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Diorganotin(IV) derivatives containing the 3,5-dimethyl-4-(4′-pyridyl)pyrazole ligand

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Abstract

3,5-Dimethyl-4-(4′-pyridyl)pyrazole, prepared by the reaction of 3-(4-pyridyl)pentane-2,4-dione with hydrazine hydrate, reacts with R_2SnCl_2 (R = Ph, Et and *n*-Bu) in a 1:1 ratio to yield 2:1 (ligand:tin) adducts. In the crystal structure of the Ph_2SnCl_2 adduct, two 3,5-dimethyl-4-(4′-pyridyl)pyrazole ligands coordinate to the tin atom through the pyridyl nitrogen atom instead of the pyrazolyl nitrogen atom, and the molecules are connected into a linear chain through intermolecular N–H···N hydrogen bonds. The reaction of 3,5-dimethyl-4-(4′-pyridyl)pyrazole with dibromomethane under phase transfer catalytic conditions affords bis[3,5-dimethyl-4-(4′-pyridyl)pyrazol-1-yl]methane. Treatment of this potential polydentate ligand with R_2SnCl_2 yields 1:1 adducts, in which bis[3,5-dimethyl-4-(4′-pyridyl)pyrazol-1-yl]methane coordinates to the tin atom through the pyridyl nitrogen atom to form six-coordinate diorganotin linkage coordination polymers, leading to a bridging instead of a general chelating metal coordination. In all new complexes, the pyridyl nitrogen atom exhibits stronger donating ability than the pyrazolyl nitrogen to the tin atom.

Keywords: Bis(pyrazol-1-yl)methane; Organotin(IV); Pyridine; X-ray structure

1. Introduction

For a long time diorganotin complexes containing nitrogen donor ligands have attracted considerable attention due to their potential biological applications [1,2]. Many complexes of the type R_2SnX_2(N–N) have been synthesized and tested for their antitumor activities [3–5]. Poly(pyrazol-1-yl)alkanes, especially bis(pyrazol-1-yl)methanes, have also been found to act as good donors to organotin compounds [6–11]. The interactions between poly(pyrazol-1-yl)alkanes and tin(IV) or organotin(IV) acceptors indicate that the donating ability of the ligands can be easily controlled by varying the substituents of the pyrazolyl ring, leading to a variable coordination geometry of the tin atom. Recently, we have also successfully prepared a variety of five and six-coordinate organotin(IV) complexes with symmetric or asymmetric bis(pyrazol-1-yl)methane [12,13], and bidentate organotin Lewis acid derivatives of bis(pyrazol-1-yl)methane [14,15], as well as novel five and six-coordinate diorganotin(IV) linkage coordination polymers with bis(1,2,4-triazol-1-yl)methane [16]. Poly(pyrazol-1-yl)alkanes containing heteroatoms such as phosphine or sulfur in the pyrazolyl rings display variable coordination modes toward different metals [17,18], which encourages us to investigate the effects of more extensive donor sets on the coordination modes of poly(pyrazol-1-yl)alkanes. Herein, we report the synthesis and structural characterization of diorganotin(IV) derivatives containing 3,5-dimethyl-4-(4′-pyridyl)pyrazole. Treatment of diorganotin(IV) chloride with this ligand yields 1:2 adducts, while employment of its

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derivative, bis(3,5-dimethyl-4-(4′-pyridyl)pyrazol-1-yl) methane, gives a 1D linkage coordination polymer.

2. Experimental

Solvents were dried by standard methods and distilled prior to use. NMR spectra (^{1}H, ^{13}C and ^{119}Sn) were recorded on a Bruker AV300 spectrometer, and the chemical shifts were reported in ppm with respect to reference standards (internal $SiMe_4$ for ^{1}H NMR and ^{13}C NMR spectra, external $SnMe_4$ for ^{119}Sn NMR). IR spectral data were obtained from a Bruker Equinox55 spectrometer in KBr pellets. Elemental analyses were carried out on a Perkin–Elmer 240C analyser. Melting points were reported with a PHMK melting-point apparatus and were uncorrected.

2.1. Preparation of 3,5-dimethyl-4-(4′-pyridyl)pyrazole (*1*)

Hydrazine hydrate (4 ml, 85%, 68 mmol) was added to a toluene solution of raw 3-(4-pyridyl)pentane-2,4-dione, obtained by the reaction of 4-methylpyridine (18.2 ml, 186 mmol) with acetyl chloride (10.6 ml, 149 mmol) according to the literature method [19], and then the mixture was stirred at room temperature overnight. After removal of the solvent under reduced pressure, the residue was recrystallized from water to yield 1.6 g of **1** as white plate crystals, m.p. 105–107 °C. ^{1}H NMR ($CDCl_3$): δ 8.63 (d, 2H, α-Py*H*), 7.24 (d, 2H, β-Py*H*), 4.30 (s, br, 1H, N*H*), 2.37 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 11.83 (*C*H_3), 100.00, 115.72, 123.71, 142.39, 149.55 (carbons of pyrazolyl and pyridyl rings). IR: ν_{NH} = 3407.0 (m); $\nu_{pyridyl\ ring}$ = 1605.7 (s) cm^{-1}. *Anal.* Calc. for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26. Found: C, 69.12; H, 6.17; N, 24.43%.

2.2. Reaction of *1* with R_2SnCl_2 (R = Ph, Et or n-Bu)

All reactions were carried out in a similar manner, so a general procedure is described. To a stirred solution of R_2SnCl_2 (1 mmol) in 15 ml ether at room temperature, a solution of **1** (1 mmol) in 15 ml ether was added. The reaction mixture was stirred continuously for 6 h at room temperature, during which time a precipitate gradually formed. The precipitate was filtered off, washed with ether and dried in vacuo. Yields, melting points and analytical data are given below.

2.2.1. [Bis(3,5-dimethyl-4-(4′-pyridyl)pyrazole)] diphenyltin dichloride (*2*)

This compound was obtained by the reaction of **1** with Ph_2SnCl_2. White solid; yield: 82%; m.p. 155–158 °C. ^{1}H NMR (CD_3COCD_3): δ 8.61 (d, 4H, α-Py*H*), 7.50 (d, 4H, β-Py*H*), 8.06, 7.41 (m, m, 4H, 6H, C_6H_5), 2.36 (s, 12H, CH_3). IR: ν_{NH} = 3294.0 (m); $\nu_{pyridyl\ ring}$ = 1612.4 (s) cm^{-1}. *Anal.* Calc. for $C_{32}H_{32}Cl_2N_6Sn$: C, 55.68; H, 4.67; N, 12.18. Found: C, 55.75; H, 4.84; N, 12.49%.

2.2.2. [Bis(3,5-dimethyl-4-(4′-pyridyl)pyrazole)] diethyltin dichloride (*3*)

This compound was obtained by the reaction of **1** with Et_2SnCl_2. Pale-yellow solid; yield: 85%; m.p. 162–165 °C. ^{1}H NMR (CD_3SOCD_3): δ 8.57 (d, 4H, α-Py*H*), 7.36 (d, 4H, β-Py*H*), 2.28 (s, 12H, CH_3), 1.56 (q, 4H, SnCH_2), 1.26 (t, 6H, CH_2 CH_3). IR: ν_{NH} = 3262.3 (m); $\nu_{pyridyl\ ring}$ = 1611.7 (s) cm^{-1}. *Anal.* Calc. for $C_{24}H_{32}Cl_2N_6Sn$: C, 48.52; H, 5.43; N, 14.14. Found: C, 48.34; H, 5.28; N, 14.29%.

2.2.3. [Bis(3,5-dimethyl-4-(4′-pyridyl)pyrazole)] di(n-butyl)tin dichloride (*4*)

This compound was obtained by the reaction of **1** with *n*-Bu_2SnCl_2. Pale-yellow solid; yield: 78%; m.p. 152–154 °C. ^{1}H NMR (CD_3SOCD_3): δ 8.56 (d, 4H, α-Py*H*), 7.35 (d, 4H, β-Py*H*), 2.27 (s, 12H, CH_3), 1.65–1.56 (m, 8H, SnCH_2CH_2), 1.36–1.24 (m, 4H, CH_2CH$_3$), 0.87 (t, 6H, CH_2CH_3). ^{13}C NMR (CD_3SOCD_3): δ 11.37, 13.62, 25.56, 27.76, 37.72 (carbons of butyl and methyl groups), 114.13, 122.41, 142.13, 149.24 (carbons of pyrazolyl and pyridyl rings). ^{119}Sn NMR (CD_3SOCD_3): δ −214 (s, br). IR: ν_{NH} = 3250.0 (m); $\nu_{pyridyl\ ring}$ = 1612.9 (s) cm^{-1}. *Anal.* Calc. for $C_{28}H_{40}Cl_2N_6Sn$: C, 51.72; H, 6.20; N, 12.92. Found: C, 51.96; H, 6.08; N, 12.69%.

2.3. Preparation of bis[3,5-dimethyl-4-(4′-pyridyl) pyrazol-1-yl]methane (*5*)

3,5-Dimethyl-4-(4′-pyridyl)pyrazole (3.25 g, 18.8 mmol), dibromomethane (1.38 ml, 9.4 mmol), tetrabutylammonium bromide (0.5 g, 1.6 mmol) and sodium hydroxide (5.7 g, 142.5 mmol) were added into a mixed solvent of water (10 ml) and benzene (50 ml). The mixture was stirred and refluxed for 48 h. After cooling to room temperature, the benzene layer was separated and the water phase was extracted with benzene (3 × 40 ml). The organic layers were combined and dried by $MgSO_4$. After evaporating the solvent, the residue was recrystallized (charcoal treatment) from benzene to yield 1.35 g of **5** (40%) as white crystals, m.p. 139–140 °C. ^{1}H NMR ($CDCl_3$): δ 8.63 (d, 4H, α-Py*H*), 7.18 (d, 4H, β-Py*H*), 6.21 (s, 2H, CH_2), 2.58, 2.27 (s, s, 6H, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 10.55, 12.75 (*C*H_3), 60.58 (*C*H_2), 117.99, 123.95, 138.29, 141.73, 146.72, 149.97 (carbons of pyrazolyl and pyridyl rings). IR: $\nu_{pyridyl\ ring}$ = 1599.7 (s) cm^{-1}. *Anal.* Calc. for $C_{21}H_{22}N_6$: C, 70.37; H, 6.19; N, 23.45. Found: C, 70.12; H, 6.11; N, 23.06%.

2.4. Reaction of **5** with R_2SnCl_2 (R = Ph, Et or n-Bu)

A general procedure was used for all preparations. The solution of **5** (0.5 mmol) in 10 ml CH_2Cl_2 was added to the stirred solution of R_2SnCl_2 (0.5 mmol) in 10 ml CH_2Cl_2 at room temperature. The reaction mixture was stirred continuously for 4 h, during which time a precipitate gradually formed. The precipitate was filtered off, washed and dried in vacuo. Yields, melting points and analytical data are given below.

2.4.1. [Bis(3,5-dimethyl-4-(4′-pyridyl)pyrazol-1-yl) methane]diphenyltin dichloride (**6**)

This compound was obtained by the reaction of **5** with Ph_2SnCl_2. White solid; yield: 90%; m.p. 131–133 °C. ^{1}H NMR (CD_3COCD_3): δ 8.63 (d, 4H, α-Py*H*), 7.39 (d, 4H, β-Py*H*), 7.96, 7.47 (m, m, 4H, 6H, C_6H_5), 6.34 (s, 2H, CH_2), 2.65, 2.23 (s, s, 6H, 6H, CH_3). IR: $\nu_{\text{pyridyl ring}}$ = 1614.7 (s) cm^{-1}. *Anal.* Calc. for $C_{33}H_{32}Cl_2N_6Sn$: C, 56.44; H, 4.59; N, 11.97. Found: C, 56.63; H, 4.73; N, 12.06%.

2.4.2. [Bis(3,5-dimethyl-4-(4′-pyridyl)pyrazol-1-yl) methane]diethyltin dichloride (**7**)

This compound was obtained by the reaction of **5** with Et_2SnCl_2. White solid; yield: 89%; m.p. 138–140 °C. ^{1}H NMR (CD_3SOCD_3): δ 8.59 (d, 4H, α-Py*H*), 7.31 (d, 4H, β-Py*H*), 6.31 (s, 2H, CH_2), 2.56, 2.18 (s, s, 6H, 6H, CH_3), 1.55 (q, 4H, $SnCH_2$), 1.26 (t, 6H, CH_2CH_3). ^{13}C NMR (CD_3SOCD_3): δ 10.14, 10.55, 12.61, 31.79 (carbons of ethyl and methyl groups), 59.30 (CH_2), 116.66, 123.52, 137.96, 141.05, 145.82, 149.61 (carbons of pyrazolyl and pyridyl rings). ^{119}Sn NMR (CD_3SOCD_3): δ −227.06 (s, br). IR: $\nu_{\text{pyridyl ring}}$ = 1612.6 (s) cm^{-1}. *Anal.* Calc. for $C_{25}H_{32}Cl_2N_6Sn$: C, 49.54; H, 5.32; N, 13.86. Found: C, 49.88; H, 5.44; N, 13.87%.

2.4.3. [Bis(3,5-dimethyl-4-(4′-pyridyl)pyrazol-1-yl) methane]di(n-butyl)tin dichloride (**8**)

This compound was obtained by the reaction of **5** with *n*-Bu_2SnCl_2. After the reaction was completed, the solvent was concentrated to ca. 5 ml, then the same volume hexane was slowly added to yield a white solid; yield: 80%; m.p. 105–106 °C. ^{1}H NMR ($CDCl_3$): δ 8.73 (d, 4H, α-Py*H*), 7.29 (d, 4H, β-Py*H*), 6.23 (s, 2H, CH_2), 2.62, 2.29 (s, s, 6H, 6H, CH_3), 1.84–1.66 (m, 8H, $SnCH_2CH_2$), 1.43–1.34 (m, 4H, CH_2CH_3), 0.92 (t, 6H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 10.67, 12.99, 13.53, 26.09, 27.84, 35.93 (carbons of butyl and methyl groups), 117.27, 124.41, 138.92, 144.27, 147.01, 148.16 (carbons of pyrazolyl and pyridyl rings). ^{119}Sn NMR ($CDCl_3$): δ −98.46, −145.68. IR: $\nu_{\text{pyridyl ring}}$ = 1621.1 (s) cm^{-1}. *Anal.* Calc. for $C_{29}H_{40}Cl_2N_6Sn$: C, 52.59; H, 6.09; N, 12.69. Found: C, 52.37; H, 5.89; N, 12.63%.

2.5. Crystal structure determinations

Crystals of complexes **2** and **6** suitable for X-ray analysis were obtained by slowly cooling hot acetone solutions of **2** and **6**. Crystals of complex **2** contain one-half of a co-crystallized acetone molecule. The methyl carbon and oxygen atoms of the acetone molecule as well as the hydrogen atom on the pyrazolyl nitrogen exhibit disorder. Satisfactory results were obtained when they were given occupancy factors of 0.5. Crystals of complex **6** have the stoichiometry **6** · H_2O · $\frac{1}{4}$ acetone, in which the phenyl group of C7–C12, pyrazolyl group of N4–N5–C28 and pyridyl group of N6–C33 are disordered, and their occupancy factors were refined to 0.594 for C7–C12 and 0.406 for C7′–C12′, 0.906 for N4–N5–C28 and 0.094 for N4′–N5′–C28′, and 0.788 for N6–C33 and 0.212 for N6′–C33′, respectively. The N4′ atom was refined to the same position with N4 by EXYZ and EADP. When acetone (occupancy factor of 0.25) appears, the disordered phenyl group locates in the position of C7–C12 (occupancy factor of 0.594). All intensity data were collected with a Bruker SMART CCD diffractometer, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were resolved by the direct method and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. A summary of the fundamental crystal data for complexes **2** and **6** is listed in Table 1.

Table 1
Crystal data for compounds **2** and **6**

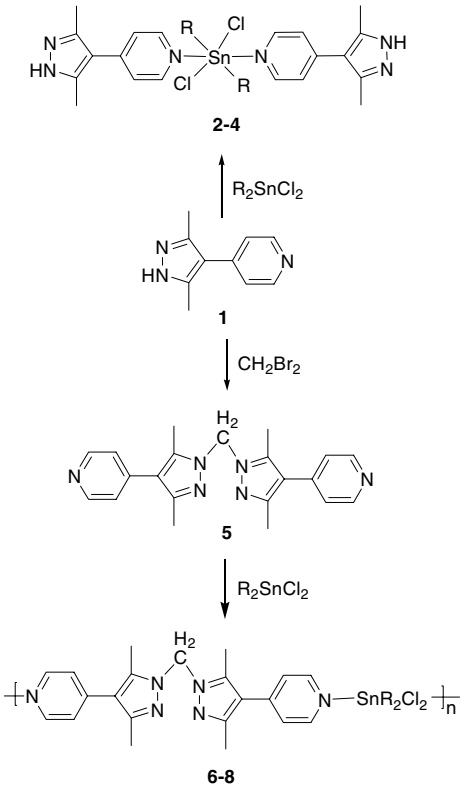
Compound	**2** · $0.5CH_3COCH_3$	**6** · H_2O · $0.25CH_3COCH_3$
Formula	$C_{33.5}H_{35}Cl_2N_6O_{0.5}Sn$	$C_{33.75}H_{35.5}Cl_2N_6O_{1.25}Sn$
Formula weight	719.27	734.77
Crystal size (mm)	0.26 × 0.24 × 0.20	0.30 × 0.25 × 0.20
Crystal class	tetragonal	monoclinic
Space group	*I*-42*d*	*P*2(1)/*c*
Cell parameters		
a (Å)	20.489(4)	7.820(3)
b (Å)	20.489(4)	17.777(6)
c (Å)	15.274(6)	29.97(1)
β (°)	90.00	91.053(6)
V (Å^3)	6412(3)	4166(2)
Z	8	4
T (K)	293(2)	293(2)
D_{calc} (Mg m^{-3})	1.490	1.172
F(000)	2928	1496
λ (Mo Kα) (Å)	0.71073	0.71073
μ (mm^{-1})	0.999	0.772
Number of reflections measured	3294	7072
Number of reflections observed ($I \geqslant 2\sigma(I)$)	3013	4216
Number of parameters	224	524
Residuals *R*, R_w	0.0231, 0.0553	0.0757, 0.2049

3. Results and discussion

3.1. Synthesis and characterization of complexes

Since 3-(4-pyridyl)pentane-2,4-dione is unstable [19], the raw pyridylpentadione was directly reacted with an excess of hydrazine hydrate to give 3,5-dimethyl-4-(4′-pyridyl)pyrazole (**1**) in a reasonable yield. Treatment of this pyrazolyl ligand with R_2SnCl_2 (R = Ph, Et or *n*-Bu) in a 1:1 ratio affords 2:1 (ligand:tin) adducts **2**–**4** (Scheme 1), according to the results of ^1H NMR data and elemental analyses. The ^1H NMR spectra of the complexes are consistent with the formulae of 2:1 adducts, which exhibit the expected proton signals for two equivalent pyridylpyrazole ligands. The chemical shifts of the protons for the ligand in the complexes are similar to those of the free ligand. Complexes **2**–**4** are insoluble in ether, chlorinated solvents, slightly soluble in acetone at room temperature, and moderately soluble in stronger polar organic solvents such as DMF and DMSO.

Reaction of **1** with CH_2Br_2 under phase-transfer conditions gives the new bridging ligand bis(3,5-dimethyl-4-(4′-pyridyl)pyrazol-1-yl)methane (**5**). Treatment of **5** with an equimolar amount of R_2SnCl_2 in CH_2Cl_2 affords 1:1 adducts **6**–**8**. Like complexes **2**–**4**, **6** and **7** are insoluble in ether, chlorinated solvents, and slightly soluble in acetone at room temperature, but complex **8** is soluble in chlorinate solvents possibly because the longer alkyl groups increase its solubility in organic solvents.



Scheme 1. R = Ph (**2**) and (**6**); R = Et (**3**) and (**7**); R = *n*-Bu (**4**) and (**8**).

It is well known that the δ (^{119}Sn) values in the ^{119}Sn NMR spectra are markedly dependent on the coordination environments around the tin atom. Owing to low solubility, only ^{119}Sn NMR spectra of complexes **4**, **7** and **8** can be clearly observed. The ^{119}Sn NMR signals of **4** and **7** in CD_3SOCD_3 occur at −214.0 and −227.1 ppm, respectively, as broad peaks, while complex **8** exhibits two ^{119}Sn NMR signals in $CDCl_3$ at −98.5 and −145.7 ppm. These data indicate that these adducts may partially dissociate in polar solutions. This kind of dissociation equilibrium can often be observed in other diorganotin derivatives containing N-donor ligands [8,12,16,20].

3.2. Crystal structures of complexes 2 and 6

The molecular structure of **2** has been confirmed by X-ray diffraction analysis as shown in Fig. 1, which clearly shows that two 3,5-dimethyl-4-(4′-pyridyl)pyrazole ligands coordinate to the tin atom through the pyridyl nitrogen atom instead of the pyrazolyl nitrogen atom. The pyridylpyrazole acts as a monodentate ligand toward the tin atom, which is six-coordinate with a slightly distorted octahedral geometry, containing two nitrogen atoms of pyridyl groups, two phenyl carbons as well as two chlorine atoms in an all-*trans* configuration. The Sn–Cl and Sn–C bond distances are similar to those in other diorganotin derivatives with monodentate or bidentate N-donor ligands [8,20,21]. The average Sn–N bond distance (2.365(3) Å) in **2** is also close to those in other diorganotin derivatives with monodentate N-donor ligands [8], such as in $Ph_2SnCl_2(Tz)_2$ (2.369(8) Å, Tz = thiazole) [20]. The dihedral angle between the two phenyl planes is 46.2°, larger than that between the two pyridyl planes (40.9°). The pyridyl group is not coplanar with the pyrazolyl ring. The dihedral angle formed by the N(1)–C(1A) pyridyl plane and the N(2)–C(5) pyrazolyl plane is 33.0°, slightly larger than the dihedral angle formed by the N(3)–C(7A) pyridyl plane and the N(4)–C(11) pyrazolyl plane (30.5°).

It is also noteworthy that molecules of complex **2** are linked into a linear chain in the solid state through intermolecular N–H···N hydrogen bond interactions (Fig. 2), while bis(pyrazole) or bis(imidazole) complexes of diorganotin dihalides tend to self-organize into chain polymers by intermolecular N–H···X hydrogen bonding (X = Cl or Br) [22–28].

Bis(3,5-dimethyl-4-(4′-pyridyl)pyrazol-1-yl)methane is a potential multidentate ligand which can act as a chelating multidentate ligand, like original bis(pyrazol-1-yl)methane using the pyrazolyl nitrogens coordinated to metals, as well as a bridging ligand by the exodentate pyridyl nitrogens. In order to confirm the coordination mode of this ligand with diorganotin halides, the

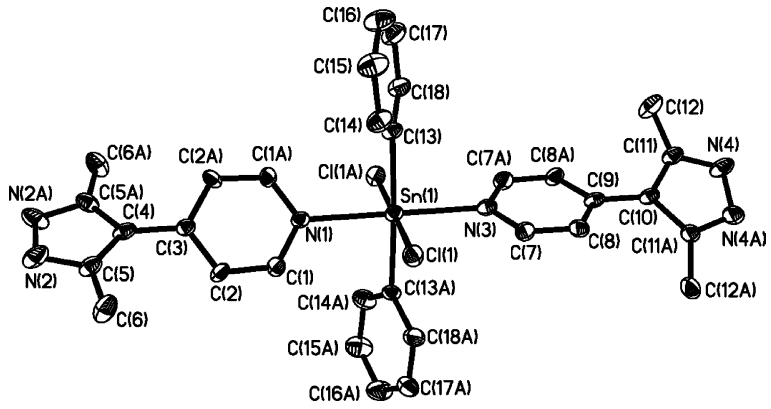


Fig. 1. The molecular structure of complex **2**. The thermal ellipsoids are drawn at the 30% probability. Selected bond distances (Å) and angles (°): Sn(1)–N(1) = 2.352(3), Sn(1)–N(3) = 2.377(3), Sn(1)–C(13) = 2.177(3), Sn(1)–Cl(1A) = 2.534(1), C(3)–C(4) = 1.478(6); C(13)–Sn(1)–C(13A) = 177.0(1), N(1)–Sn(1)–N(3) = 180.0, Cl(1)–Sn(1)–Cl(1A) = 179.11(4), C(13)–Sn(1)–N(3) = 91.50(9), C(13A)–Sn(1)–Cl(1) = 89.5(1), N(1)–Sn(1)–Cl(1A) = 89.55(2); torsion angles: C(2)–C(3)–C(4)–C(5) = 32.7(3); C(2)–C(3)–C(4)–C(5A) = −147.3(3)° (symmetry code: A = x, $-y + 1/2$, $-z + 1/4$).

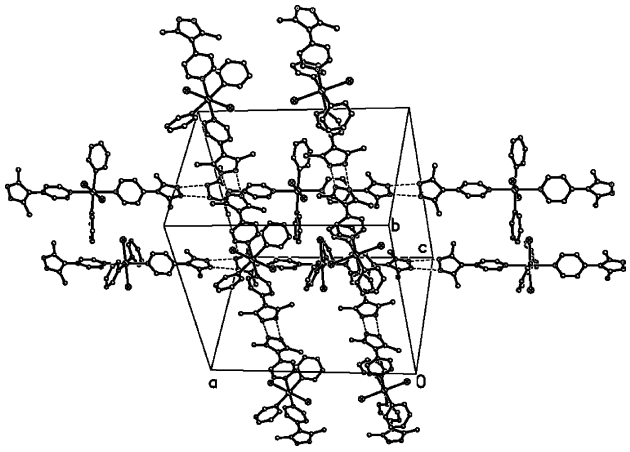


Fig. 2. The crystal packing diagram of complex **2** emphasizing the intermolecular hydrogen bonding interactions (N(2)–H···N(4)^{i} = 2.984 Å, N(4)–H···N(2)^{ii} = 2.984 Å; symmetry code: i = $x - 1$, $-y + 1/2$, $-z + 1/4$, ii = $x + 1$, $-y + 1/2$, $-z + 1/4$) and the one-dimensional chain. The solvent molecule is omitted for clarity.

X-ray diffraction analysis of complex **6** was undertaken. Fig. 3 shows that **6** is a 1D coordination polymer and bis(3,5-dimethyl-4-(4′-pyridyl)pyrazol-1-yl)methane acts as a bridged bidentate ligand by two exodentate pyridyl nitrogen atoms. The coordination environment around the tin atom is similar to that in complex **2**, i.e., a slightly distorted octahedral geometry, as well as an all-*trans* configuration of pyridyl nitrogen atoms, phenyl carbons and chlorine atoms. The Sn–Cl, Sn–C and Sn–N bond distances are also similar to those in complex **2**. The coordination mode of ligand **5** in complex **6** with the tin atom is analogous to those of bis(triazol-1-yl)methane [16] and pyrazine [28]. However, in the diorganotin derivatives of bis(triazol-1-yl)methane and pyrazine, the halide atoms as well as the coordinated nitrogen atoms are in *cis*-positions.

In conclusion, the coordination modes of 4-pyridylpyrazole and bis(4-pyridylpyrazol-1-yl)methane with diorganotin are quite different from those of the original azole and 2-pyridylpyrazole as well as bis(pyrazol-1-yl)methane. In diorganotin derivatives of pyridylpyrazole, the exodentate pyridyl nitrogen atoms have priority in coordinating to the tin atom possibly owing to their stronger donor ability over the pyrazolyl nitrogen. The coordination mode of ligand **5** to the tin atom is similar to those of 4,4-bipyridine and bis(1,2,4-triazol-1-yl)methane.

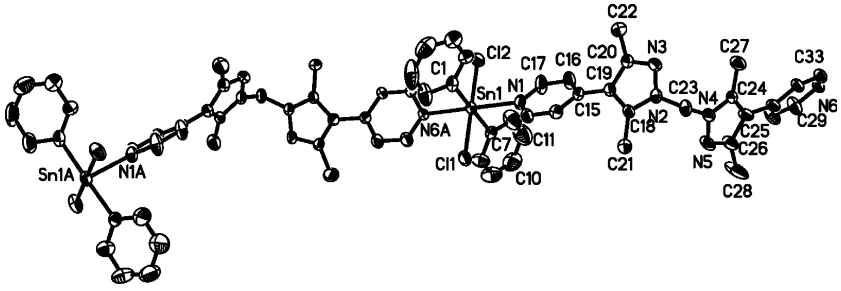


Fig. 3. The molecular structure of complex **6**. The thermal ellipsoids are drawn at 30% probability. The solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Sn1–Cl1 = 2.551(2), Sn1–Cl2 = 2.526(2), Sn1–N1 = 2.371(6), Sn1–N1A = 2.361(6), Sn1–C1 = 2.132(10), C15–C19 = 1.470(10), N2–C23 = 1.452(9), C23–N4 = 1.446(9); C1–Sn1–C7 = 177.0(4), N6A–Sn1–N1 = 178.3(3), Cl1–Sn1–Cl2 = 179.37(8), N6A–Sn1–Cl1 = 89.1(1), C1–Sn1–Cl1 = 90.2(3), C1–Sn1–Cl2 = 89.5(3), C7–Sn1–N1 = 89.0(3), C1–Sn1–N1 = 88.7(3), N4–C23–N2 = 110.9(5); torsion angles: C16–C15–C19–C20 = 40.1(13), C16–C15–C23–C18 = −142.0(10), N3–N2–C23–N4 = −81.5(8)° (symmetry code: A = $x + 1, -y + 1/2, z - 1/2$).

4. Supplementary material

Crystallographic data (CIF files) for the structures of complexes **2** and **6** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 248284 for complex **2** and CCDC No. 248283 for complex **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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