

Synthesis and spectral characterisation of bis[3,4-dichlorophenyl]tin(IV) dichloride complexes. The X-ray crystal structure of the 4,4'-dimethyl-2,2'-bipyridyl adduct of bis[3,4-dichlorophenyl]tin dichloride

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ABSTRACT The synthesis and spectroscopic data (^{119}Sn NMR, ^{119}mSn Mössbauer, IR) of a series of six-coordinated diorganotin(IV) complexes of the type $\text{R}_2\text{SnCl}_2\cdot\text{L}_2$ and $\text{R}_2\text{SnL}'_2$ where R = 3,4-dichlorophenyl, L = neutral monodentate oxygen donor ligand (containing $>\text{S}=\text{O}$, $\text{P}=\text{O}$ or $\text{As}=\text{O}$ grouping) or 1/2 bidentate donor [2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine (Me_2bipy), 1,10-phenanthroline (phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen)]; $\text{L}' = 8$ -quinolinolato (oxin) or 2-methyl-8-quinolinolato (Meoxin) are presented. The quadrupole splitting (QS) values of ca. 3.60 mm s^{-1} for the adducts with monodentate ligands are in accord with essentially *trans*- $[\text{SnR}_2]$ octahedral structures. The complexes of $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2$ with bipy and phen yielded QS values of ca. 2 mm s^{-1} which suggest *cis*- $[\text{SnR}_2]$ octahedral geometries. In contrast, the $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2 \cdot \text{Me}_4\text{phen}$ adduct has a QS value of 3.17 mm s^{-1} indicative of a distorted *trans*- $[\text{SnR}_2]$ octahedral geometry or a skew-trapezoidal bipyramidal geometry. The Mössbauer spectrum for the $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2 \cdot \text{Me}_2\text{bipy}$ indicates this to be a homogeneous mixture of *cis*- and *trans*- $[\text{SnR}_2]$ isomers. X-ray analysis of the crystalline product obtained from a toluene solution of this compound shows this to be exclusively the *trans* isomer [C-Sn-C $174.3(4)^\circ$, N1-Sn-N2 $70.0(3)^\circ$, Cl1-Sn-Cl2 $98.8(1)^\circ$; Sn-C $2.14(1)$, $2.15(1) \text{ \AA}$, Sn-Cl $2.462(3)$, $2.467(3)$ and Sn-N $2.313(9)$, $2.335(9) \text{ \AA}$]. The bischelates, $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{Sn}(\text{oxin})_2$ and $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{Sn}(\text{Meoxin})_2$ have ρ values ($\rho = QS/IS$) > 2.1 which indicate higher-than-four coordination environments at tin for these complexes. The low QS values of ca. 1.50 mm s^{-1} for the bischelates are rationalised in terms of *cis*- $[\text{SnR}_2]$ octahedral structures. The large ^{119}Sn NMR chemical shifts measured for the adducts and the bischelates in CDCl_3 (-420 ppm to -350 ppm) indicate that the diorganotin complexes retain their octahedral tin configurations in solution.

ABSTRAK Satu siri kompleks diorganostanum yang mempunyai formula, $\text{R}_2\text{SnCl}_2\cdot\text{L}_2$ dan $\text{R}_2\text{SnL}'_2$ dimana R = 3,4-diklorofenil, L = Ph_3PO , Ph_3AsO , HMPA, DMSO atau 1/2 penderrna bidentat [bipiridin (bipy), 4,4'-dimetil-2,2'-bipiridin (Me_2bipy), 1,10-fenantrolin (phen), 3,4,7,8-tetrametil-1,10-fenantrolin (Me_4phen)]; $\text{L}' = 8$ -quinolinolato (oxin) atau 2-metil-8-quinolinolato (Meoxin) telah disediakan dan dianalisis dengan kaedah spektroskopi seperti ^{119}mSn Mössbauer, ^{119}Sn NMR dan inframerah. Nilai pemecahan caturkutub (QS) bagi kompleks monodentat adalah lebih kurang 3.60 mms^{-1} , menunjukkan bahawa kompleks tersebut mempunyai struktur oktahedral dengan *trans*- $[\text{SnR}_2]$. Kompleks untuk $(3,4\text{-Cl}_2\text{-C}_6\text{H}_3)_2\text{SnCl}_2$ dengan bipy dan phen mempunyai nilai $QS \approx 2 \text{ mms}^{-1}$, menyokong geometri *cis*- $[\text{SnR}_2]$ pada atom stanum. Sebaliknya, kompleks $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2 \cdot \text{Me}_4\text{phen}$ mempunyai nilai QS 3.17 mms^{-1} ,

lebih sesuai dikelaskan sebagai kompleks dengan geometri oktahedral *trans*- $[\text{SnR}_2]$ atau bipyramid skew-trapezoidal. Spektrum Mössbauer untuk $(3,4\text{Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2 \cdot \text{Me}_2\text{bipy}$ menunjukkan kewujudan satu campuran homogenous yang mengandungi isomer *cis*- dan *trans*- $[\text{SnR}_2]$. Analisis Sinar-X untuk hablur yang diperolehi daripada penghabluran semula sebatian ini dengan pelarut toluena menunjukkan bahawa satu geometri oktahedral pada stanum dengan parameter berikut diperolehi [C-Sn-C $174.3(4)^\circ$, N1-Sn-N2 $70.0(3)^\circ$, Cl1-Sn-Cl2 $98.8(1)^\circ$; Sn-C $2.14(1)$, $2.15(1) \text{ \AA}$, Sn-Cl $2.462(3)$, $2.467(3)$ and Sn-N $2.313(9)$, $2.335(9) \text{ \AA}$]. Kompleks bikelat seperti $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{Sn}(\text{oxin})_2$ dan $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{Sn}(\text{Meoxin})_2$ mempunyai nilai ρ ($\rho = QS/IS$) > 2.1 bermakna kedua-dua kompleks ini adalah mempunyai nombor koordinasi pada stanum lebih daripada empat. Nilai anjakan kimia ^{119}Sn bagi kesemua kompleks yang dikaji adalah diantara julat -420 dan -350 ppm , menunjukkan bahawa kompleks diorganostanum ini adalah berkoordinasi enam dalam keadaan larutan.

INTRODUCTION

Diorganotin dihalides are known to readily yield coordination compounds in reactions with monodentate and bidentate ligands, in which the tin atom has an octahedral or skew-trapezoidal bipyramidal (STB) geometry [14]. These complexes having the composition $\text{R}_2\text{SnX}_2\cdot 2\text{L}$ (L = monodentate or 1/2 bidentate ligand) or R_2SnL_2 (LH = chelating ligand) have been extensively studied by spectroscopic methods which include multinuclear-NMR and ^{119}mSn Mössbauer [5-11], as well as by X-ray crystal structure analysis [12-16]. Almost invariably, the isolable complexes exist exclusively as either the *trans*- or *cis*- SnR_2 octahedral isomer for the case of $\text{R}_2\text{SnX}_2\cdot 2\text{L}$ adducts. Only one report has appeared on the successful isolation and characterisation of both isomeric forms for $(4\text{-ClC}_6\text{H}_4)_2\text{SnCl}_2 \cdot 4,4'\text{-Me}_2\text{bipy}$ [16].

For the case of bischelate complexes, particularly those involving small 'bite' angle ligands, the preferred coordination geometry at tin is the STB, in which the C-Sn-C bond angle has the value between 135 -

155°; this renders invalid either a "cis" or "trans" description of the SnR_2 skeletal arrangement based on a "distorted" octahedron.

In continuation with our studies on the coordination chemistry of organotin compounds, we report in this paper the synthesis and structures of complexes of bis[3,4-dichlorophenyl]tin dichloride with oxygen and nitrogen donor ligands. Our interest in diaryltin complexes has also been heightened by recent observations of *in-vivo* antitumour activity among several dialkyltin dichloride complexes against P-388 lymphocytic leukemia in mice [17-24].

EXPERIMENTAL SECTION

Synthesis of tetrakis(3,4-dichlorophenyl)tin A solution of 25.0 g (0.11 mole) of 3,4-dichlorobromobenzene in 50 mL dry tetrahydrofuran (THF) was added slowly to 2.55 g (0.11 mole) of magnesium suspended in 50 mL of dry THF in a three-necked flask equipped with stirrer, reflux condenser, a nitrogen supply source and a dropping funnel. Five drops of dry ethylene dibromide were added to initiate the reaction. After the reaction has subsided, the mixture was refluxed with stirring for 3 hours to give a green-coloured solution. The flask was then cooled in an ice-water bath and a solution of 2.86 mL (0.024 moles) of anhydrous stannic chloride in benzene (50 mL) was added dropwise to the reaction mixture with efficient stirring over a period of 30 minutes. The reaction mixture was subsequently refluxed for 3 hours to give a yellow brown solution. This was followed by hydrolysis with dilute hydrochloric acid solution. The organic layer was separated, washed with distilled water and dried over anhydrous magnesium sulphate. Upon removal of the solvent on a rotary evaporator, a viscous liquid was obtained, which crystallised with the addition of a small amount of ethanol. The resulting white solid was recrystallised from ethanol, m.p. 172-174°C (Lit. m.p. 165-167°C [25]). Yield, 14.0 g (81 %).

Synthesis of bis(3,4-dichlorophenyl)tin dichloride, $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2$ Tetra(3,4-dichlorophenyl)tin (6.0 g, 8.6 mmoles) and anhydrous stannic chloride (2.23g, 8.6 mmoles) were mixed together in a round-bottomed flask equipped with a reflux condenser and fitted with a calcium chloride drying tube. The reaction mixture was then heated with stirring

on an oil bath at 210-230 °C for 3 hours. The resulting brown-black viscous liquid was boiled in diethyl ether for 15 mins and filtered quickly through a Kieselguhr filter cake. 30 mL of 5M sodium hydroxide solution was then added to the filtrate and the whole was stirred for 3 hours at room temperature. The resulting white oxide was filtered, washed with water and dried, m.p. 375°C. To the oxide was added 60 mL of ether, followed by 30 mL of 5M hydrochloric acid solution and the resulting mixture stirred at room temperature until all the oxide had dissolved. The ether layer was separated, washed several times with distilled water and dried over anhydrous magnesium sulphate. This was then filtered, concentrated to a small volume and triturated with petroleum ether (60-80°C) to give a white solid, which was subsequently recrystallised from petroleum ether (60-80°C), m.p. 193-195°C. Yield, 5.3 g (65%).

Similar methods were used to prepare other neutral complexes; the following syntheses are representative:

$(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2\cdot\text{bipy}$ A solution of $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2$ (0.15 g, 0.3 mmole) in 20 mL diethyl ether was added with stirring to 2,2'-bipyridine (bipy) (0.05g, 0.3 mmole) in 20 mL ether. The solution was then chilled, whereupon a white solid precipitated. The solid was filtered off, washed with ether and air-dried, m.p. 233-235°C. Yield, 0.13 g (66%).

$(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ Equimolar amounts (0.42 mmole) of $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2$ (0.20 g) and 4,4'-dimethyl-2,2'-bipyridine (Me_2bipy) (0.08 g) were dissolved separately in ethanol and then mixed. Following cooling, a light pink solid was obtained, which was subsequently filtered, washed with cold ethanol and air-dried, m.p. 257-259°C. Yield, 0.18 g (65 %). A small portion of the product was dissolved in a minimum amount of hot toluene. Slow evaporation of the solution furnished crystals suitable for X-ray analysis.

$(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2\cdot 2\text{Ph}_3\text{PO}$ 0.15 g (0.3 mmole) of $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2$ dissolved in 20 mL of chloroform was added to 0.17 g (0.6 mmole) of triphenylphosphine oxide in 20 mL of chloroform. The solution was concentrated to a small volume, chilled and triturated with petroleum ether (60-80°C) to give a white solid which was filtered, washed with petroleum

ether and air-dried, m.p. 194-196°C. Yield, 0.22 g (70%).

(3,4-Cl₂C₆H₃)₂SnCl₂.HMPA (3,4-Cl₂C₆H₃)₂SnCl₂ (0.2 g, 0.42 mmole) was dissolved in neat hexamethylphosphoramide (HMPA) by heating on a hot plate. The mixture was chilled and triturated with methanol to give a white solid, which was filtered, washed with methanol and air-dried, m.p. 232-234°C. Yield, 0.25 g (71 %).

(3,4-Cl₂C₆H₃)₂Sn(oxin)₂ A solution of 0.2 g (0.42 mmole) of (3,4-Cl₂C₆H₃)₂SnCl₂ in 20 mL of ethanol was added to 0.12 g (0.84 mmole) of 8-hydroxyquinoline in 20 mL of ethanol. To the resulting yellow solution was added 0.1g of sodium acetate in 10 mL of 50% (v/v) aqueous ethanol, followed by 10 mL of 20% ammonia solution. A yellow solid was obtained, which was recrystallised from toluene in 69% yield (0.20 g), m.p. 245-247°C.

Physical measurements

The ^{119m}Sn Mössbauer spectra of the complexes were procured at 80K using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd., Ox-

ford) with a 512 channel data store, and a 15 mCi Ca^{119m}SnO₃ source at room temperature. The spectra were recorded on a Hewlett-Packard 7225B plotter, and fitted with Lorentzian functions by a least-squares fitting programme [26].

The infrared spectra of the complexes were recorded as nujol mulls between KBr windows using a Perkin Elmer 1760 FT-IR spectrophotometer. The infrared data are listed in Table 3.

The ¹¹⁹Sn NMR spectra were recorded on a JEOL JNM GX270 instrument equipped with multinuclear tunable probe and operating at 100.55 MHz under single pulse with hetero gated decoupling and without nuclear Overhauser effect mode. All samples were studied in CDCl₃ solution with the solvent also used as internal lock. The ¹¹⁹Sn chemical shifts were measured with resolution of 1-6 Hz relative to internal (CH₃)₄Sn.

Elemental analyses of the chloro-substituted diphenyltin complexes were performed by the Microanalytical Service, University College, London (UK). The data are given in Table 1.

Crystallographic analysis of the complex (3,4-Cl₂C₆H₃)₂SnCl₂.Me₂bipy was performed on an automated Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α (λ = 0.71703 Å)

Table 1. Analytical data for bis(3,4-dichlorophenyl)tin and related complexes.

Compound ^b	M.p. (°C)	%C	%H	%N
(3,4-Cl ₂ C ₆ H ₃) ₂ Sn	172-174	40.53(40.91)	1.50(1.70)	-
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂	193-194	29.50(28.81)	1.15(1.24)	-
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ .2L				
L = HMPA	232-234	33.86(34.24)	4.67(4.99)	9.97(9.98)
L = DMSO	167-169	31.50(30.11)	2.63(2.82)	-
L = Ph ₃ PO	194-196	55.57(55.44)	3.83(3.46)	-
L = Ph ₃ AsO	236-238	50.30(51.11)	3.58(3.19)	-
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ .L				
L = bipy	233-235	43.89(41.40)	2.78(2.19)	5.06(4.39)
L = phen	277-279	43.10(43.52)	2.21(2.12)	3.73(4.23)
L = Me ₂ bipy	257-259	41.04(43.26)	2.42(2.70)	4.12(4.21)
L = Me ₄ phen	288-290	46.69(46.82)	3.12(3.07)	3.78(3.90)
(3,4-Cl ₂ C ₆ H ₃) ₂ Sn(oxin) ₂	245-247	51.38(51.52)	2.59(2.58)	3.90(4.01)
(3,4-Cl ₂ C ₆ H ₃) ₂ Sn(Meoxin) ₂	254-256	52.80(52.84)	3.09(3.03)	3.76(3.85)

^a Calculated values in parentheses. ^b HMPA = hexamethylphosphoramide, DMSO = dimethylsulphoxide, Ph₃PO = triphenylphosphine oxide; Ph₃AsO = triphenylarsine oxide; bipy = 2,2-bipyridyl; phen = 1,10-phenanthroline; Me₂bipy = 4,4-dimethyl-2,2-dipyridyl; Me₄phen = 3,4,7,8-tetramethyl-1,10-phenanthroline; Meoxin = 2-methyl-8-hydroxyquinoline, oxin = 8-hydroxyquinoline

Table 2. ^{119m}Sn Mössbauer data^a for bis(3,4-dichlorophenyl)tin and related complexes.

Complex	IS^b	QS	Γ_1	Γ_2
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ ·2L				
L = HMPA	1.01	3.83	0.95	0.98
L = DMSO	1.13	3.63	1.20	1.38
L = Ph ₃ PO	1.01	3.46	1.30	1.45
L = Ph ₃ AsO	0.95	3.49	0.97	1.03
Ar ₂ SnCl ₂ ·bipy				
Ar = (3,4-Cl ₂ C ₆ H ₃)	0.83	2.07	1.02	1.13
Ar = (3-ClC ₆ H ₄) ^c	0.96	1.80	0.89	1.12
Ar = (4-ClC ₆ H ₄) ^c	1.20	3.53	1.10	1.12
Ar = (4-CH ₃ C ₆ H ₄) ^c	1.04	2.25	0.93	0.98
Ar ₂ SnCl ₂ ·phen				
Ar = (3,4-Cl ₂ C ₆ H ₃)	0.84	2.07	1.02	1.13
Ar = (3-ClC ₆ H ₄) ^c	0.95	2.10	1.18	0.97
Ar = (4-ClC ₆ H ₄) ^c	1.21	3.53	1.14	1.07
Ar = (4-CH ₃ C ₆ H ₄) ^c	1.24	3.58	0.99	1.03
Ar ₂ SnCl ₂ ·Me ₂ bipy				
Ar = (3,4-Cl ₂ C ₆ H ₃) ^d	0.73	2.19	1.27	0.95
	1.15	3.03	1.27	1.01
Ar = (3-ClC ₆ H ₄) ^c	1.02	3.38	1.03	0.98
Ar = (4-ClC ₆ H ₄) ^{c,e}				
<i>cis</i> -isomer	0.84	1.99	1.04	1.00
<i>trans</i> -isomer	1.14	3.49	0.91	0.96
Ar = (4-CH ₃ C ₆ H ₄) ^{c,d}	0.85	2.23	0.92	0.88
	1.14	3.59	0.81	0.88
Ar ₂ SnCl ₂ ·Me ₄ phen				
Ar = (3,4-Cl ₂ C ₆ H ₃)	1.07	3.17	1.15	1.38
Ar = (3-ClC ₆ H ₄) ^c	1.16	3.22	0.89	0.84
Ar = (4-ClC ₆ H ₄) ^c	1.16	3.38	1.05	0.99
Ar = (4-CH ₃ C ₆ H ₄) ^c	1.23	3.57	1.01	1.02
Ar ₂ Sn(oxin) ₂				
Ar = (3,4-ClC ₆ H ₃)	0.63	1.51	0.90	0.95
Ar = (4-ClC ₆ H ₄) ^c	0.71	1.66	0.97	1.16
Ar = (4-CH ₃ C ₆ H ₄) ^c	0.77	1.78	0.99	1.15
Ar ₂ Sn(2-Meoxin) ₂				
Ar = (3,4-Cl ₂ C ₆ H ₃)	0.63	1.48	1.04	1.02
Ar = (4-ClC ₆ H ₄) ^c	0.77	1.45	0.98	1.25
Ar = (4-CH ₃ C ₆ H ₄) ^c	0.77	1.75	1.14	1.14

^a Error ± 0.03 mm s⁻¹; ^b Relative to CaSnO₃ or BaSnO₃;
^c Ref. 26; ^d 3-line Mössbauer spectrum; ^e Ref. 20.

radiation, and determination of crystal class, orientation matrix and accurate cell parameters were carried out by standard procedures [27]. Unit cell constants for the compound were calculated from 25 strong reflections in the $12^\circ \leq \theta \leq 14^\circ$ thin shell. Intensity data

were collected to $2\theta_{\text{max}} = 50^\circ$. Crystal decay was monitored by using 3 standard reflections. The structure was solved by the heavy atom method and refined by full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms. The H-atoms were placed in calculated positions, assigned isotropic temperature factors of 4 Å and included in the structure-factor calculations for least-squares refinement. Weights were calculated using the weighting scheme $w = [\sigma(F)^2 + (0.02F)^2 + 1]^{-1}$ [28] and the refinement was continued until convergence. Structure solution and subsequent computations were performed with the *MoLEN* structure determination programs [29] on a DEC MicroVax minicomputer. The structure of the title compound is shown in Fig. 1. Atomic coordinates are listed in Table 5; bond distances and angles are given in Table 6. Lists of hydrogen coordinates, anisotropic temperature parameters and structure factors are available from the authors on request.

Crystal data: C₂₄H₁₈N₂Cl₆Sn, FW = 667.84, monoclinic, *P*2₁/*c*, *a* = 13.887(8), *b* = 14.6234(9), *c* = 14.864(3) Å, β = 101.08(1)°, *V* = 2962(2) Å³, *F*(000) = 298, *D*_x = 1.594 g cm⁻³ for *Z* = 4.

RESULTS AND DISCUSSION

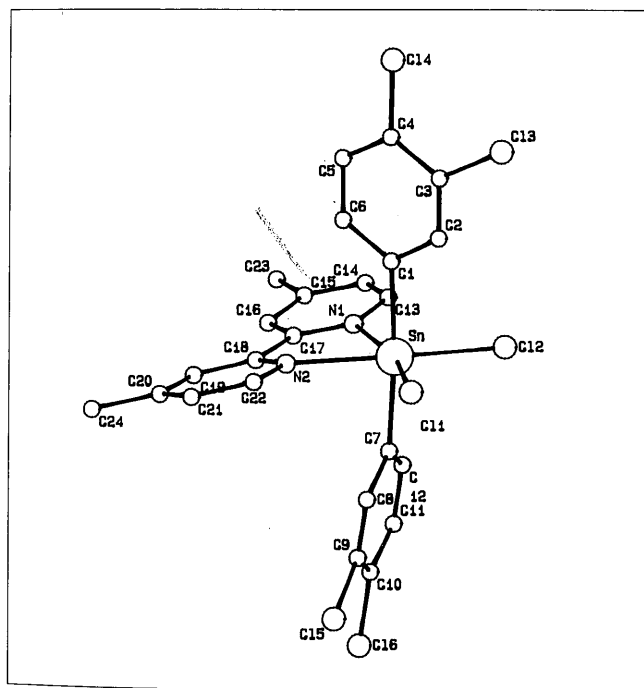
The ^{119m}Sn Mössbauer data of the complexes are listed in Table 2 together with those of some related analogues. The quadrupole splitting (*QS*) values for the (3,4-Cl₂C₆H₃)₂SnCl₂ complexes with monodentate ligands are in the range of 3.40 - 3.80 mm s⁻¹. A *trans*-[SnR₂] octahedral geometry is thus inferred for these complexes on the basis of point-charge model calculations [10,30] which specify for *trans*-[SnR₂] octahedral configurations *QS* values of *ca.* 4 mm s⁻¹ and for the *cis*-isomers *QS* values of *ca.* 2 mm s⁻¹. An all-*trans* arrangement is envisaged for these structures.

On the other hand, the complexes of (3,4-Cl₂C₆H₃)₂SnCl₂ with the bidentate ligands, bipyridine (bipy) and 1,10-phenanthroline (phen), yield *QS* values of *ca.* 2 mm s⁻¹ which support a *cis*-[SnR₂] octahedral configuration. This result is similar to that noted for the complexes of (3-ClC₆H₄)₂SnCl₂ with the same diimine ligands [31], and also augments our earlier crystallographic work on *cis*-(4-CH₃C₆H₄)₂SnCl₂·bipy [13]. By way of contrast, the corresponding complexes of (4-ClC₆H₄)₂SnCl₂ revealed *QS* values

Table 3. Selected IR bands^a for bis(3,4-dichlorophenyl)tin dichloride complexes.

Complex	vibrational bands (cm ⁻¹)			
	ν (E-O) ^b	ν (C=C)/ ν (C=N) ^c	ν (Sn-C)	ν (Sn-Cl)
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ ·2L				
L = HMPA	1193s, 1123s	-	295m	250m, 240s
L = DMSO	930s	-	320m	267s
L = Ph ₃ PO	1147s	-	311s, 298s	241s
L = Ph ₃ AsO	867s	-	308s, 289m	238s
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ ·L'				
L' = bipy	-	1598s, 1558s	287s	260s
L' = Me ₂ bipy	-	1612s, 1556s	274s	252s
L' = phen	-	1621s, 1521m, 1427m	295m	241m
L' = Me ₄ phen	-	1633m, 1556s, 1442m	299m	255m

^a IR data refer to Nujol mulls. ^b ν (E-O) values of the uncomplexed ligands are as follow: 1208(HMPA), 1192(Ph₃PO), 880(Ph₃AsO), 1053(DMSO) cm⁻¹; ^c ν (C=C/C=N) values of the uncomplexed ligands are as follow: 1575, 1470, 1420 (phen), 1615, 1536, 1430 (Me₄phen), 1550, 1435 (bipy), 1605, 1427 (Me₂bipy) cm⁻¹.

**Figure 1.** Molecular structure and atomic labelling scheme for *trans*-(3,4-Cl₂C₆H₃)₂SnCl₂·Me₂bipy.

which are indicative of a *trans*-[SnR₂] octahedral geometry [31]. Although the reasons for this structural difference are not presently clear, the varying influence of kinetic and thermodynamic controls in the complexation reaction cannot be discounted.

Table 4. ¹¹⁹Sn NMR data.

Compound	δ (¹¹⁹ Sn) ^a
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂	-35.7
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ ·2L	
L = HMPA	-375.4
L = DMSO	-379.2
L = Ph ₃ PO	-365.8
L = Ph ₃ AsO	-338.2
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ ·bipy	-366.0
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ ·Me ₂ bipy	-371.6
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ ·phen	-369.7
(3,4-Cl ₂ C ₆ H ₃) ₂ SnCl ₂ ·Me ₄ phen	-378.2
(3,4-Cl ₂ C ₆ H ₃) ₂ Sn(oxin) ₂	-406.3
(3,4-Cl ₂ C ₆ H ₃) ₂ Sn(2-Meoxin) ₂	-403.9

^a Relative to Me₄Sn.

Interestingly, the adduct of (3,4-Cl₂C₆H₃)₂SnCl₂ with 3,4,7,8-tetramethyl-1,10-phenanthroline (Me₄phen) showed a high *QS* value of 3.17 mm s⁻¹ which argues for a *trans*- or distorted *trans*-[SnR₂] octahedral geometry. The C-Sn-C bond angle for the complex

Table 5. Atomic coordinates and equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	B_{eq} (Å ²)
Sn	0.04763(6)	0.20712(5)	0.27386(5)	2.78(1)
C11	-0.0075(2)	0.2995(2)	0.3930(2)	4.67(7)
C12	0.0155(3)	0.3182(2)	0.1468(2)	4.52(7)
C13	-0.3671(3)	0.2480(3)	0.1703(4)	6.7(1)
C14	-0.4027(3)	0.0354(3)	0.1540(4)	7.0(1)
C15	0.3757(3)	0.3339(4)	0.5427(3)	8.0(1)
C16	0.5188(3)	0.3208(4)	0.4018(4)	8.4(1)
N1	0.1053(7)	0.0930(6)	0.1903(6)	2.9(2)
N2	0.1021(7)	0.0829(6)	0.3688(6)	3.1(2)
C1	-0.0960(8)	0.1484(7)	0.2371(7)	2.8(2)
C2	-0.1751(8)	0.2044(8)	0.2176(8)	3.5(2)
C3	-0.2683(9)	0.1721(9)	0.1939(8)	3.8(3)
C4	-0.2854(9)	0.0775(9)	0.1882(8)	3.9(3)
C5	-0.208(1)	0.0196(8)	0.2071(9)	4.2(3)
C6	-0.1136(9)	0.0545(8)	0.2308(8)	3.6(3)
C7	0.1976(9)	0.2524(8)	0.3129(8)	3.4(2)
C8	0.2357(9)	0.2768(9)	0.4026(8)	4.0(3)
C9	0.331(1)	0.297(1)	0.430(1)	5.0(3)
C10	0.397(1)	0.295(1)	0.369(1)	5.6(4)
C11	0.358(1)	0.272(1)	0.279(1)	5.8(4)
C12	0.260(1)	0.251(1)	0.2525(9)	4.6(3)
C13	0.0955(9)	0.0956(8)	0.0991(7)	3.5(2)
C14	0.1365(9)	0.0328(9)	0.0507(7)	3.7(3)
C15	0.1906(8)	-0.0377(8)	0.0953(8)	3.6(2)
C16	0.2009(9)	-0.0408(8)	0.1903(8)	3.5(2)
C17	0.1565(7)	0.0243(7)	0.2359(7)	2.7(2)
C18	0.1576(8)	0.0203(7)	0.3366(7)	2.9(2)
C19	0.2073(9)	-0.0453(8)	0.3933(8)	3.5(2)
C20	0.201(1)	-0.0490(9)	0.4855(8)	4.1(3)
C21	0.144(1)	0.015(1)	0.5164(8)	4.5(3)
C22	0.0958(9)	0.0801(9)	0.4578(7)	3.7(3)
C23	0.235(1)	-0.109(1)	0.0450(9)	5.5(3)
C24	0.254(1)	-0.121(1)	0.547(1)	6.4(4)

$$B_{eq} = (4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$$

predicted from the magnitude of the QS value using the Bancroft-Sham correlation [11] is 140°. This value is at the lower end of the scale for regular *trans*-octahedral angles but is higher than the basal C-Sn-C angles commonly encountered in diorganotin trigonal bipyramidal structures. The latter structures are, in principle, conceivable if the ligand adopts a unidentate bonding mode. However, this circumstance appears unlikely upon comparing with the literature values for some crystallographically authenticated five-coordinated complexes, such as Ph_2SnCl_2 ·benzthiazole [32] (angle C-Sn-C 132.5°; IS 1.36, QS 2.92 mm s⁻¹) and Ph_2SnCl_2 ·(2, 6-lutidine *N*-oxide) [33] (angle C-Sn-C 124.1°; IS

Table 6. Bond Distances (Å) and bond angles (°).

Sn	C11	2.462(3)	N1	C17	1.34(1)		
Sn	C12	2.467(3)	N1	C13	1.34(1)		
Sn	N1	2.313(9)	N2	C18	1.34(1)		
Sn	N2	2.335(9)	N2	C22	1.34(1)		
Sn	C1	2.14(1)	Sn	C7	2.15(1)		
C13	C3	1.75(1)	C14	C4	1.72(1)		
C1	C2	1.35(2)	C2	C3	1.36(2)		
C3	C4	1.40(2)	C4	C5	1.35(2)		
C5	C6	1.39(2)	C1	C6	1.40(2)		
C15	C9	1.75(1)	C16	C10	1.71(1)		
C7	C8	1.38(2)	C8	C9	1.35(2)		
C9	C10	1.40(2)	C10	C11	1.39(2)		
C11	C12	1.37(2)	C7	C12	1.37(2)		
C13	C14	1.36(2)	C14	C15	1.37(2)		
C15	C16	1.39(2)	C16	C17	1.38(2)		
C15	C23	1.48(2)	C17	C18	1.49(1)		
C18	C19	1.37(2)	C19	C20	1.39(2)		
C20	C21	1.36(2)	C21	C22	1.38(2)		
C20	C24	1.49(2)					
C11	Sn	C12	98.8(1)	C11	Sn	N1	165.7(2)
C11	Sn	N2	95.8(2)	C11	Sn	C1	90.1(3)
C11	Sn	C7	93.1(3)	C12	Sn	N1	95.4(2)
C12	Sn	N2	164.8(2)	C12	Sn	C1	92.6(3)
C12	Sn	C7	91.5(3)	N1	Sn	N2	70.0(3)
N1	Sn	C1	88.5(4)	N1	Sn	C7	87.2(4)
N2	Sn	C1	91.1(4)	N2	Sn	C7	83.9(4)
C1	Sn	C7	174.3(4)	Sn	N1	C13	123.1(7)
Sn	N1	C17	118.3(7)	Sn	N2	C18	117.2(7)
Sn	N2	C22	122.9(8)	Sn	C1	C2	119.2(8)
Sn	C1	C6	123.6(8)	C2	C1	C6	117(1)
C1	C2	C3	122(1)	C2	C3	C4	120(1)
C4	C5	C6	120(1)	C5	C6	C1	122(1)
C14	C4	C3	121(1)	C14	C4	C5	120(1)
C7	C8	C9	122(1)	C8	C9	C10	121(1)
C9	C10	C11	117(1)	C10	C11	C12	120(1)
C7	C12	C11	122(1)	C8	C7	C12	118(1)
Sn	C7	C8	120.6(9)	Sn	C7	C12	121.6(9)
C15	C9	C8	120(1)	C15	C9	C10	118(1)
C16	C10	C9	122(1)	C16	C10	C11	120(1)
C13	N1	C17	118.5(9)	C18	N2	C22	119(1)
C13	C14	C15	120(1)	C14	C15	C16	117(1)
C15	C16	C17	121(1)	C16	C17	C18	123(1)
C17	C18	C19	123(1)	N1	C13	C14	123(1)
N1	C17	C16	121(1)	N1	C17	C18	116.1(9)
C14	C15	C23	122(1)	C16	C15	C23	121(1)
N2	C18	C17	115(9)	N2	C18	C19	121(1)
C18	C19	C20	121(1)	C19	C20	C21	117(1)
C21	C20	C24	122(1)	C19	C20	C24	121(1)
C20	C21	C22	120(1)	N2	C22	C21	122(1)

1.36, QS 2.92 mm s⁻¹). It would be more appropriate to describe the structure of the Me_4phen adduct as skew-trapezoidal bipyramidal [3,4,34]. The difference in

structural type between the unsubstituted bipy and phen complexes of $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2$ with the Me_2phen complex reveals that the steric effects of the substituents in the heterocyclic ligand are particularly important.

For the Me_2bipy complex of $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2$, a three-line Mössbauer spectrum was obtained with Mössbauer parameters consistent with the presence of a homogeneous mixture of *cis*- (*IS* 0.73, *QS* 2.19 mm s^{-1}) and *trans*- (*IS* 1.15, *QS* 3.03 mm s^{-1}) octahedral isomers. This behaviour is similar to that previously observed for $(4\text{-CH}_3\text{C}_6\text{H}_4)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ [31], but contrasts sharply with $(4\text{-ClC}_6\text{H}_4)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ where both the *cis*- and *trans*-isomers were uniquely isolable [15,16]. Interestingly, the ligand Me_2bipy yielded only the *trans*- $[\text{SnR}_2]$ complex with $(3\text{-ClC}_6\text{H}_4)_2\text{SnCl}_2$ [31]. Attempts to separate the geometrical isomers of $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ by fractional recrystallisation from dimethylformamide, methanol or toluene proved unsuccessful. From the toluene medium, however, we were able to secure a suitable crystal for X-ray crystal analysis. This turned out (*vide infra*) to be exclusively the *trans*-isomer.

The complex, $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{Sn}(\text{oxin})_2$, and its 2-methyloxinato (Meoxin) analogue, have ρ values ($\rho = \text{QS/IS}$) > 2.1 which indicate higher-than-four coordination environments at tin [35]. However, the low *QS* values of *ca.* 1.50 mms^{-1} for these complexes may be rationalised in terms of a *cis*-octahedral structure, rather similar to the case for the analogous chelate complexes of $(4\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Sn}$ and $(4\text{-ClC}_6\text{H}_4)_2\text{Sn}$ [31]. By way of contrast, whereas $\text{Ph}_2\text{Sn}(\text{oxin})_2$ shows a *cis*- $[\text{SnR}_2]$ octahedral geometry (*QS* 1.69 mms^{-1}), $\text{Ph}_2\text{Sn}(\text{Meoxin})_2$ adopts a distorted-*trans* or STB structure, as indicated by its larger *QS* value of 3.50 mm s^{-1} [8].

Selected infrared data for the $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2$ complexes are listed in Table 3. For the case of the complexes with monodentate ligands, it is seen that complexation results in a decrease in the E-O (E = N, S, P or As) stretching frequency of the monodentate ligands, confirming their coordination to tin *via* the respective oxygen atoms [36,37]. Similarly, the frequencies associated with the skeletal C=C and C=N stretchings in the 1,10-phenanthroline, 3,4, 7,8-tetramethyl-1,10-phenanthroline, 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine ligands show the expected shift to higher wavenumbers following chelation to bis(3,4-dichlorophenyl)tin dichloride.

^1H and ^{13}C NMR investigations of the complexes

of $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2$ in solution were thwarted by their poor solubility in common non-donor solvents. Nevertheless, we were able to secure the ^{119}Sn NMR spectra of the complexes in dilute CDCl_3 solution (concentrations ranged from 15 mg/mL to 35 mg/mL). The ^{119}Sn chemical shift values for the complexes (Table 4) fall in the range of -420 ppm to -350 ppm, and relative to the uncomplexed bis(3,4-dichlorophenyl)tin dichloride [$\delta(^{119}\text{Sn})$ -35.7 ppm] are significantly shifted to higher field. The large magnitudes of the ^{119}Sn NMR chemical shifts indicates that the complexes largely retain their octahedral tin configurations in solution. This inference is supported by the general observation among related organotin compounds that the ^{119}Sn chemical shifts move markedly upfield over a 600 ppm range as the coordination number increases from 4 to 7 [38,39]. It is noteworthy that only a single tin signal is observed in solution for $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$, which in its solid state was deduced to be a mixture of *cis*- and *trans*-isomers. The most obvious explanation for this is that the complex exists in solution exclusively as the one isomer (presumably the *trans*-isomer).

Crystal structure analysis of $(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ The title compound crystallises in the $P2_1/c$ space group with a 13.887(8), b 14.6234(9), c 14.864(3) Å and $101.08(1)^\circ$. It is a six-coordinated, monomeric species with *trans*- $[\text{SnR}_2]$ octahedral geometry. The C-Sn-C angle is $174.3(4)^\circ$ (Fig. 1) which is in the same range as those reported for *trans*- $(c\text{-C}_5\text{H}_9)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ (C-Sn-C $174.5(1)^\circ$ [40]) and *trans*- $(4\text{-ClC}_6\text{H}_4)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ (C-Sn-C $177.4(7)^\circ$ [16]). The Cl-Sn-Cl bond angle is $98.8(1)^\circ$ and the 'bite' angle of the chelating ligand is $70.0(3)^\circ$. The 'bite' angle compares favourably with the value reported for *trans*- $(4\text{-ClC}_6\text{H}_4)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ (68.3° [16]). The steric influence of the chlorine substituents on the phenyl rings is minimal as is evidenced from the relatively short Sn-N and Sn-Cl bonds (Sn-N 2.313(9) Å, 2.335(9) Å and Sn-Cl 2.462 Å, 2.467 Å) compared with those of *trans*- $(4\text{-ClC}_6\text{H}_4)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ [Sn-N 2.402(8) Å Sn-Cl 2.482(5) Å]. The two aryl rings make an angle of $79.5(5)^\circ$ with each other. This contrasts with the structurally analogous *trans*- $(4\text{-ClC}_6\text{H}_4)_2\text{SnCl}_2\cdot\text{Me}_2\text{bipy}$ which has a dihedral angle of 4° between the two aryl rings, but is similar to *trans*- $\text{Ph}_2\text{SnCl}_2\cdot\text{bipy}$ which has a dihedral angle of 79.5° between the phenyl rings [41]. There is also a lesser torsional twist about the

C17-C18 bond of the 4,4'-Me₂bipy ligand (dihedral angle between the 4-MeC₅H₃N rings of 4,4'-Me₂bipy is 8.3° compared with 13° reported for *trans*-(4-ClC₆H₄)₂SnCl₂.Me₂bipy).

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