Journal of Organometallic Chemistry, 466 (1994) 69–75

Synthesis and spectroscopic studies (Mössbauer, IR and NMR) of $[R_2SnCl_2bipym]$ (R = butyl or phenyl) and the crystal and molecular structure of $[Ph_2SnCl_2bipym]$

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(Received July 2, 1993)

Abstract

The complexes $[R_2SnCl_2bipym]$ (R = phenyl or butyl, bipym = 2,2′,6,6′-bipyrimidine) were synthesized and studied in solution by ^{1}H- and ^{13}C-NMR spectroscopy and in the solid state by IR and Mössbauer spectroscopy. The latter was also performed in frozen ethanolic solution. The structure of the phenyl complex was determined by single crystal diffraction methods.

The value obtained for the angle C–Sn–C in the phenyl compound is 169.3(2)° (X-ray) and 151° (Mössbauer), but the assignment of an octahedral configuration by Mössbauer spectroscopy is consistent with the structure determined by diffraction. The butyl complex is also octahedral and the two techniques show better agreement. The value of the C–Sn–C angle is 171° (Mössbauer in the solid state), 163° (Mössbauer in frozen solution) and 175.1(6)° (X-ray).

The NMR coupling constant, $^1J(^{119}Sn-^{13}C)$, was also used to estimate the C–Sn–C angle. The ^{13}C-NMR spectrum for the butyl complex is markedly concentration-dependent. At the highest concentration, this angle is 138° (Lockhart) and 145° (Holeček); for less concentrated samples the angle tends to decrease. This suggests that the coordination number of tin in solution is less than six.

Key words: Tin; Mössbauer spectroscopy; Nuclear magnetic resonance; Crystal structure

1. Introduction

The established use of cisplatin in cancer chemotherapy [1–4] has led other metal complexes to be investigated as potential anticancer agents and organotin compounds have shown promising activity. Since the first report on the antitumor activity of diorganotins appeared in 1980 [5], over 2000 tin compounds have been tested by NCI [3] — more than of any other element.

Diorganotin(IV) compounds R_2SnX_2 (X = anion) are tetrahedral and with appropriate nitrogen chelating ligands form octahedral complexes [6,7] which resemble the active Pt complexes mentioned above.

Diorganotin complexes have no biological activity if they are stable and have Sn–N bonds of less than 2.39 Å. This suggests that activity is connected with dissociation of the nitrogen ligand as part of the mechanism of action [8].

Most of the active Sn compounds are effective against lymphocytic leukaemia but are less active in the successive steps of the NCI protocols. Diorganotins are the most active, followed by triorganotins. The presence of aromatic nitrogen atoms and phenyl or ethyl groups bound to tin correlates with greater activity [3].

It has been shown recently that a tetraorganotin with easily cleaved Sn–C bond is active against four tumour cell lines giving R_2Sn^{2+} or R_3Sn^+ as the biologically active species [9]. This suggests a mechanism of anti-tumour action that is different from that

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0022-328X/94/$7.00
SSDI 0022-328X(93)23996-B

TABLE 1. Summary of crystal data and intensity collection for [Ph_2SnCl_2bipym]

Formula	$C_{20}H_{16}Cl_2N_4Sn$
Formula weight	501.972
a (Å)	9.024(2)
b (Å)	13.485(3)
c (Å)	18.612(3)
α (deg)	90
β (deg)	118.60(2)
γ (deg)	90
Volume (A^3)	1988(1)
Space group	$P2_1/c$
Z	4
Crystal dimensions (mm)	0.25×0.20×0.15
Density calcd. (g. cm^{-3})	1.677
Temperature	298 K
F(000)	992.0
μ	15.729
Radiation	Mo
Data collection mode	$2\theta-\theta$
Scan speed (deg/min)	1.9
Scan range (deg)	0.8, 0.8
Background counts	1/4 of scan time at the end of scan range
2θ range (deg)	3–56
Reflections collected	4474
Reflections used, $I > 3\sigma(I)$	3678
Final no. variables	144
R_f, R_w	0.047, 0.050

accepted for Pt complexes where the Pt–N bonds are believed to be retained after interaction with DNA [10].

We report two tin complexes, [R_2SnCl_2bipym] (R = phenyl or butyl, bipym = 2,2′,6,6′-bipyrimidine) synthesized and characterized by ^1H- and ^{13}C-NMR spectroscopy in solution. These were also studied in the solid state by IR and Mössbauer spectroscopy, which was also performed in frozen solution. The molecular structure of [Ph_2SnCl_2bipym] was determined by X-ray crystallography and is discussed along with the structure of the butyl complex previously reported [11]. Bipym, which complexes other metals [12], can be bidentate at a single metal atom or it can bridge two metal atoms. We used it in order to obtain heterobimetallic organotin derivatives.

2. Experimental details

2.1. Materials and methods

Bu_2SnCl_2 was a gift from Schering AG (Bergkamen, Germany) and was recrystallized from benzene. Ph_2SnCl_2 was purchased from Fluka (Zurich, Switzerland) and used as received. 2,2′,6,6′-Bipyrimidine was purchased from Ventron-Alfa Inorganics (Beverly, USA) and recrystallized from ethanol. Deuterated chloroform was a Merck UVASOL (Darmstadt, Germany) reagent (> 99.9% deuteration).

The Mössbauer spectra were determined with apparatus and procedures described elsewhere [13], at liquid-nitrogen temperature, with a $Ca^{119}SnO_3$ source, either as solids or as quickly frozen solutions.

IR spectra were obtained using a Perkin-Elmer 983 IR spectrometer in the 4000–200 cm^{-1} region in Nujol or hexachlorobutadiene mulls between CsI disks.

The ^1H- and ^{13}C-NMR spectra were recorded either on an AC200 ($B_0 = 4.7$ T) or on an AM400 ($B_0 = 9.4$ T) Bruker spectrometer. The deuterium signal of the chloroform solvent was used for field-frequency lock. Chemical shifts are relative to TMS; the spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled.

A Nicolet R3 automatic diffractometer was used for the measurement of the cell constants and the data collection.

A summary of crystal data together with details of data collection is given in Table 1. Monitoring of four standard reflections ([1,1,0], [−1,−1,0], [1,1,−1] and [−1,−1,1]) taken every 100 reflections indicated no decay. A ψ-scan of the reflection [1,1,−4], which has the χ angle close to 90°, showed a weak absorption of about 10%. Therefore no correction for absorption was applied. Data were corrected for Lorentz and polarization effects. The structure was solved using the Patterson function to determine the positions of Sn and Cl

TABLE 2. Analytical and Mössbauer data

Compound	M.p. (°C)	C%	H%	N%	I.S. mm/s	Q.S. mm/s	$\Gamma\pm$ mm/s	C–Sn–C exp. (calcd.)
		found (calcd.)						
[Bu_2SnCl_2bipym]	104–107	41.54	5.32	12.29	1.58	4.10	0.89	175
		(41.62)	(5.24)	(12.14)				(171)
					1.50 [a]	3.98 [a]	0.85 [a]	(163) [a]
[Ph_2SnCl_2bipym]	207	47.84	3.15	11.13	1.23	3.43	0.93	169
		(47.89)	(3.21)	(11.16)				(151)

[a] Frozen ethanol solution.

atoms, and Fourier methods to locate the other non-H atoms. Refinement by least-square procedures was applied subsequently. The minimized function $\Sigma\omega(|F_o| - |F_c|)^2$ had the weighting scheme $\omega = a + F_o + cF_o^2$ where a and c are of the order of $2F_o(\text{min})$ and $2/F_o(\text{max})$ [14]. Hydrogen atoms were introduced at fixed positions, C–H distance = 0.96 Å and C–C–H angle = 120°. Only the metal and atoms bound to the metal were refined anisotropically. The calculations were performed on a VAX 3300 using the CAOS program [15]. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography.

2.2. *Synthesis of the compounds*

The adducts were obtained as white solids by mixing hot cyclohexane solutions of the reagents in equimolar amounts, and were recrystallized from a 1 : 1 dichloromethane-cyclohexane mixture. Analytical data are reported in Table 2.

2.3. *IR and Mössbauer data*

The significant bands are listed below (s = strong; m = medium; w = weak; b = broad; v = very). Some reasonable assignments are in parentheses, while absorptions due to the bipym are in italics.

[Ph_2SnCl_2bipym]: 3050–2900 groups of bands; *1587m*; *1569vs*; *1554m,s*; *1545s*; 1477m; 1428s; *1405vs*; 1308w; 1296w; 1263m; 1241m; 1206m; 1183w; 1158w; *1140m*; 1101w; 1065m; 1018m; 1012m; 1006s; 997m; *816m*; 786m; *760s*; 745vs; 735s; 679m,s; 688m; 650s; 470m,s; 458m; 278s,b $\nu(\text{Sn–Cl})_{as} + \nu(\text{Sn–Ph})_{as}$; 225s $\nu(\text{Sn–Cl})_s$.

[Bu_2SnCl_2bipym]: 3080–2900, groups of bands; *1589m*; *1569s*; *1552s*; *1407s*; 1333w; 1295w; 1263m; 1241m; 1206w; 1182vw; 1154m; *1140m*; 1114w; 1100m; 1078m; 1005s; 886w; 874m; *818m*; 807w; 784w; *761s*; 678s; 651s; 621w $\nu(\text{Sn–C})_{as}$; 578vw $\nu(\text{Sn–C})_s$; 244s $\nu(\text{Sn–Cl})_{as}$.

The Mössbauer parameters are shown in Table 2.

2.4. *Diffraction study of [Ph_2SnCl_2bipym]*

TABLE 3. Atomic coordinates (e.s.d.'s in parentheses) for [Ph_2SnCl_2bipym]

	x	*y*	*z*
Sn(1)	0.24532(4)	0.36597(2)	0.22748(2)
Cl(1)	0.2770(2)	0.4780(1)	0.1310(1)
Cl(2)	0.2105(2)	0.2019(1)	0.1647(1)
N(2A)	0.2645(5)	0.4933(3)	0.3215(2)
N(6A)	0.2901(6)	0.5289(4)	0.4516(3)
N(2B)	0.2277(5)	0.2998(3)	0.3436(2)
N(6B)	0.2977(6)	0.3303(4)	0.4814(3)
C(1)	0.5120(6)	0.3534(4)	0.3050(3)
C(2)	0.6114(7)	0.4389(4)	0.3355(3)
C(3)	0.7811(8)	0.4327(5)	0.3893(4)
C(4)	0.8565(9)	0.3413(5)	0.4139(4)
C(5)	0.7634(8)	0.2572(5)	0.3838(4)
C(6)	0.5918(7)	0.2626(4)	0.3298(3)
C(7)	−0.0212(6)	0.3918(3)	0.1691(3)
C(8)	−0.1078(7)	0.4187(4)	0.2114(3)
C(9)	−0.2807(7)	0.4343(4)	0.1711(3)
C(10)	−0.3691(7)	0.4236(4)	0.0872(3)
C(11)	−0.2863(7)	0.3964(4)	0.0441(3)
C(12)	−0.1149(6)	0.3812(4)	0.0845(3)
C(1A)	0.2778(6)	0.4667(4)	0.3937(3)
C(3A)	0.2612(7)	0.5909(4)	0.3068(3)
C(4A)	0.2719(9)	0.6604(5)	0.3630(4)
C(5A)	0.2890(9)	0.6251(5)	0.4352(4)
C(1B)	0.2690(6)	0.3593(4)	0.4073(3)
C(3B)	0.2003(7)	0.2032(5)	0.3519(4)
C(4B)	0.2201(8)	0.1696(5)	0.4264(4)
C(5B)	0.2715(8)	0.2336(5)	0.4890(4)

Atomic coordinates are given in Table 3. Figure 1 shows a computer generated drawing of the compound. The bipym is well adapted for *cis* coordination in an octahedral system, as found in this complex. The coordination sphere is completed by two *trans* phenyl and two *cis* chloro groups. Some distortion of the octahedron is observed. Thus, the angle C(1)–Sn–C(7) is 169.3(2)°, and the other two *trans* bond angles Cl(1)–Sn–N(2B) and Cl(2)–Sn–N(2A) are 163.6(1) and 160.4(1)°, respectively. The five-atom ring Sn–N(2A)–C(1A)–C(1B)–N(2B) produces a small bite angle N(2A)–Sn–N(2B) of 67.9(1)°. These five atoms lie in a plane, deviations are less than 0.09 Å. The small N–Sn–N angle induces a large Cl(1)–Sn–Cl(2) angle (103.81(5)°) so that the sum of the four bond angles in this plane is 360°. Bond distances and angles in the coordination sphere are shown in Table 4.

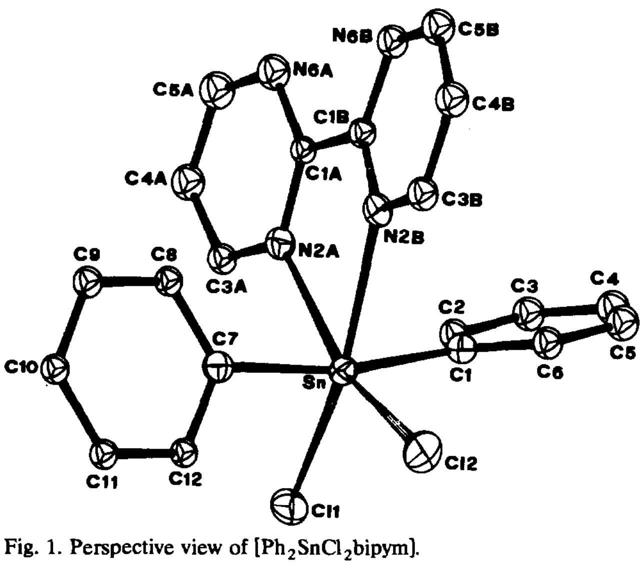

Fig. 1. Perspective view of [Ph_2SnCl_2bipym].

TABLE 4. Bond distances (Å) and angles (°) in the coordination sphere of $[Ph_2SnCl_2bipym]$

Distances	
Sn(1)-Cl(1)	2.466(2)
Sn(1)-Cl(2)	2.451(2)
Sn(1)-C(1)	2.139(7)
Sn(1)-C(7)	2.141(7)
Sn(1)-N(2A)	2.398(4)
Sn(1)-N(2B)	2.413(4)
Angles	
Cl(2)-Sn(1)-Cl(1)	103.81(5)
C(1)-Sn(1)-C(7)	169.3(2)
N(2A)-Sn(1)-N(2B)	67.9(1)
N(2A)-Sn(1)-Cl(1)	95.8(1)
N(2A)-Sn(1)-Cl(2)	160.4(1)
N(2B)-Sn(1)-Cl(1)	163.6(1)
N(2B)-Sn(1)-Cl(2)	92.6(1)
C(1)-Sn(1)-Cl(1)	93.1(1)
C(1)-Sn(1)-Cl(2)	95.5(1)
C(1)-Sn(1)-N(2A)	84.2(2)
C(1)-Sn(1)-N(2B)	84.4(2)
C(7)-Sn(1)-Cl(1)	91.4(1)
C(7)-Sn(1)-Cl(2)	92.8(1)
C(7)-Sn(1)-N(2B)	88.6(2)
C(7)-Sn(1)-N(2A)	85.7(2)

2.5. NMR spectral results

The ^{13}C- and ^{1}H-NMR data of the complexes and those of related compounds, are reported in Tables 5 and 6, respectively. The $^{1}J(^{119}Sn, ^{13}C)$ values have been used to calculate the C–Sn–C bond angle, θ, making use of either the Lockhart [16,17] or the Holeček [18] equations.

3. Discussion

The 1 : 1 compositions (Table 2) are compatible with both monomeric and polymeric formulations, but X-ray data show that both compounds are monomeric in the solid state. The crystal structure of $[Ph_2SnCl_2bipym]$ reported here (Fig. 1) may be compared to that of $[Bu_2SnCl_2bipym]$ [11]. The Sn–C bonds in the two complexes are equal, 2.139(7) and 2.141(7) Å for the phenyl compound, and 2.14(1) and 2.14(1) Å for the butyl compound, but other bonds in the coordination sphere are significantly different. Thus, the equivalent bonds Sn–N, 2.398(4) and 2.413(4) Å, for the phenyl species are shorter than 2.46(1) and 2.472(9) Å for the

TABLE 5. ^{13}C-NMR data in chloroform-d_1 solution (B_o = 4.7 or 9.4 T; T = 298 K; J in Hz; TMS δ = 0.00 ppm)

Compound	δ/ppm							$^{n}J(Sn, ^{13}C)$ [a]			
	Ph or Bu				bipym			$n = 1$	$n = 2$	$n = 3$	$n = 4$
	C_1	$C_{2,6}$	$C_{3,5}$	C_4	C_2	$C_{4,6}$	C_5				
Ph_2SnCl_2	136.8	134.9	129.5	131.7				(785) [b]	62.8	85.4	17.5
$[Ph_2SnCl_2bipym]$ [c]	145.6 [d]	135.3	128.9	129.9		157.3 [d]	123.1 [d]	[e]	67.2	97.7	19.6
bipym					162.2	157.9	121.4				
	C_α	C_β	C_γ	C_δ							
Bu_2SnCl_2	26.4	26.7	26.2	13.4				420.6	32.4	83.0	
$[Bu_2SnCl_2bipym]$											
sol.1	34.8	27.5	25.9	13.4	159.7	158.2	122.6	693.4	40.1	132.8	
sol.2	29.1	27.0	26.1	13.3	161.0	158.1	121.9	505.1	35.0	96.9	
sol.3	28.3	26.9	26.1	13.3	161.6	157.9	121.6	485.3	34.8	93.7	

[a] The value for the 119 isotope is reported, when ^{119}Sn and ^{117}Sn satellites are resolved. [b] From ref. 28; [c] T = 328 K; [d] broad to very broad resonance; [e] satellites undetectable.

TABLE 6. ^{1}H-NMR data in chloroform-d_1 solution (B_o = 4.7 or 9.4 T; T = 298 K; TMS δ = 0.00 ppm)

Compound	δ/ppm					
	Ph or Bu				bipym	
	$H_{2,6}$		$H_{3,5}$	H_4	H_5	$H_{4,6}$
Ph_2SnCl_2	7.54 [$^{3}J(Sn, ^{1}H)$ = 80 Hz]		7.7	7.54		
$[Ph_2SnCl_2bipym]$	8.0 [a] [$^{3}J(Sn, ^{1}H)$ = 92 Hz]		7.4 [b]	7.4 [b]	7.56	8.98 [a]
bipym					7.41	8.99
	αCH_2	βCH_2	γCH_2	δCH_3		
Bu_2SnCl_2	1.80	1.41 [c]	1.41 [c]	0.95		
$[Bu_2SnCl_2bipym]$						
sol.1	1.57	1.19 [c]	1.19 [c]	0.74	7.61	9.19
sol.3	1.75	1.36 [c]	1.36 [c]	0.90	7.50	9.09

[a] broad to very broad; [b] see text; [c] overlapping multiplets.

butyl complex. Crowe *et al.* [8] showed that longer Sn–N bonds are associated with higher antitumour activity, and therefore the butyl derivative should be expected to be more active than the phenyl. Also the Sn–Cl bonds are shorter in the phenyl complex (2.466(2) and 2.451(2) Å) than in the butyl complex (2.508(2) and 2.525(2) Å). The decrease in the bond lengths in the plane containing tin, the two chlorines and the two nitrogens in the phenyl species, can be ascribed to the electronegativity of the phenyl group which is higher than that of the butyl group. This decreases the s-character of the Sn–C bond so that the other bonds to tin have a higher s-character and are consequently shorter.

Comparable bond angles in the coordination sphere are C–Sn–C, which is 175.1(6)° for the butyl derivative and 169.3(2)° for the phenyl complex. The other two *trans* angles Cl–Sn–N, 161.5(3) and 158.8(2)° are less than those for the phenyl derivative, 163.6(1) and 160.4(1)°. The Cl–Sn–Cl angle is very different, 106.0(1) for the phenyl complex and 103.81(5)° for the butyl complex. The bite angles N–Sn–N are more similar, 67.9(1) and 66.4(3)°, respectively.

There are nineteen complexes of the type "$SnCl_2N_2C_2$" in the Cambridge Crystallographic Database [19] with Sn–N bond lengths ranging from 2.27 to 2.58 Å, average 2.40 Å. The values in our complex coincide with this average value. The Sn–Cl bond lengths are in the range 2.37–2.60 Å, and our values are shorter than average (2.52 Å). Finally, the Sn–C bond length range is narrower, 2.05–2.22 Å, which is probably due to the low polarizability of this bond and our values are similar to the average value, 2.13 Å. The search revealed thirteen *cis*-complexes with bis (nitrogen) chelates and six *trans* complexes of monodentate nitrogen ligands.

There are twelve complexes with chelating nitrogen ligands that have a similar five-atom Sn–N–C–C–N ring skeleton. The N–Sn–N bite angle ranges from 66.1°, for dichloro(diethyl)[3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine]-tin(IV) [20] and dichloro(diethyl)[2-(2′-pyridyl)benzothiazolyl-*N*,*N*′]tin(IV) [21] to 71.5 for (μ_2-methylene)-bipyridine(tetrachloro(dimethyl)di-tin(IV)) [22]. These three complexes have the nitrogen ligands that are derivatives of bipyridine and are very similar to bipym with two aromatic rings linked through one single C–C bond. Seven further complexes of this type were found. These complexes show an appreciable variation of Sn–N bond lengths. The complexes may be classified in two groups on the basis of Sn–N bond lengths.

(a) Short Sn–N bonds are associated with large C–Sn–C angles, between 170 and 180°; this angle is also larger than the other two *trans* N–Sn–Cl angles; (b) long Sn–N bonds are associated with small C–Sn–C angles.

This trend is also found for two complexes where the nitrogen ligand has an additional nitrogen atom available for coordination. Thus, in (2,2′-azopyridine-*N*,*N*′,*N*″)dibromodimethyltin(IV) the C–Sn–C bond angle is 162° and the three Sn–N bond lengths are 2.59, 2.79 and 2.90 Å [23]; in dichloro(diethyl)[2-(5-methyl-1,2,4-oxadiazol-3-yl)-1,10-phenanthroline]tin(IV) the values are 150°, 2.86, 2.95, and 3.01 Å [24], respectively. For these two complexes the Sn–N bonds are longer than those in the thirteen complexes having bidentate nitrogen ligands.

The lengthening of the Sn–N bond is also the driving force for the narrowing of the C–Sn–C angle. In fact, the Sn–C bonds tend to occupy the area that is left free by the leaving group (the chelating nitrogen ligand). A limiting case for this trend would be the nitrogen ligand out of the coordination sphere and the remaining four groups, two halogen and two hydrocarbon groups, around the metal in a tetrahedral conformation.

Finally, in complexes of monodentate nitrogen ligands the *trans* C–Sn–C angles are nearly 180° (range 178.1–180°). The thirteen chelate complexes have these values noticeably lower and generally two of the three *trans* bond angles are lower than 170°. The average of these three angles falls in the range 160–167°.

^{119}Sn Mössbauer I.S. values (Table 2) are typical of tin(IV) in inorganic and organometallic derivatives [25]. The Q.S. (Table 2) of [Bu_2SnCl_2bipym] is unambiguously indicative of an octahedral configuration of the tin atom with *trans* butyl groups [25]. The Q.S. in frozen ethanol solution confirms that the structure is retained. The value for [Ph_2SnCl_2bipym] also suggests an octahedral arrangement with a non-linear C–Sn–C skeleton. Using the Parish relationship between Q.S. and C–Sn–C angles [26], these angles have been estimated as 173° and 163° for the butyl derivative in the solid and the solution phase, respectively, and 151° for the phenyl adduct.

The IR spectra of the adducts show the characteristic absorptions of the 2,2′-bipyrimidine skeleton [27] (see Experimental section). In particular the strong bands (1558, 1547 cm^{-1}) assigned to C=N and C=C stretchings appear in the adducts split into three and four intense absorptions, pointing to the presence of mononuclear chelate complexes where only two of the four nitrogen atoms are coordinated. The $\nu(\text{Sn–C})_{as,s}$ have been assigned at 621 and 578 cm^{-1}, respectively, for the butyl derivative; only the $\nu(\text{Sn–C})_{as}$ has been reliably assigned for the phenyl adduct as a component of the broad band centred at 278 cm^{-1}. Two ν(Sn–Cl) bands at 278 cm^{-1}, ν_{as}, and 225 cm^{-1}, ν_s, have been assigned for the phenyl derivative, consistent with the non-linearity of the Cl–Sn–Cl system. For the butyl derivative only $\nu(\text{Sn–Cl})_{as}$ has been observed in the range of frequencies examined.

The Mössbauer and IR data are entirely consistent with the crystal structures of [Ph_2SnCl_2bipym] discussed above and of [Bu_2SnCl_2bipym] previously reported [1].

The ^{13}C-NMR data for Ph_2SnCl_2 (Table 5) are in good agreement with literature data [28] and since we could not measure $^1J(^{119}\text{Sn}, ^{13}\text{C})$ it seemed reasonable to use the published value reported in Table 5 to calculate θ in solution. The Lockhart equation [16] (eqn. (1)):

$$^1J = 11.4\theta - 875 \qquad (1)$$

yields a value of 146°, corresponding to a geometry around the tin which may be classed either as highly distorted tetrahedral or octahedral [29]. This finding is consistent with the solid state value of θ 125.5°, which we interpret as an increased amount of p character in the orbitals involved in the Sn–Cl bonds [30,31].

The ^{13}C spectrum of the 1 : 1 bipym complex exhibits both broad and sharp lines. The broad lines (phenyl C_4 and bipym carbon atoms) sharpen progressively if the temperature is raised, though the bipym C_2 resonance, the intensity of which is reduced because of the long relaxation time, is still broadened beyond detection at 328 K and the phenyl C_1 is a barely detectable fairly broad peak. The coupling constants show the commonly observed trend [32] with $^3J > {}^2J > {}^4J$.

The ^{1}H spectrum of the complex (Table 6) exhibits a similar pattern of broad (protons on C_4 and C_6 of bipym, and on C_2 and C_6 of the phenyls) and sharp (protons on C_5 of bipym and on C_3 and on C_5 of phenyls) lines. The protons on C_4 of the phenyls seem to generate a broad resonance obscured by the multiplet centred at 7.4 ppm (relative integrated intensity corresponding to 6 protons). The broad resonance at 8.0 ppm has tin satellites with $^3J(\text{Sn}, ^1\text{H})$ *ca.* 92 Hz, in the expected range for the obviously *cis* geometry [33,34]. The anomalous feature of broad and sharp lines present in the same spectrum has not been explained.

The ^{13}C-NMR parameters for Bu_2SnCl_2 (Table 5) reproduce the literature data [35] and the value of the C–Sn–C angle calculated from $^1J(^{119}\text{Sn}, ^{13}\text{C})$ using the Holeček equation [18] (eqn. (2))

$$^1J = (9.99 \pm 0.73)\theta - (746 \pm 100) \qquad (2)$$

is $(117 \pm 20)°$, whereas eqn. (1) yields 114°. X-ray diffraction data on the crystal show a distorted octahedral geometry around tin, with two bridging halogen atoms (θ is 132°) [36]. The lesser θ value in solution may be explained by medium effects, involving breaking of the halogen bridges and formation of pentacoordinate species with equatorial alkyl groups [16,37]. Comparable deviations have frequently been reported [16,18,29,38].

The ^{1}H-NMR data of Bu_2SnCl_2 are reported in Table 6: the $^2J(\text{Sn, H})$ values cannot be extracted simply from the spectrum because of the complexity of the methylene multiplets.

The ^{13}C spectrum of [Bu_2SnCl_2bipym] shows a marked concentration dependence (Table 5): the concentrations were not known, but solutions 2 and 3 were obtained from 1 by progressive dilution. In the more concentrated solution, θ calculated according to eqn. (1) (138°) or (2) $(145 \pm 21)°$ suggests a skew structure (*i.e.* distorted octahedral or trapezoidal bipyramidal) [29]. The discrepancy with θ obtained by ^{119}Sn Mössbauer spectroscopy in frozen ethanol solution (163°, Table 2) is within acceptable limits given the approximations involved; this is not true of the solid state data.

Comparable behaviour has been observed for the similar complex dibromobis(pyrazole)dimethyltin(IV), which in chloroform solution undergoes a partial dissociation to the mono(pyrazole) complex with trigonal bipyramidal structure, reverting to the octahedral stereochemistry if excess of pyrazole is present [39].

From our NMR data for the butyl complex and the previous structural studies, we conclude that the nitrogen ligand is labile and hence that the mechanism of interaction of organotin complexes in biological systems differs from that of platinum complexes which retain the Pt–N bonds when reacting with DNA. In organotin compounds the Sn–N bonds are probably cleaved before the tin reaches its ultimate target.

4. Supplementary material

Listing of F_o/F_c parameters; full listing of bond distances and angles; anisotropic and isotropic displacement parameters; hydrogen coordinates. All except the first are available from the Cambridge Crystallographic Data Centre.

Acknowledgments

Thanks are due to Miriam Rossi, Vassar College, Poughkeepsie, NY, USA for helpful discussion. The Computer Center at Vassar College provided computer facilities and assistance (Bill Wine). The Institute for Cancer Research at Fox Chase, Philadelphia, USA, provided the Cambridge Data Base facility (Jenny P. Glusker). The NMR and Microanalysis Services of the CNR Research Area of Montelibretti, Roma, Italy recorded some of the NMR spectra and performed the elemental analyses (Luca Petrilli and Franco Dianetti). Prof. M. Paci allowed use of the AM400 Bruker spectrometer.

Financial support by MURST (40% and 60% Research Projects) and CNR (research contribution no. 91.03215.CT03) is gratefully acknowledged.

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