)–Sn(1)–N(1)	85.4(2)	C(6)–Sn(1)–N(1)	83.28(19)
C(18)–Sn(1)–N(1)	159.7(2)	S(1)–Sn(1)–N(1)	59.39(11)
O(1)–Sn(2)–C(36)	109.12(18)	O(1)–Sn(2)–C(24)	109.6(2)
C(36)–Sn(2)–C(24)	123.2(2)	O(1)–Sn(2)–C(30)	93.8(2)
C(36)–Sn(2)–C(30)	108.2(2)	C(24)–Sn(2)–C(30)	108.9(2)
O(1)–Sn(2)–N(2)	53.72(14)	C(36)–Sn(2)–N(2)	85.34(18)
C(24)–Sn(2)–N(2)	85.64(18)	C(30)–Sn(2)–N(2)	147.5(2)
C(53)–Sn(3)–C(47)	116.6(3)	C(53)–Sn(3)–C(59)	107.4(3)
C(47)–Sn(3)–C(59)	105.1(2)	C(53)–Sn(3)–S(2)	114.46(19)
C(47)–Sn(3)–S(2)	111.71(18)	C(59)–Sn(3)–S(2)	99.59(17)
C(53)–Sn(3)–N(3)	82.2(2)	C(47)–Sn(3)–N(3)	86.5(2)
C(59)–Sn(3)–N(3)	158.65(19)	S(2)–Sn(3)–N(3)	59.16(10)
O(2)–Sn(4)–C(77)	112.6(2)	O(2)–Sn(4)–C(71)	91.15(19)
C(77)–Sn(4)–C(71)	111.6(2)	O(2)–Sn(4)–C(65)	111.33(19)
C(77)–Sn(4)–C(65)	117.8(2)	C(71)–Sn(4)–C(65)	109.1(2)
O(2)–Sn(4)–N(4)	52.82(14)	C(77)–Sn(4)–N(4)	85.6(2)
C(71)–Sn(4)–N(4)	143.96(19)	C(65)–Sn(4)–N(4)	87.84(19)

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

Sn(1)–C(17)	2.134(8)	Sn(1)–C(11)	2.135(7)
Sn(1)–C(5)	2.159(7)	Sn(1)–S(1)	2.4684(19)
Sn(1)–N(1)	2.693(6)	Sn(2)–O(1)	2.042(5)
Sn(2)–C(23)	2.125(8)	Sn(2)–C(35)	2.128(8)
Sn(2)–C(29)	2.138(8)	Sn(2)–N(2)	2.900(5)
S(1)–C(1)	1.745(7)		
C(17)–Sn(1)–C(11)	115.3(3)	C(17)–Sn(1)–C(5)	106.9(3)
C(11)–Sn(1)–C(5)	104.6(3)	C(17)–Sn(1)–S(1)	112.8(2)
C(11)–Sn(1)–S(1)	116.21(18)	C(5)–Sn(1)–S(1)	98.8(2)
C(17)–Sn(1)–N(1)	88.5(3)	C(11)–Sn(1)–N(1)	81.4(2)
C(5)–Sn(1)–N(1)	158.4(2)	S(1)–Sn(1)–N(1)	60.55(13)
O(1)–Sn(2)–C(23)	114.7(3)	O(1)–Sn(2)–C(35)	106.3(3)
C(23)–Sn(2)–C(35)	117.7(3)	O(1)–Sn(2)–C(29)	93.7(3)
C(23)–Sn(2)–C(29)	108.4(3)	C(35)–Sn(2)–C(29)	113.7(3)
O(1)–Sn(2)–N(2)	50.82(18)	C(23)–Sn(2)–N(2)	84.6(2)
C(35)–Sn(2)–N(2)	87.3(3)	C(29)–Sn(2)–N(2)	143.7(3)

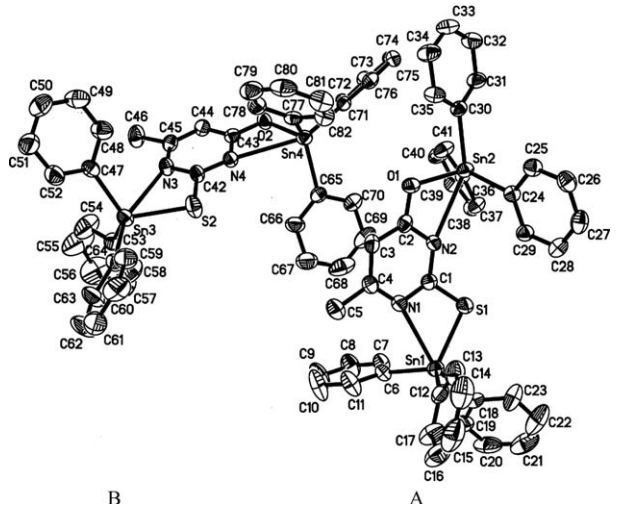


Fig. 1. Molecular structure of complex **2**.

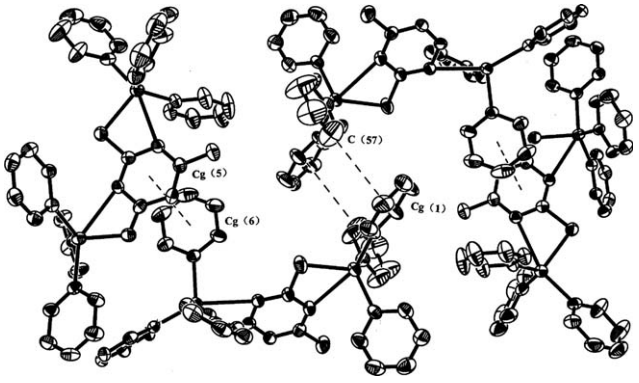


Fig. 2. Perspective view of complex **2** showing π···π stacking interactions (Cg(5): N(1)–C(1)–N(2)–C(2)–C(3)–C(4); ·Cg(6): C(65)–C(66)–C(67)–C(68)–C(69)–C(70)) and edge- or point-to-face C–H···π interactions (C(57)–H(57)···Cg(1)) (Cg(1): C(59a)–C(60a)–C(61a)–C(62a)–C(63a)–C(64a)).

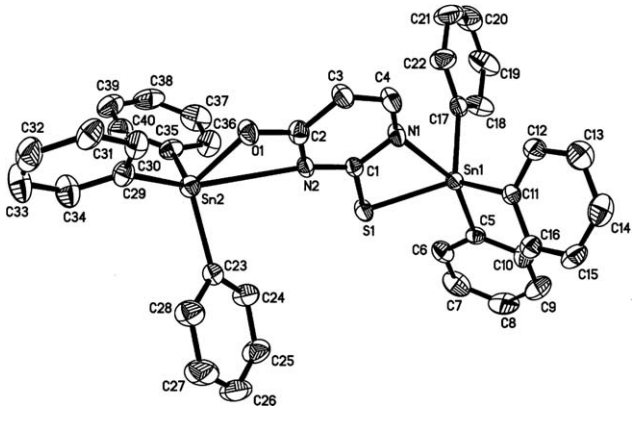


Fig. 3. Molecular structure of complex **5**.

Sn(2)–O(1) 2.071(4) Å, Sn(2)–N(2) 2.721(5) Å, Sn(3)–S(2) 2.4280(17) Å, Sn(3)–N(3) 2.853(5) Å, Sn(4)–O(2) 2.076(4) Å and Sn(4)–N(4) 2.756(5) Å in complex **2**, and Sn(1)–S(1) 2.4684(19) Å, Sn(1)–N(1) 2.693(6) Å, Sn(2)–O(1) 2.042(5) Å and Sn(2)–N(2) 2.900(5) Å in **5**. All these Sn–N and Sn–S bond lengths are comparable with those found in $Ph_3Sn(SC_5H_5N_2)$ (Sn(1)–S(1) 2.4228(16) Å, Sn(1)–N(2) 2.907(4) Å) [12c] and $Ph_3Sn(Hthpu)$ (H_2thpu is 2-thio-6-hydroxypurine) (Sn(1)–S(1) 2.4661(17) Å, Sn(1)–N(1) 2.653(5) Å) [22]. And they lie in the range of the sum of the covalent radii and the van der Waals radii of Sn and S (2.42–4.0 Å) [23] and Sn and N (2.15–3.74 Å) [24]. The Sn–O bond lengths are also comparable with those in $[SnMe_2(Salop)]$ (H_2salop is 2-{[(2-hydroxyphenyl)imino]methyl}phenol) Sn–O(1) 2.117(2) Å, $[SnVi_2(Salop)]$ 2.117(2) Å, $[SnCl_2(Salop)(CH_3OH)]\cdot CH_3OH$ (2.009(2) Å and $[SnBr_2(Salop)(CH_3OH)]$ (2.005(2) Å [25]. The sum of equatorial angles of central tin atoms are 342.97° for Sn(1), 341.92° for Sn(2), 342.77° for Sn(3) and 341.73° for Sn(4) in **2**, and 346.31° for Sn(1) and 338.7° for Sn(2) in **5**. The axial angles are C(18)–Sn(1)–N(1) 159.7(2)° for Sn(1), C(30)–Sn(2)–N(2) 147.5(2)° for Sn(2), C(59)–Sn(2)–N(3) 159.65(19)° for Sn(3), C(71)–Sn(2)–N(4) 143.96(19)° for Sn(4) in **2**, and C(5)–Sn(1)–N(1) 158.4(2)° for Sn(1) and C(29)–Sn(2)–N(2) 143.7(3)° for Sn(2) in **5**. They deviate more or less from standard 360° and 180°, indicating the distortion of the geometry.

The complexes exhibit interesting intermolecular interactions as shown in Figs. 2 and 4: the molecules of **2** and **5** are connected via offset π···π stacking interactions of approximately parallel phenyl rings and pyrimidine rings and edge- or point-to-face C–H···π interactions (Table 4). In complex **2**, π···π stacking interactions occur between ring (C65–C70) and ring (C1–C4, N1, N2) (symmetry codes: x, y, z) at a ring centroid distance of 3.811 Å (dihedral angle 6.0°). Evidence for a C–H···π interaction is also found in the structure. The C(57)–H atom is directed towards the symmetry related ($1-x$, $1-y$, $1-z$) aromatic ring containing the C(59a)–C(64a) atoms. The

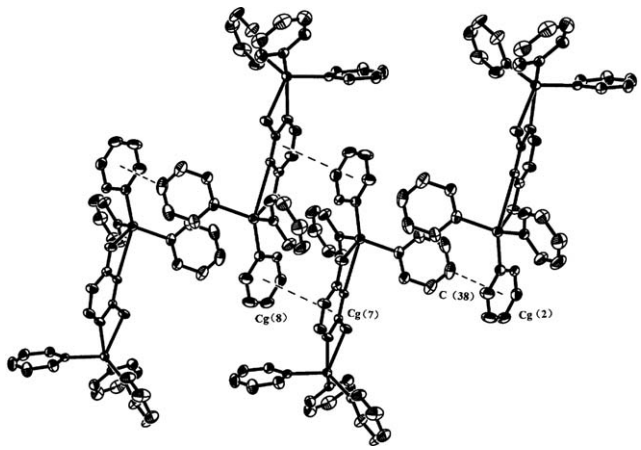


Fig. 4. Perspective view of complex **5** showing π···π stacking interactions (Cg(7): N(1)–C(1)–N(2)–C(2)–C(3)–C(4); Cg(8): C(29a)–C(30a)–C(31a)–C(32a)–C(33a)–C(34a)) and edge- or point-to-face C–H···π interactions (C(38)–H(38)···Cg(2)) (Cg(2): C(29b)–C(30b)–C(31b)–C(32b)–C(33b)–C(34b)).

Table 4
π···π, C–H···π and intra-hydrogen bonds for **2**, **5** and **8**

	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
5	C(22)–H(22)···N(1)	0.93	2.61	3.290	131
	C(36)–H(36)···N(2)	0.93	2.50	3.706	120
	C(30)–H(30)···O(1)	0.93	2.58	3.267	131
8	C(6)–H(6)···N(2)	0.93	2.56	3.231	129
	C–H···π		H···Cg (Å)	C···Cg (Å)	C–H···Cg (°)
2	C(57)–H(57)···Cg(1)[i]		3.128	3.943	147.34
5	C(38)–H(38)···Cg(2)[ii]		2.829	3.527	132.75
8	C(20a)–H(20a)···Cg(3)[iii]		2.912	3.660	138.47
	C(2a)–H(2a)···Cg(4)[iv]		2.710	3.599	160.50
	π(i)···π(j)[a]	Dihedral angle (i,j) (°)	Centroid separation Cg···Cg[b] (Å)	Cg(i)···perp[c] (Å)	Cg(j)···perp[d] (Å)
2	Cg(5)···Cg(6)[v]	6.0	3.811	3.4505	3.5955
5	Cg(7)···Cg(8)[vi]	16.2	3.859	3.3018	3.6995

[a] Where Cg(1), Cg(2), Cg(3), Cg(4), Cg(5), Cg(6), Cg(7) and Cg(8) are referred to the centroids of C(59a)–C(60a)–C(61a)–C(62a)–C(63a)–C(64a), C(29b)–C(30b)–C(31b)–C(32b)–C(33b)–C(34b), C(11)–C(12)–C(13)–C(14)–C(15)–C(16), C(35)–C(36)–C(37)–C(38)–C(39)–C(40), N(1)–C(1)– N(2)–C(2)–C(3)–C(4), C(65)–C(66)–C(67)–C(68)–C(69)–C(70), N(1)–C(1)– N(2)–C(2)–C(3)–C(4) and C(29a)–C(30a)–C(31a)—C(32a)–C(33a)–C(34a), respectively.
[b] Cg···Cg is the distance between ring centroids; symmetry transformation: (i) $1-x, 1-y, 1-z$; (ii) $2-x, -y, 1-z$; (iii) $-1/2+x, 3/2-y, z$; (iv) x, y, z; (v) x, y, z and (vi) $1-x, -y, -z$.
[c] Cg(i)···perp is the perpendicular distance of Cg(i) on ring j.
[d] Cg(j)···perp is the perpendicular distance of Cg(i) on ring i.

distance of C(57)···Cg and H(57)···Cg are 3.943 and 3.128 Å, respectively. The angle of C(57)–H(57)···Cg is 147.34°. Similarly in complex **5**, ring (C29a–C34a) and ring (C1–C4, N1, N2) (symmetry codes: $1-x, -y, -z$) are stacked at a ring centroid distance of 3.859 Å (dihedral angle 16.2°). C–H···π interaction occurs between C(38)–H and ring (C29b–C34b) (symmetry codes: $2-x, -y, 1-z$). The data are C(38)···Cg 3.527 Å, H(57)···Cg 2.829 Å, C(38)–H(38)···Cg 132.75°. In addition to the mentioned π-interactions, the molecules of **5** are involved in weak intramolecular C–H···N and C–H···O hydrogen bonds (C(22)–H(22)···N(1) 3.290(12) Å, 131°; C(36)–H(36)···N(2) 3.267(11) Å, 131°; C(30)–H(30)···O(1) 3.706(10) Å, 120°). All the above weak but significant interactions stabilize these crystal structures.

3.2.2. $Ph_3Sn(C_4H_2N_2S_2)SnPh_3$ (**8**)

Selected bond lengths (Å) and bond angles (°) for **8** are given in Table 5, and its molecular structure and network are shown in Figs. 5 and 6, respectively.

Table 5
Selected bond lengths (Å) and bond angles (°) for **8**

Sn(1)–C(17)	2.118(3)	Sn(1)–C(5)	2.136(3)
Sn(1)–S(1)	2.4444(7)	Sn(1)–C(11)	2.152(3)
Sn(2)–C(23)	2.112(3)	Sn(2)–C(35)	2.125(3)
Sn(2)–C(29)	2.136(3)	Sn(2)–S(2)	2.4495(8)
S(1)–C(1)	1.751(3)	S(2)–C(4)	1.739(3)
C(17)–Sn(1)–C(5)	116.94(11)	C(17)–Sn(1)–C(11)	108.93(11)
C(5)–Sn(1)–C(11)	108.26(11)	C(17)–Sn(1)–S(1)	107.31(8)
C(5)–Sn(1)–S(1)	118.73(8)	C(11)–Sn(1)–S(1)	93.99(7)
C(23)–Sn(2)–C(35)	113.93(11)	C(23)–Sn(2)–C(29)	107.83(11)
C(35)–Sn(2)–C(29)	110.84(10)	C(23)–Sn(2)–S(2)	116.57(8)
C(35)–Sn(2)–S(2)	111.59(7)	C(29)–Sn(2)–S(2)	94.20(8)

Complex **8** is also a monomer with one ligand coordinated to two triphenyltin moiety. The central tin atoms are five-coordinated with distorted trigonal bipyramidal

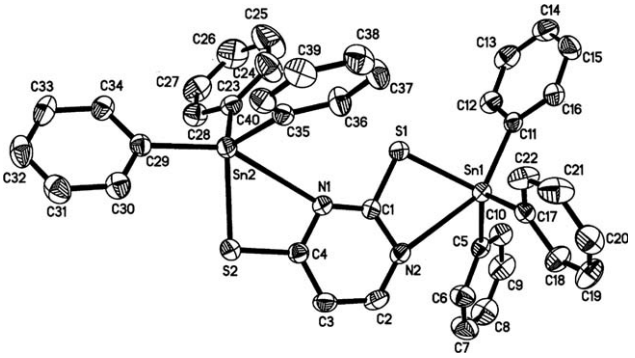


Fig. 5. Molecular structure of complex **8**.

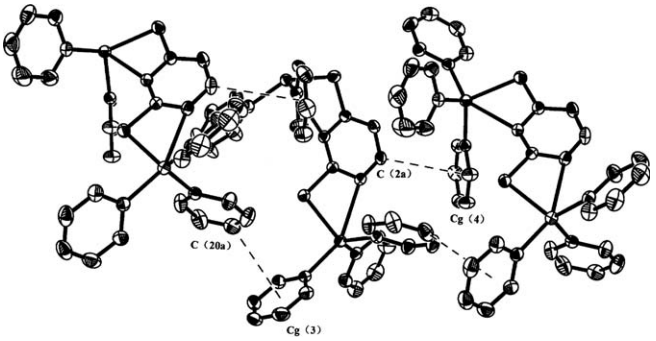


Fig. 6. Perspective view of complex **8** showing edge- or point-to-face C–H···π interactions (C(20a)–H(20a)···Cg(3)) (Cg(3): C(11)–C(12)–C(13)–C(14)–C(15)–C(16)) (C(2a)–H(2a)···Cg(4)) (Cg(4): C(35)–C(36)–C(37)–C(38)–C(39)–C(40)).

geometry. The ligands adopt its thiol sulfur atom and heterocyclic nitrogen atoms to coordinate to the central tin atoms. The equatorial plane are defined by S(1), C(5) and C(17) for Sn(1), S(2), C(23) and C(35) for Sn(2) with the sum of 342.99° (S(1)–Sn(1)–C(5) 118.73°, S(1)–Sn(1)–C(17) 103.72°, C(17)–Sn(1)–C(5) 116.94°) and 342.09° (S(2)–Sn(1)–C(35) 111.59°, S(2)–Sn(1)–C(23) 116.56°, C(35)–Sn(1)–C(23) 113.94°). The axial positions are occupied by C(11), N(2) for Sn(1), and C(29), N(1) for Sn(2) with the angles of 153.35° and 151.92°. The Sn–S and Sn–N bond lengths are Sn(1)–S(1) 2.4444(7) Å, Sn(2)–S(2) 2.4495(8) Å, Sn(2)–N(1) 2.926 Å and Sn(1)–N(2) 2.814 Å. They are comparable with those of **2** and **5**, and the Sn–S bond length (2.476(8) Å) lies in the range reported for tri-phenyltin heteroarenethiolates (2.405–2.481 Å) [26], and approaches the sum of the covalent radii of tin and sulfur (2.42 Å), which proves that sulfur atoms coordinated to tin atom by strong covalent bonds. Besides, the Sn–N distance is comparable with that of complex $Ph_3Sn(Me_2$-Pymt) (2.835(7) Å) [27], and still shorter than the sum of the van der Waals radii of tin and nitrogen (3.74 Å).

The molecules of **8** associate via edge- or point-to-face C–H···π interactions. The C(20a)–H atom is directed towards the symmetry related $(-1/2 + x, 3/2 - y, z)$ aromatic ring containing the C(11)–C(16) atoms. The distance of C(20a)···Cg and H(20a)···Cg are 3.660 and 2.912 Å, respectively. The angle of C(20a)–H(20a)···Cg is 138.47°. Another C–H···π interaction occurs between C(2a)–H and ring (C35–C40) (symmetry codes: x, y, z). The data are C(2a)···Cg 3.599 Å, H(2a)···Cg 2.710 Å, C(2a)–H(2a)···Cg 160.50°. Further, intramolecular C–H···N hydrogen bonds (C(6)–H(6)···N(2) 3.231(4) Å, 129°) stabilize the structure.

4. Conclusions

In summary, a series of triorganotin(IV) complexes based on substituent pyrimidine ligands have been synthesized and characterized. Detailed studies on the structures of these complexes indicate that complexes **2**, **5** and **8** exhibit fascinating self-assembled structural topologies via cooperative hydrogen bonds and offset π···π stacking interactions and edge- or point-to-face C–H···π interactions. Therefore, the understanding and utilization of the non-covalent interactions including hydrogen bonds, π···π stacking interactions and C–H···π interactions may cast light on the further development of supramolecular chemistry and the tuning and prediction of crystal structures.

Acknowledgement

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper (**2**, **5**, **8**) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC Nos. 257750, 257759, 274749, respectively. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.ck). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.12.054.

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