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Synthesis and characterization of some organotin(IV) adducts containing a related series of pyridines: Crystal structure of $[SnMe_2Cl_2(bu_2bpy)]$

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ABSTRACT

Organotin(IV) complexes of $[SnR_{(4-n)}Cl_n]$ (n = 2, R = Me, ^{n}Bu; n = 1, R = Ph) react with the bidentate pyridyl ligand 4,4′-di-*tert*-butyl-2,2′-bipyridine (bu_2bpy) to give hexa-coordinated adducts with the general formula $[SnR_{(4-n)}Cl_n(bu_2bpy)]$. However, the reaction of these organotin(IV) complexes with the corresponding monodentate ligand 4-*tert*-butylpyridine (bupy) resulted in the formation of the hexa-coordinated complex $[SnMe_2Cl_2(bupy)_2]$ and the penta-coordinated complexes $[SnR_{(4-n)}Cl_n(bupy)]$ (n = 2, R = ^{n}Bu; n = 1, R = Ph). Moreover, the reaction of the above organotin(IV) complexes with 4,4′-trimethylenedipyridine (tmdp) yields hexa-coordinated adducts with the general formula $[SnR_2Cl_2(tmdp)]$ (R = Me, ^{n}Bu) and the penta-coordinated complex $[ClPh_3Sn\text{-}\mu\text{-}(tmdp)SnPh_3Cl]$ in the solid state. The resulting complexes have been characterized by multinuclear NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopy and elemental analysis. NMR data shows that the triphenyltin(IV) adducts are not stable in solution and dissociate to give tetra-coordinated tin(IV) complexes. The X-ray crystal structure determination of $[SnMe_2Cl_2(bu_2bpy)]$ reveals that the tin atom is hexa-coordinated in an octahedral geometry with a *trans*-$[SnMe_2]$ configuration.

1. Introduction

It has long been known that tin(IV) compounds are one of the most convenient systems for the investigation of Lewis acid–base interactions [1–4]. They usually form 1:1 and 1:2 adducts, and the resulting adducts exist in trigonal bipyramidal or octahedral geometries [5]. The formation of adducts depends upon the nature of the organic group R on the organotin compounds, nature of the donor ligand, donor ratio, halide or pseudohalide, reaction temperature and solvent [5]. The organotin halides have a tendency to form 1:1 adducts with monodentate ligands in solution. The equilibrium constants for the formation of 1:1 adducts are strongly dependent upon the size of the substituents. The greater insolubility of 1:2 adducts and an excess of base can result in the formation of 1:2 adducts in the solid state [6]. Many organotin(IV) adducts dissociate in solution and the behavior in solution is dependent upon the organotin(IV) acceptor and solvent [7]. There are many complexes of organotin halides with ligands such as sulfoxides, phosphines, phosphine oxides and phosphine sulfides, and their structure and stability have been investigated [5–7]. Monodentate or bidentate pyridyl ligands are one of the strongest bases towards organotin(IV) halides and form both stable 1:1 and 1:2 complexes. For example, $SnMe_2Cl_2$ reacts with 2,2′-bipyridine (bpy) or pyridine (py) to form the 1:1 complex of $[SnMe_2Cl_2(bpy)]$ or the 1:2 complex of $[SnMe_2Cl_2(py)_2]$ [2]. These complexes have been shown to exhibit anti-tumor activity. There is a relation between the Sn–N bond length and the anti-cancer activity [8,9].

Herein, we report on the preparation and NMR data of some organotin(IV) complexes with a related series of the monodentate pyridyl ligand 4-*tert*-butylpyridine (bupy) and the corresponding bidentate ligand 4,4′-di-*tert*-butyl-2,2′-bipyridine (bu_2bpy). Also, the reactions of the organotin(IV) complexes with the 4,4′-trimethylenedipyridine (tmdp) ligand were investigated, where the ligand can act as a monodentate ligand or bridge two tin atoms (Scheme 1). We used these three nitrogen-donor ligands to obtain more information about the relative reactivities of organotin(IV) complexes. The molecular structure of $[SnMe_2Cl_2(bu_2bpy)]$ was determined by X-ray crystallography and is discussed.

2. Experimental

2.1. General remarks

Dimethyltin dichloride, dibutyltin dichloride and triphenyltin chloride were purchased from Merck. 4,4′-Di-*tert*-butyl-2,2′-bipyridine, 4-*tert*-butylpyridine and 4,4′-trimethylenedipyridine were purchased from Aldrich and were used without further purifica-

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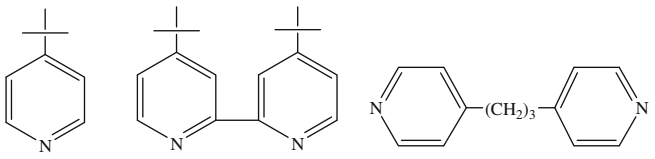


Scheme 1.

tion. Diethyl ether was distilled from sodium/benzophenone ketyl and dichloromethane was distilled from P_2O_5. Elemental analyses were performed on a Perkin–Elmer 2400 II elemental analyzer. NMR data were recorded using Bruker Avance DRX 500 or DPX 250 MHz spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported relative to the residual solvent signal, and ^{119}Sn NMR chemical shifts are reported relative to $SnMe_4$. All the chemical shifts and coupling constants are reported in ppm and Hz, respectively.

2.2. Preparation of $[SnMe_2Cl_2(bu_2bpy)]$, **1a**

A solution of 4,4′-di-*tert*-butyl-2,2′-bipyridine (61 mg, 0.23 mmol) in diethyl ether (5 mL) was added to a solution of $SnMe_2Cl_2$ (50 mg, 0.23 mmol) in diethyl ether (5 mL) to afford a white crystalline solid. The product was then filtered off and washed with diethyl ether and air dried. Yield: 85%; m.p. 235–236 °C. *Anal.* Calc. for $C_{20}H_{30}Cl_2N_2Sn$: C, 49.20; H, 6.20; N, 5.74. Found: C, 49.93; H, 6.35; N, 5.83%. NMR data in $CDCl_3$: δ(^{1}H) 1.06 [s, 6H, ^2J($^{119/117}$Sn–H) = 106.4 Hz, Sn–Me], 1.48 [s, 18H, ^{t}Bu], (bu_2bpy group) 7.67 [d, 2H, ^3J(HH) = 5.6 Hz, H$^{5,5'}$], 8.23 [s, 2H, H$^{3,3'}$], 9.40 [d, 2H, ^3J(HH) = 5.4 Hz, H$^{6,6'}$]; δ (^{13}C) 25.3 [s, ^1J(^{119}Sn–C) = 1092 Hz, ^1J(^{117}Sn–C) = 1043 Hz, Sn–Me], 30.4 [s, terminal C atoms of ^{t}Bu groups], 35.7 [s, central C atoms of ^{t}Bu groups], (bu_2bpy group) 165.4 (C_2), 118.9 (C_3), 148.7 (C_4), 123.8 (C_5), 148.0 (C_6); δ(^{119}Sn) −251 (sh). Crystals suitable for X-ray structure determination were grown from a chloroform solution.

2.3. Preparation of $[Sn^nBu_2Cl_2(bu_2bpy)]$, **2a**

Following the same procedure as for the preparation of **1a**, a solution of 4,4′-di-*tert*-butyl-2,2′-bipyridine (44 mg, 0.16 mmol) in diethyl ether (5 mL) was added to a solution of $Sn^nBu_2Cl_2$ (50 mg, 0.16 mmol) in diethyl ether (5 mL) to give a white solid. Yield: 81%; m.p. 188–190 °C. *Anal.* Calc. for $C_{26}H_{42}Cl_2N_2Sn$: C, 54.55; H, 7.40; N, 4.90. Found: C, 54.69; H, 7.59; N, 4.81%. NMR data in $CDCl_3$: δ (^{1}H) 1.47 [s, 18H, ^{t}Bu], 1.58 [m, 4H, Sn*CH*$_2$], 1.41 [m, 4H, SnCH$_2$*CH*$_2$], 1.14 [m, 4H, ^3J(HH) = 7.2 Hz, *CH*$_2$CH$_3$], 0.71 [t, 6H, ^3J(HH) = 7.2 Hz, CH$_3$], (bu_2bpy group) 7.61 [dd, 2H, ^3J(HH) = 5.5 Hz, ^4J(HH) = 1.5 Hz, H$^{5,5'}$], 8.19 [d, 2H, ^4J(HH) = 1.2 Hz, H$^{3,3'}$], 9.31 [d, 2H ,^3J(HH) = 5.5 Hz, H$^{6,6'}$]; δ (^{13}C) 29.4 [s, terminal C atoms of ^{t}Bu groups], 34.6 [s, central C atoms of ^{t}Bu groups], 40.2 [s, ^1J($^{119/117}$Sn–C) not resolved, Sn*C*H$_2$], 27.0 [s, SnCH$_2$*C*H$_2$], 24.9 [s, *C*H$_2$CH$_3$], 12.5 [s, CH$_3$], (bu_2bpy group) 164.1 (C_2), 117.5 (C_3), 148.6 (C_4), 122.4 (C_5), 147.6 (C_6); δ(^{119}Sn) −232 (br).

2.4. Preparation of $[SnPh_3Cl(bu_2bpy)]$, **3a**

A solution of 4,4′-di- *tert*-butyl-2,2′-bipyridine (50 mg, 0.19 mmol) in diethyl ether (5 mL) was added to a solution of $SnPh_3Cl$ (72 mg, 0.19 mmol) in diethyl ether (5 mL). The solution was stirred for 10 hours. The resultant colorless solution was evaporated to dryness to afford a white solid, which was filtered off. The solid was washed with diethyl ether and air dried. Yield: 85%; m.p. 83–85 °C. *Anal.* Calc. for $C_{36}H_{39}ClN_2Sn$: C, 66.11; H, 6.02; N, 4.29. Found: C, 66.09; H, 5.77; N, 4.32%.

2.5. Preparation of $[SnMe_2Cl_2(bupy)_2]$, **1b**

4-*tert*-Butyl pyridine (0.07 mL, 0.46 mmol) was added to a solution of $SnMe_2Cl_2$ (50 mg, 0.23 mmol) in diethyl ether (5 mL). The solution was stirred for 15 h, during which time a white solid was formed. The solid was filtered and washed with diethyl ether and air dried. Yield: 77%; m.p. 133–135 °C. *Anal.* Calc. for $C_{20}H_{32}Cl_2N_2Sn$: C, 48.99; H, 6.58; N, 5.72. Found: C, 49.18; H, 6.76; N, 5.62%. NMR data in $CDCl_3$: δ (^{1}H) 1.32 [s, 6H, ^2J($^{119/117}$Sn–H) = 100.8 Hz, Sn–Me], 1.33 [s, 18H, ^{t}Bu], (bupy groups) 7.46 [d, 4H, ^3J(HH) = 5.0 Hz, H^3], 8.85 [d, 4H, H^2]; δ (^{13}C) 29.2 [s, terminal C atoms of ^{t}Bu groups], 34.2 [s, central C atom of ^{t}Bu groups], 20.4 [s, ^1J($^{119/117}$Sn–C) = 1087 Hz, Sn–Me], (bupy groups) C_2 (146.3), C_3 (121.0), C_4(162.7); δ (^{119}Sn) −217 (br).

2.6. Preparation of $[Sn^nBu_2Cl_2(bupy)]$, **2b**

To a solution of $Sn^nBu_2Cl_2$ (60 mg, 0.20 mmol) in diethyl ether (5 mL) was added 4-*tert*-butyl pyridine (0.06 mL, 0.40 mmol). The resultant solution was stirred for 24 h. The solvent was evaporated and a white solid was produced. Then, the solid was filtered off and washed with diethyl ether and air dried. Yield: 75%; m.p. 67–69 °C. *Anal.* Calc. for $C_{17}H_{31}Cl_2NSn$: C, 46.48; H, 7.12; N, 3.19. Found: C, 47.38; H, 7.27; N, 3.95%. NMR data in $CDCl_3$: δ(^{1}H) 1.32 [s, 9H, ^{t}Bu], 1.80 [m, 4H, SnCH$_2$], 1.61 [q, 4H, ^3J(HH) = 7.2 Hz, SnCH$_2$*CH*$_2$], 1.26 [m, 4H, ^3J(HH) = 7.4 Hz, *CH*$_2$CH$_3$], 0.79 [t, 6H, ^3J(HH) = 7.3 Hz, CH$_3$], (bupy group) 7.43 [d, 2H, ^3J(HH) = 6.4 Hz, H^3], 8.78 [d, 2H, H^2]; δ (^{13}C) 30.3 [s, terminal C atoms of ^{t}Bu group], 35.6 [s, central C atom of ^{t}Bu group], 32.8 [s, ^1J($^{119/117}$Sn–C) not resolved, SnCH$_2$], 27.8 [s, ^2J($^{119/117}$Sn–C) = 41 Hz, SnCH$_2$*C*H$_2$], 26.1 [s, ^3J($^{119/117}$Sn–C) = 131 Hz, *C*H$_2$CH$_3$], 13.5 [s, CH$_3$], (bupy group) 147.7 (C_2), 120.1 (C_3), 160.4 (C_4); δ(^{119}Sn) −84 (br), −90 (sh), −137 (sh).

2.7. Preparation of $[SnPh_3Cl(bupy)]$, **3b**

To a solution of $SnPh_3Cl$ (100 mg, 0.26 mmol) in dichloromethane (10 mL) was added 4-*tert*-butyl pyridine (0.04 mL, 0.26 mmol). The solution was stirred for 48 h and then the solvent was evaporated to afford a white solid. This was recrystallized from CH_2Cl_2/*n*-hexane and air dried. Yield: 85%; m.p. 66–68 °C. *Anal.* Calc. for $C_{27}H_{28}ClNSn$: C, 62.26; H, 5.42; N, 2.69. Found: C, 61.43; H, 5.25; N, 2.44%. NMR data in $CDCl_3$: δ (^{13}C) 30.5 [s, terminal C atoms of ^{t}Bu group], (bupy group) 149.4 (C_2), 120.9 (C_3), (Ph groups) 137.9 [s, C_1], 136.2 [s, ^2J($^{119/117}$Sn–C) = 48 Hz, C_2], 129.1 [s, ^3J($^{119/117}$Sn–C) = 64 Hz, C_3], 130.3 [s, ^4J($^{119/117}$Sn–C) = 14 Hz, C_4]; δ (^{119}Sn) in CH_2Cl_2/$CDCl_3$: −71 (sh).

2.8. Preparation of $[SnMe_2Cl_2(tmdp)]$, **1c**

Following the same procedure as for the preparation of **1a**, a solution of 4,4′-trimethylenedipyridine (45 mg, 0.23 mmol) in diethyl ether (5 mL) was added to a solution of Me_2SnCl_2 (50 mg, 0.23 mmol) in diethyl ether (5 mL) to give a white solid. Yield: 87%; m.p. 174–176 °C. *Anal.* Calc. for $C_{15}H_{20}Cl_2N_2Sn$: C, 43.12; H, 4.78; N, 6.71. Found: C, 43.06; H, 4.69; N, 6.64%. NMR data in CD_2Cl_2: δ(^{1}H) 2.73 [t, 4H ,^3J(HH) = 7.8 Hz, terminal CH_2 of tmdp], 2.03 [q, 2H, ^3J(HH) = 4.6 Hz, central CH_2 of tmdp], 1.26 [t, 6H, ^2J($^{119/117}$Sn–H) = 84.1, Sn–Me], (tmdp group) 8.62 [d, 4H, ^3J(HH) = 5.9 Hz, H^2], 7.26 [d, 4H, ^3J(HH) = 6.0 Hz, H^3]; δ (^{13}C) 38.1 [s, terminal C atoms of tmdp], 34.1 [s, central C atom of tmdp], 24.1 [s, ^1J($^{119/117}$Sn–C) not resolved, Sn–Me], (tmdp group) 152.9 (C_2), 127.8 (C_3), 155.0 (C_4); δ(^{119}Sn) −66 (sh), −116 (sh).

2.9. Preparation of [$Sn^nBu_2Cl_2$(tmdp)], **2c**

Following the same procedure as for the preparation of **1a**, a solution of 4,4′-trimethylenedipyridine (65 mg, 0.33 mmol) in diethylether (5 mL) was added to a solution of $Sn^nBu_2Cl_2$ (100 mg, 0.33 mmol) in diethyl ether (5 mL) to afford a white solid. The product was filtered off and then washed with ether and dried in air. Yield: 82%; m.p. 137–139 °C. *Anal.* Calc. for $C_{21}H_{32}Cl_2N_2Sn$: C, 50.21; H, 6.43; N, 5.58. Found: C, 50.64; H, 6.56; N, 5.59%. NMR data in $CDCl_3$: δ (^{1}H) 2.70 [t, 4H ,^3J(HH) = 7.8 Hz, terminal CH_2 of tmdp], 2.02 [q, 2H, ^3J(HH) = 7.8 Hz, central CH_2 of tmdp], 1.80 [m, 4H, $SnCH_2$], 1.76 [m, 4H, $SnCH_2CH_2$], 1.60 [m, 4H, ^3J(HH) = 7.0 Hz, CH_2CH_3], 0.93 [t, 6H, ^3J(HH) = 7.9 Hz, CH_3], (tmdp group) 8.59 [d, 4H ,^3J(HH) = 5.8 Hz, H^2], 7.18 [d, 4H , ^3J(HH) = 6.0 Hz, H^3]; δ (^{13}C) 35.3 [s, terminal C atoms of tmdp], 34.6 [s, central C atom of tmdp], 30.2 [s, ^1J($^{119/117}$Sn–C) not resolved, $SnCH_2$], 27.7 [s, ^2J($^{119/117}$Sn–C) = 41 Hz, $SnCH_2CH_2$], 26.1 [s, ^3J($^{119/117}$Sn–C) = 131 Hz, CH_2CH_3], 13.5 [s, CH_3], (tmdp group) 148.4 (C_2), 124.6 (C_3), 153.0 (C_4); δ (^{119}Sn) −90 (sh),-105 (br), −137 (sh).

2.10. Preparation of [$ClPh_3Sn$-μ-(tmdp)$SnPh_3Cl$], **3c**

A solution of 4,4′-trimethylenedipyridine (51 mg, 0.26 mmol) in dichloromethane (3 mL) was added to a solution of $SnPh_3Cl$ (200 mg, 0.52 mmol) in dichloromethane (10 mL) and stirred for 48 h. The solvent was evaporated to afford a white solid. The solid was filtered off and air dried. Yield: 81%; m.p. 119–120 °C. *Anal.* Calc. for $C_{49}H_{44}Cl_2N_2Sn_2$: C, 60.70; H, 4.58; N, 2.89. Found: C, 60.39; H, 4.39; N, 2.66%. NMR data in $CDCl_3$: δ (^{1}H) 2.64 [t, 4H ,^3J(HH) = 8.0 Hz, terminal CH_2 of tmdp], 1.98 [q, 2H, ^3J(HH) = 7.8 Hz, central CH_2 of tmdp], 8.48 [d, 4H ,^3J(HH) = 4.3 Hz, H^2], 7.10 [d, 4H ,^3J(HH) = 5.8 Hz, H^3], 7.46, 7.68 [m, Ph groups]; δ (^{13}C) 34.4 [s, terminal C atoms of tmdp], 30.4 [s, central C atom of tmdp], (tmdp group) 149.6 (C_2), 123.9 (C_3), 150.9 (C_4), (Ph groups) 137.9 [s, C_1], 136.2 [s, ^2J($^{119/117}$Sn–C) = 49 Hz, C_2], 129.1 [s, ^3J($^{119/117}$Sn–C) = 65 Hz, C_3], 130.3 [s, ^4J($^{119/117}$Sn–C) = 14 Hz, C_4]; δ (^{119}Sn) in CH_2Cl_2/$CDCl_3$: −80 (sh).

2.11. X-ray crystal structure determination

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo Kα radiation. The colorless block crystal with dimensions of 0.40 × 0.38 × 0.32 mm was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 6841 unique reflections. Data were collected at a temperature of 298(2) K to a maximum 2θ value of 58.48° and in a series of ω scans with 1° oscillations and integrated using the STOE X-AREA [10] software package. The numerical absorption coefficient, μ, for Mo-Kα radiation is 1.373 mm^{-1} for **1a**. A numerical absorption correction was applied using X-RED [11] and X-SHAPE [12] software. The data were corrected for Lorentz and Polarizing effects. The structure was solved by direct methods and subsequent difference Fourier map and then refined by a full-matrix least-squares on F^2 [13]. All of the H atoms except H21 were positioned geometrically, with C–H = 0.93 and 0.96 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms with Uiso(H) = 1.2Ueq(C). H21 was located in a difference Fourier map and then refined isotropically. Subsequent refinement then converged with *R* factors and parameter errors significantly better than for all attempts to model the solvent disorder. Atomic factors are from International Tables for X-ray Crystallography [14]. All refinements were performed using the SHELXTL crystallographic software package [15]. A summary of the crystal data, experimental details and refinement parameters is given in Table 1.

Table 1
Experimental details, crystal data and refinement parameters for complex **1a**.

Empirical formula	$C_{20}H_{30}Cl_2N_2Sn{\cdot}0.5CHCl_3$
Formula weight (g/mol)	1095.47
Crystal size (mm)	0.32 × 0.38 × 0.40
Crystal system	monoclinic
Space group	*C*2/*c*
θ range (°)	29.2
a (Å)	33.560(2)
b (Å)	11.5983(5)
c (Å)	11.5983(5)
β (°)	90.556(6)
Volume (Å^3)	5113.9(5)
Z	4
D_{calc} (g/cm^3)	1.423
μ (mm^{-1})	1.373
F (0 0 0)	2216
Index ranges	$-46 \leqslant h \leqslant 46$, $-15 \leqslant k \leqslant 15$, $-15 \leqslant l \leqslant 17$
Reflections collected	19 478
Independent reflections [R_{int}]	6841 [0.057]
Observed reflections	5875 ($I > 2\sigma(I)$)
Parameters/restraints	279/24
Goodness-of-fit (GOF)	1.11
R_1 (observed data)	0.0459
wR_2 (all data)[a]	0.1206

[a] $w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 7.039P]$, where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

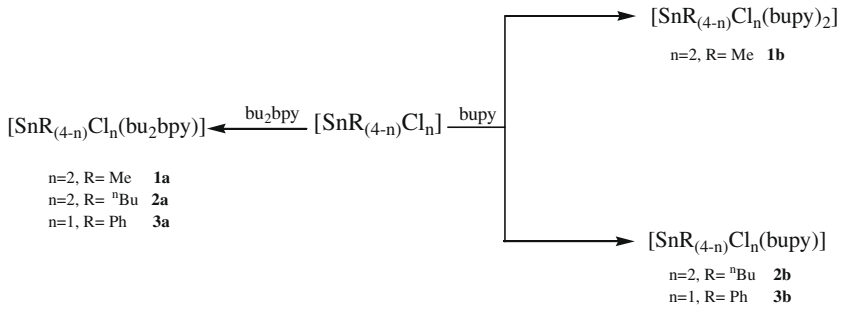
3.1. Solution studies

The reactions of organotin(IV) chlorides [$SnR_{(4-n)}Cl_n$] (n = 2, R = Me, ^{n}Bu; n = 1, R = Ph) with the bidentate pyridyl ligand bu_2bpy gave the hexa-coordinated complexes [$SnR_{(4-n)}Cl_n$(bu_2bpy)] (**1a**–**3a**), as shown in Scheme 2. Moreover, the above organotin(IV) chlorides reacted with the corresponding monodentate pyridyl ligand bupy to afford hexa- or penta-coordinated organotin(IV) complexes **1b**–**3b** (Scheme 2). These complexes were typically prepared by mixing a diethyl ether or dichloromethane solution of the appropriate organotin chloride with the ligands in a 1:1 or 1:2 mole ratio.

The reaction of dimethyltin(IV) dichloride with bu_2bpy in a 1:1 mole ratio in diethyl ether yields the white complex [$SnMe_2Cl_2$-(bu_2bpy)], **1a**, which was fully characterized by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. The ^{1}H NMR spectrum of complex **1a** in $CDCl_3$ shows a signal at δ 1.06 with ^2J($^{119/117}$Sn–H) = 106.4 Hz, different from that of the starting complex $SnMe_2Cl_2$ which has ^2J(^{119}Sn–H) = 68.6 Hz and ^2J(^{117}Sn–H) = 65.7 Hz in $CDCl_3$ [16]. It is well-known that the magnitude of the magnetic coupling constant of the methyl protons with ^{119}Sn is a useful guide for the determining the geometry of the tin atom. This coupling constant is in the range of other hexacoordinate dimethyltin(IV) complexes [16,17]. The ^{13}C NMR spectrum of **1a** in $CDCl_3$ displayed a signal at δ = 25.3 with ^1J(^{119}Sn–C) = 1092 Hz and ^1J(^{117}Sn–C) = 1043 Hz, which were used to calculate θ (C–Sn–C) by the Lockhart and Manders equation (Eq. (1)), giving a value of 172.54° [18]. The magnitude of θ is very close to the observed value in the solid state from analysis of the X-ray crystallography data (174.22°).

$$^1J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C}) = 11.4\theta - 875 \quad (1)$$

The ^{119}Sn NMR spectrum of complex **1a** showed a sharp signal at δ = −251. A range of δ values from +200 to −60 have been reported for four-coordinated, −90 to −190 for five-coordinated and −210 to −400 for six-coordinated diorganotin(IV) complexes in solution [19]. Thus, the signal at −251 is consistent with those



Scheme 2.

reported for other hexa-coordinated diorganotin(IV) complexes. The chemical shift of **1a** is significantly more upfield than that for the starting complex $SnMe_2Cl_2$ (δ = 137.2 in $CDCl_3$) [20], resulting from the coordination of two N atoms to the tin center. These data, in combination with the spin–spin coupling constants, indicate that the hexa-coordinated geometry persists in solution. In addition, the reaction of dibutyltin(IV) dichloride with bu_2bpy resulted in the formation of the complex $[Sn(^nBu)_2Cl_2(bu_2bpy)]$ (**2a**). The ^{119}Sn NMR spectrum of **2a** in $CDCl_3$ shows a signal at $\delta = -231$, which indicates the presence of a hexa-coordinated adduct of tin(IV) in solution [19].

The ^{119}Sn NMR spectrum of the complex $[SnPh_3Cl(bu_2bpy)]$, **3a**, in $CDCl_3$ displayed a sharp signal at $\delta = -46$, which is in agreement with the reported value for free $SnPh_3Cl$ ($\delta = -44.7$) [21]. These data indicate that the interaction between $SnPh_3Cl$ and bu_2bpy is not maintained in solution and it strongly dissociates in chloroform solution to give triphenyltin chloride. This is consistent with other triphenyltin(IV) adducts which are not stable in solution [7]. Therefore, the assignment of the stoichiometry of complex **3a** was based on the elemental analysis.

Additionally, $SnMe_2Cl_2$ reacts with bupy in a mole ratio of 1:2 to give the hexa-coordinated complex $[SnMe_2Cl_2(bupy)_2]$, **1b**. However, the reaction of $SnBu_2Cl_2$ with bupy in a mole ratio of 1:2 affords the penta-coordinated complex $[SnBu_2Cl_2(bupy)]$, **2b** (Scheme 2). The ^{119}Sn spectrum of **2b** in $CDCl_3$ shows a broad signal at $\delta = -84$ and two sharp signals at $\delta = -89$ and -137, which are more upfield than the starting complex $SnBu_2Cl_2$ (δ = 126 in $CDCl_3$) [21]. The presence of several signals indicates the presence of geometric isomers [22]. In the case of $[SnPh_3Cl]$, a penta-coordinated crystalline tin complex of $[SnPh_3Cl(bupy)]$, **3b**, could be isolated. The ^{119}Sn NMR spectrum of **3b** in dichloromethane shows a signal at $\delta = -71$, which is in the observed range of tetra-coordinated triphenyltin compounds ($\delta = -40$ to -120 ppm) [23]. It should be mentioned that the formation of an adduct between $[SnPh_3Cl]$ and pyridine has been observed only in solution [24]. We attribute it to the increased basicity of bupy relative to that pyridine, which can form a stable adduct in the solid state. The formation of stronger complexes results in higher formation constants of the complexes [24,25].

The organotin(IV) chlorides $[SnR_{(4-n)}Cl_n]$ reacted with tmdp to give the complexes $[SnR_{(4-n)}Cl_n(tmdp)]$ (n = 2; R = Me, ^{n}Bu) (**1c**–**2c**) or $[ClPh_3Sn$-μ-(tmdp)$SnPh_3Cl]$ (**3c**) in the solid state (Eqs. (2 and 3)).

$$[SnR_2Cl_2] + tmdp \longrightarrow [SnR_2Cl_2(tmdp)] \quad (2)$$

R = Me **1c**
R = ^{n}Bu **2c**

$$2[SnPh_3Cl] + tmdp \longrightarrow [ClPh_3Sn\text{-}\mu\text{-}(tmdp)SnPh_3Cl] \quad (3)$$

3c

The elemental analysis data show a ligand to metal ratio of 1:1 for complexes **1c** and **2c**, whereas a 1:2 ligand to metal ratio is observed for **3c**. The ^{119}Sn NMR spectrum of **1c** showed a signal at $\delta = -116$ (in $CDCl_3$), and three signals at $\delta = -90$, -105 and -137 (in $CDCl_3$) were observed for **2c**, typical for five-coordinated diorganotin(IV) adducts ($\delta = -90$ to -190 ppm) [19]. Therefore, penta-coordinated diorganotin(IV) adducts are present in solutions of **1c** and **2c**. Moreover, the ^{119}Sn NMR spectrum of **3c** displayed a signal at $\delta = -80$ (in $CH_2Cl_2/CDCl_3$) in the region of four-coordinated triphenyltin(IV) compounds ($\delta = -40$ to -120 ppm for four-coordinated and $\delta = -180$ to -260 ppm for five-coordinated triphenyltin(IV) compounds) [23]. Therefore, a tetra-coordinated tin(IV) compound persists in the solution of **3c**. On the basis of combined analytical data and spectral data, we suggest a penta-coordinated geometry in the solid state for the organotin(IV) adduct of $[ClPh_3Sn$-μ-(tmdp)$SnPh_3Cl]$, **3c**, which dissociates in solution to afford a tetra-coordinated compound of tin(IV). However, a hexa-coordinated solid state structure is reasonably assumed for **1c** and **2c**, which is probably a polymeric chain of $\cdots$Sn–tmdp–Sn–tmdp$\cdots$ which dissociates in solution to give the penta-coordinated complexes of $[SnR_2Cl_2(tmdp\text{-}\kappa^1N)]$ (R = Me, ^{n}Bu). It should be mentioned that in the case of **1c**, a signal at $\delta = -66$ was also observed, and this value is "unnatural" [19]. It can be assigned to the equilibrium of the four-coordinated complex $[SnMe_2Cl_2]$ and the five-coordinated complex $SnMe_2Cl_2$.tmdp.

The ^1H and ^{13}C NMR assignments for the butyl moiety in **2a**–**c**, the phenyl groups in **1**–**3c** and the bu_2bpy ligand were made according to literature data [23,26,27].

The ^1H NMR spectrum of **1c** in $CDCl_3$ solution and in the presence of a few drops of DMSO showed a singlet at δ = 1.18 with ^2J(Sn–H) = 102.8 Hz. The magnitude of the observed coupling constant is consistent with an octahedral structure for the $SnMe_2Cl_2$ adduct, which is likely to be $[SnMe_2Cl_2(tmdp\text{-}\kappa^1N)(DMSO)]$. Additionally, the ^{119}Sn NMR spectrum of complex **1c** in $CDCl_3$/DMSO showed a broad signal at $\delta = -155$, in the range of other penta-coordinated complexes [19]. This indicates that the proposed complex $[SnMe_2Cl_2(tmdp\text{-}\kappa^1N)(DMSO)]$ is not stable in solution for a long time and dissociates to give a penta-coordinated complex.

It is also interesting to note that the reaction of triphenyltin(IV) chloride with these nitrogen-donor ligands requires a longer reaction time than the corresponding reaction of diorganotin(IV) chlorides, which is consistent with a previous observation [7].

The preparation of all the complexes were attempted with different stoichiometries in order to determine if more than one kind of complex can be formed between a particular organotin(IV) halide and ligand. It can be seen that the formation of penta- or hexa-coordinated species is influenced by the nature of alkyl groups R on the organotin(IV) compounds as well as the nature of the ligand. They are more significant factors than the ratio of the ligand to metal for the formation of adducts in the solid state.

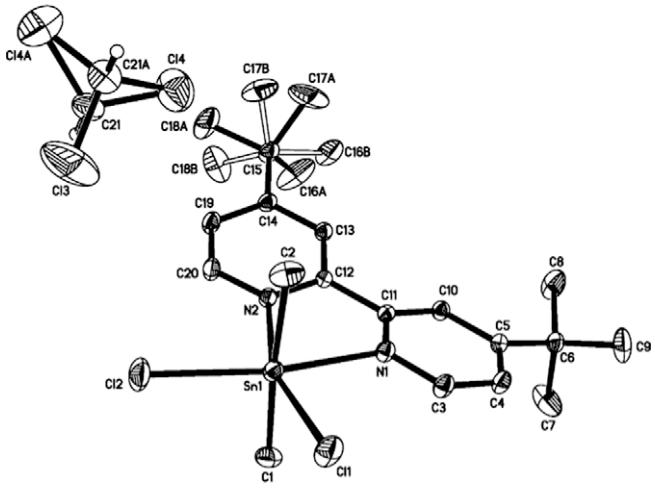


Fig. 1. The molecular structure of complex **1a**, showing 30% probability displacement ellipsoids and the atomic numbering. The hydrogen atoms (except for the solvent) are omitted for clarity. The open bonds show the minor component.

3.2. Description and discussion of the crystal structure of *1a*

The molecular structure of $[SnMe_2Cl_2(bu_2bpy)]$ (**1a**) is shown in Fig. 1. Selected bond distances and angles are given in Table 2. Complex **1a** was crystallized as the chloroform solvate $[SnMe_2Cl_2(bu_2bpy)]\cdot 0.5CHCl_3$. One of the *tert*-butyl groups of the bu_2bpy ligand is disordered rotationally over two positions with a refined site-occupancy ratio of 0.58(2)/0.42(2). In addition, the chloroform solvent of crystallization is also disordered along the crystallographic twofold rotation axis which passes through the Cl3 atom. The coordination geometry about the Sn(IV) atom is octahedral, as revealed by the C(1)–Sn–C(2) angle which deviates insignificantly from linearity (174.22(19)°). The chlorine atoms are *cis* to each other, while the methyl groups are *trans*. Bu_2bpy acts in a bidentate manner through N(1) and N(2), adopting a *cis* conformation. The Sn–C bond distances are not equal (2.126 and 2.127 Å).

Table 2
Selected bond lengths (Å) and angles (°) for complex **1a**.

Sn(1)–C(2)	2.126(4)
Sn(1)–C(1)	2.127(4)
Sn(1)–N(2)	2.379(2)
Sn(1)–N(1)	2.405(2)
Sn(1)–Cl(2)	2.4971(11)
Sn(1)–Cl(1)	2.5538(10)
N(1)–C(3)	1.336(4)
C(2)–Sn(1)–C(1)	174.22(19)
C(2)–Sn(1)–N(2)	86.43(14)
C(1)–Sn(1)–N(2)	89.97(15)
C(2)–Sn(1)–N(1)	89.20(16)
C(1)–Sn(1)–N(1)	85.28(14)
N(2)–Sn(1)–N(1)	68.66(8)
C(2)–Sn(1)–Cl(2)	93.97(16)
C(1)–Sn(1)–Cl(2)	90.75(14)
N(2)–Sn(1)–Cl(2)	93.56(6)
N(1)–Sn(1)–Cl(2)	161.74(7)
C(2)–Sn(1)–Cl(1)	89.90(14)
C(1)–Sn(1)–Cl(1)	91.97(14)
N(2)–Sn(1)–Cl(1)	160.15(6)
N(1)–Sn(1)–Cl(1)	91.81(6)
Cl(2)–Sn(1)–Cl(1)	106.16(4)
C(3)–N(1)–Sn(1)	123.1(2)
C(11)–N(1)–Sn(1)	118.32(18)
C(20)–N(2)–C(12)	117.9(3)
C(20)–N(2)–Sn(1)	122.5(2)
C(12)–N(2)–Sn(1)	118.84(18)
Sn(1)–C(1)–H(1A)	109.5
Sn(1)–C(1)–H(1B)	109.5
Sn(1)–C(1)–H(1C)	109.5
N(1)–C(3)–C(4)	123.5(3)
N(1)–C(3)–H(3)	118.2
C(11)–C(10)–C(5)	120.7(3)
N(1)–C(11)–C(10)	121.6(2)
N(1)–C(11)–C(12)	116.1(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$.

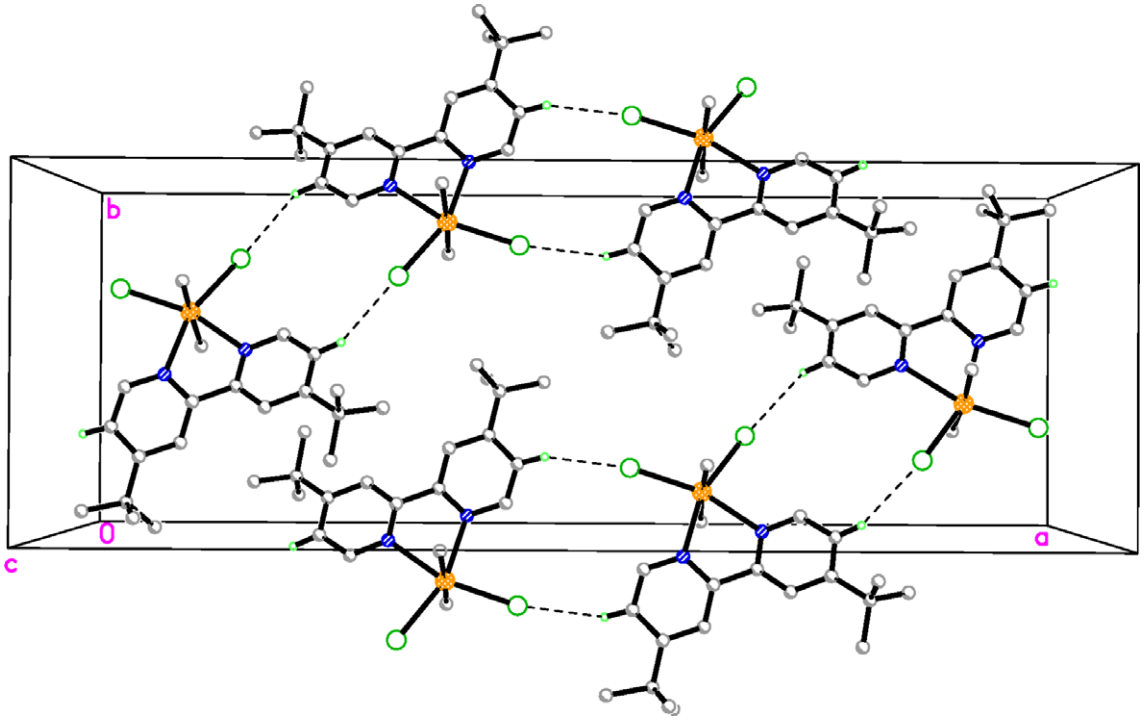


Fig. 2. The crystal packing of complex **1a**, viewed down the *c*-axis, showing linking of the neighboring molecules through intermolecular C–H···Cl interactions along the *a*-axis. The H-atoms except those involved in interactions are omitted for clarity. Intermolecular interactions are shown as dashed lines.

The Sn–Cl bonds are also inequivalent ([2.5538 and 2.4971 Å). The bond lengths of the two Sn–N bonds are different with the Sn–N(1) bond length (2.405(2) Å) being longer than that for Sn–N(2) (2.379(2) Å), which is due to the packing of the crystal. The N1–Sn–N2 bite angle is 68.66(8)°, which is consistent with those observed for other chelating diimine ligands [16]. The *trans*-[$SnMe_2$] stereochemistry for **1a** is expected, consistent with other adducts of dialkyltin(IV) dihalides with the general formula [$SnR_2X_2L_n$] (X = monoanion; $n = 2$, L = monodentated ligand; $n = 1$, L = bidentate ligand) [1,25]. The interesting features of the crystal structure are short intermolecular C–H···Cl contacts, which link neighboring molecules together into chains along the *a*-axis (Fig. 2) and seems to be effective in the stabilization of the crystal packing.

4. Supplementary data

CCDC 746807 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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