

Thiazole complexes of diorganotin(IV) dihalides: the crystal structure of dichlorodiphenylbis(thiazole)tin(IV)

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Abstract

The reaction of thiazole (Tz) with diorganotin(IV) dihalides yielded compounds of type $[\text{SnR}_2\text{X}_2(\text{Tz})_2]$ ($\text{R} = \text{Me, Et, Ph}$; $\text{X} = \text{Cl, Br}$). The structure of dichlorodiphenylbis(thiazole)tin(IV) was determined by X-ray diffraction. The crystals are monoclinic (space group $P2_1/c$) and consist of discrete *trans*- $\text{SnPh}_2\text{Cl}_2(\text{Tz})_2$ units with the metal atom coordinated to two Cl atoms, two phenyl carbons, and the N atoms of two thiazole rings. Mössbauer and IR spectra suggest similar *trans*-stereochemistry for the other complexes prepared. The behavior of these compounds in solution was studied by conductimetry and NMR techniques.

Keywords: Tin; Thiazole; Mössbauer spectroscopy; Nuclear magnetic resonance; Crystal structure

1. Introduction

In previous work [1] we prepared and in some cases studied the crystallography of several dialkyltin(IV) complexes of type $[\text{SnR}_2\text{X}_2\text{L}_2]$ ($\text{R} = \text{Me, Et, Bu}$; $\text{X} = \text{Cl, Br}$; L an imidazole or pyrazole) in order to investigate the steric influence of the different substituents on the structure of the compounds. This study was recently extended to diaryltin(IV) derivatives by the preparation of dichlorodiphenylbis(pyrazole)tin(IV) [2]. In all these compounds the ligands L have an N–H group that can take part in hydrogen bonding, and hydrogen bonds were in fact detected in the compounds studied crystallographically. To investigate the influence of the absence of such bonds on the orientation of the azole ring and the overall structure, we prepared the complexes $[\text{SnR}_2\text{X}_2(\text{Tz})_2]$ ($\text{R} = \text{Me, Et, Ph}$; $\text{X} = \text{Cl, Br}$; $\text{Tz} = \text{thiazole}$). This paper describes their preparation and characterization, and the crystal structure of the dichlorodiphenyl compound.

2. Experimental section

2.1. Materials

Dimethyltin dichloride (Ventron), dimethyltin dibromide (Ventron), diethyltin dichloride (Ventron), diethyltin dibromide (Ventron), diphenyltin dichloride (Aldrich) and thiazole (Aldrich) were used as supplied. Diphenyltin dibromide was prepared by treating diphenyltin dichloride with sodium bromide. Solvents were purified by the usual methods.

2.2. Preparation of compounds

$[\text{SnMe}_2\text{Cl}_2(\text{Tz})_2]$. A solution of SnMe_2Cl_2 (4.4 mmol) in 15 ml CH_2Cl_2 was added dropwise to a stirred solution of thiazole (8.8 mmol) in 15 ml of the same solvent. The mixture was stirred for a short time and the white solid formed then filtered off and dried in vacuo. Analysis: found, C 23.5, H 2.8, N 6.3%; Calculated for $\text{C}_8\text{H}_{12}\text{Cl}_2\text{N}_2\text{S}_2\text{Sn}$, C 24.6, H 3.1, N 7.2%. M.p. 134°C, Λ_{M} (MeCN, 10^{-3} M) 9.0 $\text{S cm}^2 \text{mol}^{-1}$.

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$[\text{SnMe}_2\text{Br}_2(\text{Tz})_2]$. A white solid was prepared from SnMe_2Br_2 (3.3 mmol) and thiazole (6.6 mmol) by the procedure used for $[\text{SnMe}_2\text{Cl}_2(\text{Tz})_2]$. Analysis: found, C 20.1, H 2.7, N 5.6%; Calculated for $\text{C}_8\text{H}_{12}\text{Br}_2\text{N}_2\text{S}_2\text{Sn}$, C 20.1, H 2.5, N 5.8%. M.p. 156°C , Λ_{M} (MeCN, 10^{-3} M) $57.0 \text{ S cm}^2 \text{ mol}^{-1}$.

$[\text{SnEt}_2\text{Cl}_2(\text{Tz})_2]$. A solution of SnEt_2Cl_2 (2.2 mmol) in 15 ml CH_2Cl_2 was added dropwise to a stirred solution of thiazole (4.4 mmol) in 15 ml of the same solvent. The mixture was stirred for a short time and the solvent then partly evaporated off; the white solid formed was filtered off and dried in vacuo. Analysis: found, C 28.7, H 4.1, N 6.2%; Calculated for $\text{C}_{10}\text{H}_{16}\text{Cl}_2\text{N}_2\text{S}_2\text{Sn}$, C 28.7, H 3.9, N 6.7%. M.p. 109°C , Λ_{M} (MeCN, 10^{-3} M) $8.5 \text{ S cm}^2 \text{ mol}^{-1}$.

$[\text{SnEt}_2\text{Br}_2(\text{Tz})_2]$. A white solid was prepared from SnEt_2Br_2 (3.6 mmol) and thiazole (7.2 mmol) by the procedure used for $[\text{SnEt}_2\text{Cl}_2(\text{Tz})_2]$. Analysis: found, C 24.0, H 3.2, N 5.3%; calculated for $\text{C}_{10}\text{H}_{16}\text{Br}_2\text{N}_2\text{S}_2\text{Sn}$, C 23.7, H 3.2, N 5.5%. M.p. 120°C , Λ_{M} (MeCN, 10^{-3} M) $8.6 \text{ S cm}^2 \text{ mol}^{-1}$.

$[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$. A solution of SnPh_2Cl_2 (2.7 mmol) in 10 ml CH_2Cl_2 was added dropwise to a stirred solution of thiazole (5.5 mmol) in 10 ml of the same solvent. The mixture was stirred for a short time, the solvent then partly evaporated off, and the white solid formed filtered off and dried in vacuo. Crystals suitable for X-ray analysis were obtained from the filtrate. Analysis: found, C 42.1, H 3.0, N 5.4%; Calculated for $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{N}_2\text{S}_2\text{Sn}$, C 42.1, H 3.1, N 5.4%. M.p. 159°C , Λ_{M} (MeCN, 10^{-3} M) $10.0 \text{ S cm}^2 \text{ mol}^{-1}$.

$[\text{SnPh}_2\text{Br}_2(\text{Tz})_2]$. A white solid was prepared from SnPh_2Br_2 (1.4 mmol) and thiazole (2.9 mmol) by the procedure used for $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$. Analysis: found, C 35.9, H 2.1, N 4.1%; Calculated for $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{N}_2\text{S}_2\text{Sn}$, C 35.9, H 2.7, N 4.6%. M.p. 138°C , Λ_{M} (MeCN, 10^{-3} M) $32.0 \text{ S cm}^2 \text{ mol}^{-1}$.

2.3. Physical measurements

Elemental analyses were performed with a Carlo-Erba 1108 apparatus. Melting points were determined using a Büchi apparatus. IR spectra were recorded with Nujol mulls or KBr discs on a Nicolet FT-IR 55XC20F spectrometer. Conductivities were determined with a WTW-LF3 conductivity meter. Mössbauer spectra were determined at 80.0 K in a constant acceleration apparatus with a $\text{Ca}^{119\text{m}}\text{SnO}_3$ source and δ referred to SnO_2 . ^1H (250.13 MHz) and ^{13}C (62.83 MHz) NMR spectra were recorded in CDCl_3 at room temperature on a Bruker WM-250 and referred to TMS.

2.4. Determination of the crystal structure of $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$

X-ray data collection and reduction. A colourless prismatic crystal was mounted on a glass fibre for data collection in an Enraf-Nonius CAD4 automatic diffractometer [3]. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range $6.8^\circ < \theta < 13.6^\circ$. Data were collected at 293 K using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and the $\omega/2\theta$ scan technique, and were corrected for Lorentz and polarization effects. An empirical absorption correction was made [4]. Table 1 summarizes the crystal data, experimental details and refinement results.

Table 1
Crystal data, data collection and structure refinement parameters for $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$

Crystal shape	Prismatic
Size (mm)	$0.30 \times 0.25 \times 0.30$
Chemical formula	$\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{N}_2\text{S}_2\text{Sn}$
Formula weight	514.07
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	9.263(2)
b (Å)	14.146(2)
c (Å)	16.032(4)
β (deg)	105.77(1)
Volume of unit cell (Å ³)	2021.6(7)
Z	4
D (g cm ⁻³)	1.689
$F(000)$	1016
Linear absorption coefficient (cm ⁻¹)	17.371
Minimum, maximum and average absorption correction	0.664, 1.159, 1.002
Maximum value of $(\sin \theta)/\lambda$ reached in intensity measurement (Å ⁻¹)	0.617
Range of h, k, l	$0 \rightarrow 11,$ $0 \rightarrow 17,$ $-19 \rightarrow 19$
Standard reflections	$4, 0, 2; -2, -2, 7$
Interval standard reflections measured	7200s
Total number of reflections measured, θ range (deg)	4161, 3–26
Number of unique reflections, R_{int}	3710, 0.040
Number of observed reflections	2252
Criterion for observed reflections	$I > 3\sigma(I)$
Weighting scheme	$1/\sigma^2(F)$
Parameters refined	227
Value of R	0.051
Value of R_w	0.053
Ratio of maximum LS shift to e.s.d. (Δ/σ)	0.001
Maximum $\Delta\rho$ in final difference electron density map (e Å ⁻³)	1.255 (around Sn)
Error in an observation of unit weight	2.848
Secondary extinction coefficient	3.731×10^{-8}

Structure solution and refinement. The structure was solved by direct methods [5], which revealed the positions of all non-hydrogen atoms, and refined on F by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were located in the Fourier difference maps and included in the structure factor calculations as fixed contributions ($B_{\text{iso}} = 4.0 \text{ \AA}^2$) but their positional parameters were not refined. A secondary extinction correction was applied [6]. When all shift/e.s.d. ratios were less than 0.001, the agreement factors were those listed in Table 1. Atomic scattering factors were taken from Ref. [7]. Molecular graphics were obtained with SCHAKAL [8]. Final atomic parameters and bond distances and angles are listed in Tables 2 and 3 respectively.

3. Results and discussion

3.1. Description of the structure of $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$

The molecular structure of $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$ is shown in Fig. 1 together with the numbering scheme. The Sn atom is octahedrally coordinated to two Cl atoms, two phenyl C atoms, and the N atoms of two thiazole ligands in an all-trans configuration. The deviation from the ideal octahedral angles is small (Table 3).

Table 2
Positional parameters for $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$, and their estimated standard deviations

Atom	x	y	z	$B(\text{\AA}^2)$
Sn	0.26067(7)	0.13965(5)	0.75150(5)	3.15(1)
Cl1	0.3771(3)	0.0959(2)	0.6327(2)	4.10(5)
Cl2	0.1444(3)	0.1842(2)	0.8745(2)	4.53(6)
S11	0.1073(5)	0.4082(3)	0.5630(2)	7.13(9)
S21	0.4179(7)	−0.1734(3)	0.8508(4)	11.6(2)
N11	0.1783(9)	0.2847(6)	0.6808(5)	3.9(2)
N21	0.3369(9)	−0.0067(6)	0.8214(5)	3.6(2)
C11	0.0490(9)	0.0804(7)	0.6801(6)	3.5(2)
C12	−0.083(1)	0.1226(8)	0.6847(7)	4.5(2)
C13	−0.220(1)	0.0837(9)	0.6376(7)	5.1(3)
C14	−0.223(1)	0.0040(9)	0.5882(7)	5.4(3)
C15	−0.093(1)	−0.0377(8)	0.5834(7)	4.9(3)
C16	0.044(1)	−0.0001(7)	0.6302(7)	4.2(2)
C17	0.175(1)	0.3013(8)	0.6007(7)	4.5(2)
C18	0.124(1)	0.3628(9)	0.7140(7)	5.5(3)
C19	0.079(1)	0.4372(7)	0.6582(6)	5.2(3)
C21	0.469(1)	0.2013(7)	0.8264(6)	3.6(2)
C22	0.604(1)	0.1587(8)	0.8283(7)	4.4(2)
C23	0.738(1)	0.197(1)	0.8755(7)	5.8(3)
C24	0.738(1)	0.279(1)	0.9223(8)	6.1(3)
C25	0.605(1)	0.3220(8)	0.9209(8)	6.0(3)
C26	0.470(1)	0.2836(8)	0.8733(7)	4.8(3)
C27	0.381(2)	−0.0799(9)	0.7860(7)	6.2(3)
C28	0.342(1)	−0.027(1)	0.9039(7)	6.6(3)
C29	0.388(1)	−0.1262(6)	0.9353(5)	4.0(2)

Table 3

Selected bond distances ($\text{\AA}$) and angles (deg) in $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$, with estimated standard deviations in parentheses

Sn–Cl1	2.508(3)
Sn–Cl2	2.569(3)
Sn–N11	2.368(8)
Sn–N21	2.370(8)
Sn–C11	2.154(8)
Sn–C21	2.158(8)
S11–C17	1.68(2)
S11–C19	1.67(1)
S21–C27	1.66(1)
S21–C29	1.60(1)
N11–C17	1.30(1)
N11–C18	1.38(2)
N21–C27	1.30(2)
N21–C28	1.34(1)
C18–C19	1.38(2)
C28–C29	1.51(2)
Cl1–Sn–Cl2	179.33(7)
Cl1–Sn–N11	90.0(2)
Cl1–Sn–N21	90.5(2)
Cl1–Sn–C11	91.0(3)
Cl1–Sn–C21	91.2(3)
Cl2–Sn–N11	90.4(2)
Cl2–Sn–N21	89.1(2)
Cl2–Sn–C11	89.6(3)
Cl2–Sn–C21	88.3(3)
N11–Sn–N21	178.7(3)
N11–Sn–C11	87.4(3)
N11–Sn–C21	92.2(4)
N21–Sn–C11	91.3(3)
N21–Sn–C21	89.1(4)
C11–Sn–C21	177.9(4)
C17–S11–C19	91.6(5)
C27–S21–C29	98.2(7)
C17–N11–C18	108.8(9)
C27–N21–C28	110(1)
S11–C17–N11	115.3(8)
N11–C18–C19	116(2)
S11–C19–C18	108.1(9)
S21–C27–N21	113.4(9)
N21–C28–C29	118(2)
S21–C29–C28	101.7(7)

The Sn–Cl and Sn–C bond lengths are similar to those in other octahedral dichlorodiphenyltin(IV) compounds [2,9] and in octahedral dichlorodiorganotin(IV) complexes in general [1]. The Sn–N bonds (average 2.369(8) $\text{\AA}$) are close in length to those in other $\text{SnR}_2\text{X}_2\text{L}_2$ systems with N-coordinated L [1], but slightly longer than the average value (2.328 $\text{\AA}$) in $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ [2].

The phenyl rings are practically coplanar, forming dihedral angles of 35.7° (ring 1) and 38.8° (ring 2) with the Cl(1)C(11)Cl(2)C(21) plane. The thiazole rings are essentially planar, with negligible deviation from the best least-squares plane, and do not undergo significant structural modifications on coordination [10]. The dihedral angles of these rings with the Cl(1)N(11)Cl(2)N(21) plane (14.2° (ring 1) and 16.1° (ring 2)) show that the

Table 4
Mössbauer effect parameters at 80.0 K for $[\text{SnR}_2\text{X}_2(\text{Tz})_2]$ complexes

Compound	δ^a (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})	$\Gamma_{2/1}$
$[\text{SnMe}_2\text{Cl}_2(\text{Tz})_2]$	1.52	3.75	0.94	0.94
$[\text{SnMe}_2\text{Br}_2(\text{Tz})_2]$	1.60	3.89	1.11	1.04
$[\text{SnEt}_2\text{Cl}_2(\text{Tz})_2]$	1.70	3.87	0.92	1.01
$[\text{SnEt}_2\text{Br}_2(\text{Tz})_2]$	1.77	3.89	1.08	1.09
$[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$	1.48	3.49	0.91	1.02
$[\text{SnPh}_2\text{Br}_2(\text{Tz})_2]$	1.52	3.50	0.82	0.94

^a Relative to room temperature SnO_2 .

$\text{SnCl}_2(\text{Tz})_2$ moiety is closer to planar than *trans*- $[\text{PtCl}_2(\text{Tz})_2]$ [11], probably owing to the steric influence of the phenyl ring in the tin compound.

Comparison of this structure with that of $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ shows opposite rings to be more coplanar in $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$. This suggests that intramolecular or intermolecular hydrogen bonds have significant structural influence when present in this type of complex.

3.2. Mössbauer spectra

Table 4 shows the Mössbauer parameters of the adducts. The variation of the isomer shift is typical of organometallic tin(IV) derivatives, the δ values increasing on going from the phenyl complexes (average value 1.50 mm s^{-1}) to the methyl complexes (average value 1.56 mm s^{-1}) and finally to the ethyl compounds (aver-

Table 5
Significant IR bands ($600\text{--}100 \text{ cm}^{-1}$) for $[\text{SnR}_2\text{X}_2(\text{Tz})_2]$ complexes

Compound	$\nu_{\text{as}}(\text{Sn-C})$	$\nu_{\text{sym}}(\text{Sn-C})$	$\nu_{\text{as}}(\text{Sn-X})$
$[\text{SnMe}_2\text{Cl}_2(\text{Tz})_2]$	567 s	—	242 m,b
$[\text{SnMe}_2\text{Br}_2(\text{Tz})_2]$	563 s	—	165 m,b
$[\text{SnEt}_2\text{Cl}_2(\text{Tz})_2]$	530 s	—	227 m
$[\text{SnEt}_2\text{Br}_2(\text{Tz})_2]$	525 s	—	171 m
$[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$	288 s	245 s	232 s
$[\text{SnPh}_2\text{Br}_2(\text{Tz})_2]$	288 s	239 s	172 m

b broad, s strong, m medium.

age value 1.74 mm s^{-1}). Moreover, the bromide adducts have values ca. 0.06 mm s^{-1} higher than the chlorides, as expected on electronegativity grounds.

The ΔE_Q values are typical of *trans* octahedral complexes and, as expected, those of the alkyl derivatives are higher than those of the aryl derivatives. Moreover, the ΔE_Q of the two aryl species are almost identical, as are most of those of the alkyl species, suggesting that all these compounds have the same structure. To check this conclusion, the bond angles obtained by X-ray analysis of $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$ were used with the corresponding experimental value of ΔE_Q to calculate the p.q.s. value for the N-bonded thiazole molecule according to the point charge model. The value obtained, -0.20 mm s^{-1} was then used for the alkyl derivatives to calculate a ΔE_Q of 3.78 mm s^{-1} , in good agreement with the experimental value (average 3.85 mm s^{-1}). This supports the view that all these adducts have very similar structure.

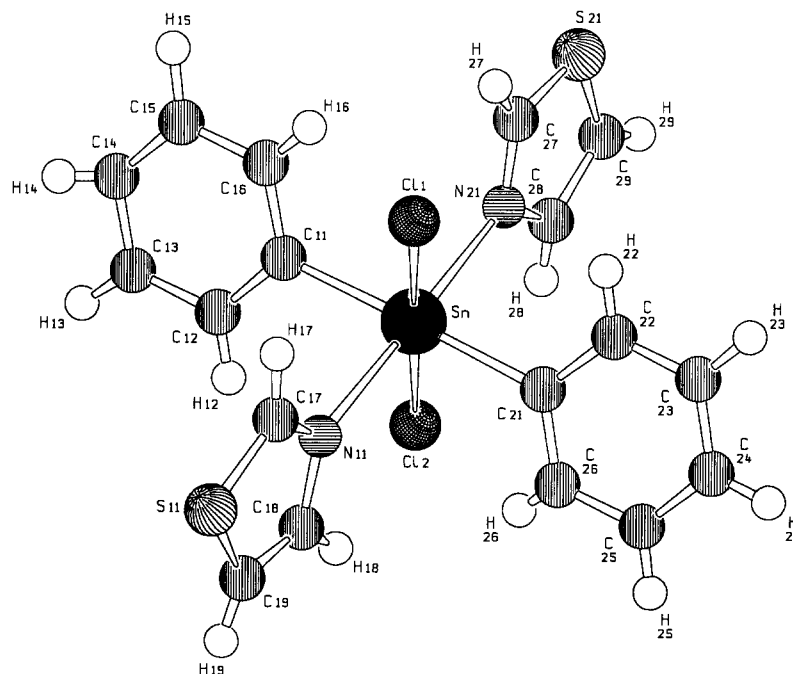
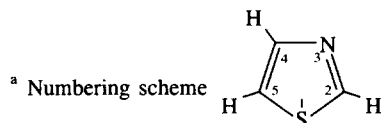


Fig. 1. Perspective view of $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$, showing the atom numbering scheme and the coordination geometry about the tin atom. The rings referred to as 1 in the text have atom numbers beginning with 1, those referred to as 2 have atom numbers beginning with 2.

Table 6

¹H NMR parameters (δ in ppm, J in Hz) for $[\text{SnR}_2\text{X}_2(\text{Tz})_2]$ complexes in CDCl_3

Compound	$\delta(\text{CH}_3)$	$\delta(\text{CH}_2)$	$^2J(^{119}\text{Sn}-^1\text{H})$	$^3J(^{119}\text{Sn}-^1\text{H})$	$\delta(\text{Ligand})^a$
Tz	—	—	—	—	7.41(H5,q) 7.97(H4,d) 8.87(H2,d)
$[\text{SnMe}_2\text{Cl}_2(\text{Tz})_2]$	1.22(s)	—	73.8	—	7.46(H5,s,b) 7.99(H4,s,b) 8.95(H2,s,b)
$[\text{SnMe}_2\text{Br}_2(\text{Tz})_2]$	1.39(s)	—	69.7	—	7.44(H5,q) 8.00(H4,d) 8.93(H2,d)
$[\text{SnEt}_2\text{Cl}_2(\text{Tz})_2]$	1.36(t)	1.77(q)	57.8	145.8	7.47(H5,q) 8.03(H4,d) 9.02(H2,d)
$[\text{SnEt}_2\text{Br}_2(\text{Tz})_2]$	1.35(t)	1.86(q)	52.5	145.7	7.44(H5,q) 8.03(H4,d) 8.98(H2,d)
	$\delta H(3,4,5)$	$\delta H(2,6)$			
$[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$	7.50(m)	7.71(m)	—	83.2	7.42(H5,q) 7.93(H4,d) 8.87(H2,s,b)
$[\text{SnPh}_2\text{Br}_2(\text{Tz})_2]$	7.51(m)	7.70(m)	—	76.7	7.41(H5,q) 7.94(H4,d) 8.86(H2,d)



3.3. Vibrational spectra

The shifts in the thiazole bands [12] on coordination are similar to those found for other complexes with N-bonded ligands [13]. Significant IR bands for the SnR_2X_2 fragment ($600\text{--}100\text{ cm}^{-1}$) are listed in Table 5. Their positions and intensities (the high intensity of the band identified as $\nu_{\text{sym}}(\text{Sn}-\text{C})$ for the phenyl derivatives is probably due to a contribution from a ligand vibration) are similar to those found for other systems for which all-trans octahedral $\text{SnR}_2\text{X}_2\text{L}_2$ stereochem-

istry has been confirmed by X-ray diffraction studies [1, 2, 9 and references therein, 14].

3.4. Characteristics in solution

The molar conductivities of 10^{-3} M solutions of the complexes in MeCN show them all to be non-ionogenic in this solvent [15].

Tables 6 and 7 list the salient results of ^1H and ^{13}C NMR studies in CDCl_3 . The slight differences between the Tz signals of the free ligand and the complexes

Table 7

 ^{13}C NMR parameters (δ in ppm, J in Hz) for $[\text{SnR}_2\text{X}_2(\text{Tz})_2]$ complexes in CDCl_3

Compound	$\delta(\text{CH}_3)$	$\delta(\text{CH}_2)$	$\delta(\text{Ph})$	$^nJ(^{119}\text{Sn}-^{13}\text{C})$				$\delta(\text{Ligand})$
				$n = 1$	$n = 2$	$n = 3$	$n = 4$	
Tz								118.9(C5), 143.4(C4), 152.9(C2)
$[\text{SnMe}_2\text{Cl}_2(\text{Tz})_2]$	12.3			646.9				120.0(C5), 142.8(C4), 154.2(C2)
$[\text{SnMe}_2\text{Br}_2(\text{Tz})_2]$	9.6			500.2				119.1(C5), 143.3(C4), 153.3(C2)
$[\text{SnEt}_2\text{Cl}_2(\text{Tz})_2]$	9.7	21.3		525.8				119.4(C5), 143.3(C4), 153.7(C2)
$[\text{SnEt}_2\text{Br}_2(\text{Tz})_2]$	10.7	25.5		570.5	44.7			119.6(C5), 143.3(C4), 154.4(C2)
$[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$			139.5(Ci) 135.3(Co) 131.5(Cp) 129.7(Cm)	NO	63.7	18.1	90.5	119.3(C5), 143.5(C4), 153.7(C2)
$[\text{SnPh}_2\text{Br}_2(\text{Tz})_2]$			138.0(Ci) 135.2(Co) 131.7(Cp) 129.7(Cm)	NO	NO	NO	NO	119.0(C5), 143.6(C4), 153.4(C2)

NO not observed.

suggest that the donor–acceptor interaction between SnR_2X_2 and thiazole partially persists in solution. However the $^2J(\text{Sn}-\text{H})$ values for the methyl derivatives are only slightly greater than those of the free acceptors in this solvent (66.82/69.82 for SnMe_2Cl_2 and 65.70/68.92 for SnMe_2Br_2 [16]), suggesting that extensive dissociation of the thiazole ligand occurs. For $[\text{SnMe}_2\text{X}_2(\text{HPz})_2]$ we found [1a] that the dissociative process $[\text{SnMe}_2\text{X}_2(\text{HPz})_2] \rightarrow [\text{SnMe}_2\text{X}_2(\text{HPz})] + \text{HPz}$ led to the pentacoordinated $[\text{SnMe}_2\text{X}_2(\text{HPz})]$ species predominating in solution; the lower $^2J(\text{Sn}-\text{H})$ values obtained for the Tz compounds suggest [17] that both $[\text{SnMe}_2\text{X}_2(\text{Tz})_2]$ and $[\text{SnMe}_2\text{X}_2(\text{Tz})]$ undergo dissociation increasing the concentration of free SnMe_2X_2 in solution. This conclusion is further supported by the values of the $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants [18].

Similar behaviour is exhibited by the ethyl derivatives. The $J(\text{Sn}-\text{H})$ coupling constants are again only slightly greater than those for the free acceptors [16], suggesting that dissociation is more extensive than for the analogous pyrazole complexes [1b], and this is again confirmed by the values of the $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants [19].

The ^1H NMR spectra of the phenyl derivatives show two multiplets attributable to the H(2, 6) and H(3, 4, 5) protons. Comparison of the positions of these signals for $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$ and SnPh_2Cl_2 [20] shows only very slight shielding of H(2, 6) on coordination, less than in the analogous complex with the N-donor ligand bipyrimidine [20]. As in other dichlorodiphenyltin(IV) complexes [9,20,21], the resonance of the ipso carbon of the phenyl groups shifts towards higher frequencies on coordination, but the small magnitude of the shift (1.2 ppm) is again suggestive [21] of extensive dissociation.

In conclusion, in chloroform solution the dialkyl- and diaryltin(IV) complexes of thiazole prepared in this work lose the six-coordination observed in the solid state, and the pentacoordinated species $[\text{SnR}_2\text{X}_2(\text{Tz})]$ that are initially formed also undergo extensive dissociation, even though the presence of only one set of signals for the Tz ligand in both ^1H and ^{13}C NMR spectra shows that the free and coordinated ligand are involved in fast interchange.

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