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Syntheses, Characterizations, and Crystal Structures of Organotin(IV) Chloride Complexes with 4,4′-Bipyridine

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ABSTRACT: *The organotin(IV) chlorides R_nSnCl_{4-n} ($n = 3$, R = Ph, $PhCH_2$, n-Bu; and $n = 2$, R = n-Bu, Ph, $PhCH_2$) react with 4,4′-bipyridine (4′4-bpy) to give $[(Ph_3SnCl)_2(4,4'\text{-bpy})_{1.5}(C_6H_6)_{0.5}]$ (**1**), $[(PhCH_2)_3SnCl]_2$ (4,4′-bpy) (**2**), $[(n\text{-Bu})_3SnCl]_2(4,4'\text{-bpy})$ (**3**), $[(n\text{-Bu})_2SnCl_2(4,4'\text{-bpy})]$ (**4**), $[Ph_2SnCl_2(4,4'\text{-bpy})]$ (**5**), and $[(PhCH_2)_2SnCl_2(4,4'\text{-bpy})]$ (**6**). The new complexes have been characterized by elemental analyses, IR, ^1H, ^{13}C, ^{119}Sn NMR spectroscopy. The structures of (**1**), (**2**), (**4**), and (**6**) have been determined by X-ray crystallography. Crystal structures of (**1**) and (**2**) show that the coordination number of tin is five. In complex (**1**), two different molecules exist: one is a binuclear molecule bridged by 4,4′-bpy and another is a mononuclear one, only one N of 4,4′-bpy coordinate to tin. Complex (**2**) contains an infinite 1-D polymeric binuclear chain by weak Sn···Cl intermolecular interactions with neighboring molecules. In the complexes (**4**) and (**6**), the tin is six-coordinate, and the 4,4′-bpy moieties bridge adjacent dialkyltin(IV)dichloride molecules to form a linear chain.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:338–346, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20016

INTRODUCTION

Recent development in coordination chemistry has produced numerous polymers and supramolecular complexes through the election of appropriate coordination geometry of metal ions and the chemical structure of organic ligands [1]. Ligands with particular symmetry and stereochemistry have led to different specific architectures. For example, *exo*-bidentate, such as pyrazine, 4,4′-bipyridine (4,4′-bpy), 1,2-bis(4-pyridyl)ethylene, 1,2-bis(4-pyridy)-ethane, are widely used for constructing chains [2,3]. Focusing only on 4,4′-bipyridine as a ligand, a survey of the recent literature reveals a plethora of homopolymetallic complexes with very interesting supramolecular architectures [4–7].

Although 4,4′-bpy has been extensively used in transition metal chemistry for construction of chains, rectangular grids, and cages [8,9], its use in main-group chemistry and crystallographic investigation appears to be limited [10]. Moreover, the coordination chemistry of organotin(IV) acceptors has been extensively studied due to the interest toward factors that influence the coordination number and geometry of molecule as well as for the important biological and catalytic properties of these compounds [11].

Because of the above consideration, we decided to investigate the donating ability of 4,4′-bpy toward organotin(IV) acceptors with different numbers of R-groups linked to metal center. We have synthesized six organotin(IV) derivatives of 4,4′-bpy and characterized them by elemental analysis, IR, ^1H, ^{13}C, ^{119}Sn

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NMR spectroscopy. Complexes (**1**), (**2**), (**4**), and (**6**) have also been studied by X-ray crystallography. The synthesis method used is shown in Scheme 1.

EXPERIMENTAL

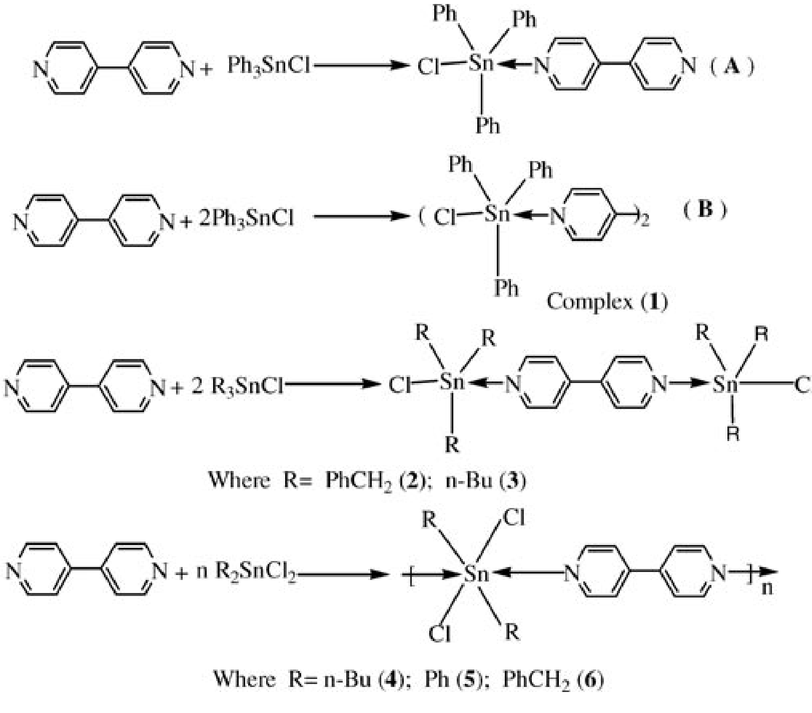
Materials and Methods

Triphenyltin chloride, tributyltin chloride, diphenyltin dichloride, di-*n*-butyltin dichloride, and 4,4′-bipyridine were commercially available, and they were used without further purification. Tribenzyltin chloride and dibenzyltin dichloride were prepared by a standard method reported in the literature [12]. The melting points were obtained with Kofler micro melting point apparatus and are uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300, 75.3, and 111.9 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C 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 ^{1}H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400II apparatus.

Syntheses

*[(Ph$_3$SnCl)$_2$(4,4′-bpy)$_{1.5}$(C$_6$H$_6$)$_{0.5}$] (**1**).* The reaction was carried out under nitrogen atmosphere. The 4,4′-bipyridine (0.234 g, 1.5 mmol) was added to a solution of absolute benzene (20 ml) in a Schlenk flask and stirred for 10 min. After triphenyltin chloride (0.770 g, 2 mmol) was added to the reactor, the reaction mixture was stirred for 12 h at 40°C. After cooling down to room temperature, the mixture was filtered. The filtered solution was gradually evaporated under vacuum until a solid product was obtained. The solid was then recrystallized from ether–dichloromethane. Colourless crystal complex (**1**) was formed: Yield, 89%. m.p. 132–134°C. Anal. Found: C, 61.88; H, 4.40; N, 9.20. Calc. for $C_{54}H_{45}Cl_2N_3Sn_2$: C, 61.51; H, 4.33; N, 9.26. IR (KBr) ν_{max}: 3020 (w, Ph—H), 2930 (m, C—H), 1597 (s, C=N), 1382 (s, C—N), 372 (w, Sn—N), 243 (m, Sn—Cl), 277, 229 (Sn—C) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ: 8.82 (d, 4H), 7.62 (d, 2H), 7.59 (d, 2H), 7.51 (d, 2H), 7.45 (d, 2H), 7.12–7.70 (m, 33H, aromatic-H, $^{3}J\,^{119}$Sn-^{1}H = 78 Hz). ^{13}C (CDCl$_3$) δ: 156.0, 145.9, 145.3, 122.3, 120.9 ($C_{10}H_8N_2$); 129.0, 129.8, 135.9, 137.7 (C—Ph, $^{2}J\,^{119}$Sn-^{13}C = 57 Hz, $^{3}J\,^{119}$Sn-^{13}C = 69 Hz). ^{119}Sn(CDCl$_3$) δ: −125.9.

*[(PhCH$_2$)$_3$SnCl]$_2$(4,4′-bpy) (**2**).* Complex (**2**) was prepared similarly to complex (**1**), by using 4,4′-bpy (0.156 g, 1 mmol) and tribenzyltin chloride (0.854 g, 2 mmol) in benzene (30 ml). The solid was



SCHEME 1

recrystallized from dichloromethane–hexane. Yield, 80%. m.p. 136–138°C. Anal. Found: C, 61.88; H, 4.40; N, 9.20. Calc. for $C_{52}H_{50}Cl_2\ N_2Sn_2$: C, 61.51; H, 4.33; N, 9.26. IR (KBr) ν_{max}: 3017 (w, Ph—H), 2916 (m, C—H), 1598 (s, C=N), 1384 (s, C—N), 555, 532 (Sn—C), 408 (w, Sn—N), 234 (m, Sn—Cl) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.78 (d, 4H), 7.63 (d, 4H), 7.10–7.75 (m, 30H), 3.22 (m, 12H, $^2J\ ^{119}$Sn-^{1}H = 75.0 Hz). ^{13}C ($CDCl_3$) δ: 156.2, 145.9, 122.3 ($C_{10}H_8N_2$); 128.1, 128.7, 128.9, 129.5, 137.8 (C—Ph), 37.9 (CH_2-Ph, $^1J\ ^{119}$Sn-^{13}C = 493 Hz). ^{119}Sn ($CDCl_3$) δ: −127.7.

[(n-Bu)$_3$SnCl]$_2$(4,4′-bpy) (**3**). Complex (**3**) was prepared similarly to complex (**1**), by using 4,4′-bpy (0.156 g, 1 mmol) and tributyltin chloride (0.650 g, 2 mmol) in benzene (20 ml). Stirred for 16 h at 40°C. It was recrystallized from ether–dichloromethane. Yield, 89%. m.p. 126–128°C. Anal. Found: C, 57.76; H, 8.74; N, 3.93. Calc. for $C_{34}H_{62}Cl_2N_2Sn_2$: C, 57.80; H, 8.77; N, 3.96. IR (KBr) ν_{max}: 2910 (m, C—H), 1599 (s, C=N), 1380 (s, C—N), 550, 536 (Sn—C), 410 (m, Sn—N), 280 (Sn—Cl) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.46 (d, 4H), 7.71 (d, 4H), 1.10–1.50 (t, 36H, $-CH_2$). 0.84 (t, 18H, $-CH_3$), ^{13}C ($CDCl_3$) δ: 156.1, 145.8, 122.2 ($C_{10}H_8N_2$); 13.06, 16.40, 27.10, 27.73 (^{n}Bu, $^2J\ ^{119}$Sn-^{13}C = 45.9 Hz). ^{119}Sn($CDCl_3$) δ: −106.8 ppm.

(n-Bu)$_2$SnCl$_2$(4,4′-bpy) (**4**). Complex (**4**) was prepared similarly to complex (**1**), by using 4,4′-bpy (0.156 g, 1 mmol) and *n*-dibutyltin dichloride (0.303 g, 1 mmol) in benzene (20 ml). Stirred for 10 h at 40°C. It was recrystallized from ether–dichloromethane. Yield, 89%. m.p. 162–164°C. Anal. Found: C, 46.98; H, 5.67; N, 6.03. Calc. for $C_{18}H_{26}Cl_2\ N_2Sn$: C, 47.00; H, 5.70; N, 6.09. IR (KBr) ν_{max}: 1610 (s, C=N), 565 (s, Sn—C), 418 (m, Sn—N), 250 (s, Sn—Cl) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.79 (d, 4H), 7.60 (d, 4H), 1.80–1.41 (m, 12H, $^2J\ ^{119}$Sn-^{1}H = 95.7 Hz), 0.96 (m, 6H). ^{13}C ($CDCl_3$) δ: 156.2, 150.0, 122.5 ($C_{10}H_8N_2$); 13.8, 26.7, 28.5, 33.9 (^{n}Bu, $^1J\ ^{119}$Sn-^{13}C = 889 Hz, $^2J\ ^{119}$Sn-^{13}C = 37.6 Hz, $^3J\ ^{119}$Sn-^{13}C = 108 Hz). ^{119}Sn($CDCl_3$) δ: −264.3 ppm.

Ph$_2$SnCl$_2$(4,4′-bpy) (**5**). Complex (**5**) was prepared similarly to complex (**4**), by using 4,4′-bpy (0.156 g, 1 mmol) and diphenyltin dichloride (0.343 g, 1 mmol) in benzene (20 ml). It was recrystallized from ether–dichloromethane. Yield, 89%. m.p. 136–138°C. Anal. Found: C, 52.81; H, 3.58; N, 5.57. Calc. for $C_{20}H_{18}Cl_2\ N_2Sn$: C, 52.85; H, 3.60; N, 5.60. IR(KBr)ν_{max}: 1612 (s, C=N), 409 (w, Sn—N), 287, 232 (Sn—C), 256 (m, Sn—Cl) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.60 (d, 4H), 7.62 (d, 4H), 7.12–7.68 (m, 10H, $^3J\ ^{119}$Sn-^{1}H = 94.8 Hz). ^{13}C ($CDCl_3$) δ: 157.0, 150.6, 122.9 ($C_{10}H_8N_2$); 128.3, 129.5, 136.2, 143.8 ($^1J\ ^{119}$Sn-^{13}C = 886 Hz, *i*-C). ^{119}Sn($CDCl_3$) δ: −390.4 ppm.

(PhCH$_2$)$_2$SnCl$_2$(4,4′-bpy) (**6**). Complex (**6**) was prepared similarly to complex (**4**), by using 4,4′-bpy (0.156 g, 1 mmol) and dibenzyltin dichloride (0.371 g, 1 mmol) in benzene (20 ml). It was then recrystallized from ether–dichloromethane. Yield, 89%. m.p. 170–172°C. Anal. Found: C, 54.56; H, 4.15; N, 5.26. Calc. for $C_{24}H_{22}Cl_2\ N_2Sn$: C, 54.59; H, 4.17; N, 5.30. IR (KBr) ν_{max}: 3019 (w, Ph—H), 1598 (s, C=N), 555 (s, Sn—C), 411 (m, Sn—N), 254 (Sn—Cl) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.41 (d, 4H), 7.61 (d, 4H), 7.12–7.68 (m, 10 H), 3.24 (4H, CH_2-Ph, $^2J\ ^{119}$Sn-^{1}H = 95.1 Hz). ^{13}C ($CDCl_3$) δ: 156.1, 145.9, 122.1 ($C_{10}H_8N_2$); 128.1, 129.3, 136.5, 148.6, 37.5 (CH_2-Ph, $^1J\ ^{119}$Sn-^{13}C = 870 Hz). ^{119}Sn($CDCl_3$) δ: −385.2 ppm.

X-Ray Crystallography

Data were collected at 298 K on a Bruker SMART CCD 1000 X-diffractometer fitted with MoKα radiation. The structures were solved by direct-methods and refined by a full-matrix least squares procedure based on F^2 using the SHELXL-97 program system. All non-H atoms were included in the model at their calculated positions. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included.

RESULTS AND DISCUSSION

IR

In the triorganotin(IV) derivatives (**2**) and (**3**), two strong or medium absorptions are observed at 555 and 532, 550 and 536 cm^{-1} respectively. They are due to ν_{asym} and ν_{sym} Sn—C stretching vibrations and are consistent with an essentially trigonal pyramidal arrangement of organic groups [13]. The spectra of (**1**) is also consistent with an essentially pyramidal arrangement of phenyl groups, the ν_{asym} and ν_{sym} Sn—C being observed at ca 277 and 229 cm^{-1}, respectively.

The appearance of only a single Sn—C band in the spectra of diakyltin(IV) complexes (**4**) and (**6**) at ca 565 and 554 cm^{-1} respectively, is in accordance with a *trans*-octahedral configuration of the two alkyl groups [14]. Instead, in the diphenyltin(IV) dichloride complex (**5**), the ν_{asym} and ν_{sym} Sn—C stretching vibrations are observed at ca 287 and 232 cm^{-1} respectively, which are lower than those found in *trans*-R_2 octahedral diphenyltin(IV) complexes containing N-donor ligands [15].

The tin-chloride stretching frequencies in the mono- (**1, 2**, and **3**) and dichlorotin(IV) complexes

(**4, 5**, and **6**) fall in the region 243–228 cm^{-1}, and 256–250 cm^{-1} respectively. These bands are lower than those observed in the spectra of the starting tin(IV) reagents [16].

We noted some weak absorption in the region of 372–418 cm^{-1}, which were absent in the spectrum of the free donor. They were assigned to ν (Sn—N) stretches [17].

NMR

The spectra of the triorganotin(IV) complexes (**1**), (**2**), and (**3**) indicate a complete dissociation into the starting reagents. In fact, the Δ (difference in chemical shift for the same type of proton in the free base and in its organotin(IV) complex) value is in the range 0.11–0.34 ppm. The tin–proton and tin–carbon coupling constants observed are of the same order of magnitude as those reported for the starting triorganotin(IV) acceptors [18]. In the spectra of diorganotin(IV) complexes (**4**), (**5**), and (**6**), the signals of the ligand are generally displaced to lower fields. This is likely to be due to the N atoms coordinating to metal tin center. The tin–proton and tin–carbon coupling constants observed are different from those observed for the starting organotin(IV) derivatives [19], similar to those found in the literature for undissociated *trans*-octahedral diorganotin(IV) complexes [20].

In the ^{13}C NMR spectra of the complexes (**1**)–(**6**), which are generally consistent with the conclusions drawn from ^{1}H NMR results, the signals of ligand are shifted only very slightly from their position in the spectrum of free donor ligand. However, the magnitude of J_{Sn-C} and the values of chemical shift of the carbons band to organotin(IV) are different from those reported for starting organotin(IV) derivatives and are similar to those indicated for petra- or hexacoordinate tin(IV) complexes [21].

The ^{119}Sn NMR spectra of complexes (**1**), (**2**), and (**3**) exhibit a single resonance, typical for five-coordinate central tin atom [22]. These signals are shifted upfield with respect to those reported for starting acceptor (Ph_3SnCl: −44.7 ppm [22]). The ^{119}Sn chemical shift of dialkyltin(IV) complexes (**4**), (**5**), and (**6**) range from −264.3 to −390.4 ppm, shifting upfield with respect to those reported for starting acceptor (n-Bu_2SnCl_2: 126.2 ppm, Ph_2SnCl_2: −32 ppm [23]) too, typical for *trans*-octahedral structures [18].

TABLE 1 Crystal Data and Refinement Details for Complexes **1** and **2**

Complexes	**1**	**2**
Chemical formula	$C_{54}H_{45}Cl_2N_3Sn_2$	$C_{52}H_{50}Cl_2N_2Sn_2$
Formula weight	1044.21	1011.22
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2(1)/n
a (Å)	9.2549(19)	13.148(4)
b (Å)	14.040(3)	14.775(4)
c (Å)	18.664(4)	23.868(6)
α (°)	82.203(3)	
β (°)	81.226(3)	97.790 (4)
γ (°)	82.216(3)	
V (Å^3)	2358.4(9)	4594(2)
D_c (g cm^{-3})	1.211	1.462
λ (Å)	0.71073	0.71073
Z	2	4
F(000)	1048	2040
Crystal size (mm)	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.20
θ range (°)	1.47 to 23.44	1.63 to 24.81
Absorption (mm^{-1})	1.407	1.240
T (K)	298(2)	298(2)
Reflections	10411/6815	23395/7858
Collected/unique	[$R_{int} = 0.0209$]	[$R_{int} = 0.0860$]
Parameters	550	523
Goodness-of-fit on F^2	1.047	0.899
Final R indices [$I > 2.0\sigma(I)$]	$R_1 = 0.0425$, w$R_2 = 0.1135$	$R_1 = 0.0558$, w$R_2 = 0.1308$
R indices (all data)	$R_1 = 0.0641$, $wR_2 = 0.1251$	$R_1 = 0.1450$, w$R_2 = 0.1652$
Largest diff. peak and hole (e Å^{-3})	0.588 and −0.385	0.832 and −0.673
Max. and min. transmission	0.7937 and 0.7126	0.7895 and 0.7073

TABLE 2 Crystal Data and Refinement Details for Complexes **4** and **6**

Complexes	**4**	**6**
Chemical formula	$C_{18}H_{26}Cl_2N_2Sn$	$C_{24}H_{22}Cl_2N_2Sn$
Formula weight	460	528.03
Crystal system	Triclinic	Monoclinic
Space group	P1	C2/c
a (Å)	9.202(5)	15.869(4)
b (Å)	9.350(5)	11.845(3)
c (Å)	9.563(5)	13.295(3)
α (°)	85.434(9)	
β (°)	61.316(9)	112.972(3)
γ (°)	79.615(9)	
V (Å^3)	710.0(7)	2300.9(9)
D_c (g cm^{-3})	1.076	1.524
λ (Å)	0. 71073	0.71073
Z	1	4
$F(000)$	232	1056
Crystal size (mm)	0.25 × 0.13 × 0.08	0.30 × 0.20 × 0.10
θ range (°)	2.56 to 26.37	2.21 to 23.33
Absorption (mm^{-1})	1.0 89	1.355
T (K)	298(2)	293(2)
Reflections Collected/unique	3579/3075 [$R_{int} = 0.0436$]	5154/1656 [$R_{int} = 0.0299$]
Parameters	208	134
Goodness-of-fit on F^2	0.750	1.036
Final R indices [$I > 2.0\sigma(I)$]	$R_1 = 0.0551$, w$R_2 = 0.0797$	$R_1 = 0.0274$, w$R_2 = 0.0596$
R indices (all data)	$R_1 = 0.0928$, $wR_2 = 0.0905$	$R_1 = 0.0341$, w$R_2 = 0.0627$
Largest diff. peak and hole (e Å^{-3})	0.377 and −0.3 63	0.645 and −0.430
Max. and min. transmission	0.9180 and 0.7725	0.8764 and 0.6866

Crystal Structures

The crystal data and refinement details of complexes (**1**), (**2**), (**4**), and (**6**) are given in Tables 1 and 2, respectively. Selected bond distances and angles are shown in Tables 3–5, respectively. The crystal structures and unit cells packing figures are shown in Figs. 1–8.

For complex (**1**), the molecular structure and the atom numbering scheme is shown in Fig. 1. The symmetric unit cell contains two different crystallographically independent molecules **A** and **B**, and there is also a moiety phenyl solvent molecule in complex (**1**). Molecule **A** is a mononuclear through one nitrogen of 4,4′-bpy coordinated to the tin atom,

TABLE 3 Selected Bond Lengths (Å) and Angles (°) for $[(Ph_3SnCl)_3(4,4'\text{-bpy})_2]$ **1**

*Molecule **A***		*Molecule **B***	
Sn(1)–Cl(1)	2.5153(17)	Sn(2)–Cl(2)	2.4927(16)
Sn(1)–N(1)	2.475(5)	Sn(2)–N(3)	2.540(5)
Sn(1)–C(17)	2.139(6)	Sn(2)–C(46)	2.123(6)
Sn(1)–C(11)	2.149(7)	Sn(2)–C(34)	2.154(6)
Sn(1)–C(23)	2.157(6)	Sn(2)–C(40)	2.156(6)
Cl(1)–Sn(1)–N(1)	176.40(12)	Cl(2)–Sn(2)–N(3)	175.21(14)
C(17)–Sn(1)–C(11)	117.0(2)	C(46)–Sn(2)–C(34)	117.1(2)
C(17)–Sn(1)–C(23)	122.1(3)	C(46)–Sn(2)–C(40)	117.4(2)
C(11)–Sn(1)–C(23)	120.5(3)	C(34)–Sn(2)–C(40)	123.0(2)
C(17)–Sn(1)–Cl(1)	93.52(17)	C(46)–Sn(2)–Cl(2)	99.37(15)
C(11)–Sn(1)–Cl(1)	94.14(18)	C(34)–Sn(2)–Cl(2)	92.67(17)
C(23)–Sn(1)–Cl(1)	88.51(16)	C(40)–Sn(2)–Cl(2)	93.90(17)
C(17)–Sn(1)–N(1)	88.3(2)	C(46)–Sn(2)–N(3)	85.21(19)
C(11)–Sn(1)–N(1)	87.7(2)	C(34)–Sn(2)–N(3)	86.4(2)
C(23)–Sn(1)–N(1)	87.9(2)	C(40)–Sn(2)–N(3)	82.7(2)

TABLE 4 Selected Bond Lengths (Å) and Angles (°) for [(PhCH$_2$)$_3$SnCl]$_2$(4,4′-bpy) **2**

Sn(1)–Cl(1)	2.474(2)	Sn(1)–C(25)	2.161(9)
Sn(2)–Cl(2)	2.503(3)	Sn(1)–C(11)	2.169(10)
Sn(1)–N(1)	2.543(7)	Sn(1)–C(18)	2.179(9)
Sn(2)–N(2)	2.548(7)	Sn(2)–C(32)	2.180(10)
Cl(1)–Sn(1)–N(1)	171.47(18)	Cl(2)–Sn(2)–N(2)	169.6(2)
C(25)–Sn(1)–C(11)	128.2(4)	C(39)–Sn(2)–C(46)	114.1(4)
C(25)–Sn(1)–C(18)	114.5(4)	C(39)–Sn(2)–C(32)	114.0(4)
C(11)–Sn(1)–C(18)	114.2(3)	C(46)–Sn(2)–C(32)	131.6(3)
C(25)–Sn(1)–Cl(1)	93.3(2)	C(39)–Sn(2)–Cl(2)	89.2(3)
C(11)–Sn(1)–Cl(1)	94.0(3)	C(46)–Sn(2)–Cl(2)	93.9(3)
C(18)–Sn(1)–Cl(1)	100.9(3)	C(32)–Sn(2)–Cl(2)	92.2(3)
C(11)–Sn(1)–N(1)	83.4(3)	C(39)–Sn(2)–N(2)	101.2(3)
C(25)–Sn(1)–N(1)	82.1(3)	C(46)–Sn(2)–N(2)	82.3(3)
C(18)–Sn(1)–N(1)	87.6(3)	C(32)–Sn(2)–N(2)	83.3(3)

while another N is not coordinated, and the dihedral angles of two pyridine rings of 4,4′-bpy is 41.4°, while **B** consists of centrosymmetric binuclear species with a bridging 4,4′-bpy molecule. However, the coordination geometry about Sn(IV) of molecules **A** and **B** is a trigonal bipyramid in which three phenyl groups form the equatorial plane, while one nitrogen of the ligand and the halogen occupy the apical positions. And in molecule **B**, the tin–tin separation across 4,4′-bpy is 7.048 Å and the pyridine rings of 4,4′-bpy are coplanar (0° dihedral angle), two chlorine and two nitrogen atoms are located in the chain, the angles Cl(2)—Sn(2)—N(3) 175.21(19)° and Cl(2A)—Sn(2A)—N(3A) 175.35(19)° are all very close to 180°, therefore forming a Cl—Sn—N—N—Sn—Cl beeline configuration. The Sn—N distances are 2.475(5) Å in molecule **A** and 2.548(7) Å in molecule **B** respectively, longer than those found in [$Me_3SnN(SO_2Me)_2 \cdot 4,4'$-bpy] (2.411 and 2.420 Å) [24]. The Sn—Cl distances are 2.5153(17) Å for molecule **A** and 2.4927(16) Å for molecule **B** respectively, and are in the ranges reported in the literature for five-coordinated organotin(IV) chloride (2.432–2.613) [25]. The average Sn—C bond lengths are in the range of 2.123(6) Å–2.157(6) Å, in good agreement with published values [26].

As shown in Fig. 3, the formation of complex (**2**) is similar to that of (**1**), Sn has a trigonal bipyramid

TABLE 5 Selected Bond Lengths (Å) and Angles (°) for Complexes **4** and **6**

4		6	
Sn(1)–C(15)	2.120(12)	Sn(1)–C(7)	2.169(4)
Sn(1)–C(11)	2.13(3)	Sn(1)–C(7A)	2.169(4)
Sn(1)–N(1)	2.449(16)	Sn(1)–N(1)	2.359(4)
Sn(1)–N(2)	2.33(2)	Sn(1)–N(2)	2.433(4)
Sn(1)–Cl(1)	2.566(6)	Sn(1)–Cl(1)	2.5429(10)
Sn(1)–Cl(2)	2.564(8)	Sn(1)–Cl(1A)	2.5429(10)
C(15)–Sn(1)–C(11)	172.7(2)	C(7)–Sn(1)–C(7A)	171.15(19)
N(1)–Sn(1)–N(2)	178.3(10)	N(1)–Sn(1)–N(2)	180.00(1)
Cl(1)–Sn(1)–Cl(2)	178.1(4)	Cl(1)–Sn(1)–Cl(1A)	179.81(4)
C(15)–Sn(1)–N(1)	88.8(6)	C(7)–Sn(1)–N(1)	94.42(9)
C(11)–Sn(1)–N(1)	87.4(9)	C(7A)–Sn(1)–N(1)	94.42(9)
C(15)–Sn(1)–N(2)	89.8(7)	C(7)–Sn(1)–N(2)	85.58(9)
C(11)–Sn(1)–N(2)	93.9(10)	C(7A)–Sn(1)–N(2)	85.58(9)
C(15)–Sn(1)–Cl(1)	93.2(6)	C(7)–Sn(1)–Cl(1)	89.99(11)
C(1)–Sn(1)–Cl(1)	93.1(8)	C(7A)–Sn(1)–Cl(1)	90.03(11)
N(2)–Sn(1)–Cl(1)	89.7(5)	N(2)–Sn(1)–Cl(1)	90.10(2)
N(1)–Sn(1)–Cl(1)	91.4(5)	N(1)–Sn(1)–Cl(1)	89.90(2)
C(15)–Sn(1)–Cl(2)	85.0(6)	C(7)–Sn(1)–Cl(1A)	90.03(11)
C(11)–Sn(1)–Cl(2)	88.7(8)	C(7A)–Sn(1)–Cl(1A)	89.99(11)
N(2)–Sn(1)–Cl(2)	89.5(5)	N(2)–Sn(1)–Cl(1A)	90.10(2)
N(1)–Sn(1)–Cl(2)	89.4(5)	N(1)–Sn(1)–Cl(1A)	89.90(2)

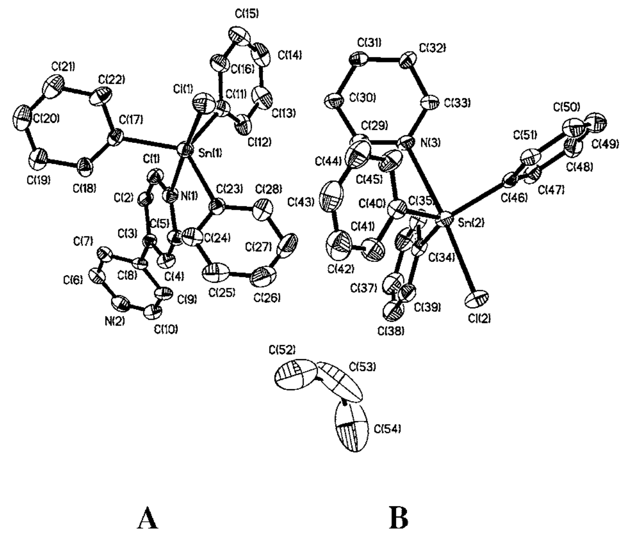


FIGURE 1 The molecular structure of complex **1**.

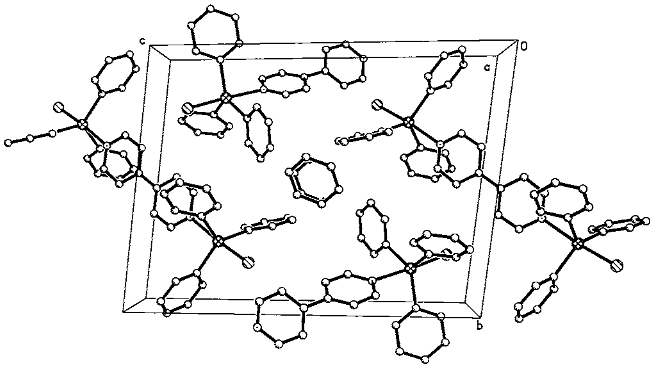


FIGURE 2 The unit cell of complex **1**.

geometry. But it is worthy to note that the structure of (**2**) consists of centrosymmetric binuclear $[(PhCH_2)_3SnCl]_2\cdot$4,4′-bpy units that are bridged by the weak intermolecular Sn···Cl contacts which give rise to polymeric infinite chains, within which tin atoms are linked alternatively by double chlorides and 4,4′-bpy bridges. The intermolecular bond lengths are 4.134 Å for Sn(1A)···Cl(2), and 3.932 Å for Sn(2)···Cl(1), little longer than the sum of the tin and chloride van der Waals radii (3.85 Å) [27], and hence tin is truly five-coordinate. Three C of benzyl groups forming the equatorial position, chlorine and nitrogen atoms occupy the axial positions, and the tin–tin separation across 4,4′-bpy being (7.057 Å) a value which is much longer than the shorter intermolecular one (4.998 Å) through the pathway Sn(1A)—Cl(1A)···Sn(2), the pyridine rings of 4,4′-bpy twist by 17.7°, and two rings twist the chains by 3.5° and 14.2° respectively.

From the Figs. 5 and 7, respectively, we can see that, contrast to above triorganotin(IV) complexes (**1**) and (**2**), the geometry of diorganotin(IV) complexes (**4**) and (**6**) are different from them. The 4,4′-bpy moiety in (**4**) and (**6**) bridges adjacent dialkyltin(IV)dichloride molecules to form a linear chain, whose six-coordinate Sn atom exists in an *all-trans* octahedral geometry. Two C atoms of *n*-butyl or benzyl groups and two Cl atoms exist in equatorial positions, while two N atoms of 4,4′-bpy occupy the axial chain position. The angles N(1)—Sn(1)—N(2) 178.3(10)°, Cl(1)—Sn(1)—Cl(2) 178.1(4)°, C(15)—Sn(1)—C(11) 172.7(11)° for (**4**), and N(1)—Sn(1)—N(2) 180.00(1)°, Cl(1)—Sn(1)—Cl(1A) 179.81(4)°, C(7)—Sn(1)—C(7A) 171.15(19)° for (**6**),

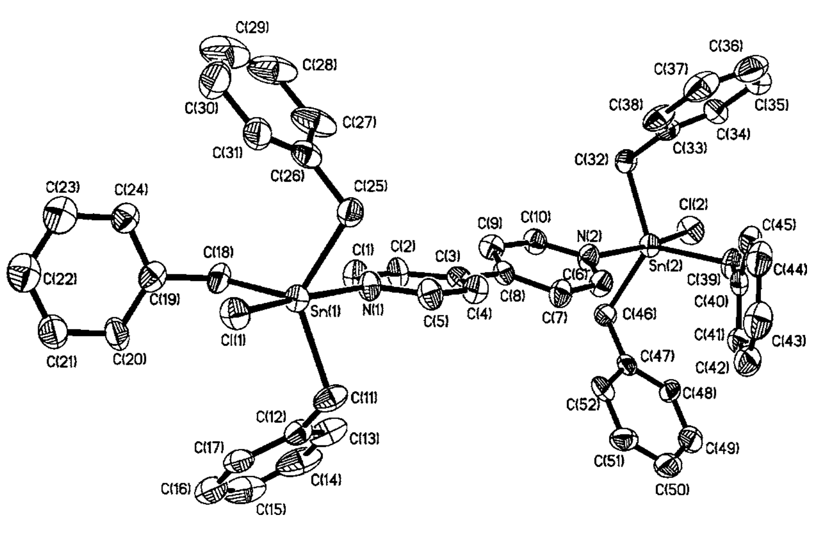


FIGURE 3 The molecular structure of complex **2**.

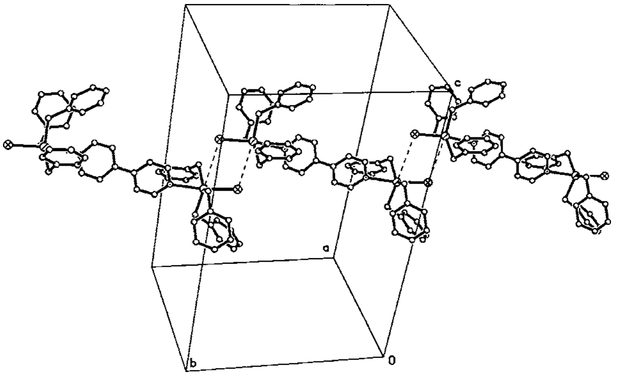


FIGURE 4 The unit cell of complex **2**.

respectively, which are all close to 180°, so two C, two Cl, two N atoms are all lie in *trans*-geometry, respectively. Seen from the Table 5, both Sn—N bond lengths in (**4**) and (**6**) are all shorter than those in complexes (**1**) and (**2**), shorter Sn—N bond lengths 2.33(2) for (**4**) and 2.359(4) for (**6**) are in good agreement with those found in [Ph_2SnCl_2(2,2′-bpy)] 2.344(6) and 2.375(6) Å [28], while another longer Sn—N bond length 2.449(16) Å for (**4**) and 2.433(4) Å for (**6**), are similar to those found in [Ph_2SnCl_2(mepirizole)] 2.581(4) and 2.430(4) Å [29]. The Sn—Cl distances are 2.564(8) and 2.566(6) Å for (**4**), 2.5429(10) Å for (**6**), longer than those found in ($SnPh_2Cl_2 \cdot Pyz)_n (n = \infty)$ (2.404(4) and 2.379(4) Å) [30], the Sn—C distances are 2.120(12), 2.13(3) Å for (**4**) and 2.169(4) Å for (**6**), in the range found for other dialkyltindichloride complexes with bidentate N,N′-donor ligands [31].

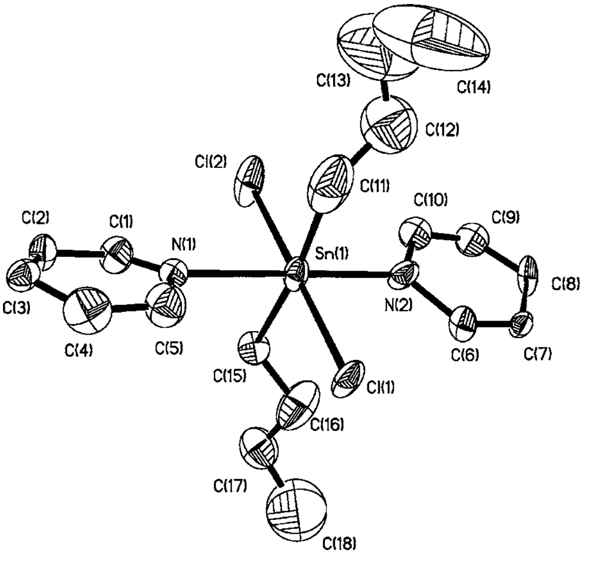


FIGURE 5 The molecular structure of complex **4**.

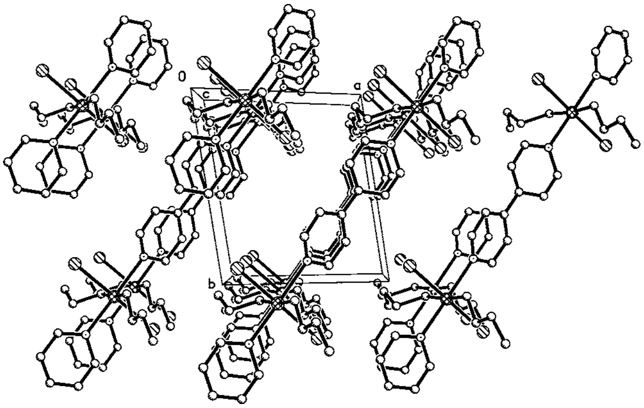


FIGURE 6 The unit cell of complex **4**. Flack parameters: 0.03(7) showing 30% thermal ellipsoid probability.

In view of the above description, we can conclude that in triorganotin(IV) complexes, 4,4′-bpy ligand acts as a bridge to link binuclear. But based on the stereochemical constraints sequence, phenyl > benzyl, so complex (**2**) forms an infinite polymeric chain, while complex (**1**) dose not form a chain. However, in diorganotin(IV) complexes, 4,4′-bpy moiety bridge adjacent dialkyltin(IV)dichloride molecules to form a linear chain.

Examination of the structures of Sn (IV) complexes containing a N-donor atom and tested for antitumor activity revealed that in the active Sn complexes the average Sn—N bond lengths were >2.39 Å, whereas the inactive complexes had Sn—N bonds <2.39 Å, which implies that predissociation of the

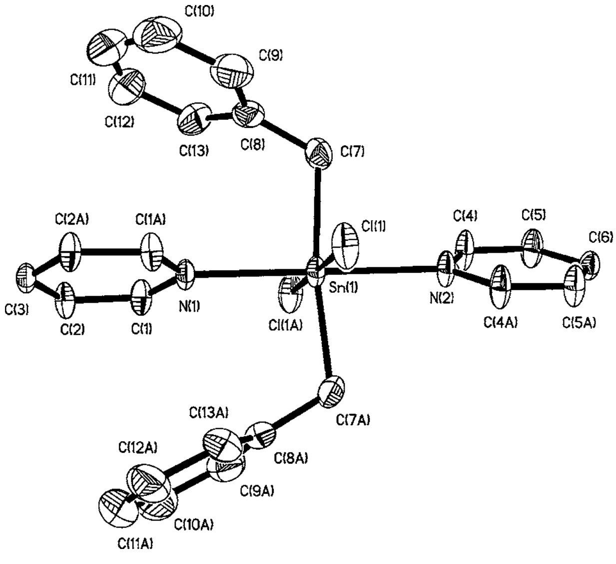


FIGURE 7 The molecular structure of complex **6**.

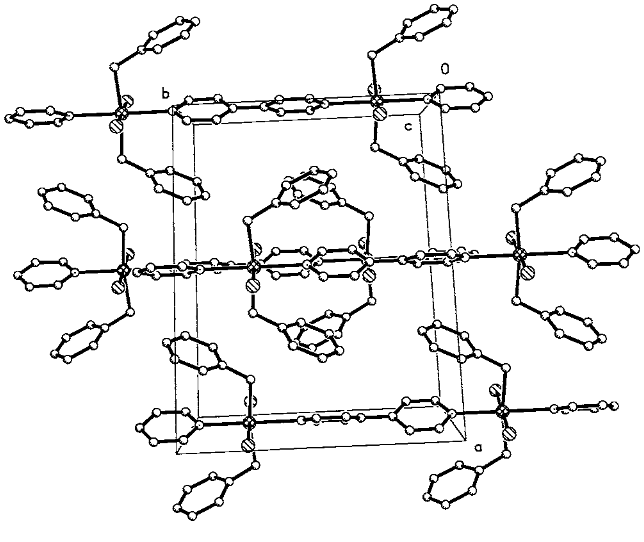


FIGURE 8 The unit cell of complex **6**.

ligand may be an important step in the mode of action of these complexes, while the coordinated ligand may favor transport of the active species to the site of action in the cells, where they are released by hydrolysis [32]. From Tables 3–5, we can see that the average Sn—N bond lengths are all longer than 2.39 Å, and the results of bioactivity measurement show that complexes (**1**), (**2**), (**4**), and (**6**) all have antitumor activity against culture cells, which is in accord with correlation of Sn—N bond length with antitumor activity.

SUPPLEMENTARY DATA

Atomic coordinates, thermal parameters, and bond lengths and angles for complexes (**1**), (**2**), (**4**), and (**6**) have been deposited the Cambridge Crystallographic Data Center, CCDC nos. CCDC 183590, 183592, 207120, and 192504. Copies of this information may be obtained free of charge from the Director, CCDC, 2 Union Road, Cambridge CB2 1EZ, UK on request (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www. http://www ccdc. cam.ac.uk), quoting the deposition numbers for (**1**), (**2**), (**4**), and (**6**), respectively.

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