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Multi-site coordination ligands assembled on organostannoxane supports

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Abstract

The reactions of bis(pyrazol-1-yl) acetic acid LCOOH (**1**) (L = (Pz)$_2$CH–) and bis(3,5-dimethylpyrazol-1-yl)acetic acid L′COOH (**2**) (L = (3,5-Me$_2$Pz)$_2$CH–) with organotin oxide (hydroxide) precursors, n-BuSn(O)(OH), n-Bu$_2$SnO, (n-Bu$_3$Sn)$_2$O and (Ph$_3$Sn)$_2$O has led to the isolation of several organotin compounds containing bispyrazolyl unit(s) on the periphery of the stannoxane structure [n-BuSn(O)O$_2$CL]$_6$ (**3**), [n-BuSn(O)O$_2$CL′]$_6$ (**4**), [n-Bu$_3$SnO$_2$CL]$_n$ (**5**), [n-Bu$_3$SnO$_2$CL′]$_n$ (**6**), [Ph$_3$SnO$_2$CL]$_n$ (**7**), [Ph$_3$SnO$_2$CL′]$_n$ (**8**), [{n-Bu$_2$SnO$_2$CL}$_2$O]$_2$ (**9**) and [{n-Bu$_2$SnO$_2$CL′}$_2$O]$_2$ (**10**). Compounds **5**, **7**, **9** and **10** have been structurally characterized by X-ray crystallography. In the solid state, these compounds possess interesting 3-D and 2-D supramolecular networks as a result of intermolecular C–H···O, C–H···N, C–H···Cl and C–H···π interactions.
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1. Introduction

The utility of inorganic rings and cages to function as scaffolds or supports for the assembly of *dendrimer-like* molecules are being increasingly exploited as evidenced by the recent spurt of activity in this area [1]. Thus, inorganic rings such as cyclophosphazenes [2], cyclosiloxanes [3], borazines [4] or inorganic cages that contain Si–O, Al–N or Al–C bonds have been used recently as supports for the preparation of novel compounds which contain a central inorganic core and a periphery of judiciously placed functional substituents [5]. Recently, we have shown that multi-ferrocenyl and multi-porphyrinyl assemblies can be readily assembled in nearly quantitative yields by a single-pot synthesis involving the reaction of n-BuSn(O)OH and the corresponding carboxylic acid [6]. The novelty and simplicity of the aforementioned synthetic design has

prompted us to explore this *stannoxane synthetic route* for the assembly of new multi-site coordination ligands. Hitherto, the synthesis of such ligands has been carried out by usually a multi-step procedure. We have attempted to achieve this assembly by a one-step synthetic methodology. Bis(pyrazol-1-yl) acetic acid is an interesting new multi-dentate ligand that binds through two of its pyrazolyl nitrogen atoms and the carboxylate oxygen [7]. It was therefore of interest to build assemblies that contain in their periphery multiple bis(pyrazolyl) motifs. Accordingly, we have investigated the reactions of bis(pyrazol-1-yl) acetic acid LCOOH (**1**) (L = (Pz)$_2$CH–) and bis(3,5-dimethylpyrazol-1-yl) acetic acid L′COOH (**2**) (L = (3,5-Me$_2$PzCH–)) with organotin oxide (hydroxide) precursors, n-BuSn(O)(OH), n-Bu$_2$SnO, (n-Bu$_3$Sn)$_2$O and (Ph$_3$Sn)$_2$O. We report herein the synthesis and characterization of [n-BuSn(O)O$_2$CL]$_6$ (**3**), [n-BuSn(O)O$_2$CL′]$_6$ (**4**), [n-Bu$_3$SnO$_2$CL]$_n$ (**5**), [n-Bu$_3$SnO$_2$CL′]$_n$ (**6**), [Ph$_3$SnO$_2$CL]$_n$ (**7**) and [Ph$_3$SnO$_2$CL′]$_n$ (**8**). We have also synthesized (and structurally characterized) [{n-Bu$_2$SnO$_2$CL}$_2$O]$_2$ (**9**) and [{n-Bu$_2$SnO$_2$CL′}$_2$O]$_2$ (**10**). However, very recently there has been a report describing the molecular structures of **9** and **10**

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without any mention of their supramolecular structures [8]. We report in the following the supramolecular structural details of **9** and **10**.

2. Experimental

2.1. Materials and methods

All the organotin precursors were purchased (Aldrich, USA) and used as such without further purification. The carboxylic acids bis-pyrazolyl acetic acid (LCOOH) and bis-(3,5-dimethyl)pyrazolyl acetic acid (L′COOH) were prepared according to the literature procedures [7a]. Solvents were stored over appropriate reagents and distilled under nitrogen prior to use. Melting points were measured using the JSGW apparatus and are uncorrected. Elemental analyses were carried out by using a Thermo quest CE instrument model EA/110 CHNS-O elemental analyzer. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT-IR spectrophotometer operating from 400 to 4000 cm^{-1}. ^{1}H and ^{119}Sn NMR were recorded on a JEOL-JNM LAMBDA 400 model NMR spectrometer in CDCl$_3$ and CD$_3$OD solutions. The chemical shifts are referenced with respect to tetramethylsilane (^{1}H) and tetramethyltin (^{119}Sn), respectively.

2.2. Synthesis

2.2.1. [n-BuSn(O)O₂CL]₆ (3)

Compound **1** (0.38 g, 2 mmol) and *n*-BuSn(O)(OH) (0.42 g, 2 mmol) were heated under reflux in a mixture of toluene and ethanol (80:20) for 8 h The mixture was cooled to room temperature and an insoluble white colored solid (0.22 g) was filtered away. The filtrate was evaporated to dryness to afford a white solid. Recrystallization of this solid from acetonitrile/methanol (60/40) yielded pure **3**. Yield: 65% (0.52 g), m.p.: 270 °C (d). Anal. Calc. for C$_{72}$H$_{96}$N$_{24}$O$_{18}$Sn$_6$ (%): C, 37.64; H,4.21; N, 14.63. Found: C, 36.90; H,3.80; N, 14.21. IR(KBr, cm^{-1}): 1664, ν_{asym}-(COO); 1420, ν_{sym}(COO). ^{1}H NMR (CD$_3$OD, ppm): 0.67 and 1.13 (m; CH_2–CH_2–CH_2–CH_3, 54H); 6.16, 7.49 and 7.86 (m, protons of the pyrazole rings, 36H); 6.88 (–CH–COO), ^{119}Sn NMR (CDCl$_3$, ppm): −452.0 (s).

2.2.2. [n-BuSn(O)O₂CL′]₆ (4)

Compound **4** was prepared following a procedure similar to that used for **3**. The quantities involved and the characterization data are as follows. *n*-BuSnO(OH) (0.42 g, 2 mmol) and **2** (0.50 g, 2 mmol). Yield of **4**: 78% (0.72 g), m.p.: 240 °C (charring). Anal. Calc. for (%): C$_{96}$H$_{144}$-N$_{24}$O$_{18}$Sn$_6$ (%): C, 43.77; H, 5.51; N, 12.76. Found: C,

Table 1
Crystal data collection and structure parameters for complexes **5, 7, 9** and **10**

Compound number	5	7	9	10
Empirical formula	C$_{18}$H$_{18}$N$_4$O$_4$Sn	C$_{28}$H$_{26}$Cl$_4$N$_4$O$_2$Sn	C$_{64}$H$_{100}$N$_{16}$O$_{10}$Sn$_4$	C$_{81}$H$_{133}$N$_{16}$O$_{10}$Sn$_4$
Formula weight	481.22	711.04	1728.36	1965.87
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P121/n1 (14)	P121/c1 (14)	P1̄ (2)	C12/c1 (15)
Unit cell dimensions	a = 10.8793(8) Å	a = 12.5479(7) Å	a = 12.8238(8) Å	a = 19.2520(17) Å
	b = 9.9739(7) Å	b = 17.7820(10) Å	b = 13.2945(8) Å	b = 21.6288(19) Å
	c = 21.7182(16) Å	c = 13.9689(8) Å	c = 13.6141(8) Å	c = 23.573(2) Å
	α = 90°	α = 90°	α = 62.2490(10)°	α = 90°
	β = 101.59(10)°	β = 93.03(10)°	β = 72.6300(10)°	β = 98.765(2)°
	γ = 90°	γ = 90°	γ = 64.5330(10)°	γ = 90°
Volume (Å^3)	2308.6(3)	3112.5(3)	1840.37(19)	9700.9(15)
Z	4	4	1	4
Density (calculated) (Mg/m^3)	1.385	1.517	1.559	1.341
Absorption coefficient (mm^{-1})	1.127	1.196	1.406	1.076
F(000)	992	1424	876	1032
Crystal size (mm)	0.2 × 0.1 × 0.1	0.1 × 0.2 × 0.1	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
Theta range for data collection (°)	2.30–28.29	1.99–28.31	1.96–28.30	2.08–28.31
Reflections collected	14,783	20,416	12,388	32,115
Independent reflections	5711 [R_{int} = 0.0225]	7693 [R_{int} = 0.0293]	8768 [R_{int} = 0.0173]	11,969 [R_{int} = 0.0261]
Completeness to theta (%)	99.5	99.4	95.8	99.1
Absorption correction	SADABS	SADABS	SADABS	SADABS
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restrains/parameters	5711/0/247	7693/0/352	8768/0/428	11,969/0/505
Goodness-of-fit on F^2	1.095	1.035	1.033	1.072
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0320, wR_2 = 0.0736	R_1 = 0.0394, wR_2 = 0.1019	R_1 = 0.0330, wR_2 = 0.0809	R_1 = 0.0576, wR_2 = 0.1745
R indices (all data)	R_1 = 0.0356, wR_2 = 0.0752	R_1 = 0.0479, wR_2 = 0.1064	R_1 = 0.0380, wR_2 = 0.0835	R_1 = 0.0630, wR_2 = 0.1787
Largest difference peak and hole (e Å^3)	1.579 and −1.363	1.234 and −0.958	3.127 and −0.830	3.143 and −1.142

42.90; H, 5.56; N, 11.94. IR(KBr, cm^{-1}): 1685, v_{asym}-(COO); 1428 v_{sym}(COO). ^{1}H NMR (CDCl$_3$, ppm): 0.68, 0.79 (m, CH_2–CH_2–CH_2–CH_3, 54H); 2.09 and 2.29 (m, C–CH_3, methyl substituents on pyrazolyl ring, 72H); 5.68 (m, C–H, pyrazolyl hydrogens, 12H); 6.69 (s, CH–COO, 6H). ^{119}Sn NMR (CDCl$_3$): −460.0 (s).

2.2.3. [n-Bu$_3$SnO$_2$CL]$_n$ (5)

[(n-Bu$_3$Sn)$_2$O] (0.60 g, 1 mmol) and **1** (0.38 g, 2 mmol) were heated together under reflux in toluene (100 mL) for 6 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness to obtain a colorless solid. This was dissolved in dichloro-methane (20 mL) and kept in refrigerator for a period of one week to afford crystals of **5**. Yield: 85% (0.83 g), m.p.: 78 °C. Anal. Calc. for C$_{20}$H$_{34}$N$_4$O$_2$Sn (%): C, 49.92; H, 7.12; N, 11.64. Found: C, 49.11; H, 6.82; N, 11.03. IR(KBr, cm^{-1}): 1664, v_{asym}(COO); 1408, v_{sym}(COO). ^{1}H NMR (CDCl$_3$, ppm): 0.83 and 1.23 (CH_2–CH_2–CH_2–CH_3, 27H); 6.33, 7.55 and 7.65 (m, C–H, pyrazolyl hydrogens, 6H); 7.26 (s, CH(COO), 1H).

2.2.4. [n-Bu$_3$SnO$_2$CL′]$_n$ (6)

Compound **6** was prepared following a procedure used for **5**, using [(n-Bu$_3$Sn)$_2$O] (0.60 g, 1 mmol) and **2** (0.50 g, 2 mmol). Recrystallization of **6** from dichloromethane
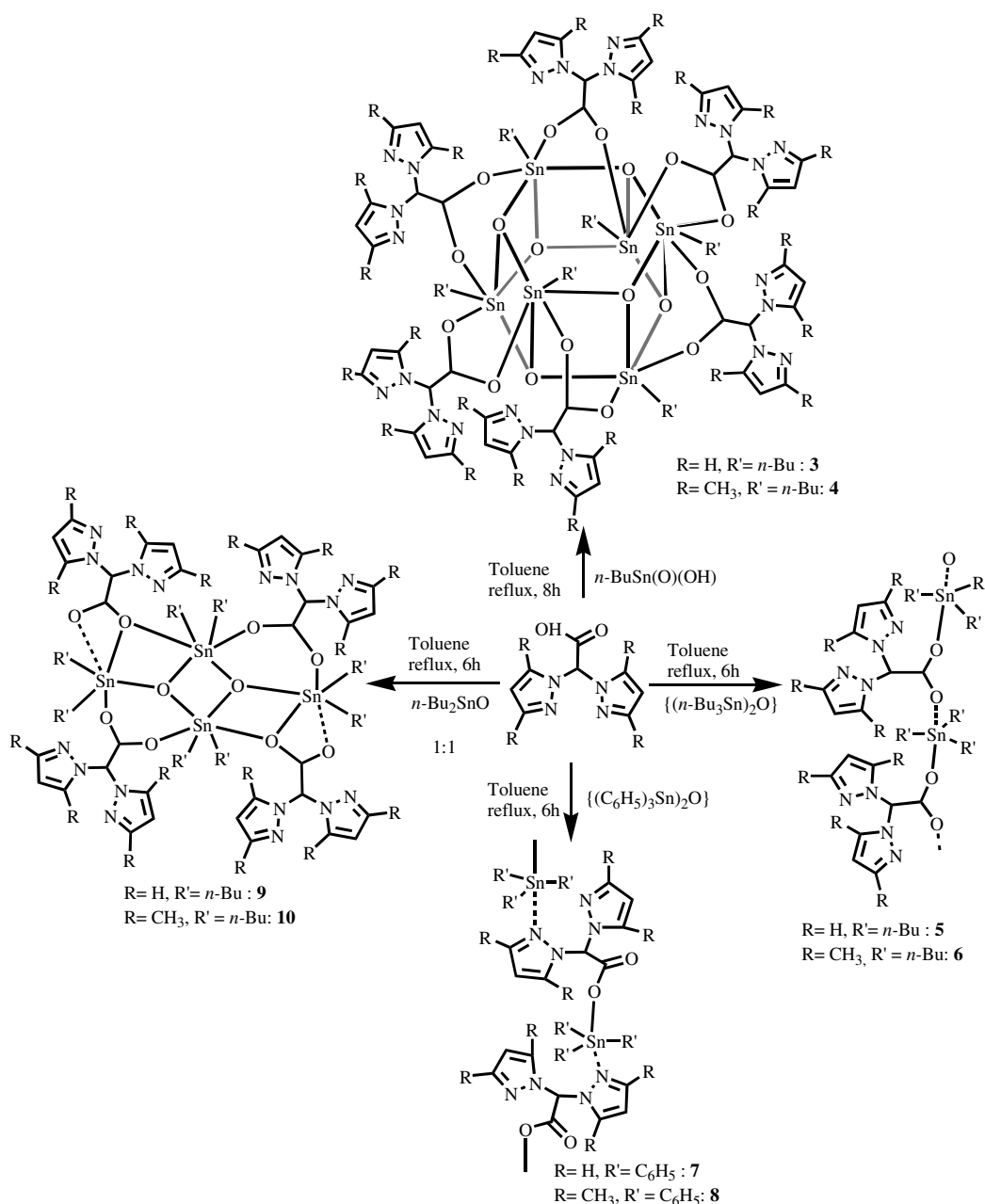
Scheme 1.

yields the pure product. Yield: 90% (0.99 g), m.p.: 70 °C. Anal. Calc. for $C_{24}H_{42}N_4O_2Sn$ (%): C, 53.63; H, 7.88; N, 10.42. Found: C, 53.10; H, 7.12; N, 10.13. IR (KBr, cm^{-1}): 1680, v_{asym}(COO); 1415, v_{sym}(COO). ^{1}H NMR (CDCl$_3$, ppm): 0.89 (t, CH$_2$–CH$_3$, 9H), 1.3 (m, –CH$_2$–CH$_2$–CH$_2$–CH$_3$, 12H), 1.6 (m, CH$_2$–CH$_2$–CH$_2$–CH$_3$, 6H), 2.16 (s, C–CH$_3$, 6H), 2.17 (s, C–CH$_3$, 6H), 5.79 (s, CH, pyrazolyl protons, 2H), 6.85 (s, 1H, CH(COO)). ^{119}Sn NMR (CDCl$_3$): 140.4 (s).

2.2.5. Synthesis of: [Ph₃SnO₂CL]ₙ (7)

Compound **7** was prepared following a procedure used for **5** using [(Ph$_3$Sn)$_2$O] (0.72 g, 1 mmol) and **1** (0.38 g, 2 mmol). Recrystallization of **7** from dichloromethane afforded crystals of **7**. Yield: 90% (0.99 g). m.p.: 120 °C (d). Anal. Calc. for $C_{26}H_{22}N_4O_2Sn$ (%): C, 57.71; H, 4.10; N, 10.35. Found: C, 57.15; H, 3.81; N, 10.12. IR(KBr, cm^{-1}): 1660, v_{asym}(COO); 1410, v_{sym}(COO). ^{1}H NMR (CDCl$_3$, ppm): 6.19, 7.46, and 7.59 (m, CH, pyrazolyl protons, 6H), 7.37 and 7.66 (m, C–H, protons of the phenyl substituent, 15H). ^{119}Sn NMR (CDCl$_3$): −88.4 (s), −90.3 (s).

2.2.6. [Ph₃SnO₂CL′]ₙ (8)

Compound **8** was prepared following a procedure used for **5**, using [(Ph$_3$Sn)$_2$O] (0.72 g, 1 mmol) and **2** (0.50 g, 2 mmol). Recrystallization of **8** was carried out from chloroform. Yield: 95% (1.16 g), m.p.: 100 °C. Anal. Calc. for $C_{30}H_{30}N_4O_2Sn$ (%): C, 60.33; H, 5.06; N, 9.38. Found: C, 59.65; H, 4.81; N, 9.01. IR(KBr, cm^{-1}): 1690 and 1640, v_{asym}(COO); 1430 and 1420, v_{sym}(COO). ^{1}H NMR (CDCl$_3$, ppm): 2.03 (s, CH$_3$, 6H); 2.09 (s, CH$_3$, 6H); 5.71 (s, C–H, pyrazolyl proton, 2H); 6.88 (s, CH(COO)) 7.35 and 7.64 (m, C–H, phenyl substituent on tin, 15H). ^{119}Sn NMR (CDCl$_3$): −92.9 (s).

2.2.7. [{n-Bu₂SnO₂CL}₂O]₂ (9)

Compound **9** was prepared following a procedure used for **5**, using n-Bu$_2$SnO (0.50 g, 2 mmol) and **1** (0.38 g, 2 mmol). Recrystallization of **9** was carried out from dichloromethane. Yield: 80% (0.70 g), m.p.: 135–140 °C. Anal. Calc. for $C_{64}H_{100}N_{16}O_{10}Sn_4$ (%): C, 44.48; H, 5.83; N, 12.97. Found: C, 44.00; H, 5.60; N, 12.40. IR(KBr cm^{-1}): 1670, 1615 v_{asym}(COO) and 1415, 1395 v_{sym}(COO). ^{1}H NMR (CDCl$_3$, ppm): 0.80, 0.96, 1.15 and 1.31 (m, CH$_2$–CH$_2$–CH$_2$–CH$_3$, 72H); 6.19, 7.44 and 7.57 (m, C–H, pyrazolyl protons, 24H); 6.76 (s, CH–COO, 4H). ^{119}Sn NMR (CDCl$_3$): −171.1 (s), −194.5 (s).

2.2.8. [{n-Bu₂SnO₂CL′}₂O]₂ (10)

Compound **10** was prepared following a procedure used for **5**, using n-Bu$_2$SnO (0.50 g, 2 mmol) and **2** (0.50 g, 2 mmol). Recrystallization of **10** was carried out from dichloromethane. Yield: 85% (0.85 g), m.p.: 120 °C. Anal. Calc. for $C_{80}H_{132}N_{16}O_{10}Sn_4$ (%): C, 49.21; H, 6.81; N, 11.48. Found: C, 48.50; H, 6.03; N, 10.79. IR(KBr cm^{-1}): v_{asym}(COO), 1680, 1180 and v_{sym}(COO) 1415,

1380. ^{1}H NMR (CDCl$_3$, ppm): 0.86, 1.34 and 1.51 (m, CH$_2$–CH$_2$–CH$_2$– CH$_3$, 72H); 2.10 (s, C–CH$_3$, 24H); 2.15 (s, C–CH$_3$, 24H); 5.79 (s, C–H, pyrazolyl protons, 8H); 6.86 (s, CH(COO), 4H). ^{119}Sn NMR (CDCl$_3$): −177.5 (s), 196.2(s).

2.3. X-ray crystallography

The crystal data for **5**, **7**, **9** and **10** are given in Table 1. These were collected on a Bruker Smart diffractometer. All the structures were solved by direct methods using SHELXS-97 [9] and refined by full-matrix least squares on F^2 using SHELXL-97. All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. In structure **10** one of the butyl groups is disordered over two positions.

3. Results and discussion

Various organostannoxane compounds **3**–**10** were prepared by reaction of the ligands **1** and **2** with appropriate organotin precursors (Scheme 1). These were characterized by analytical and spectroscopic procedures. In the case of **5**, **7**, **9** and **10** X-ray crystallography was also carried out. The reaction of [n-BuSnO(OH)] with LCOOH or L′COOH leads to the predominant formation of the hexameric

Fig. 1. (a) A portion of the crystal structure of compound **5**. Only the alpha carbon atom of the butyl groups is shown. Hydrogen atoms have been removed for clarity. (b) Coordination environment around tin atom in **5**.
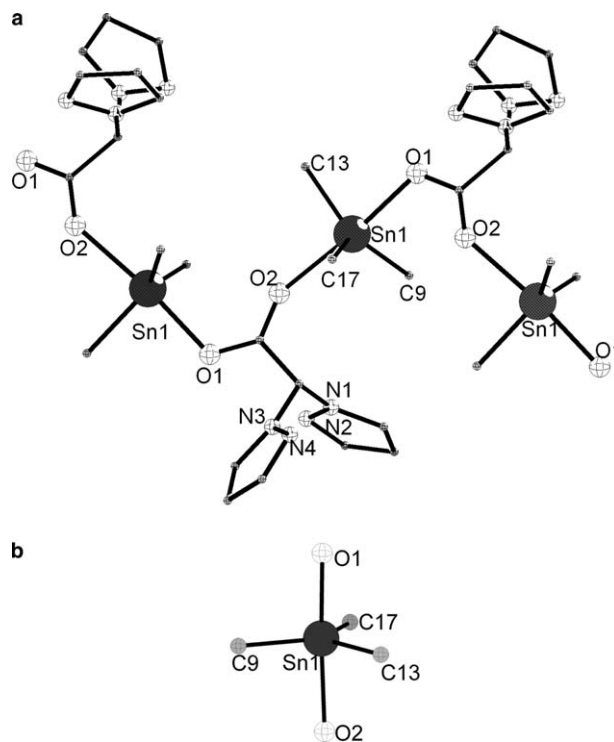
Fig. 2. (a) A portion of the crystal structure of compound **7**. Only the alpha carbon atom of the butyl groups is shown. Hydrogen atoms have been removed for clarity. (b) Coordination environment around tin atom in **7**.
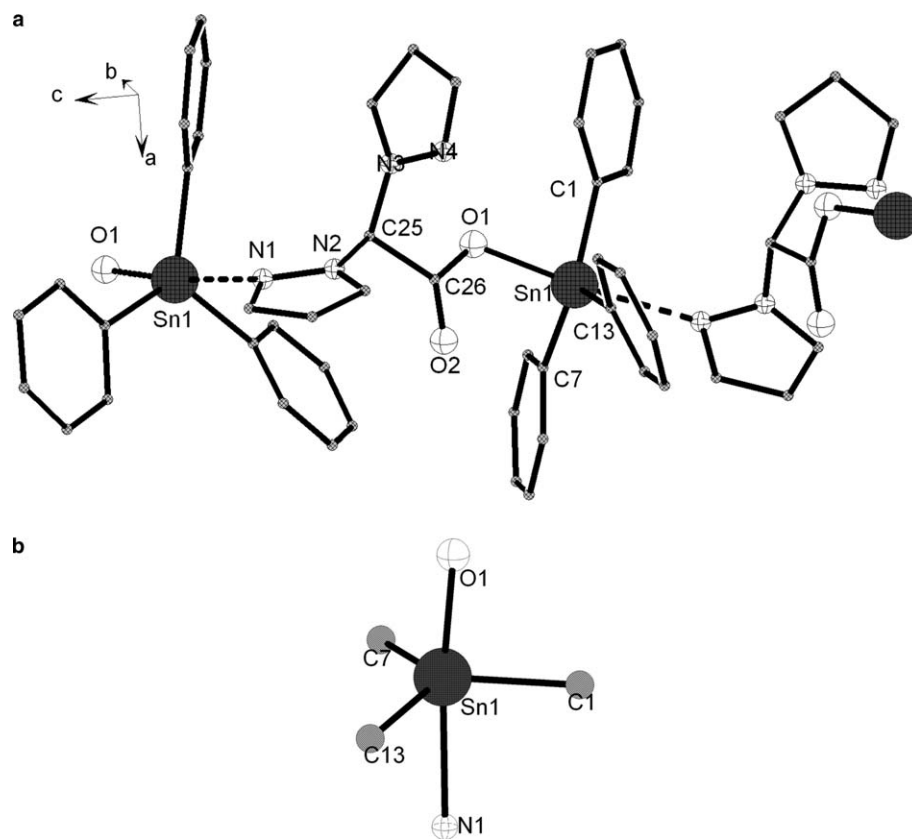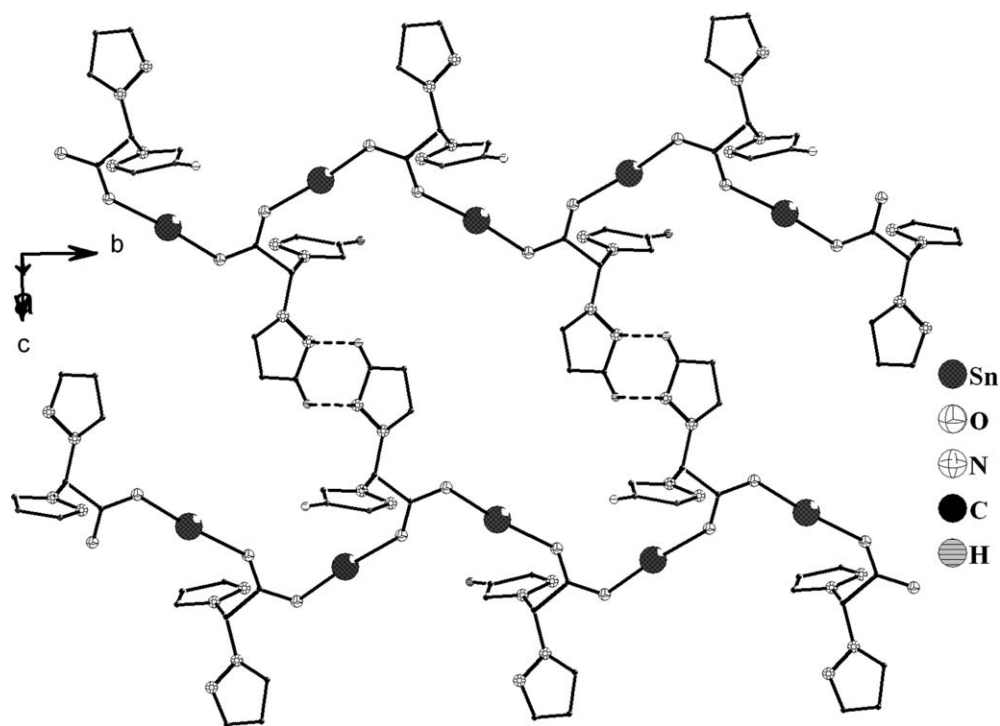

Fig. 3. C–H···N hydrogen bonding between the adjacent chains of **5**. The butyl groups on tin and the hydrogen atoms not involved in hydrogen bonding have been removed for the sake of clarity.

prismane compounds $[n\text{-BuSn(O)O}_2\text{CL}]_6$ (**3**) and $[n\text{-BuSn(O)-O}_2\text{CL}']_6$ (**4**). The ^{119}Sn NMR of **3** and **4** shows a single peak around −452.0 and −460.0 ppm characteristic of these class of compounds where the tin is hexa-coordinate (5O,1C) [10]. This also implies that the nitrogen atoms of the pyrazole rings do not involve in coordination to tin and are available for further interaction with transition metal ions (Scheme 1).

The reaction of $[(n\text{-Bu}_3\text{Sn})_2\text{O}]$ with LCOOH and L′COOH in a 1:2 stoichiometric ratio affords $[n\text{-Bu}_3\text{Sn-O}_2\text{CL}]_n$ (**5**) and $[n\text{-Bu}_3\text{SnO}_2\text{CL}']_n$ (**6**) (Scheme 1). Similarly

the reactions of $[(\text{Ph}_3\text{Sn})_2\text{O}]$ with LCOOH and L′COOH affords $[\text{Ph}_3\text{SnO}_2\text{CL}]_n$ (**7**) and $[\text{Ph}_3\text{SnO}_2\text{CL}']_n$ (**8**). In the solid-state **5**, **6**, **7**, and **8** exist as polymeric compounds. This has been confirmed by the X-ray crystal structural analysis on **5** and **7**. However, solution ^{119}Sn NMR spectra of these compounds (see Section 2) are consistent with monomeric structures in solution [10]. The reaction of $n\text{-Bu}_2\text{SnO}$ with LCOOH and L′COOH in a 1:1 stoichiometry afforded $[\{n\text{-Bu}_2\text{SnO}_2\text{CL}\}_2\text{O}]_2$ (**9**) and $[\{n\text{-Bu}_2\text{SnO}_2\text{CL}'\}_2\text{O}]_2$ (**10**). The solution ^{119}Sn NMR spectra of these compounds (see Seection 2) reveals that the tetrameric

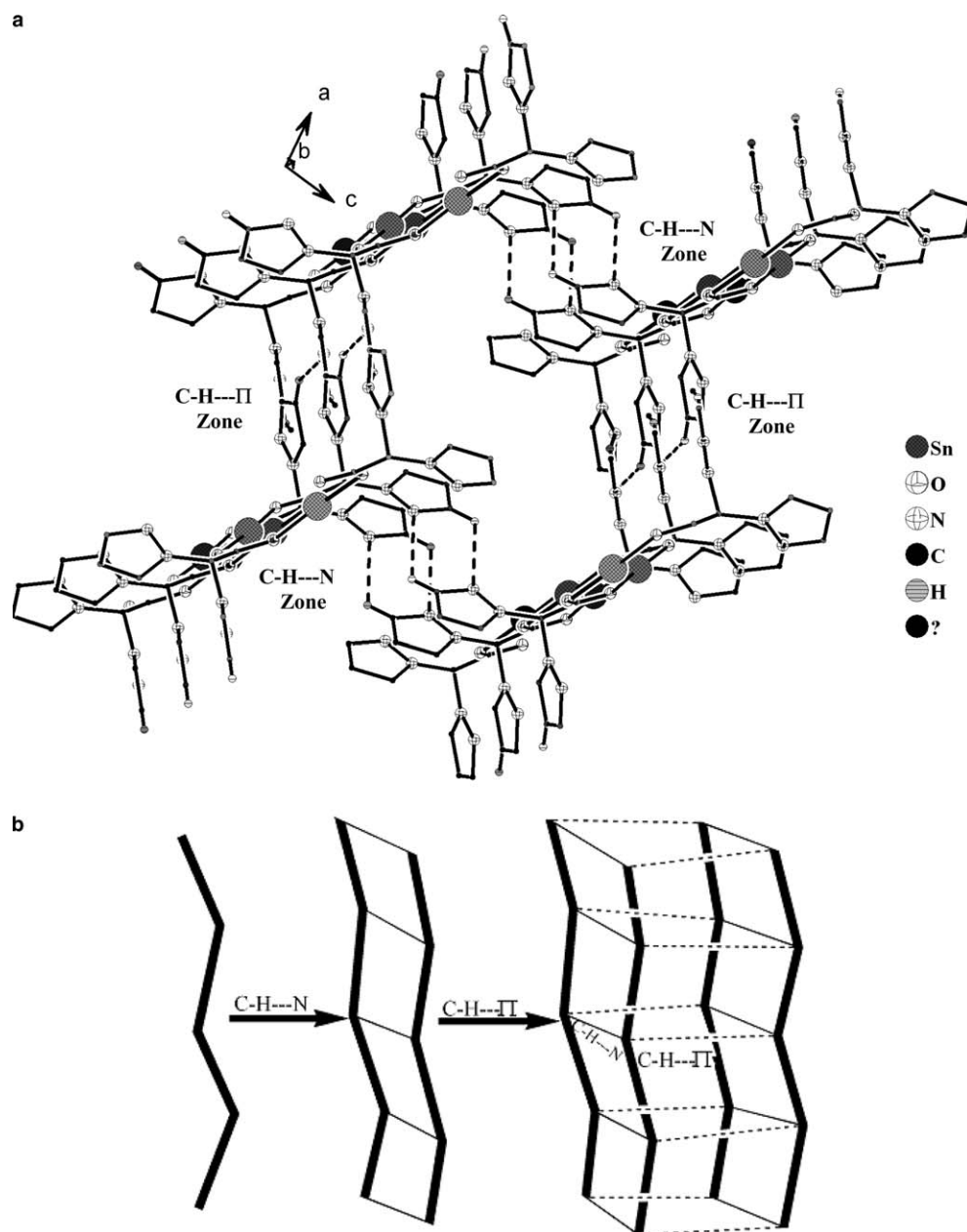Fig. 4. (a) The formation of three-dimensional columnar network in **5** by intermolecular C–H···N and C–H···π interactions between the adjacent chains. All the butyl groups on tin and hydrogen atoms not involved in hydrogen bonding have been removed for the sake of clarity. (b) Pictorial representation of 3D network formation in **5**.

structures found in the solid-state (vide infra) are retained in solution.

3.1. X-ray crystal structures of 5, 7, 9 and 10

The molecular structure of **5**, **7**, **9** and **10** are shown in Figs. 1–4 along with the atom numbering schemes. The crystallographic data for these compounds are given in Table 1. Selected bond distance/bond angle data for **5**, **7**, **9** and **10** are listed in Tables 2–5.

The crystal and molecular structures of **5** and **7** show that these compounds exist as coordination polymers. Compound **7** crystallizes with two molecules of dichloromethane. In both of these compounds tin is present in trigonal bipyramidal geometry. While in **5** the coordination environment is 3C,2O in **7** the coordination environment is 3C,1N and 1O (Figs. 1 and 2). The coordination around tin in **5** is made up of three covalently bound butyl substituents and one covalently bound oxygen. The fifth coordination is through an intermolecularly interacting oxygen atom. In the case of **7**, the fifth coordination site is taken up by an intermolecular interaction through one of the pyrazolyl nitrogen atoms. In compound **5**, the tin atom is 0.06 Å above the trigonal plane formed by the three alpha carbons of *n*-butyl groups while in **7** the tin atom is −0.18 Å below the trigonal plane formed by the three

Table 3
Selected interatomic bond length (Å) and bond angles (°) for **7**

Bond length (Å)		Bond angle (°)	
Sn(1)–C(7)	2.113(3)	C(19)–N(1)–N(2)	104.30(2)
Sn(1)–C(1)	2.125(3)	C(19)–N(1)–Sn(1)	124.96(17)
Sn(1)–O(1)	2.126(19)	N(2)–N(1)–Sn(1)	128.34(16)
Sn(1)–C(13)	2.127(3)	C(21)–N(2)–N(1)	111.60(2)
Sn(1)–N(1)	2.574(2)	C(21)–N(2)–C(25)	127.00(2)
O(1)–C(26)	1.287(3)	N(1)–N(2)–C(25)	121.30(2)
O(2)–C(26)	1.215(3)	C(22)–N(3)–N(4)	112.50(2)
N(1)–C(19)	1.340(3)	C(22)–N(3)–C(25)	127.50(2)
N(1)–N(2)	1.359(3)	C(6)–C(1)–C(2)	118.50(3)
N(2)–C(21)	1.351(3)	C(6)–C(1)–Sn(1)	123.40(2)
N(2)–C(25)	1.449(3)	C(2)–C(1)–Sn(1)	118.10(2)
N(3)–C(22)	1.353(4)	C(12)–C(7)–C(8)	118.800(3)
N(3)–N(4)	1.360(3)	C(12)–C(7)–Sn(1)	121.00(2)
N(3)–C(25)	1.445(3)	C(8)–C(7)–Sn(1)	120.00(3)
N(4)–C(24)	1.328(4)	C(9)–C(8)–C(7)	120.80(4)
C(1)–C(6)	1.394(4)	C(18)–C(13)–C(14)	118.80(3)
C(1)–C(2)	1.397(4)	C(18)–C(13)–Sn(1)	118.70(2)
C(7)–C(12)	1.380(5)	C(14)–C(13)–Sn(1)	122.50(2)
C(7)–C(8)	1.407(5)	C(15)–C(14)–C(13)	120.10(3)
C(13)–C(18)	1.391(4)	N(3)–C(25)–C(26)#1	110.50(2)
C(13)–C(14)	1.392(4)	N(2)–C(25)–C(26)#1	111.40(2)
C(25)–C(26)#1	1.550(4)	O(2)–C(26)–O(1)	127.50(3)
C(26)–C(25)#2	1.551(4)	O(2)–C(26)–C(25)#2	121.10(2)
		O(1)–C(26)–C(25)#2	111.30(2)

Table 4
Selected interatomic bond length (Å) and bond angles (°) for **9**

Bond length (Å)		Bond angle (°)	
Sn(2)–C(9)	2.130(3)	O(5)–Sn(1)–C(1)	106.33(9)
Sn(2)–C(13)	2.133(3)	O(5)–Sn(1)–C(5)	106.36(9)
Sn(2)–O(3)	2.206(18)	C(1)–Sn(1)–C(5) 1	46.77(11)
Sn(2)–O(2)	2.255(19)	O(5)–Sn(1)–O(5)#1	76.69(8)
O(1)–C(30)	1.245(3)	C(1)–Sn(1)–O(5)#1	95.52(9)
O(2)–C(30)	1.251(3)	C(5)–Sn(1)–O(5)#1	97.56(9)
O(3)–C(32)	1.295(3)	O(5)–Sn(1)–O(1)	91.11(7)
O(4)–C(32)	1.225(3)	C(1)–Sn(1)–O(1)	84.72(9)
O(5)–Sn(1)#1	2.170(18)	C(5)–Sn(1)–O(1)	88.87(9)
N(1)–C(17)	1.330(4)	O(5)#1–Sn(1)–O(1)	167.39(7)
N(1)–N(2)	1.358(3)	O(5)–Sn(2)–C(9)	110.29(10)
N(2)–C(19)	1.354(3)	O(5)–Sn(2)–C(13)	110.31(10)
N(3)–C(20)	1.356(3)	C(9)–Sn(2)–C(13)	138.70(12)
N(3)–N(4)	1.359(3)	O(5)–Sn(2)–O(3)	80.08(7)
N(4)–C(22)	1.335(4)	C(9)–Sn(2)–O(3)	97.32(9)
N(5)–C(23)	1.321(4)	C(13)–Sn(2)–O(3)	96.71(9)
N(6)–C(25)	1.347(4)	O(5)–Sn(2)–O(2)	88.87(7)
N(7)–C(26)	1.356(3)	C(9)–Sn(2)–O(2)	82.47(9)
N(7)–N(8)	1.361(3)	C(13)–Sn(2)–O(2)	91.06(9)
N(8)–C(28)	1.327(4)	O(3)–Sn(2)–O(2)	168.17(7)
C(1)–C(2)	1.530(4)	C(30)–O(1)–Sn(1)	131.80(17)
C(5)–C(6)	1.526(4)	C(30)–O(2)–Sn(2)	135.89(18)
C(9)–C(10)	1.522(4)	C(32)–O(3)–Sn(2)	109.43(16)
C(10)–C(11)	1.528(4)	Sn(2)–O(5)–Sn(1)	138.45(9)
C(11)–C(12)	1.518(4)	Sn(2)–O(5)–Sn(1)#1	117.99(8)
C(13)–C(14)	1.527(4)	Sn(1)–O(5)–Sn(1)#1	103.30(8)
		C(6)–C(5)–Sn(1)	112.02(18)
		C(10)–C(9)–Sn(2)	118.97(19)
		C(14)–C(13)–Sn(2)	117.30(2)
		C(19)–C(18)–C(17)	104.50(3)
		N(2)–C(19)–C(18)	107.00(2)
		O(4)–C(32)–C(31)	121.00(2)
		O(3)–C(32)–C(31)	114.90(2)

Table 2
Selected interatomic bond length (Å) and bond angles (°) for **5**

Bond length (Å)		Bond angle (°)	
Sn(1)–C(9)	2.139(2)	C(9)–Sn(1)–C(13)	118.10(9)
Sn(1)–C(13)	2.142(2)	C(9)–Sn(1)–C(17)	125.40(9)
Sn(1)–C(17)	2.148(2)	C(13)–Sn(1)–C(17)	116.30(8)
Sn(1)–O(1)	2.2282(14)	C(9)–Sn(1)–O(1)	90.87(7)
Sn(1)–O(2)#1	2.382(15)	C(13)–Sn(1)–O(1)	87.52(7)
O(1)–C(1)	1.258(2)	C(17)–Sn(1)–O(1)	95.75(7)
O(2)–C(1)	1.249(2)	C(9)–Sn(1)–O(2)#1	90.60(7)
O(2)–Sn(1)#2	2.3824(15)	C(13)–Sn(1)–O(2)#1	87.39(7)
N(1)–N(2)	1.351(3)	C(17)–Sn(1)–O(2)#1	87.45(7)
N(1)–C(3)	1.354(3)	O(1)–Sn(1)–O(2)#1	174.81(5)
N(1)–C(2)	1.448(3)	C(1)–O(1)–Sn(1)	118.61(13)
C(1)–C(2)	1.536(3)	C(1)–O(2)–Sn(1)#2	39.23(14)
C(5)–C(4)	1.391(3)	N(2)–N(1)–C(3)	112.55(18)
C(6)–C(7)	1.368(3)	N(2)–N(1)–C(2)	119.18(17)
C(7)–C(8)	1.403(4)	C(3)–N(1)–C(2)	127.65(19)
C(9)–C(10)	1.523(3)	N(1)–C(3)–C(4)	106.80(2)
C(13)–C(14)	1.536(3)	O(2)–C(1)–O(1)	124.94(19)
C(17)–C(18)	1.527(3)	O(2)–C(1)–C(2)	117.77(18)
		O(1)–C(1)–C(2)	117.29(18)
		N(3)–C(2)–N(1)	111.54(17)
		N(3)–C(2)–C(1)	114.45(17)
		N(1)–C(2)–C(1)	108.73(16)
		N(4)–C(8)–C(7)	111.90(2)
		C(10)–C(9)–Sn(1)	115.71(16)
		C(9)–C(10)–C(11)	113.10(2)
		C(14)–C(13)–Sn(1)	115.14(15)
		C(15)–C(14)–C(13)	113.04(19)
		C(18)–C(17)–Sn(1)	112.70(2)
		C(19)–C(18)–C(17)	112.95(15)

Table 5
Selected interatomic bond length (Å) and bond angles (°) for **10**

Bond length (Å)		Bond angle (°)	
Sn(1)–O(1)	2.018(3)	O(1)–Sn(1)–C(41)	115.03(17)
Sn(1)–C(41)	2.117(5)	O(1)–Sn(1)–C(45)	110.65(18)
Sn(1)–C(45)	2.128(5)	C(41)–Sn(1)–C(45)	134.00(2)
Sn(1)–O(4)	2.201(3)	O(1)–Sn(1)–O(4)	79.690(12)
Sn(1)–O(3)	2.246(4)	C(41)–Sn(1)–O(4)	96.580(17)
Sn(2)–O(1)	2.048(3)	C(45)–Sn(1)–O(4)	96.1(2)
Sn(2)–C(35)	2.114(5)	O(1)–Sn(1)–O(3)	90.36(13)
Sn(2)–C(31)	2.124(5)	C(41)–Sn(1)–O(3)	86.17(17)
Sn(2)–O(1)#1	2.172(3)	C(45)–Sn(1)–O(3)	88.8(2)
Sn(2)–O(2)	2.288(3)	O(4)–Sn(1)–O(3)	169.92(13)
O(1)–Sn(2)#1	2.172(3)	O(1)–Sn(2)–C(35)	105.86(16)
O(2)–C(13)	1.240(6)	O(1)–Sn(2)–C(31)	105.91(16)
O(3)–C(13)	1.253(6)	C(35)–Sn(2)–C(31)	147.74(18)
O(4)–C(1)	1.297(6)	O(1)–Sn(2)–O(1)#1	75.56(13)
O(5)–C(1)	1.215(7)	C(35)–Sn(2)–O(1)#1	93.92(16)
N(1)–C(3)	1.287(17)	C(31)–Sn(2)–O(1)#1	99.25(16)
N(1)–N(2)	1.440(12)	O(1)–Sn(2)–O(2)	89.73(12)
N(1)–C(2)	1.439(8)	C(35)–Sn(2)–O(2)	85.89(16)
N(2)–C(5)	1.256(16)	C(31)–Sn(2)–O(2)	88.77(16)
N(7)–N(8)	1.360(6)	O(1)#1–Sn(2)–O(2)	164.67(12)
N(7)–C(14)	1.433(6)	Sn(1)–O(1)–Sn(2)	136.50(16)
N(8)–C(22)	1.321(7)	Sn(1)–O(1)–Sn(2)#1	118.69(15)
C(31)–C(32)	1.525(7)	Sn(2)–O(1)–Sn(2)#1	104.44(13)
C(41)–C(42)	1.532(7)	C(13)–O(2)–Sn(2)	131.90(3)
C(45)–C(46)	1.513(8)	C(13)–O(3)–Sn(1)	132.80(3)
		C(1)–O(4)–Sn(1)	108.80(3)
		C(5)–N(2)–N(1)	104.90(13)
		N(4)–N(3)–C(10)	110.80(5)
		N(4)–N(3)–C(2)	121.00(5)
		O(5)–C(1)–O(4)	124.30(5)
		O(5)–C(1)–C(2)	120.40(5)
		O(4)–C(1)–C(2)	114.80(5)
		O(2)–C(13)–O(3)	127.30(4)
		O(2)–C(13)–C(14)	115.60(4)

alpha carbons of the phenyl rings. The O–Sn–O bond angle in **5** and the O–Sn–N bond angles in **7** are 174.8(5)° and 174.6(7)°, respectively.

Compound **5** shows interesting supramolecular structure formed via C–H⋯π and C–H⋯N interactions (Figs. 3 and 4). As shown in Fig. 3 two coordination polymers interact with each other through (pyrazole) C–H⋯N interactions to afford a two-dimensional sheet type structure. The C–H⋯N distance involved in this interaction is 2.4858(33) Å while the C–H⋯N angle is 142.6(2)°. These parameters are consistent with such weak hydrogen bonds [11]. The two-dimensional sheets thus formed, further interact intermolecularly with each other via C–H⋯π (pyrazolyl C–H and the pyrazolyl ring) interactions to afford a three-dimensional columnar network along the crystallographic b-axis (Fig. 4). The columnar space in this three-dimensional network is effectively filled by the alkyl substituents on tin.

Compound **7** crystallizes along with two molecules of dichloromethane solvent. These solvent molecules assist in the formation of the supramolecular structure via C–H–Cl [2.8929(12) Å, 121.4(2)°] interactions. Additional intermolecular C–H⋯O [2.2429(19) Å, 118.2(2)°] interac-

tions augment the supramolecular formation (Fig. 5). Thus, the CH_2Cl_2 molecules bridge two coordination polymers by forming Cl⋯H–C(phenyl) hydrogen bonds with one polymer and (dichloromethane) C–H⋯O (carboxylate oxygen) interactions with the adjacent coordination polymer. Interestingly both the hydrogens of the CH_2Cl_2 molecule are involved in this C–H⋯O bonding. In this manner, the solvent dichloromethane molecules are able to effectively bridge the coordination polymers to generate a two-dimensional network which contain pentagonal-shaped voids [11]. These voids are further occupied by the additional dichloromethane molecule (Fig. 7).

Compounds **9** and **10** adopt ladder structures and contain a tetranuclear tin frame work (Figs. 6 and 7). The ladder framework contains a central distannoxane (Sn_2O_2) unit. The oxygen atoms present in this distannoxane unit are involved in further coordination to one terminal tin each. The four carboxylates present in these compounds function in two different types of binding. In one mode of binding, the carboxylate ligand bridges two tin centers through one oxygen atom. In the other mode of binding, the carboxylate ligand bridges two tin centers in an isobidentate manner.

Both **9** and **10** form interesting supramolecular structures as a result of intermolecular C–H⋯N, C–H⋯π and C–H⋯O interactions (Figs. 8 and 9) . Thus, in **9** C–H⋯O interactions [C–H⋯O 2.6060(29) Å, 130.7(2)°] between the pyrazolyl C–H and the carboxylate oxygen atoms leads to the formation of a one-dimensional ribbon. Adjacent ribbons are intermolecularly bridged via C–H⋯N [C–H⋯N: 2.4858(53) Å, 142.605(3)°] and C–H⋯π interactions [C–H⋯π: 3.8938(2) Å] to afford a two-dimensional ribbon (Fig. 8). The formation of discrete 12-membered rings as a result of exclusive C–H⋯N interactions may be noticed within the two-dimensional ribbons. The supramolecular formation in **10** is mediated by intermolecular C–H⋯π [C–H⋯π, 2.9652(2) Å] and C–H⋯O interactions [2.6691(40) Å, 152.103(5)°] and results in the formation of a two-dimensional ribbon (Fig. 9). The pyrazolyl C–H which is involved in this supramolecular formation interacts by a bifurcated hydrogen bonding [11] with a carboxylate oxygen as well as the π-ring of a neighboring pyrazole unit.

4. Conclusions

The reaction of LCOOH and L′COOH with various organotin precursors leads to the generation of potentially multi-site coordination ligands. The number of coordination units assembled on the stannoxane periphery depends on the type of stannoxane assembled. Thus, the modulation of the coordination periphery is readily accomplished by the choice of the organotin precursor. The coordination properties of these new multi-site coordination ligands are in progress.
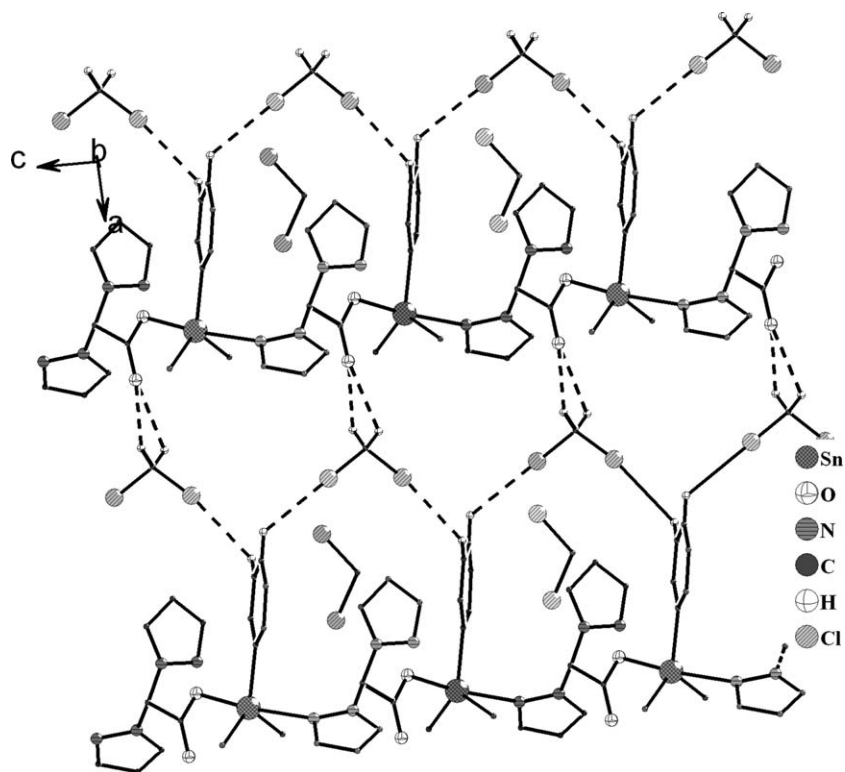
Fig. 5. C–H···Cl and C–H···O interactions between the guest molecules (dichloromethane) and the host (stannoxane) in **7**. Two of the phenyl rings on tin atom has been removed for the sake of clarity.
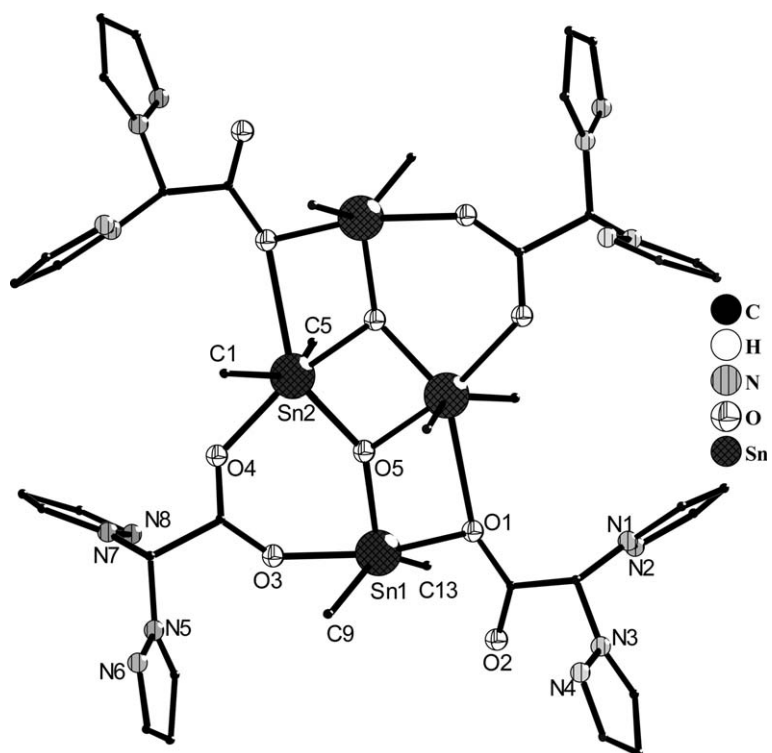

Fig. 6. Molecular structure of compound **9**. Only alpha carbons of the butyl groups are shown, other carbons of the butyl groups and hydrogen atoms have been removed for the sake of clarity.
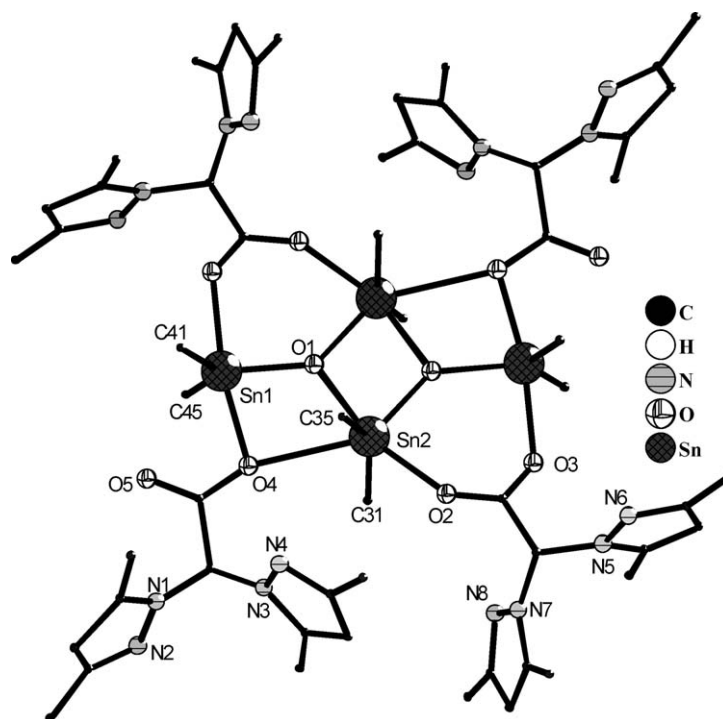
Fig. 7. Molecular structure of **10** with atom numbering. Only alpha carbon atom of the butyl groups is shown and other carbon atoms as well as all the hydrogen atoms have been removed for clarity.
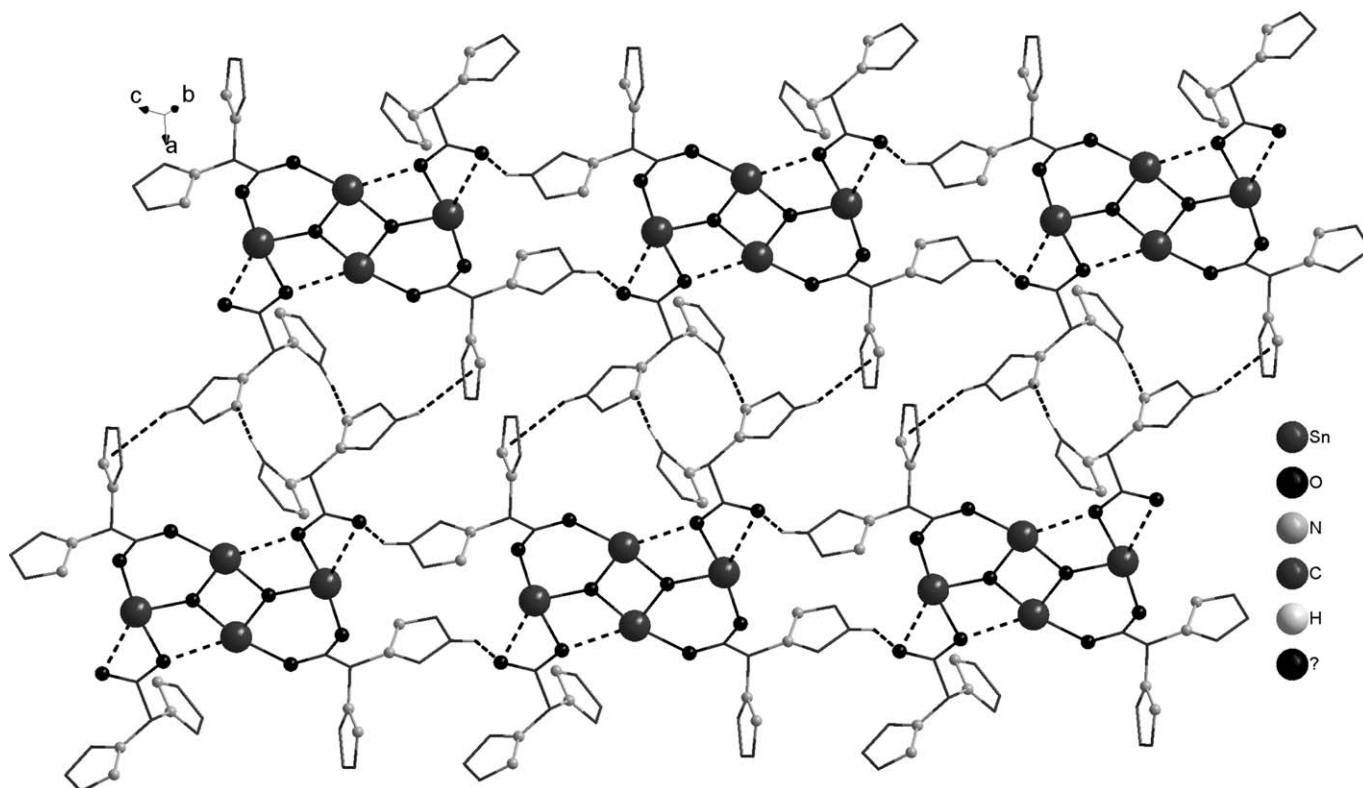

Fig. 8. 2D supramolecular ribbon formation in **9** via intermolecular C–H···N, C–H···π and C–H···O interactions.
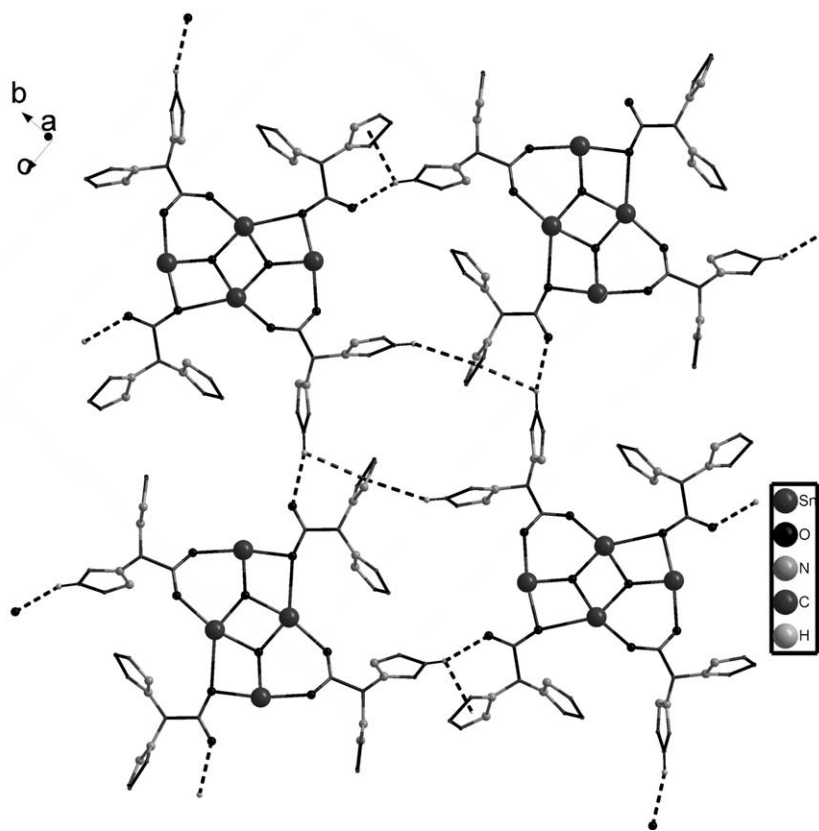
Fig. 9. 2D supramolecular ribbon formation in **10** via intermolecular C–H···π and C–H···O interactions.

5. Supplementary material

Crystallographic data for the structure analysis of complexes **5**, **7**, **9** and **10** have been deposited with the Cambridge crystallographic data center, CCDC Nos. 286419, 286420, 286421 and 286422, respectively. Copies of these information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposite@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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