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Organotin compounds with 1-methyl-2(3*H*)-imidazolinethione. The crystal and molecular structure of dichlorobis[1-methyl-2(3*H*)-imidazolinethione]diphenyltin(IV)

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Abstract

The compounds [$SnPh_2Cl_2$(Hmimt)], [$SnPh_2Cl_2$(Hmimt)$_2$] and (Et_4N)[$SnPh_2Cl_3$(Hmimt)] (Hmimt = 1-methyl-2(3*H*)-imidazolinethione) have been prepared and characterized by conductivity measurements and by IR, Raman, mass, Mössbauer and ^1H, ^{13}C, and ^{119}Sn NMR spectroscopies. The structure of the all-*trans*-octahedral [$SnPh_2Cl_2$(Hmimt)$_2$] complex was determined by X-ray crystallography. Coordination bond lengths (Å) are: Sn–Cl 2.587(1), Sn–C 2.154(3) and Sn–S 2.705(1).

1. Introduction

The compound 1-methyl-2(3*H*)-imidazolinethione (Hmimt) has been studied both for its pharmacological (it is a potent antithyroid drug [1]) and chemical properties [2]. Because the study of sulfhydryl ligands may help us understand the biological properties of diorganotin(IV) compounds [3,4], we prepared and characterized [$SnMe_2$(Hmimt)$_4$](NO_3)$_2$ [5] and studied the reaction of Hmimt with dimethyltin(IV) dihalides, obtaining the complexes [$SnMe_2X_2$(Hmimt)], [$SnMe_2X_2$(Hmimt)$_2$] and (Et_4N)[$SnMe_2X_3$(Hmimt)] (X = Cl or Br) [6,7]. The complex [$SnMe_2X_2$(Hmimt)] is pentacoordinate, with tin in a distorted trigonal bipyramidal environment (with Sn–X–Sn bridges between units when X = Cl), whereas Mössbauer and vibrational data suggested an all-*trans* octahedral structure for [$SnMe_2X_2$(Hmimt)$_2$]. In this paper we report the preparation and structural characterization of [$SnPh_2Cl_2$(Hmimt)], [$SnPh_2Cl_2$(Hmimt)$_2$] and (Et_4N)[$SnPh_2Cl_3$(Hmimt)] (including the crystal structure of [$SnPh_2Cl_2$(Hmimt)$_2$]), and compare these results with those obtained previously for the corresponding dimethyltin derivatives.

2. Experimental section

2.1. Materials

Diphenyldichlorotin (Aldrich), tetraethylammonium chloride monohydrate (Merck) and Hmimt (Aldrich) were used as supplied. Solvents were purified by the usual methods.

2.2. Preparation of compounds

2.2.1. [$SnPh_2Cl_2$(Hmimt)]

A solution of Hmimt (1.71 mmol) in 10 ml of CH_2Cl_2 was added dropwise to a solution of $SnPh_2Cl_2$ (1.71 mmol) in 10 ml of the same solvent. After stirring, the

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solvent was partially evaporated off and the yellow solid so obtained was filtered off and dried *in vacuo*. Anal.: found, C 41.2, H 3.6, N 6.2; calc. for $C_{16}H_{16}Cl_2N_2SSn$, C 42.0, H 3.5, N 6.1%. M.p.: 155°C. Λ_M (MeCN, 10^{-3} M): 2.6 s cm^2 mol^{-1}. The mass spectra showed peaks at *m/z* (ion, intensity) (based on isotope ^{120}Sn): 69 (HIm + H, 4.2); 77 (Ph, 69.9); 81 (Hmimt − S − H, 18,2); 82 (Hmimt − S, 17.3); 114 (Hmimt, 100.0); 120 (Sn, 10.5), 155 (SnCl, 60.5); 190 ($SnCl_2$, 4.1); 197 (SnPh, 11.8); 232 (SnPhCl, 38.5); 267 ($SnPhCl_2$, 21.4); 309 ($SnPh_2Cl$, 28.6); 344 ($SnPh_2Cl_2$, 16.8); 388 [$SnPh_2$(Hmimt), 1.4], (HIm = imidazole).

2.2.2. *[SnPh₂Cl₂(Hmimt)₂]*

A solution of $SnPh_2Cl_2$ (1.64 mmol) in 15 ml of CH_2Cl_2 was added dropwise to a solution of Hmimt (3.28 mmol) in 15 ml of the same solvent. After stirring for a few days, the solvent was partially evaporated off and the yellow solid so obtained was filtered off and dried *in vacuo*. Crystals suitable for the X-ray analysis were obtained from the filtrate. Anal.: found, C 42.3, H 3.8, N 9.9; calc. for $C_{20}H_{22}Cl_2N_4S_2Sn$, C 42.0, H 3.9, N 9.8%. M.p.: 160°C. Λ_M (MeCN, 10^{-3} M): 2.8 s cm^2 mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity): 69 (HIm + H, 9.8); 72 ($C_3H_8N_2$, 17,8); 77 (Ph, 35.5); 81 (Hmimt − S − H, 8.6); 99 (Hmimt − Me, 2.5); 114 (Hmimt, 100.0); 155 (SnCl, 27.6); 197 (SnPh, 3.3); 232 (SnPhCl, 13.2); 267 ($SnPhCl_2$, 8.7); 309 ($SnPh_2Cl$, 7.4); 344 ($SnPh_2Cl_2$, 8.6); 388 [$SnPh_2$(Hmimt), 0.2].

2.2.3. *(Et₄N)[SnPh₂Cl₃(Hmimt)]*

A solution of Hmimt (3.71 mmol) in 15 ml of acetone was added dropwise to a solution of $SnPh_2Cl_2$ (3.71 mmol) in 15 ml of the same solvent. After stirring for 3 days, a solution of $Et_4NCl \cdot H_2O$ (3.71 mmol) in 15 ml of MeOH was added dropwise. After stirring for one more day, the solvent was evaporated off and the orange solid so obtained was filtered off and dried *in vacuo*. Anal.: found, C 46.2, H 5.7, N 6.6; calc. for $C_{24}H_{36}Cl_3N_3SSn$, C 46.2, H 5.8, N 6.7%. M.p.: 105°C. Λ_M(MeCN, 10^{-3} M): 191.9 s cm^2 mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity): 69 (HIm + H, 41.0); 72 ($C_3H_8N_2$, 25.8); 77 (Ph, 76.3); 81 (Hmimt − S − H, 25.5); 83 (Hmimt − S + H, 26.0); 114 (Hmimt, 100.0); 130 (Et_4N, 12.1); 155 (SnCl, 66.5); 197 (SnPh, 8.3); 232 (SnPhCl, 23.1); 267 ($SnPhCl_2$, 12.5); 309 ($SnPh_2Cl$, 15.7); 344 ($SnPh_2Cl_2$, 15.2).

2.3. *Physical Measurements*

Elemental analyses were performed with a Carlo-Erba 1108 apparatus. Melting points were measured on a Büchi apparatus. IR spectra were recorded in Nujol mulls or KBr discs on a Perkin-Elmer 1330 spectrophotometer, and Raman spectra were obtained with a Dilor Omars 89 spectrometer (argon ion laser, 5145 Å) using powdered samples in capillary tubes. Conductivities were measured in a WTW-LF3 conductivity meter. Mass spectra were recorded on a Kratos MS50 TC spectrometer connected to a DS90 system and operating under EI conditions (direct insertion probe, 70 eV, 250°C); all ions were identified by DS90 software. Mössbauer spectra were determined at 80.0 K in a constant acceleration apparatus with a $Ca^{119m}SnO_3$ source and δ referred to SnO_2. ^{1}H (250.13 MHz), ^{13}C (62.83 MHz) and ^{119}Sn (93.28 MHz) NMR spectra were recorded in $CDCl_3$ at room temperature on a Bruker WM-250 spectrometer. ^{1}H and ^{13}C chemical shifts were referred to TMS and the ^{119}Sn chemical shift to tetramethyltin.

2.4. *Determination of the structure*

A crystal of maximum dimension 0.2 mm was used for the X-ray analysis. Data were collected on a Philips PW 1100 diffractometer using Mo Kα radiation. Cell dimensions were determined by least-squares refinement of 25 medium angle settings. The crystals were stable under irradiation. The structure was solved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. All hydrogen atoms were located on the Fourier difference maps and were refined with fixed isotropic temperature factors (U_{iso} = 0.08 Å^2). Anisotropy was introduced for all non-hydrogen atoms. Scale factor and positional and thermal parameters were refined by minimizing the function $\Sigma w(\Delta F)^2$, with $w = 1$. At convergence, the largest parameter shift of the refined parameters of the non-hydrogen atoms was 0.2 times the standard deviation. No significant electron density residue was observed in the final electron density map. Form factors for the atoms were supplied internally by the SHELX program system [8]. Crystal and intensity data, final atomic parameters and bond distances and angles are listed in Tables 1, 2 and 3 respectively and complete lists are available from the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. *Description of the structure of [SnPh₂Cl₂(Hmimt)₂]*

The molecular structure of the *trans*-[$SnPh_2Cl_2$(Hmimt)$_2$] is shown in Fig. 1 together with the adopted numbering scheme. The molecule is centrosymmetric, and in the crystal the Sn atom occupies a special position at a crystallographic inversion centre.

The Sn–Cl and Sn–C bond lengths are very similar to those found in other octahedral dichlorodiphenyltin (IV) compounds [10] and in octahedral dichlorodi-

TABLE 1. Crystal and intensity data for $[SnPh_2Cl_2(Hmimt)_2]$

Formula	$C_{20}H_{22}Cl_2N_4S_2Sn$
Formula weight	572.15
Cell constants	$a = 8.632(2)$ Å
	$b = 9.441(2)$ Å
	$c = 14.504(3)$ Å
	$\beta = 97.66(3)°$
	$U = 1171$ Å^3
Density (calcd.)	$D_c = 1.62$ g cm^{-3}
Molecules per cell	$Z = 2$
Crystal system	monoclinic
Space group	$P2_1/c$
Absorption (Mo Kα)	$\mu = 14$ cm^{-1}
Wave length (Mo Kα)	$\lambda = 0.7107$ Å
Scan method	$\theta/2\theta$
2θ limits	$3° < 2\theta < 58°$
Scan speed	2°/min
Data collected	3593
Data with $I > 3\sigma(I)$	3120
Corrections applied	Lp, absorption [9]
Discrepancy factor	$R = 0.022$

TABLE 2. Fractional coordinates with equivalent isotropic thermal parameters (Å^2) [a]

Atom	x	y	z	U_{eq}
Sn	0.5	0.0	0.0	0.03314(7)
S(1)	0.6512(1)	0.17152(9)	−0.10788(6)	0.0486(3)
Cl(1)	0.70307(9)	0.0690(1)	0.14043(6)	0.0500(3)
N(1)	0.6096(3)	−0.0443(3)	−0.2361(2)	0.0485(9)
N(2)	0.8219(3)	0.0732(3)	−0.2392(2)	0.0436(8)
C(1)	0.6937(3)	0.0639(3)	−0.1963(2)	0.0393(9)
C(2)	0.6854(5)	−0.1044(5)	−0.3041(3)	0.063(1)
C(3)	0.8161(5)	−0.0312(4)	−0.3066(3)	0.060(1)
C(4)	0.9478(4)	0.1765(4)	−0.2181(3)	0.055(1)
C(5)	0.6423(3)	−0.1780(3)	−0.0284(2)	0.0341(8)
C(6)	0.8036(3)	−0.1643(4)	−0.0216(2)	0.043(1)
C(7)	0.8942(4)	−0.2799(4)	−0.0408(3)	0.055(1)
C(8)	0.8248(5)	−0.4081(4)	−0.0651(3)	0.057(1)
C(9)	0.6656(5)	−0.4219(4)	−0.0724(3)	0.054(1)
C(10)	0.5728(4)	−0.3073(3)	−0.0546(2)	0.043(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

organotin(IV) complexes in general [11–13]. The Sn–S bonds (2.705(1) Å), though close in length to those found in related $SnR_2X_2L_2$ systems [10,11,14], are rather longer than in the $[SnMe_2X_2(Hmimt)]$ compounds [6,7], and in fact longer than the sums of the covalent (2.42 Å) and atomic (2.45 Å) radii. This suggests that the Sn–S bond is relatively weak.

The structure of the imidazoline ring is unremarkable [5]. The S–C bond length, 1.714(3) Å, is slightly shorter than the 1.75 Å generally accepted for the S–C(sp^2) single bond [15], showing that the S–C bond retains some double bond character. The C(5)–Sn–S(1)–C(1) torsion angle is 34.7°. The orientation of the imidazoline ring seems both to prevent steric hindrance involving the methyl substituent and to facilitate intramolecular hydrogen bonding between Cl(1)^i and the H atom attached to N(1) (Cl ··· H 2.35 Å; see Table 3). No other hydrogen bonds are present.

The phenyl planes approximately bisect the S(1)–Sn–Cl(1) angle, the S(1)–Sn–C(5)–C(10) torsion angle being 47.5°. This orientation presumably minimizes repulsion between the phenyls and the equatorial ligands.

3.2. *Mass spectra*

The presence in the spectra of an intense (Hmimt) ion signal (the most intense) and several others due to its fragmentation, and the absence of any signal due to the molecular ion, are in keeping with the fast fragmentation of the tin compounds under EI conditions following a pathway in which the breaking of the Sn–S bond is an essential step.

TABLE 3. Bond lengths (Å) and angles (°) for $[SnPh_2Cl_2(Hmimt)_2]$. E.s.d's in parentheses refer to the last significant digit

Sn–Cl(1)	2.587(1)	Sn–S(1)	2.705(1)
Sn–C(5)	2.154(3)	S(1)–C(1)	1.714(3)
N(1)–C(1)	1.339(4)	N(1)–C(2)	1.376(5)
C(2)–C(3)	1.328(6)	N(2)–C(3)	1.385(5)
N(2)–C(1)	1.342(4)	N(2)–C(4)	1.462(4)
Cl(1)–Sn–C(5)	90.19(8)	S(1)–Sn–C(5)	91.41(8)
S(1)–Sn–Cl(1)	88.63(4)	Sn–S(1)–C(1)	104.2(1)
N(1)–C(1)–N(2)	106.5(3)	C(1)–N(1)–C(2)	110.0(3)
N(1)–C(2)–C(3)	107.0(3)	N(2)–C(3)–C(2)	107.6(3)
C(1)–N(2)–C(3)	109.0(3)	C(1)–N(2)–C(4)	125.6(3)
C(3)–N(2)–C(4)	125.4(3)	S(1)–C(1)–N(1)	128.1(2)
S(1)–C(1)–N(2)	125.4(2)		
N(1)–H ··· Cl(1)^i	160	N(1)–H 0.89, H ··· Cl(1)^i 2.35, N(1) ··· Cl(1)^i 3.204	

Symmetry code: none $= x, y, z$; i $= 1 - x, -y, -z$.

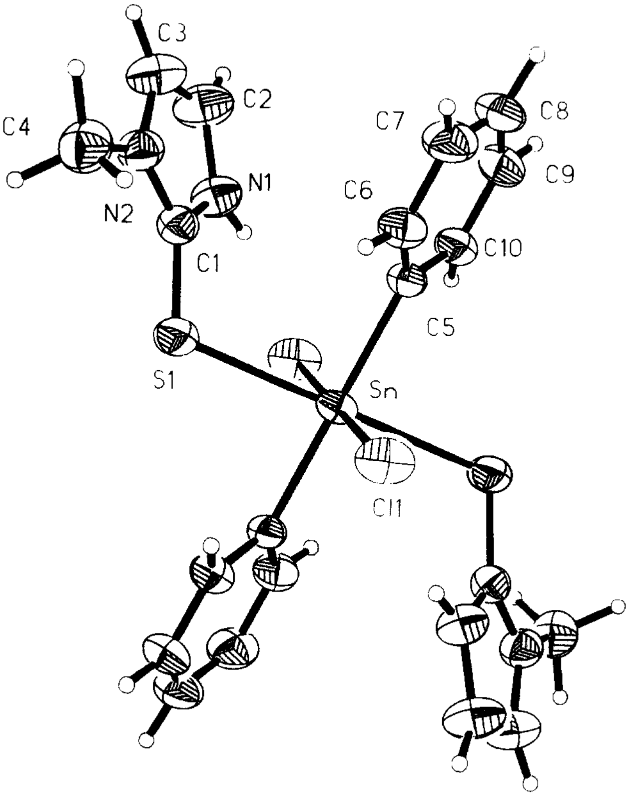

Fig. 1. Molecular structure of $[SnPh_2Cl_2(Hmimt)_2]$ showing the atom numbering scheme.

3.3. Mössbauer spectra

Table 4 lists the values of the Mössbauer parameters δ and ΔE_Q for the compounds prepared. For $[SnPh_2Cl_2(Hmimt)_2]$, ΔE_Q is in keeping with the all-*trans* octahedral structure determined by X-ray diffraction, and both ΔE_Q and δ are close to the values found in similar tin $SnPh_2Cl_2S_2$ environments [10]. The ΔE_Q value for this compound, together with the structural data, was used to calculate the partial quadrupole splitting (p.q.s.) for the imidazolinethione (−0.36 mm/s). The high value for the line width (1.30 mm/s) can be explained by a small positional disorder of the ligands around the tin. This is not in contradiction with the centrosymmetric arrangement of the crystal structure, because the sample for the Mössbauer measurements was obtained by powder material, and not from single crystals.

TABLE 4. Mössbauer parameters [a] (80.0 K)

Compound		δ [b]	ΔE_Q	Γ
$[SnPh_2Cl_2(Hmimt)]$	**1**	1.52	2.76	1.05 0.97
$[SnPh_2Cl_2(Hmimt)_2]$	**2**	1.59	3.32	1.37 1.23
$(Et_4N)[SnPh_2Cl_3(Hmimt)]$	**3**	1.49	3.32	0.91 0.93

[a] mm s^{-1}. [b] relative to room temperature SnO_2

A similar *trans* C–Sn–C arrangement in an octahedral environment is suggested by the values of δ and ΔE_Q for $(NEt_4)[SnPh_2Cl_3(Hmimt)]$. The point charge model using the calculated p.q.s. value for Hmimt and a C–Sn–C angle of 160°, gives a value of 3.35 mm/s for ΔE_Q. Both δ and ΔE_Q are greater than for the $[SnPh_2Cl_3]^-$ anion ($\delta = 1.20$; $\Delta E_Q = 2.56$) [16], from which the complex may be considered as derived, in keeping with an increase in s-electron density on the Sn atom and the change from an equatorial C–Sn–C fragment placed in a trigonal bipyramidal structure to a *trans* C–Sn–C fragment in a distorted octahedral arrangement, (*cf.* the values $\delta = 1.33$, $\Delta E_Q = 3.42$ for the ion $[SnPh_2Cl_4]^{2-}$ [16]).

The δ value for $[SnPh_2Cl_2(Hmimt)]$ falls between those of compounds **2** and **3** which undoubtedly have an octahedral coordination (Table 4). Thus a similar s-electron density at tin is likely in all the three complexes and a similar coordination can be inferred. To rationalize the low value for the quadrupole splitting, and bearing in mind that the related compound $[SnMe_2Cl_2(Hmimt)]$ [7] is an octahedral dimer with Sn–Cl–Sn bridges, calculations based on the point charge model have been performed by using the p.q.s. value obtained from compound **2** for imidazolinethione. For a dimeric complex with two apical and one equatorial chloro atoms, one Hmimt and two phenyl groups, and C–Sn–C angle of 130°, ΔE_Q was

TABLE 5. Significant IR and Raman bands (600–200 cm^{-1})

Compound		ν(Sn–S)	ν_{as}(Sn–C)	ν_{sym}(Sn–C)	ν_{as}(Sn–Cl)
$[SnPh_2Cl_2(Hmimt)]$	IR	350m [a]	280sh	225m	260m
	R	347w	–	227m	262m
$[SnPh_2Cl_2(Hmimt)_2]$	IR	–	290sh, 280s	230sh	220m
	R	–	–	225m	220sh
$(Et_4N)[SnPh_2Cl_3(Hmimt)]$	IR	–	280s	235m	260m
	R	–	–	232m	256m

[a] s = strong; m = medium; sh = shoulder; w = weak.

calculated to be 2.71 mm/s, in good agreement with experiment.

3.4. Vibrational spectra

The shifts that Hmimt bands in the range 2000–600 cm^{-1} undergo upon coordination are similar to those found in other dialkyltin complexes [5,7]. Bands typical of phenyltin compounds at around 1070, 1020, 1000, 730 and 700 cm^{-1} [17] were exhibited by all the compounds prepared. As for other 1:1 systems [17], a strong band at 460 cm^{-1} is split in the spectrum of $[SnPh_2Cl_2(Hmimt)]$, but not in those of the other two compounds.

The significant bands in the range 600–200 cm^{-1} are listed in Table 5. The positions and intensities of ν_{as}(Sn–C) and ν_{sym}(Sn–C) in the IR and Raman spectra of $[SnPh_2Cl_2(Hmimt)_2]$ are in keeping with the X-ray and the Mössbauer data and with previous data for compounds with an all-*trans* octahedral structure [10] or at least a *trans* C–Sn–C fragment [17]. The position of ν(Sn–Cl) is typical of all-*trans* octahedral complexes [10].

For $(Et_4N)[SnPh_2Cl_3(Hmimt)]$ too, the positions and intensities of ν_{as}(Sn–C) and ν_{sym}(Sn–C) are consistent with the Mössbauer data. As in the related methyl derivative, ν(Sn–Cl) shifts to lower wavenumbers than in the corresponding $SnR_2Cl_3^-$ ion [18], showing an increase in the coordination number of tin.

For $[SnPh_2Cl_2(Hmimt)]$, the positions of ν_{as}(Sn–C) and ν_{sym}(Sn–C) are close to those found in the spectra of other compounds of $SnPh_2Cl_2$ of similar stoichiometry in which, as in this case, C–Sn–C is thought to be non-linear [10,17]. Unlike these compounds, $[SnPh_2Cl_2(Hmimt)]$ has no IR or Raman bands attributable to ν(Sn–Cl) at > 300 cm^{-1} (a medium IR and Raman band at 350 cm^{-1} should probably be attributed to ν(Sn–S) [7]). This supports the Mössbauer data in suggesting a dimeric structure with Cl bridges, similar to $[SnMe_2Cl_2(Hmimt)]$ [7].

3.5. NMR spectra

The main ^{13}C NMR parameters of $[SnPh_2Cl_2(Hmimt)_2]$ and $(Et_4N)[SnPh_2Cl_3(Hmimt)]$ in $CDCl_3$ solution are listed in Table 6 together with those of $SnPh_2Cl_2$ and Hmimt; the values for Hmimt are close to those reported in ref. [19]. $CDCl_3$ was used, rather than donor solvents such as D_2O and DMSO-d_6, to avoid the possible displacement of Hmimt from the coordination sphere of the tin [5]. Due to the low solubility of the two compounds in deuterated chloroform, saturated solutions (*ca.* 10^{-2} M) were used.

Regarding the 1:1 adduct, its ^1H NMR spectrum indicates that the interaction of the solid compound with the $CDCl_3$ solvent is not a simple solution process. Hmimt seems to dissolve so as to give rise to a solution with practically a 1:2 acceptor:donor mole ratio and with spectral parameters like those of $[SnPh_2Cl_2(Hmimt)_2]$ solutions. Therefore Table 6 does not include data for this compound.

In the ^{13}C NMR spectrum of the 1:2 adduct the Hmimt signals are shifted only very slightly from their positions in the spectrum of the free donor, as in the case of $[SnMe_2Cl_2(Hmimt)_2]$ [7]. As has been observed in other dichlorodiphenyltin(IV) adducts [20], the resonance of *ipso* carbon of the phenyl groups (C(5)) shifts towards higher frequencies upon coordination, though the small magnitude of the shift in $[SnPh_2Cl_2(Hmimt)_2]$ (*ca.* 2.5 ppm, suggestive of five-coordination [20]) indicates that the six-coordination observed in the solid state is lost in solution. A similar conclusion was reached for $[SnMe_2Cl_2(Hmimt)_2]$ [7]. Though the poor solubility of the phenyl compound prevented measurement of ^1J(Sn–C) to confirm pentacoordination, this question was further explored by ^{119}Sn NMR spectroscopy of mixtures of acceptor and donor in various mole ratios in chloroform. Table 7 shows the observed $\delta(^{119}Sn)$ values. The progressive shift to lower frequencies as the proportion of Hmimt increases indicates a concomitant increase in the coordination number of the tin atom [21], but the small value of $\delta(^{119}Sn)$ suggests that hexacoordination is not reached even in the 1:3 mixture [21], so corroborating the dissociation of $[SnPh_2Cl_2(Hmimt)_2]$ in chloroform. The fact that interaction between diphenyldichlorotin(IV) and Hmimt shielded the metallic nucleus rather less than the formation of other adducts [22–24] is possibly due to the weaker donor properties of the thione group.

TABLE 6. ^{13}C NMR parameters (δ in ppm, J in Hz)

Compound	C(1)	C(2)	C(3)	N(1)–CH_3	C(5)	C(6,10)	C(7,9)	C(8)	^2J(Sn–C)
Hmimt	160.2	119.0	114.0	34.0	–	–	–	–	–
$SnPh_2Cl_2$	–	–	–	–	136.8	134.9	129.7	131.8	63.3
$[SnPh_2Cl_2(Hmimt)_2]$	159.8	119.6	114.4	34.5	139.3	135.2	129.5	131.4	64.1
$(Et_4N)[SnPh_2Cl_3(Hmimt)]$	–	119.3	114.3	34.4	148.2	136.3	128.1	129.4	68.6
$[SnPh_2Cl_3]^-$ [a]	–	–	–	–	147.0	136.4	128.5	129.9	67.0

[a] $SnPh_2Cl_2 + Et_4NCl$ (1:1 mole ratio, *ca.* 2.5 10^{-2} M).

TABLE 7. ^{119}Sn NMR data for various mole ratios of $SnPh_2Cl_2$ (A), Hmimt (D) and for Et_4NCl (Cl) in chloroform

A:D	$\delta(^{119}Sn)$	A:D:Cl	$\delta(^{119}Sn)$
1:0 [a]	−37.0	1:0:1	−258 [b]
1:1	−83.6	1:1:1	−251.1
1:2	−117.8		
1:3	−139.7		

[a] Concentration *ca.* 2.5×10^{-2} M. [b] Ref [22].

The ^{119}Sn chemical shift for a mixture of $SnPh_2Cl_2$, Hmimt and Et_4NCl (Table 7) is practically the same as that observed for $SnPh_2Cl_3^-$, suggesting that $[SnPh_2Cl_3(Hmimt)]^-$ also dissociates in chloroform:

$$[SnPh_2Cl_3(Hmimt)]^- \rightleftharpoons [SnPh_2Cl_3]^- + Hmimt$$

The differences between the ^{13}C NMR spectra (Table 6) of this system and $SnPh_2Cl_2$ are ascribed mainly to the effect of the additional chloride [see in Table 6 the values for $SnPh_2Cl_2 + Et_4NCl$ mixture (1:1 mole ratio)].

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