Journal of Organometallic Chemistry, 327 (1987) 311–326
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Structural studies on octahedral diorganotin(IV) complexes: the influence of substituents in carbon- and heteroatom-donor ligands on [SnR_2] skeletal geometry

V.G. Kumar Das*, Yap Chee-Keong
Department of Chemistry, University of Malaya, 59100 Kuala Lumpur (Malaysia)

and Peter J. Smith
International Tin Research Institute, Kingston Lane, Uxbridge, Middlesex UB8 3PJ (Great Britain)

(Received November 20th, 1986)

Abstract

The synthesis and spectroscopic characterization are described of six-coordinated diorganotin(IV) complexes of the type $RR'SnX_2 \cdot L_2$ and $RR'SnL'_2$ where RR′ = diphenyl, bis(*p*-tolyl), bis(*m*-chlorophenyl), bis(*p*-chlorophenyl), MeEt, Et(n-Pr); X = Cl or NCS; L = neutral monodentate oxygen donor (containing $>$S=O, $>$N → O, $>$P=O or $>$As=O grouping) or 1/2 bidentate donor (2,2′-bipyridyl, 4,4′-dimethyl-2,2′-bipyridyl, 1,10-phenanthroline or 3,4,7,8-tetramethyl-1,10-phenanthroline); L′ = 8-quinolinolato or 2-methyl-8-quinolinolato. The spectroscopic (in particular, the ^{119m}Sn Mössbauer) data have been used to infer the stereochemistry of the [SnR_2] skeleton in these complexes, with confirmation from recent X-ray studies in a few cases. The results indicate that substituents in the carbon- and heteroatom-donor ligands attached to tin have a strong influence on the stereochemical preference for *trans*- or *cis*-[SnR_2] configurations in the six-coordinated octahedral complexes.

Introduction

Diorganotin(IV) dihalides and diisothiocyanates readily yield complexes with neutral oxygen and nitrogen donor ligands of formula $R_2SnX_2 \cdot 2L$ (L = monodentate or 1/2 bidentate ligand). The tin is in an octahedral coordination environment in these structures [1–4], as it is, because of intermolecular halogen bridging [5,6], in several complexes of 1:1 stoichiometry involving non-sterically demanding ligands containing $>$C=O, $>$S=O, $>$N → O, $>$P=O or $>$As=O groupings.

0022-328X/87/$03.50

The structural features of the above complexes, in particular the stereochemistry of the R_2Sn skeleton, have been investigated by a combination of IR, NMR and ^{119m}Sn Mössbauer spectroscopic studies, as well as by X-ray analysis in suitable cases. The results, although largely restricted to dimethyl- and diphenyl-tin systems, suggest a preponderant tendency towards a *trans*-[SnR_2] skeletal array for $R_2SnX_2 \cdot 2L$ complexes (L = monodentate donor) [1,2,7,8]. This has been ascribed to the σ-donor ability of the methyl groups which tends to maximize the tin 5*s* character in the Sn–C bond, resulting in a linear C–Sn–C structure [9,10]. Indeed, this preference for *trans*-[SnR_2] geometry has been observed also with bulkier alkyl groups [11] and for mixed (alkyl)(aryl) systems [12–14].

With bidentate ligands of the α-diimine type, the *trans*- or distorted *trans*-[SnR_2] configuration is exclusively formed for the dialkyltin dihalide and diisothiocyanate complexes and, with the recent exception of (p-tolyl)$_2SnCl_2 \cdot$ bipy [15], also for the diphenyltin dihalide series, as shown by Mössbauer and X-ray data [1,2,16–18]. However, for the corresponding diaryltin(IV) diisothiocyanate complexes, only *cis*-[SnR_2] geometries have so far been encountered [18,19] and this has been attributed to steric effects introduced by the NCS groups [20]. The mixed (alkyl)(aryl)tin dihalide complexes, $RPhSnCl_2 \cdot L'$ (R = Me, Et, n-Pr, n-Bu; L′ = bipy, phen), although not extensively studied, appear from spectroscopic evidence to have a *trans*-[SnR_2] geometry [12–14], a preference which is manifested also by the diisothiocyanate complexes, e.g. $BuPhSn(NCS)_2 \cdot L'$ (L′ = bipy, phen) [12]. It has been suggested, however, that in such mixed diorganotin systems the C–Sn–C bond angles depart significantly from the ideal *trans* angle of 180° [12–14]. It is noteworthy that in cases where the structural distortion of the octahedron is severe, *cis*/*trans* designations would be of questionable validity and, indeed, configurations intermediate between these have been assigned to dimethyltin(IV) bis(*N*-Me-*N*-acetylhydroxylamine) [21] and dimethyltin(IV) bis(*N*,*N*-dimethyldithiocarbamate) [22]. Bis-(quinolin-8-olato)dimethyltin(IV) (C–Sn–C bond angle (X-ray) 110.7°) [23] and bis(*N*-acetylhydroxylamino)dimethyltin(IV) (C–Sn–C bond angle (X-ray) 109.1°) [24], on the other hand, are marked exceptions among dialkyltin bis-chelates in having *cis*-[SnR_2] octahedral geometries. This difference has been rationalised on steric grounds, and this is supported by semi-theoretical arguments based on the ligand–ligand repulsion model [10,25], which predicts *cis*-structures to be more favourable when the chelating ligands have small 'bite' angles. Bancroft and coworkers [10] have observed that with 1,3-dicarbonyl donors (RCOCHCOR), the *cis*-preference follows the order $Ph_2SnL_2 > PhMeSnL_2 > Me_2SnL_2$. These authors have suggested the possibility that *cis*/*trans* energy differences could be somewhat small for dialkyltin bis-chelates relative to diaryltin analogues, so that both these configurations could conceivably coexist in certain circumstances. Studies on the $Ph_2Sn/PhBuSn/Bu_2Sn$ series [12] have also confirmed the trends in *cis*-preference.

Our work on the effects of substituents in the carbon- and heteroatom-donor ligands attached to tin was prompted by our somewhat puzzling earlier Mössbauer observation [26] that the steric presence of a 2-methyl substituent on the oxin ligand (oxinH = 8-hydroxyquinoline) causes the Me_2Sn skeleton to adopt the *trans*-configuration in the bis-chelate, $Me_2Sn(quin)_2$ (quinH = 2-methyl-8-hydroxyquinoline), as opposed to the *cis*-structure in $Me_2Sn(oxin)_2$ [23]. This was subsequently confirmed by X-ray diffraction for the case of $Et(n\text{-}Pr)Sn(quin)_2$ [27], which showed a C–Sn–C angle of 145.2° and an average ligand bite angle of 70.5°, which is ca. 3°

lower than that in $Me_2Sn(oxin)_2$. It appeared from this study that steric effects, as manifested in the unequal Sn–donor bond distances in the complex, were responsible for enforcing the *trans*-[SnR_2] configuration, rather than the reassertion of electronic effects as expressed by Bent's rule [9]. Extension of such work to other hexacoordinated diorganotin complexes containing structured R groups, such as phenyl carrying substituents on the ring, yielded the unexpected result of a *cis*-[SnR_2] geometry for the 1:1 complex of $(p\text{-tolyl})_2SnCl_2$ with bipy [15], and, even more impressively, allowed us to isolate for the first time both the *cis*- and *trans*-isomers of an octahedral diorganotin complex for the case of dichlorobis(4-chlorophenyl)tin(IV) · 4,4′-dimethyl-2,2′-bipyridyl [28,29]. In this paper, we report our work on a range of related complexes directed towards the general question of *cis-trans* preference in organotin(IV) hexacoordination.

Experimental

The starting diorganotin dichlorides {$(p\text{-tolyl})_2SnCl_2$, m.p. 48–49 °C (lit. m.p. 49–50 °C [30]); $(p\text{-}ClC_6H_4)_2SnCl_2$, m.p. 85–86 °C (lit. m.p. 88 °C [31]); $(m\text{-}ClC_6H_4)_2SnCl_2$, m.p. 74–75 °C; Ph_2SnCl_2, m.p. 43 °C (lit. m.p. 42–44 °C [3]); $MeEtSnCl_2$, m.p. 51–52 °C (lit. m.p. 53 °C [32]); $Et(n\text{-}Pr)SnCl_2$, m.p. 50–52 °C (lit. m.p. 52–53 °C [33])} were prepared by published methods. The diisothiocyanate derivatives {$(p\text{-tolyl})_2Sn(NCS)_2$, m.p. 148–150 °C; $(p\text{-}ClC_6H_4)_2Sn(NCS)_2$, m.p. 215–217 °C; $Ph_2Sn(NCS)_2$, m.p. 177–179 °C; $MeEtSn(NCS)_2$, m.p. 172–174 °C} were prepared from the corresponding chlorides by Seyferth and Rochow's method [34]. Except for pyridine *N*-oxide and quinoline *N*-oxide, which were prepared by Ochiai's method [35], all other ligands were obtained commercially and used without further purification. Acetonitrile was purified by a standard procedure [36].

Supplementary material. Tables of IR and mass spectral data for the complexes are available from the authors on request.

Preparation of the complexes

Most of the neutral complexes were formed by mixing the appropriate diorganotin dihalides or diisothiocyanates with the monodentate or bidentate ligands in a suitable solvent. The bis-oxinates were prepared by the method of Westlake and Martin [37]. The 1:1 and 1:2 complexes with neutral monodentate and bidentate ligands were isolated as stable white solids in 60–80% yields. The bis-oxinates were obtained as beige or yellow-coloured solids. Elemental analyses of the complexes (Tables 1, 2 and 3) were performed by the Australian Microanalytical Service, Melbourne, and by the Microanalytical Service of University College, London. The melting points listed are uncorrected. The following abbreviations are used for the ligands: 2,2′-bipyridine (bipy); 1,10-phenanthroline (phen); 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy); 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen); quinoline *N*-oxide (quinO); pyridine *N*-oxide (pyO); hexamethylphosphoramide (HMPA); triphenylphosphine oxide (Ph_3PO); dimethylsulphoxide (DMSO); triphenylarsine oxide (Ph_3AsO); 8-hydroxyquinoline (oxinH); 2-methyl-8-hydroxyquinoline (quinH).

The following syntheses are representative:

$MeEtSnCl_2 \cdot Me_2bipy$. A solution of $MeEtSnCl_2$ (0.70 g, 3 mmol) in 20 ml ethanol was added to Me_2bipy (0.72 g, 3 mmol) in 40 ml ethanol. A precipitate of

Table 1

Analytical data (found (calc) (%)) for diorganotin(IV) dihalide and diisothiocyanate complexes of nitrogen-donor ligands

Complex	M.p. (°C) [a]	C	H	N
Et(n-Pr)$SnCl_2$·bipy	193–194	43.30 (43.11)	4.64 (4.79)	6.32 (6.71)
EtMe$SnCl_2$·bipy	196–197	39.80 (40.05)	4.13 (4.11)	6.97 (7.19)
(*p*-tolyl)$_2SnCl_2$·bipy	218–220	53.81 (54.59)	4.00 (4.17)	5.01 (5.31)
(*p*-$ClC_6H_4)_2SnCl_2$·bipy	236–238	45.64 (46.44)	2.96 (2.81)	4.87 (4.93)
(*m*-$ClC_6H_4)_2SnCl_2$·bipy	224–226	46.24 (46.43)	2.94 (2.81)	4.72 (4.92)
Et(n-Pr)$SnCl_2$·phen	198–199	46.30 (46.21)	4.47 (4.53)	6.05 (6.34)
EtMe$SnCl_2$·phen	215–217	43.74 (43.53)	3.76 (3.87)	6.42 (6.77)
(*p*-tolyl)$_2SnCl_2$·phen	281–283	55.89 (56.57)	4.28 (3.99)	5.01 (5.08)
(*p*-$ClC_6H_4)_2SnCl_2$·phen	282–284	48.21 (48.61)	2.69 (2.70)	4.58 (4.73)
(*m*-$ClC_6H_4)_2SnCl_2$·phen	248–249	48.50 (48.60)	2.77 (2.70)	4.61 (4.73)
Et(n-Pr)$SnCl_2$·Me_2bipy	195–196	46.09 (45.79)	5.40 (5.39)	6.30 (6.29)
EtMe$SnCl_2$·Me_2bipy	230–232	43.48 (43.11)	4.77 (4.79)	6.67 (6.71)
(*p*-tolyl)$_2SnCl_2$·Me_2bipy	232–235	56.02 (56.17)	4.84 (4.68)	4.96 (5.04)
(*p*-$ClC_6H_4)_2SnCl_2$·Me_2bipy	241–243	47.91 (48.27)	3.15 (3.35)	4.70 (4.69)
(*m*-$ClC_6H_4)_2SnCl_2$·Me_2bipy	230–231	48.39 (48.27)	3.36 (3.35)	4.57 (4.69)
Ph_2SnCl_2·Me_2bipy	228–230	54.36 (54.59)	4.29 (4.17)	5.41 (5.31)
Et(n-Pr)$SnCl_2$·Me_4phen	298–300	49.76 (50.65)	5.58 (5.63)	5.37 (5.63)
EtMe$SnCl_2$·Me_4phen	302–304	48.10 (48.56)	5.11 (5.11)	5.68 (5.96)
(*p*-tolyl)$_2SnCl_2$·Me_4phen	300–302	58.20 (59.26)	4.81 (4.94)	4.24 (4.61)
(*p*-$ClC_6H_4)_2SnCl_2$·Me_4phen	319–320	51.42 (51.81)	3.78 (3.70)	4.13 (4.32)
(*m*-$ClC_6H_4)_2SnCl_2$·Me_4phen	290–291	51.68 (51.80)	3.58 (3.70)	4.10 (4.32)
Ph_2SnCl_2·Me_4phen	282–283 (267–268) [b]	58.08 (57.97)	4.52 (4.49)	4.79 (4.83)
(*p*-tolyl)$_2$Sn(NCS)$_2$·bipy	168–170	54.42 (54.49)	3.84 (3.84)	9.68 (9.78)
(*p*-$ClC_6H_4)_2$Sn(NCS)$_2$·bipy	208–209	46.68 (46.94)	2.56 (2.61)	8.96 (9.13)
EtMeSn(NCS)$_2$·phen	198–199	44.46 (44.49)	3.64 (3.49)	12.07 (12.21)
(*p*-tolyl)$_2$Sn(NCS)$_2$·phen	214–215	56.18 (56.32)	3.82 (3.69)	9.12 (9.39)
(*p*-$ClC_6H_4)_2$Sn(NCS)$_2$·phen	245–246	48.87 (48.94)	2.59 (2.51)	8.70 (8.78)
(*p*-tolyl)$_2$Sn(NCS)$_2$·Me_2bipy	220–222	56.9 (55.94)	4.07 (4.33)	9.19 (9.32)
(*p*-$ClC_6H_4)_2$Sn(NCS)$_2$·Me_2bipy	208–210	48.05 (48.63)	3.47 (3.12)	8.27 (8.73)
Ph_2Sn(NCS)$_2$·Me_2bipy	202–204	53.08 (54.49)	3.86 (3.84)	8.76 (8.78)
(*p*-tolyl)$_2$Sn(NCS)$_2$·Me_4phen	271–272	58.59 (58.84)	4.75 (4.60)	8.62 (8.58)

[a] With decomposition. [b] Ref. 17.

the complex appeared immediately, and was filtered off, washed with cold diethyl ether, and dried in air. Yield, 1.0 g (80%).

(p-tolyl)$_2SnCl_2$ · phen. Equimolar quantities (5 mmol) of (*p*-tolyl)$_2SnCl_2$ (1.86 g) and 1,10-phenanthroline (0.99 g) were dissolved separately in ethanol and mixed to give an immediate white precipitate, which was filtered off, washed with ethanol, and air-dried. Yield, 2.21 g (80%).

(p-tolyl)$_2SnCl_2$ · 2HMPA. (*p*-Tolyl)$_2SnCl_2$ (0.50 g, 1.3 mmol) was dissolved in neat HMPA by brief warming and the mixture set aside to stand overnight in the freezer. The white solid formed was filtered off, washed with petroleum ether (60–80 °C), and dried in air. Yield, 0.57 g (60%).

(p-tolyl)$_2SnCl_2$ · 2quinO. A solution of 0.40 g (1 mmol) of (*p*-tolyl)$_2SnCl_2$, in 20 ml dichloromethane was added to 0.38 g (2 mmol) of quinoline *N*-oxide in 20 ml dichloromethane. The solution was concentrated to a small volume, chilled, and

Table 2

Analytical data (found (calc) (%)) for diorganotin(IV) dihalide complexes of oxygen-donor ligands

Complex	M.p. (°C) [a]	C	H	N
$(p\text{-tolyl})_2SnCl_2 \cdot 2quinO$	156–158	57.09 (58.04)	4.29 (4.23)	4.18 (4.23)
$(p\text{-}ClC_6H_4)_2SnCl_2 \cdot 2quinO$	166–168	50.05 (51.24)	3.10 (3.13)	3.72 (3.99)
$(p\text{-tolyl})_2SnCl_2 \cdot 2pyO$	176–178	49.99 (51.28)	4.29 (4.27)	4.86 (4.98)
$(p\text{-}ClC_6H_4)_2SnCl_2 \cdot 2pyO$	180–182	43.71 (43.81)	3.07 (2.99)	4.45 (4.65)
$(p\text{-tolyl})_2SnCl_2 \cdot 2HMPA$	116–117	42.50 (42.75)	6.71 (6.85)	11.46 (11.51)
$(p\text{-}ClC_6H_4)_2SnCl_2 \cdot 2HMPA$	212–213	37.05 (37.37)	5.67 (5.71)	11.10 (10.90)
$(m\text{-}ClC_6H_4)_2SnCl_2 \cdot 2HMPA$	197–199	37.01 (37.37)	5.81 (5.71)	11.16 (10.90)
$(p\text{-tolyl})_2SnCl_2 \cdot 2Ph_3PO$	145–146	64.43 (64.68)	4.78 (4.74)	
$(p\text{-}ClC_6H_4)_2SnCl_2 \cdot 2Ph_3PO$	178–180	59.07 (59.47)	3.94 (3.92)	
$(m\text{-}ClC_6H_4)_2SnCl_2 \cdot 2Ph_3PO$	168–170	59.53 (59.47)	4.08 (3.92)	
$(p\text{-tolyl})_2SnCl_2 \cdot 2DMSO$	150–152	40.17 (40.94)	4.87 (4.93)	
$(p\text{-}ClC_6H_4)_2SnCl_2 \cdot 2DMSO$	152–154	33.89 (33.77)	3.57 (3.52)	
$(p\text{-tolyl})_2SnCl_2 \cdot 2Ph_3AsO$	210–212	57.75 (59.09)	4.29 (4.33)	
$(p\text{-}ClC_6H_4)_2SnCl_2 \cdot 2Ph_3AsO$	227–229	54.22 (54.52)	3.62 (3.60)	
$(m\text{-}ClC_6H_4)_2SnCl_2 \cdot 2Ph_3AsO$	192–194	54.36 (54.52)	3.64 (3.60)	

[a] With decomposition.

triturated with petroleum ether (60–80 °C) to give a white solid which was filtered off, washed with petroleum ether, and air-dried. Yield, 0.5 g (70%).

$(p\text{-}ClC_6H_4)_2SnCl_2 \cdot 2DMSO$. 2.89 g (0.7 mmol) of $(p\text{-}ClC_6H_4)_2SnCl_2$ was heated with neat DMSO until the solid dissolved. The solution was chilled, than triturated with ethanol to give a white solid, which was filtered off, washed with ethanol and air-dried. Yield, 2.39 g (60%).

Et(n-Pr)Sn(quin)$_2$. Solutions of Et(n-Pr)$SnCl_2$ (0.52 g, 2.0 mmol) and 2-methyl-8-hydroxyquinoline (0.64 g, 4.0 mmol) in ethanol were mixed and a solution of 0.2 g of sodium acetate in 20 ml of 50% (v/v) aqueous ethanol was added, followed by 20 ml of 25% aqueous ammonia. The beige-coloured solid obtained was recrystallised from toluene in 60% yield (0.61 g). Mass spectrum [70 eV, *m/e* (relative intensity)]: $[M - Et]^+$ 479(9); $[M - n\text{-}Pr]^+$ 465(7.4); $[Sn(quin)_2]^+$ 436(13); $[M - quin]^+$ 350(7.5); $[Sn(quin)]^+$ 278(100); $[quinH]^+$ 159 (58.8); $[Sn]^+$ 120(3).

Table 3

Analytical data (found (calc) (%)) for diorganotin(IV) oxinates

Compound	M.p. (°C) [a]	C	H	N
$Et(n\text{-}Pr)Sn(oxin)_2$	130–131	57.67 (57.43)	4.99 (5.41)	5.75 (5.82)
$Et(n\text{-}Pr)Sn(quin)_2$	287–289	59.14 (58.98)	5.39 (5.89)	5.57 (5.51)
$EtMeSn(oxin)_2$	184–186	56.09 (55.68)	4.52 (4.86)	6.09 (6.19)
$EtMeSn(quin)_2$	306–308	57.56 (57.43)	4.92 (5.41)	5.82 (5.83)
$(p\text{-tolyl})_2Sn(oxin)_2$	293–295	64.73 (65.02)	4.53 (4.74)	4.57 (4.74)
$(p\text{-tolyl})_2Sn(quin)_2$	271–273	65.39 (65.96)	4.89 (5.17)	4.47 (4.53)
$(p\text{-}ClC_6H_4)_2Sn(oxin)_2$	285–287	58.94 (60.39)	3.56 (3.69)	4.55 (4.69)
$(p\text{-}ClC_6H_4)_2Sn(quin)_2$	280–281	57.96 (58.22)	3.52 (3.94)	4.54 (4.25)

[a] With decomposition.

MeEtSn(quin)$_2$. This was prepared by the same procedure. Mass spectrum (m/e, rel. int.): $[M-Me]^+$ 465(0.4); $[M-Et]^+$ 451(1); $[Sn(quin)_2]^+$ 436(1.8); $[M-quin]^+$ 322(2.3); $[EtSn(quin)]^+$ 307(0.3); $[MeSn(quin)]^+$ 293(0.5); $[Sn(quin)]^+$ 278(25.3); $[quin-H]^+$ 159(100); $[SnMe]^+$ 135(1.8); $[Sn]^+$ 120(3.1).

Mössbauer spectra

The ^{119m}Sn Mössbauer spectra of the complexes were obtained at 80 K on a constant acceleration microprocessor spectrometer using a 15 mCi $Ca^{119}SnO_3$ 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 [38].

Infrared spectra

The infrared spectra of the compounds were recorded as Nujol mulls between NaCl or polyethylene windows using a Perkin–Elmer 1300 spectrometer, and were calibrated with polystyrene.

Ultraviolet spectra

The ultraviolet spectra were recorded on a Beckman DU-7 spectrometer with 1-cm quartz cells. The temperature was maintained at $26 \pm 1°C$.

The determination of the formation constants (K) of the complexes of $MeEtSnCl_2$ and Et(n-Pr)$SnCl_2$ with 2,2′-bipyridine (bipy) and its 4,4′-dimethyl derivative (Me_2bipy) was carried out spectroscopically in acetonitrile (λ range: 250 to 320 nm) by use of the following equation:

$$1-(D_0/D)/A_0 = -K + K(E_{AB}/E_B)(D_0/D) \quad (1)$$

where E_B and E_{AB} are, respectively, the molar extinction coefficients of the free and complexed ligands (bipy or Me_2bipy), D_0 is the absorbance of a solution containing only the ligand and D is the absorbance of the solution containing a definite amount of the ligand and an arbitrary amount of the mixed dialkyltin dichloride. The concentrations used were 1×10^{-5} M for the ligands and ca. 1.0×10^{-5} to 6.0×10^{-3} M for the mixed dialkyltin dichlorides.

As is evident from eq. 1, a plot of (D_0/D) against $1-(D_0/D)/A_0$ gives a straight line, from which K is obtained as the intercept at $(D_0/D) = 0$. A programmable calculator was used for least-squares treatment of the data and to derive the K values listed in Table 8.

Results and discussion

1. Complexes with monodentate ligands

Selected infrared data for the 1:2 complexes of Ar_2SnCl_2 (Ar = *m*-ClC_6H_4, *p*-ClC_6H_4, *p*-MeC_6H_4) are listed in Table 4, together with literature data for the corresponding complexes of Ph_2SnCl_2. It is apparent that complexation leads to a decrease in the E–O (E = N, S, P or As) stretching frequencies of the ligands, confirming their coordination to tin via oxygen [7,40]. Application of the generalization that, for a given ligand, the larger the magnitude of $\Delta\ \nu$(E–O) the stronger the donor interaction [41], leads to the following order of acceptor strengths:

(*p*-tolyl)$_2SnCl_2$ < Ph_2SnCl_2 < (*p*-ClC_6H_4)$_2SnCl_2$ < (*m*-ClC_6H_4)$_2SnCl_2$

Table 4

Selected IR bands [a] for diorganotin(IV) dihalide complexes of oxygen-donor ligands

Complex	ν(E–O) [b]	ν(Sn–C)	ν(Sn–Cl)
(*p*-tolyl)$_2$SnCl$_2$·2quinO	1220m, 1235m	280s	255m,br
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2quinO	1218m, 1232m	308s; 294sh	240s,br
Ph$_2$SnCl$_2$·2pyO [c]	1200, 1209	283s	
(*p*-tolyl)$_2$SnCl$_2$·2pyO	1200s	280s	255m,br
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2pyO	1210s	305s; 295sh; 230m	250s
(*p*-tolyl)$_2$SnCl$_2$·2HMPA	1195s; 1136vs	284s; 220s,br	250m,sh
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2HMPA	1196s, 1130vs	312m	250w,sh; 230m
(*m*-ClC$_6$H$_4$)$_2$SnCl$_2$·2HMPA	1198s, 1124vs	294w	238s,br
Ph$_2$SnCl$_2$·2Ph$_3$PO [c]	1143s, 1137s	267m	
(*p*-tolyl)$_2$SnCl$_2$·2Ph$_3$PO	1148vs	280s; 220s,br	238m,sh
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2Ph$_3$PO	1150vs	306s; 295w,sh	245s,br
(*m*-ClC$_6$H$_4$)$_2$SnCl$_2$·2Ph$_3$PO	1145s	290w; 270m,sh	246s,br
Ph$_2$SnCl$_2$·2DMSO [c]	946s	264m, 244sh	
(*p*-tolyl)$_2$SnCl$_2$·2DMSO	950, 935s	284s; 222s,br	240m,sh
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2DMSO	945s	310w	260vs,br
Ph$_2$SnCl$_2$·2Ph$_3$AsO [c]	860s	293s, 280sh	
(*p*-tolyl)$_2$SnCl$_2$·2Ph$_3$AsO	885vs	295m,sh; 280s; 215s,br	240m,sh
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2Ph$_3$AsO	884vs	298sh; 284s	240s,br
(*m*-ClC$_6$H$_4$)$_2$SnCl$_2$·2Ph$_3$AsO	874vs	294s	238s,br

[a] IR data (cm^{-1}) refer to Nujol mulls. [b] E = N, P, S, As, ν(P–O)(Ph$_3$PO) 1190, ν(S–O)(DMSO) 1047, ν(N–O)(pyO) 1244, ν(P–O)(HMPA) 1218, ν(N–O)(quinO) 1230 and 1210, ν(As–O)(Ph$_3$AsO) 890 cm^{-1} for the free ligands. [c] Ref. 7.

The ^{119m}Sn Mössbauer data of the complexes are listed in Table 5. Inspection of their quadrupole splitting (QS) values reveals essentially *trans*-[SnR$_2$] octahedral structures for the complexes, in keeping with point-charge model calculations [42,43], which specify values of ca. 4 mm s^{-1} for *trans*- and ca. 2 mm s^{-1} for

Table 5

^{119m}Sn Mössbauer data [a] for diorganotin(IV) dihalide complexes of oxygen-donor ligands

Complex	IS [b]	QS	Γ_1	Γ_2
(*p*-tolyl)$_2$SnCl$_2$·2quinO	1.21	3.86	1.05	1.03
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2quinO	1.17	3.67	1.13	1.05
(*p*-tolyl)$_2$SnCl$_2$·2pyO	1.24	3.89	1.22	1.07
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2pyO	1.13	3.71	1.13	1.12
(*p*-tolyl)$_2$SnCl$_2$·2HMPA	1.22	3.92	0.86	0.89
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2HMPA	1.05	3.72	1.05	1.00
(*m*-ClC$_6$H$_4$)$_2$SnCl$_2$·2HMPA	0.97	3.70	1.01	0.86
(*p*-tolyl)$_2$SnCl$_2$·2Ph$_3$PO	1.06	3.95	0.94	0.90
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2Ph$_3$PO	1.08	3.81	0.99	1.02
(*m*-ClC$_6$H$_4$)$_2$SnCl$_2$·2Ph$_3$PO	1.07	4.01	0.97	0.99
(*p*-tolyl)$_2$SnCl$_2$·2DMSO	1.22	3.91	1.12	0.99
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2DMSO	1.14	3.64	1.14	1.10
(*p*-tolyl)$_2$SnCl$_2$·2Ph$_3$AsO	1.08	3.64	1.01	0.98
(*p*-ClC$_6$H$_4$)$_2$SnCl$_2$·2Ph$_3$AsO	0.99	3.51	0.86	0.90
(*m*-ClC$_6$H$_4$)$_2$SnCl$_2$·2Ph$_3$AsO	1.01	3.70	0.99	1.01

[a] Error ±0.03 mm s^{-1}. [b] Relative to CaSnO$_3$ or BaSnO$_3$.

cis-[SnR_2] configurations. Further, on the basis of the Bancroft correlation [44] that for diorganotin(IV) octahedral structures the *QS* values decrease smoothly from 4 mm s^{-1} as the C–Sn–C angle decreases from linearity, it is obvious that the ring substituents do not impose any appreciable steric distortion of the R–Sn–R angle relative to the diphenyltin case. Nevertheless, some degree of distortion from ideal geometry is generally inferred for the complexes from the multiplicity of the Sn–C bands observed in the infrared (Table 4). The ν(Sn–Cl) bands were too poorly resolved to allow unambiguous stereochemical assignments of the chloro groups. The pattern of higher *QS* values for the *p*-tolyltin complexes over *p*-chlorophenyltins is reflected also in the isomer shift (*IS*) values, indicating the Mössbauer nucleus to be subject to the normal mesomeric electronic effects of the aryl groups bound to it.

2. Complexes with bidentate ligands

The frequencies associated with the skeletal C=C and C=N stretches in the 1,10-phenanthroline and 2,2′-bipyridine ligands show the expected shift to higher wavenumbers following chelation to the diaryltin dihalides and diisothiocyanates (Table 6). In the case of the diisothiocyanates, complexation is also accompanied by a shift to lower frequencies of the asymmetric C=N stretch of the NCS moiety (Table 6). The latter complexes reveal *QS* values of about 2 mm s^{-1} in their Mössbauer spectra (Table 7), which argue strongly for *cis*-[SnR_2] configurational assignments. This is corroborated by the presence of the both the asymmetric and symmetric Sn–C stretching bands (Table 6) in the infrared spectra of these adducts.

For the diaryltin dichloride complexes, including the previously reported complex (p-$ClC_6H_4)_2SnCl_2 \cdot Me_2$bipy (entry 18, Table 7) [28], the *QS* values in the majority of the cases are around 3.40 mm s^{-1} (Table 7), and are typical of distorted *trans*-[SnR_2] geometries [17,44]. *Cis*-geometries, such as were revealed by crystallographic data for (p-tolyl)$_2SnCl_2 \cdot$ bipy [15] and (p-$ClC_6H_4)_2SnCl_2 \cdot Me_2$bipy (entry 17, Table 7) [29], seem to be indicated by the Mössbauer data (*QS* ca. 2 mm s^{-1}) for the related complexes of (m-$ClC_6H_4)_2SnCl_2$ with bipy and phen. Literature reports of *cis*-[SnR_2] octahedral structures among diorganotin dihalide complexes have previously been limited to the bis(heteroaryl)tin(IV) dihalide adducts, (3-$C_4H_3O)_2SnX_2 \cdot$ bipy (X = Cl (*QS* 2.02 mm s^{-1}); X = Br (*QS* 2.13 mm s^{-1})) and (3-$C_4H_3S)_2SnCl_2 \cdot$ bipy (*QS* 2.00 mm s^{-1}) [45], and the crystallographically characterized complex, $Ph_2Sn(NCS)_2 \cdot$ bipy [19].

It is of interest that (p-tolyl)$_2SnCl_2 \cdot Me_2$bipy gave a three-line Mössbauer spectrum which was resolved into two Lorentzian doublets with Mössbauer parameters consistent with *cis*- (*IS* 0.85, *QS* 2.23 mm s^{-1}) and *trans*- (*IS* 1.14, *QS* 3.59 mm s^{-1}) [SnR_2] assignments (entry 16; Table 7). An alternative assignment for the set of lower *IS* and *QS* values is a five-coordinated tin structure involving a unidentate bonding mode for the ligand, which would be unprecedented. We consider this bonding mode to be unlikely in view of the reluctance of the ligand even to participate in bridging [46,47]. Further, the predicted C–Sn–C bond angle on the Brancroft model [44] associated with the *QS* value of 2.23 mm s^{-1} is 110.7°, which agrees closely with documented *cis*-octahedral values but is at the lower end of the scale for basal angles commonly encountered for trigonal bipyramidal coordination. Thus, the calculated value agrees favourably with the experimentally determined values for *cis*-(p-tolyl)$_2SnCl_2 \cdot$ bipy (111° (calc) vs. 108.7° (expt)) and

Table 6

Selected IR bands [a] (cm^{-1}) for diorganotin(IV) dihalide and diisothiocyanate complexes of nitrogen-donor ligands

Complex	ν(C=C) + ν(C=N)	ν(Sn–C)	ν(Sn–Cl)
Et(n-Pr)$SnCl_2$·bipy	1594s; 1435vs	552w; 526w; 500w	230s,br
EtMe$SnCl_2$·bipy	1594s; 1434s	550m; 525w	240s,br
Et(n-Pr)$SnCl_2$·phen	1620m; 1515s; 1430s	550w; 530w; 502w	235s
EtMe$SnCl_2$·phen	1622ms; 1512vs; 1420vs	544m; 522w	240s
Et(n-Pr)$SnCl_2$·Me_2bipy	1610vs; 1405ms	545ms	245s,br; 220s
EtMe$SnCl_2$·Me_2bipy	1610vs; 1400ms	542ms	242s,br
Et(n-Pr)$SnCl_2$·Me_4phen	1610m; 1522s; 1430s	555m	238s,br; 218s
EtMe$SnCl_2$·Me_4phen	1606m; 1520s; 1430s	550m	240s,br
EtMeSn$(NCS)_2$·phen	1624m; 1518ms; 1425s	568s; 555sh	2030vs,br [b]
(*p*-tolyl)$_2SnCl_2$·bipy	1595ms; 1436s	286w; 214m	256s,br
(*p*-$ClC_6H_4)_2SnCl_2$·bipy	1600m; 1435s	296m	258s; 240s
(*m*-$ClC_6H_4)_2SnCl_2$·bipy	1590ms; 1432s	284s; 230w	258ms,sh
(*p*-tolyl)$_2SnCl_2$·phen	1620m; 1515ms; 1422s	248m,sh	260s,br
(*p*-$ClC_6H_4)_2SnCl_2$·phen	1620m; 1525ms; 1420s	290m,sh	250s,br
(*m*-$ClC_6H_4)_2SnCl_2$·phen	1616m; 1510ms; 1420s	284s; 232w	256m,sh; 238w
(*m*-$ClC_6H_4)_2SnCl_2$·Me_2bipy	1605s	280s	256m,sh
Ph_2SnCl_2·Me_2bipy	1615s; 1426ms	295ms; 270vs,br	240s,br
(*p*-tolyl)$_2SnCl_2$·Me_4phen	1616m; 1526s; 1430ms	284m,sh; 206m,br	260s,br; 246m
(*p*-$ClC_6H_4)_2SnCl_2$·Me_4phen	1615m; 1536s; 1430s	280m,sh	258s; 240s
(*m*-$ClC_6H_4)_2SnCl_2$·Me_4phen	1530m	285ms,sh; 275s	260ms,sh
Ph_2SnCl_2·Me_4phen	1620w; 1528m; 1430s	294m	260s; 240s
(*p*-tolyl)$_2Sn(NCS)_2$·bipy	1605s; 1440s	295m,br; 220m,br	2000vs,br [b], 2030vs
(*p*-$ClC_6H_4)_2Sn(NCS)_2$·bipy	1602ms; 1440s	295w; 275s; 230vw	2030vs,br [b]
(*p*-tolyl)$_2Sn(NCS)_2$·phen	1585w; 1430m	298m,br; 215m,br	2040vs [b]; 2000vs
(*p*-$ClC_6H_4)_2Sn(NCS)_2$·phen	1625w; 1520m; 1425s	295m; 280sh; 240m	2045vs [b]; 2002vs
(*p*-tolyl)$_2Sn(NCS)_2$·Me_2bipy	1615ms; 1415w	270s; 210m,sh	2030vs,br [b]
(*p*-$ClC_6H_4)_2Sn(NCS)_2$·Me_2bipy	1606s; 1450s	285sh; 275ms; 225m,br	2030vs,br [b]; 1995vs
$Ph_2Sn(NCS)_2$·Me_2bipy	1616s; 1428ms;	275m; 230m	2030vs,br [b]
(*p*-tolyl)$_2Sn(NCS)_2$·Me_4phen	1620w; 1532s; 1432ms	290m,br; 230w	2040vs [b]; 2008vs

[a] IR data refer to Nujol mulls. [b] ν(C–N) stretching vibrations.

cis-(*p*-$ClC_6H_4)_2SnCl_2$ · Me_2bipy (100° (calc) vs. 106.2° (expt)), but less so with the literature values for five-coordinated complexes, namely Ph_2SnCl_2 · (benzthiazole) [48] (angle C–Sn–C (X-ray) 132.5°; *IS* 1.36, *QS* 2.92 mm s^{-1}) and Ph_2SnCl_2 · (2,6-lutidine *N*-oxide) [49] (angle C–Sn–C (X-ray) 124.1°; *IS* 1.36, *QS* 2.92 mm s^{-1}). Interestingly, the coexistence of *cis*-R_2SnX_4 octahedral and *cis*-R_2SnX_3 trigonal bipyramidal structures has been inferred [17] from a Mössbauer study for Ph_2SnF_2 · 0.5phen, and explained in terms of fluorine bridging. It should be noted, however, that chlorine bridging which dominates the structure of Me_2SnCl_2 [50] is conspicuously absent in Ph_2SnCl_2 [51], and by inference also in (*p*-tolyl)$_2SnCl_2$.

While a quantitative estimate of the amount of each isomer present in (*p*-tolyl)$_2SnCl_2$ · Me_2bipy cannot be made from the Mössbauer spectrum, a higher proportion of *trans*-isomer is qualitatively evident. Attempts to separate the geometrical isomers by recrystallisation from methanol or dimethylformamide were unsuccessful. On the other hand, recrystallisation from hot toluene gave a product whose Mössbauer spectrum indicated almost equal amounts of both isomers. A similar

Table 7

^{119m}Sn Mössbauer data [a] for diorganotin(IV) dihalide and diisothiocyanate complexes of nitrogen-donor ligands

Complex	*IS* [b]	*QS*	Γ_1	Γ_2
1. Et(n-Pr)$SnCl_2$·bipy	1.57	4.07	0.99	1.00
2. EtMe$SnCl_2$·bipy	1.51	4.04	1.10	1.03
3. Et(n-Pr)$SnCl_2$·phen	1.57	4.14	1.13	1.07
4. EtMe$SnCl_2$·phen	1.51	4.01	1.24	1.23
5. Et(n-Pr)$SnCl_2$·Me_2bipy	1.52	4.04	1.08	1.03
6. EtMe$SnCl_2$·Me_2bipy	1.49	4.07	1.05	0.97
7. Et(n-Pr)$SnCl_2$·Me_4phen	1.52	4.11	1.09	0.97
8. EtMe$SnCl_2$·Me_4phen	1.49	3.97	1.00	0.99
9. EtMeSn$(NCS)_2$·phen	1.42	4.28	1.14	1.07
10. (p-tolyl)$_2SnCl_2$·bipy	1.04	2.25	0.93	0.98
11. (p-ClC_6H_4)$_2SnCl_2$·bipy	1.20	3.53	1.10	1.12
12. (m-ClC_6H_4)$_2SnCl_2$·bipy	0.96	1.80	0.89	1.07
13. (p-tolyl)$_2SnCl_2$·phen	1.24	3.58	0.99	1.03
14. (p-ClC_6H_4)$_2SnCl_2$·phen	1.21	3.53	1.14	1.07
15. (m-ClC_6H_4)$_2SnCl_2$·phen	0.95	2.10	1.18	0.97
16. (p-tolyl)$_2SnCl_2$·Me_2bipy [c]	0.85	2.23	0.92	0.88
	1.14	3.59	0.81	0.88
(p-ClC_6H_4)$_2SnCl_2$·Me_2bipy				
17. *cis*-isomer	0.84	1.99	1.04	1.00
18. *trans*-isomer	1.14	3.49	0.91	0.96
19. (m-ClC_6H_4)$_2SnCl_2$·Me_2bipy	1.02	3.38	1.03	0.98
20. (C_6H_5)$_2SnCl_2$·Me_2bipy	1.10	3.33	0.92	0.91
21. (p-tolyl)$_2SnCl_2$·Me_4phen	1.23	3.57	1.01	1.02
22. (p-ClC_6H_4)$_2SnCl_2$·Me_4phen	1.16	3.38	1.05	0.99
23. (m-ClC_6H_4)$_2SnCl_2$·Me_3phen	1.16	3.22	0.89	0.84
24. Ph_2SnCl_2·Me_4phen	1.26	3.50	1.11	0.99
25. (p-tolyl)$_2$Sn$(NCS)_2$·bipy	0.70	2.42	0.93	0.91
26. (p-ClC_6H_4)$_2$Sn$(NCS)_2$·bipy	0.82	2.18	0.89	0.91
27. (p-tolyl)$_2$Sn$(NCS)_2$·phen	0.77	2.47	0.94	0.98
28. (p-ClC_6H_4)$_2$Sn$(NCS)_2$·phen	0.80	2.22	0.93	1.06
29. (p-tolyl)$_2$Sn$(NCS)_2$·Me_2bipy	0.78	2.34	0.87	0.86
30. (p-ClC_6H_4)$_2$Sn$(NCS)_2$·Me_2bipy	0.72	2.17	0.96	0.91
31. Ph_2Sn$(NCS)_2$·Me_2bipy	0.83	2.08	1.19	0.97
32. (p-tolyl)$_2$Sn$(NCS)_2$·Me_4phen	0.69	2.32	0.88	0.98

[a] Error ±0.03 mm s^{-1}. [b] Relative to $CaSnO_3$ or $BaSnO_3$. [c] 3-line Mössbauer spectrum fitted as a pair of Lorentzian doublets.

result was obtained when the complex was prepared at 0 °C in ethanol. Another approach involved the displacement of a weaker ligand with Me_2bipy in a complex which is unequivocally *trans*; this approach with *trans*-(p-tolyl)$_2SnCl_2$·2DMF (*IS* 1.22, *QS* 3.63 mm s^{-1}) also failed to yield the expected *trans* isomer. An attempted separation of the isomers by column chromatography (silica gel) was thwarted by the poor solubility of the complex. The difficulty encountered in separating the isomers of (p-tolyl)$_2SnCl_2$·Me_2bipy, in contrast to the case of (p-ClC_6H_4)$_2SnCl_2$·Me_2bipy [28,29], may be due in part to the small *cis-trans* energy difference for the complex.

Data for complexes of the mixed dialkyltin dihalides are also included in Table 7, and show *QS* values in the 4 mm s^{-1} range, comparable to those of the correspond-

ing symmetrical dialkyltin(IV) complexes [17]. *Trans*-[SnR_2] geometries are therefore postulated for these, as well as for $MeEtSn(NCS)_2 \cdot$ phen. Seemingly, the tendency (on steric grounds) for the NCS groups to the influence *cis*-[SnR_2] stereochemistry in Ph_2Sn chelates [18] and in divinyltins [52] is masked for the mixed alkyl complex by the influence of the stronger electronic effects of the alkyl groups.

Selected IR data for the complexes are given in Table 6. The uncomplexed Lewis acids, $MeEtSnCl_2$ and $Et(n\text{-}Pr)SnCl_2$, show dual Sn–C stretching frequencies at 554, 550 and 552, 510 cm^{-1} respectively. Their Sn–Cl stretching bands are found at 350 and 348 cm^{-1}, respectively. These values are comparable to those obtained for the symmetrical dialkyltin dihalides [53]. The Sn–C stretching frequencies for the mixed dialkyltin dihalide adducts and $MeEtSn(NCS)_2 \cdot$ phen are assigned as shown in Table 6. A single ν(Sn–C) band (the asymmetric stretch) corroborates the *trans*-[SnR_2] geometry deduced earlier from Mössbauer *QS* values. The Sn–C symmetric stretch is IR forbidden, but may appear as a weak band as a result of structural distortion. Although the observation of a second (or third) band in some cases may attest to this, the picture is complicated by the possibility of rotational isomers (*trans / gauche*) with alkyl groups higher than methyl [33]. The tin–halogen stretching frequencies of the mixed dialkyltin dichlorides are lowered by ca. 100 cm^{-1} on complexation with phen or bipy derivatives (Table 6), as has been observed

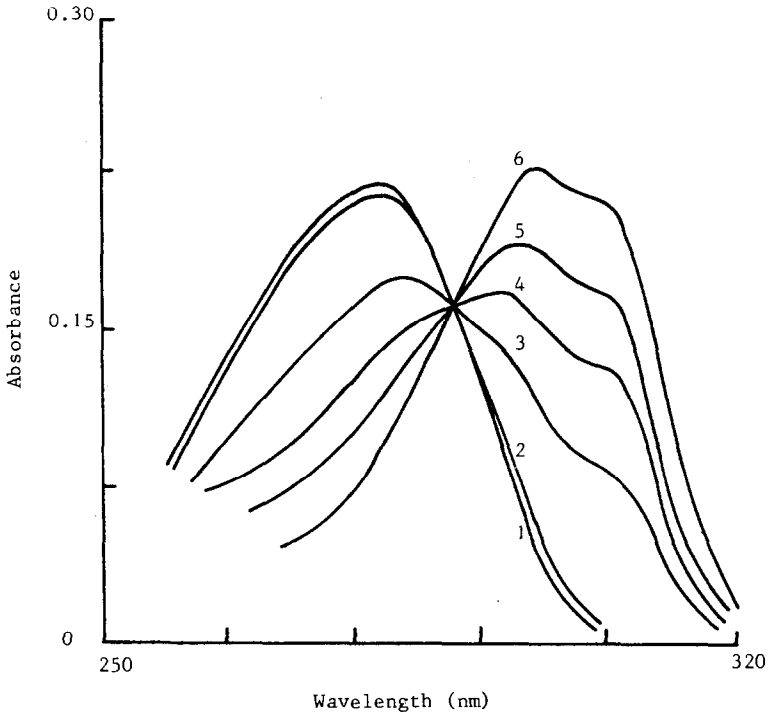

Fig. 1. The absorption spectra of 2,2′-bipyridyl (1.5×10^{-5} *M*) in acetonitrile at $26 \pm 1°C$, in the presence of varying amounts of $MeEtSnCl_2$: (1) 0; (2) 1.5×10^{-5}; (3) 3.0×10^{-4}; (4) 7.5×10^{-4}; (5) 1.5×10^{-3}; (6) 6.0×10^{-3} *M*.

Table 8

Formation constants for complexes of dialkyltin dichloride with bipy and Me_2bipy at 26 °C in acetonitrile

Complex	$\log K\ (r)$ [a]	Ref.
$Me_2SnCl_2 \cdot$ bipy	3.30 [b]	39
$MeEtSnCl_2 \cdot$ bipy	3.39 (0.985)	This work
$Et_2SnCl_2 \cdot$ bipy	3.47 [b]	39
$Et(n\text{-}Pr)SnCl_2 \cdot$ bipy	3.18 (0.990)	This work
$n\text{-}Pr_2SnCl_2 \cdot$ bipy	3.07 [b]	39
$n\text{-}Bu_2SnCl_2 \cdot$ bipy	3.03 [b]	39
$Me_2SnCl_2 \cdot Me_2$bipy	3.98 [b]	54
$MeEtSnCl_2 \cdot Me_2$bipy	3.81 (0.978)	This work
$Et(n\text{-}Pr)SnCl_2 \cdot Me_2$bipy	3.78 (0.991)	This work

[a] Correlation coefficient in parentheses. [b] At 26 ± 1 °C.

for the analogous symmetrical dialkyltin dichloride complexes [53,54]. However, the bands are broad, and their resolution into ν_{asym} and ν_{sym}(Sn–Cl) stretches could not be made unambiguously. The broadness of the tin–chlorine bands has been commented upon in an earlier study [53].

The formation constants of the adducts of $MeEtSnCl_2$ and $Et(n\text{-}Pr)SnCl_2$ with bipyridyl ligands were determined spectroscopically at 26 °C in acetonitrile as outlined in the experimental section. Figure 1 shows, as an example, the way the ultraviolet spectrum of 2,2′-bipyridine changes in the presence of various concentrations of the methylethyltin(IV) dichloride. Only one isosbestic point is observed in all four cases, indicating the formation of a 1 : 1 adduct for $RR'SnCl_2$ to ligand ratios $< 10^{-3}/1$.

The formation constants for the bipyridyl complexes are listed in Table 8, together with those for some related complexes taken from the literature. Previous studies on the bipy adducts of symmetrical dialkyltin dichlorides have indicated that the formation constants generally increase with increasing electronegativity of the alkyl group [39]. (The abnormally large formation constant for $Et_2SnCl_2 \cdot$ bipy, however, was regarded as an anomaly [39].) Our results for the mixed dialkyltin dichloride complexes confirm the trend and suggest the following order of stabilities: $Et_2 > MeEt > Me_2 > Et(n\text{-}Pr) > (n\text{-}Pr)_2 > (n\text{-}Bu)_2$.

The ligand Me_2bipy, being a stronger base than bipy [55], is expected to form stronger complexes with the diorganotins. This is reflected in the higher formation constants of these complexes relative to those of bipy (Table 8).

3. Complexes with bidentate (N,O) ligands

The ultraviolet spectral data for the oxinate and 2-methyloxinate (quin) complexes in chloroform are shown in Table 9. The oxinates show a strong band at ca. 380 nm, and the 2-methyloxinates at ca. 363 nm. These bands, which are at higher wavelengths than those for the uncomplexed ligands, are strongly indicative of chelation [37,56,57]. Except for the mixed dialkyltin complexes of quin, all the other complexes additionally show either or both of two peaks located at 335 and 320 nm. The observation of the latter peaks in the case of the above complexes suggests the possibility of a coordination lower than six in solution as a result of departure from chelating behaviour of the ligand.

Table 9

Ultraviolet absorption spectra [a,b]

Compound	λ_{max} (nm)
MeEtSn(oxin)$_2$	378 (3.69), 335 (3.51)
Et(n-Pr)Sn(oxin)$_2$	379 (3.70), 335 (3.54)
(*p*-tolyl)$_2$Sn(oxin)$_2$	381 (3.72), 335 (3.50), 320 (3.44)
(*p*-ClC$_6$H$_4$)$_2$Sn(oxin)$_2$	380 (3.77), 335 (3.50)
MeEtSn(quin)$_2$	363 (3.69)
Et(n-Pr)Sn(quin)$_2$	364 (3.68)
(*p*-tolyl)$_2$Sn(quin)$_2$	361 (3.56), 336 (3.54), 319 (3.55)
(*p*-ClC$_6$H$_4$)$_2$Sn(quin)$_2$	364 (3.62), 320 (3.58)

[a] Spectral data refer to oxin and quin bands in $CHCl_3$. [b] Log ϵ values are given in parentheses.

The chemical shifts of the 2-H, 3-H and 4-H ring protons (Table 10) in the mixed dialkyltin bischelates are in close agreement with those reported for the symmetrical dialkyltins [58], and differ only slightly from those for the free ligand. Since considerable downfield shifts of the 2-H and 4-H protons are expected for strong chelation in the case of the oxinates [59], the results indicate that the bisoxinates are not strongly chelated in solution. For the mixed dialkyltin bis(quin) complexes, upfield shifts in the 4-H resonances (Table 10) are observed, indicative of weakened Sn–N interactions [58]. The chemical shifts of the oxinato protons for the diaryltin complexes were not assigned because of the complexity of the spectra. A similar spectral complexity was also reported previously by Kawasaki [58], who has attributed the effect to the anisotropy of the aryl groups bonded to the metal.

In the infrared, the Sn–O and Sn–N stretching bands are expected in the region 600–200 cm^{-1} [57,60], but assignments of these bands proved to be generally tenuous. However, for the case of MeEtSn(quin)$_2$ and Et(n-Pr)Sn(quin)$_2$, the medium intensity bands located at 310 and 320 cm^{-1}, respectively, may be reasonably assigned to Sn–N vibrations. In Me$_2$Sn(oxin)$_2$, ν(Sn–N) appears at 395 cm^{-1} [57]. The Sn–N bond distance in this complex is 2.35 Å [23], which is shorter than that (2.542, 2.597 Å) in Et(n-Pr)Sn(quin)$_2$ [27]. The longer Sn–N bonds in the latter

Table 10

^{1}H NMR chemical shifts [a] for the oxinate moiety complexed to symmetrical and mixed dialkyltins

Compound	δ(2-H)	δ(3-H)	δ(4-H)	Ref.
Hoxin	8.73	7.38	8.04	[b]
Hquin	–	7.22	7.98	[b]
Me$_2$Sn(oxin)$_2$ [c]	8.45	7.08	8.10	[d]
MeEtSn(oxin)$_2$	8.48	7.07	8.05	[b]
Et$_2$Sn(oxin)$_2$ [c]	8.44	7.07	8.06	[d]
Et(n-Pr)Sn(oxin)$_2$	8.45	7.05	8.05	[b]
(n-Pr)$_2$Sn(oxin)$_2$ [c]	8.42	7.07	8.05	[d]
MeEtSn(quin)$_2$	–	7.06	8.12	[b]
Et(n-Pr)Sn(quin)$_2$	–	7.05	8.11	[b]

[a] In $CDCl_3$. [b] This work. [c] In CH_2Cl_2. [d] Ref. 58.

Table 11

^{119m}Sn Mössbauer data [a] for diorganotin(IV) oxinates

Compound	*IS* [b]	*QS* [c]	ρ (*QS*/*IS*)	Ref.
$Me_2Sn(oxin)_2$	0.88	1.98		[d]
$MeEtSn(oxin)_2$	0.71	1.996	2.81	[e]
		(−1.96)		
$Et_2Sn(oxin)_2$	0.99	2.02		[d]
$Et(n\text{-}Pr)Sn(oxin)_2$	0.94	2.09	2.22	[e]
		(−1.96)		
$n\text{-}Pr_2Sn(oxin)_2$	0.98	2.08		[d]
$Ph_2Sn(oxin)_2$	0.78	1.64		[d]
$(p\text{-tolyl})_2Sn(oxin)_2$	0.77	1.78	2.31	[e]
		(−1.80)		
$(p\text{-}ClC_6H_4)_2Sn(oxin)_2$	0.71	1.66	2.34	[e]
		(−1.80)		
$Me_2Sn(quin)_2$	1.29	3.15		26
$MeEtSn(quin)_2$	1.15	3.14	2.73	[e]
		(+3.92)		
$Et_2Sn(quin)_2$	1.39	2.79		[f]
$Et(n\text{-}Pr)Sn(quin)_2$	1.24	3.17	2.56	[e]
		(+3.92)		
$Ph_2Sn(quin)_2$	1.04	3.50		26
$(p\text{-tolyl})_2Sn(quin)_2$	0.77	1.75	2.27	[e]
		(−1.80)		
$(p\text{-}ClC_6H_4)_2Sn(quin)_2$	0.77	1.45	1.88	[e]
		(−1.80)		

[a] Error ±0.03 mm s^{-1}. [b] Relative to $CaSnO_3$ or $BaSnO_3$. [c] Calculated [52,62] *QS* values appropriate for *cis*- and *trans*-[SnR_2] configurations are given in parentheses. [d] R.C. Poller and J.N.R. Ruddick, J. Chem. Soc. A, (1969) 2273. [e] This work. [f] S.N. Bhide, P. Umapathy. M.P. Gupta and D.N. Sen, J. Inorg. Nucl. Chem., 40 (1978) 1003.

complex thus appear to be in accord with the lower value of the Sn–N stretching frequency.

The ^{119m}Sn Mössbauer data for the complexes are listed in Table 11. Within experimental error all the compounds show ρ values ($\rho = QS/IS$) whose magnitudes indicate higher than four-coordinated environments at tin. Only the $(p\text{-}ClC_6H_4)_2Sn(quin)_2$ complex with a ρ value of 1.9, represents a borderline case in terms of the rule which says that values below 1.8 indicate four-coordinated tin(IV) while those above 2.1 are associated with higher-than-four coordination [61]. That the Sn–N interaction is weak in the latter complex is indicated by the presence of a non-chelated ligand band in its UV spectrum. The quadrupole splitting (*QS*) values for the diaryl- and dialkyl-tin bisoxinates and the diaryltin bis(quin) complexes (Table 11) are in the region 2 mm s^{-1}, while those for $MeEtSn(quin)_2$ and $Et(n\text{-}Pr)Sn(quin)_2$ are much higher. On the basis of the point charge model arguments [42,43], *trans*- or distorted *trans*-[SnR_2] geometries may be assigned to the above two mixed dialkyltin bis(quin) complexes, and *cis*-structures * to the

* We have recently confirmed the *cis*-structure by X-ray diffraction for the mixed diaryltinbisoxinate $(p\text{-tolyl})(p\text{-}ClC_6H_4)Sn(oxin)_2$: C–Sn–C 106.8(2), N–Sn–O 74.59(7)°, Sn–N 2.322(2), Sn–O 2.084(2) Å.

remainder. The observed *QS* values are in close agreement with calculated values [56,62] for the *cis*-structure (Table 11). It is interesting to note that the *QS* values for $(p\text{-tolyl})_2Sn(quin)_2$ and $(p\text{-}ClC_6H_4)_2Sn(quin)_2$ complexes are similar to that for $Ph_2Sn(oxin)_2$, whilst a larger *QS* value is observed for $Ph_2Sn(quin)_2$ which has been assigned a distorted *trans*-$[SnR_2]$ geometry [26]. Seemingly, in the last case, the steric congestion imposed by the methyl substituent in the ligand in the regular *cis*-structure is relieved in a distorted *trans*-arrangement in which one end of the bidentate ligand (N atom) is pushed farther away from the tin atom [26]. But the presence of substituents in the phenyl ring introduces additional steric effects which are apparently better accomodated in a *cis*-structure.

For both $MeEtSn(quin)_2$ and $Et(n\text{-}Pr)Sn(quin)_2$, the observed values differ from the calculated values for ideal *cis*- (1.96 mm s^{-1}) or *trans*- (3.92 mm s^{-1}) geometries (Table 11), but appear to be essentially in accord with *trans*-geometry. In this respect, a parallel may be drawn with $Me_2Sn(quin)_2$, which was assigned a distorted *trans*-configuration on the basis of its Mössbauer (*QS* 3.15 mm s^{-1}) and NMR data ($^2J(^{119}Sn\text{–}Me)$ 88.7 Hz [26]; $\delta(^{119}Sn)$ −228 ppm [62]; cf. ^2J 71.2 Hz [63]; $\delta(^{119}Sn)$ −237 ppm [62] for $Me_2Sn(oxin)_2$). In the present case, the bulkier ethyl or propyl groups could be expected to present greater steric repulsions. On the basis of the point-charge model [44], the estimated C–Sn–C bond angle for the mixed alkyl complexes is about 133° (cf. 138° for $Me_2Sn(quin)_2$ [26]), which is intermediate between the values for regular *cis*- and *trans*-geometries. Kepert [64] has labelled such intermediate geometries (having C–Sn–C angles of 135–155°) as skew (or trapezoidal bipyramidal) structures.

Acknowledgement

We are grateful to the Institute of Advanced Studies of the University of Malaya for generous support of this research.

References

1 P.J. Smith, J. Organomet. Chem. Libr., 12 (1981) 97.
2 J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 24 (1978) 251.
3 R.C. Poller, The Chemistry of Organotin Compounds, Logos Press, London, 1970; Rev. Silicon, Germanium, Tin, Lead Compounds, 3 (1978) 243.
4 V.S. Petrosyan, N.S. Yashina and O.A. Reutov, Adv. Organomet. Chem., 14 (1976) 63.
5 S.W. Ng, C.L. Barnes, M.B. Hossain, D. van der Helm, J.J. Zuckerman and V.G. Kumar Das, J. Am. Chem. Soc., 104 (1982) 5359.
6 S.W. Ng, C.L. Barnes, D. van der Helm and J.J. Zuckerman, Organometallics, 2 (1983) 600.
7 V.G. Kumar Das and W. Kitching, J. Organomet. Chem., 13 (1968) 523.
8 B.V. Liengme, R.S. Randall and J.R. Sams, Can. J. Chem., 50 (1972) 3212.
9 H.A. Bent, J. Inorg. Nucl. Chem, 19 (1961) 43.
10 J.S. Tse, T.K. Sham and G.M. Bancroft, Can. J. Chem., 57 (1979) 2223.
11 F.P. Mullins, Can. J. Chem., 49 (1971) 2719.
12 V.G. Kumar Das, S.W. Ng, P.J. Smith and R. Hill, J. Chem. Soc., Dalton Trans., (1981) 552.
13 T.K. Sham, J.S. Tse, V. Wellington and G.M. Bancroft, Can. J. Chem., 55 (1977) 3487.
14 K.L. Jaura and V.K. Verma, J. Inorg. Nucl. Chem., 36 (1973) 2361.
15 V.G. Kumar Das, Chen Wei, C.K. Yap and T.C.W. Mak, J. Organomet. Chem., 299 (1986) 41.
16 R.C. Poller, J.N.R. Ruddick, M. Thevarasa and W.R. McWhinnie, J. Chem. Soc. A, (1969) 2327.
17 A.J. Crowe and P.J. Smith, J. Organomet. Chem., 224 (1982) 223.
18 M.A. Mullins and C. Curran, Inorg. Chem., 7 (1968) 2584.

19 E.J. Gabe, L. Prasad, Y. Le Page and F.E. Smith, Acta Crystallogr., Sect. B, 38 (1982) 256.
20 R.V. Parish and C.E. Johnson, J. Chem. Soc. A, (1971) 1906.
21 P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc., Dalton Trans., (1975) 826.
22 T. Kimura, N. Yasuoka, N. Kasai and M. Kakudo, Bull. Chem. Soc. Jpn., 45 (1972) 1649.
23 E.O. Schlemper, Inorg. Chem., 6 (1967) 2012.
24 P.G. Harrison, T.J. King and R.C. Phillips, J. Chem. Soc., Dalton Trans., (1976) 2317.
25 D.L. Kepert, J. Organomet. Chem., 107 (1976) 49.
26 V.G. Kumar Das, S.W. Ng, Joginder Singh, P.J. Smith and R. Hill, J. Organomet. Chem., 214 (1981) 183.
27 V.G. Kumar Das, C. Wei, C.K. Yap and E. Sinn, J. Chem. Soc., Chem. Commun., (1984) 1418.
28 V.G. Kumar Das, C.K. Yap and P.J. Smith, J. Organomet. Chem., 291 (1985) C17.
29 V.G. Kumar Das, C.K. Yap, C. Wei, P.J. Smith and T.C.W. Mak, J. Chem. Soc., Dalton Trans., (1987) 129.
30 K.A. Kocheshkov and M.M. Nad, Chem. Ber., 67B (1934) 717; CA 28 (1934) 4711.
31 R.K. Ingham, S.D. Rosenberg and H. Gilman, Chem. Rev., 60 (1960) 459; O.A. Ptitsyna, O.A. Reutov and M.F. Turchinskii, Dokl. Akad. Nauk SSSR, 114 (1957) 110; CA 52 (1957) 1090.
32 K.L. Jaura and K. Lal, Inorg. Nucl. Chem. Letts., 13 (1977) 297.
33 K.L. Jaura, K.K. Dhingra, R.K. Mahajan and K. Lal, Z. Anorg. Allg. Chem., 445 (1978) 242.
34 D. Seyferth and E.G. Rochow, J. Am. Chem. Soc., 77 (1955) 1302.
35 E. Ochiai, J. Org. Chem., 18 (1953) 534.
36 D.D. Perrin, W.l.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, 2nd Edition, Pergamon Press, Oxford, 1980.
37 A.H. Westlake and D.F. Martin, J. Inorg. Nucl. Chem., 27 (1965) 1579.
38 F.W.D. Woodhams, Software Microsyst., 1 (1982) 108.
39 M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, J. Organomet. Chem., 4 (1965) 308.
40 R.S. Drago and D.W. Meek, J. Phys. Chem., 65 (1961) 1446.
41 F.A. Cotton, R. Francis and W.D. Horrocks, J. Phys. Chem., 64 (1960) 1534.
42 B.W. Fitzsimmons, N.J. Seeley and A.W. Smith, J. Chem. Soc. A, (1969) 143.
43 B.W. Fitzsimmons, N.J. Seeley and A.W. Smith, J. Chem. Soc. A, (1970) 935.
44 T.K. Sham and G.M. Bancroft, Inorg. Chem., 14 (1975) 2281.
45 D.W. Allen, D.J. Derbyshire, J.S. Brooks, S.J. Blunden and P.J. Smith, J. Chem. Soc., Dalton Trans., (1984) 1889.
46 A.S. Mufti and R.C. Poller, J. Organomet. Chem., 3 (1965) 99.
47 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, J. Inorg. Nucl. Chem., 28 (1966) 2937.
48 P.G. Harrison and K.C. Molloy, J. Organomet. Chem., 152 (1978) 63.
49 A.L. Rheingold, S.W. Ng and J.J. Zuckerman, Organometallics, 3 (1984) 233.
50 A.G. Davies, H.J. Milledge, D.C. Puxley and P.J. Smith, J. Chem. Soc. A, (1970) 2862.
51 P.T. Greene and R.F. Bryan, J. Chem. Soc. A, (1971) 2549.
52 G.M. Bancroft and R.H. Platt, Adv. Inorg. Chem. Radiochem., 15 (1972) 59.
53 R.J.H. Clark and C.S. Williams, Spectrochim. Acta, 21 (1965) 1861.
54 W.D. Honnick, M.C. Hughes, C.D. Schaeffer, Jr. and J.J. Zuckerman, Inorg. Chem., 15 (1976) 1391.
55 T.B.W. Einstein and B.R. Penfold, J. Chem. Soc. A, (1968) 3019.
56 T. Moeller and F.L. Pundsack, J. Am. Chem. Soc., 76 (1954) 617.
57 K. Kawasaki and R. Okawara, J. Organomet. Chem., 6 (1966) 249.
58 Y. Kawasaki, Org. Mag. Res., 2 (1970) 165.
59 H.A. Meinema, E. Rivarola and J.G. Noltes, J. Organomet. Chem., 17 (1969) 71.
60 T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, J. Organomet. Chem., 1 (1964) 484.
61 R.H. Herber, H.A. Stöckler and W.T. Reichle, J. Chem. Phys., 42 (1965) 2447.
62 J. Otera, J. Organomet. Chem., 221 (1981) 57.
63 M.M. McGrady and R.S. Tobias, J. Am. Chem. Soc., 87 (1965) 1909.
64 D.L. Kepert, Prog. Inorg. Chem., 23 (1977) 1.