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Synthesis, crystal structures and spectroscopic properties of dichloroethylphenyltin(IV) and its phenanthroline adduct

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The reaction of dichloroethylphenyltin(IV), $Ph(Et)SnCl_2$, with phenanthroline monohydrate ($phen{\cdot}H_2O$) in chloroform, in 1:1 mole ratio, afforded $[Ph(Et)SnCl_2(phen)]$. The crystal structures of dichloroethylphenyltin(IV) and its phenanthroline adduct were studied by X-ray diffraction. In $Ph(Et)SnCl_2$ the tin atom is in a distorted tetrahedral environment, the distortion probably being imposed by weak intermolecular $Sn \cdots Cl$ interactions. In $[Ph(Et)SnCl_2(phen)]$ the tin atom is in an octahedral *trans*-C_2, *cis*-Cl_2, N_2 environment and weak intermolecular $C{-}H \cdots Cl$ interactions connect the molecules throughout the lattice. Spectroscopic studies in solution (^1H, ^{13}C and ^{119}Sn NMR) were also carried out; the ^1H and ^{13}C NMR data in dimethylsulfoxide suggest that $[Ph(Et)SnCl_2(phen)]$ remains at least partially undissociated in this solvent.

KEYWORDS: crystal structure; ^1H NMR; ^{13}C NMR; ^{119}Sn NMR; mixed diorganotin complexes; phenanthroline complexes

INTRODUCTION

The coordination behaviour of R_2Sn^{2+} derivatives (R = alkyl or aryl groups) with ligands coordinating through oxygen, sulfur or nitrogen donor atoms has been widely explored, and a large number of the complexes obtained have been characterized structurally in the solid state by X-ray diffraction.[1–3] Such studies are of both chemical and pharmaceutical interest, since some of these complexes show biological activity[4] (mainly *in vitro* carcinostatic activity). In particular, structural and biological studies of $R_2Sn{-}N$ compounds have shown a structure–activity relationship between carcinostatic activity and Sn–N bond length.[5,6]

In continuance of our structural studies of mixed diorganotin(IV) derivatives,[7,8] in the work described here we studied the crystal structures of $Ph(Et)SnCl_2$ and its phenanthroline adduct.

EXPERIMENTAL

Materials

All chemicals were reagent grade and were used as received. Et_4Sn, $PhSnCl_3$ and 1,10-phenanthroline monohydrate were purchased from Aldrich.

Measurements

Analytical data were obtained with a Fisons Instruments EA1108 CHNS-O microanalyser. Melting points were determined using a Büchi apparatus. Mass spectra were recorded on a Kratos MS50 TC spectrometer connected to a MACH30 system and operating under fast atom bombardment (FAB) conditions (NBA matrix). ^1H and ^{13}C NMR spectra were run on a Bruker AMX 300 apparatus at 300.14 MHz and 75.48 MHz respectively and were referred to the solvent signals [^1H: 7.26 ($CDCl_3$), 2.49 (dimethylsulfoxide, DMSO-d_6) ppm; ^{13}C: 39.5 (DMSO-d_6) ppm]. ^{119}Sn NMR spectra in $CDCl_3$, CD_2Cl_2 or DMSO were recorded on a Bruker AMX 500 spectrometer at 186.50 MHz and referred to external pure Me_4Sn, and ^{15}N NMR spectra in DMSO-d_6 were obtained on a Bruker AMX 500 at 50.59 MHz by means of an HMBC ($^1H{-}^{15}N$) experiment and were referred to external pure CH_2NO_2. All chemical shifts are reported as δ (ppm) values.

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Synthesis

Ph(Et)$SnCl_2$ was prepared by a published method[9] by reacting Et_4Sn (1.98 g, 8.46 mmol) and $PhSnCl_3$ (1.4 ml, 8.46 mmol). Yield: 70%. Anal. Found: C, 32.34; H, 3.40. Calc. for $C_8H_{10}Cl_2Sn$: C, 32,49; H, 3.41%.

^{1}H NMR ($CDCl_3$): 1.52 (t, 3H, CH_3), 1.97 (c, 2H, CH_2), 7.52 (m, 3H, $H_{m,p}$–Ph), 7.64 (m, 2H, H_o–Ph), $^2J[^1H(CH_2)-^{119}Sn] = 61.22$ Hz, $^3J[^1H(CH_3)-^{119}Sn] = 147.4$ Hz; ^{1}H NMR (DMSO-d_6): 1.31 (t, 3H, CH_3), 1.69 (c, 2H, CH_2), 7.35 (m, 3H, $H_{m,p}$–Ph), 7.84 (m, 2H, H_o–Ph), $^2J[^1H(CH_2)-^{117/119}Sn] = 115.0/119.4$ Hz, $^3J[^1H(CH_3)-^{117/119}Sn] = 196.2/205.2$ Hz, $^3J[^1H(H_o-Ph)-^{119}Sn] = 101.3$ Hz. ^{13}C NMR (DMSO-d_6): 10.9 (CH_3), 34.2 (CH_2), 127.2 (C_m–Ph), 127.7 (C_p–Ph), 134.9 (C_o–Ph), 155.0 (C_{ipso}–Ph); $^1J[^{13}C(CH_2)-^{117/119}Sn] = 1062/1110$ Hz, $^1J[^{13}C(C_o-Ph)-^{117/119}Sn] = 1267/1324$ Hz, $^2J[^{13}C(CH_3)-^{119}Sn] = 58.8$ Hz, $^2J[^{13}C(C_o-Ph)-^{117/119}Sn] = 64.7/67.6$ Hz, $^3J[^{13}C(C_m-Ph)-^{117/119}Sn] = 103.9/108.2$ Hz, $^4J[^{13}C(C_p-Ph)-^{119}Sn] = 21.1$ Hz. ^{119}Sn NMR: 39.6 ($CDCl_3$); 44.4 (CD_2Cl_2), −316.0 (DMSO).

Crystallization from CH_2Cl_2 at 4 °C yielded colourless crystals suitable for study by X-ray diffraction.

[Ph(Et)$SnCl_2$(phen)]

A solution of 0.067 g (0.34 mmol) of phenanthroline monohydrate in chloroform (5 ml) was added to a solution of 0.1 g (0.34 mmol) of Ph(Et)$SnCl_2$ in the same solvent. After a few minutes of stirring, a white solid was formed which was filtered out and vacuum dried. Yield: 90%, m.p.: 230 °C. Anal. Found: C, 50.45; H, 4.12; N, 5.93. Calc. for $C_{20}H_{18}Cl_2N_2Sn$: C, 50.47; H, 3.80; N, 5.89%.

The main metallated ions in the FAB spectrum were at *m/z* (%) 447 ([Ph$SnCl_2$(phen)], 26), 441 ([Ph(Et)SnCl(phen)], 46.7), 399 ([Et$SnCl_2$(phen)], 10.2), 335 ([SnCl(phen)], 42.8), 181 ([phen + H], 100).

^{1}H NMR (0.1 M in DMSO, see Fig. 3 for numbering scheme): 0.95 (t, 3H, CH_3), 1.54 (c, 2H, CH_2), 7.04 (m, 3H, $H_{m,p}$–Ph), 7.58 (m, 2H, H_o–Ph), 8.15 (dd, 2H, H10,19), 8.19 (s, 2H, H14,15), 8.85 (d, 2H, H11,18), 9.52 (d, 2H, H9,20), $^2J[^1H(CH_2)-^{119}Sn] = 117.8$ Hz, $^3J[^1H(CH_3)-^{119}Sn] = 207.2$ Hz, $^3J[^1H(H_o-Ph)-^{119}Sn] = 104.2$ Hz. ^{13}C NMR (0.1 M in DMSO): 10.5 (CH_3), 35.7 (CH_2), 125.2 (C10,19), 127.4 (C_m–Ph), 127.5 (C14,15), 127.6 (C_p–Ph), 129.5 (C12,16), 133.8 (C_o–Ph), 139.7 (C11,18), 141.0 (C13,17), 148.6 (C9,20), 155.4 (C_{ipso}–Ph); $^1J[^{13}C(CH_2)-^{117/119}Sn] = 1120/1176$ Hz, $^2J[^{13}C(CH_3)-^{119}Sn] = 60.3$ Hz, $^2J[^{13}C(C_o-Ph)-^{119}Sn] = 67$ Hz, $^3J[^{13}C(C_m-Ph)-^{119}Sn] = 110$ Hz. ^{119}Sn NMR: −320.2 (CD_2Cl_2), −323.0 (DMSO).

Crystals suitable for study by X-ray diffraction were obtained by recrystallization in acetone–chloroform.

Crystallographic data collection and structure determination

X-ray crystallography was performed using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation ($\lambda = 1.54184$ Å). The absorption corrections were empirical[10] for Ph(Et)$SnCl_2$ and analytical[11] for [Ph(Et)$SnCl_2$(phen)]. The structures were solved by direct methods and refined on F^2 by a full-matrix least-squares procedure using SHELX97.[12] Each hydrogen atom was positioned stereochemically and was refined riding on the atom to which it was bound. In the refinement procedure, all non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from Ref. 13. Illustrations were drawn with ORTEP.[14] The crystal data, data-collection procedure and refinement results are summarized in Table 1.

RESULTS AND DISCUSSION

Crystal structure of Ph(Et)$SnCl_2$

The molecular structure of Ph(Et)$SnCl_2$ is represented in Fig. 1. Selected bond lengths and angles are listed in Table 2.

Table 1. Crystal and structure refinement data

	Ph(Et)$SnCl_2$	[Ph(Et)$SnCl_2$(phen)]
Empirical formula	$C_8H_{10}Cl_2Sn$	$C_{20}H_{18}Cl_2N_2Sn$
Formula weight	295.75	475.95
Temperature (K)	293(2)	293(2)
Crystal system/space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Unit cell dimensions		
a (Å)	9.193(2)	9.007(2)
b (Å)	10.744(5)	11.906(3)
c (Å)	11.170(8)	18.251(7)
β (°)	105.78(3)	93.60(2)
Volume (Å^3)	1061.7(9)	1953.4(10)
Z	4	4
D_c (Mg m^{-3})	1.850	1.618
Absorption coefficient (mm^{-1})	23.286	12.949
Crystal size (mm^3)	0.14 × 0.16 × 0.22	0.1 × 0.1 × 0.1
θ range for data collection (°)	5–67.0	4.4–67.1
Reflections collected	1996	3718
Independent reflections (R_{int})	1891 (0.0351)	3485 (0.0487)
Final R indices, R_1, wR_2 [$I > 2\sigma(I)$]	0.037, 0.092	0.045, 0.118
Largest diff., peak (e$^-$ Å^{-3})	0.84, −0.69	1.15, −0.49
CCDC no.	170845	170846

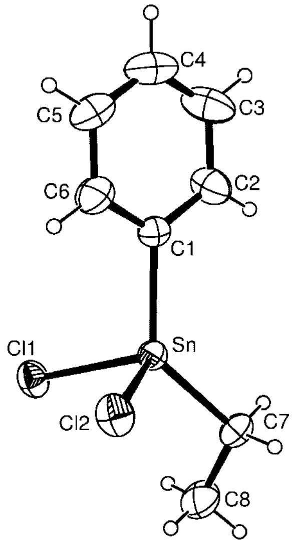

Figure 1. ORTEP drawing showing the molecular structure of Ph(Et)SnCl$_2$, with the numbering scheme used. The ellipsoids correspond to 30% probability.

Table 2. Selected bond lengths (Å) and bond angles (°)

	Ph(Et)SnCl$_2$	[Ph(Et)SnCl$_2$(phen)]
Sn–C(1)	2.112(7)	2.155(7)
Sn–C(7)	2.108(8)	2.121(10)
Sn–Cl(1)	2.367(3)	2.489(2)
Sn–Cl(2)	2.359(2)	2.4646(18)
Sn–N(1)		2.386(5)
Sn–N(2)		2.367(5)
C(1)–Sn–Cl(1)	104.8(2)	93.3(2)
C(1)–Sn–Cl(2)	105.2(2)	92.89(17)
C(1)–Sn–N(1)		98.2(2)
C(1)–Sn–N(2)		88.0(2)
C(7)–Sn–C(1)	131.5(3)	173.9(3)
C(7)–Sn–Cl(1)	108.8(2)	91.9(2)
C(7)–Sn–Cl(2)	105.0(2)	89.1(2)
C(7)–Sn–N(1)		85.0(3)
C(7)–Sn–N(2)		88.2(3)
N(1)–Sn–Cl(1)		165.59(13)
N(1)–Sn–Cl(2)		91.01(13)
N(2)–Sn–N(1)		70.12(17)
N(2)–Sn–Cl(1)		95.76(13)
N(2)–Sn–Cl(2)		161.10(13)
Cl(2)–Sn–Cl(1)	95.83(8)	103.03(8)

The tin atom is bound to two carbon and two chlorine atoms in a highly distorted tetrahedral arrangement, the most distorted geometric parameters being the C(7)–Sn–C(1) and Cl(2)–Sn–Cl(1) angles [131.5(3)° and 95.83(8)° respectively].

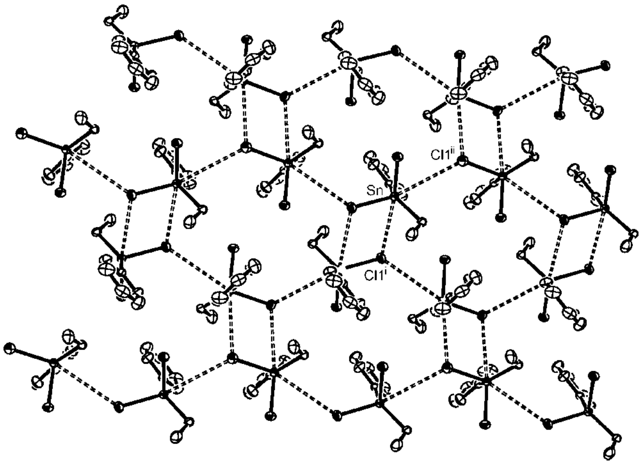

Figure 2. ORTEP plot showing the weak intermolecular Sn$\cdots$Cl interactions in Ph(Et)SnCl$_2$.

The distance from the tin to Cl(1)^i (i $= 2 - x, -y, 1 - z$) is 3.52 Å, less than the sum of the van der Waals radii (3.9–4.1 Å),[15] and this weak intermolecular bond links the molecules in dimers (Fig. 2). An additional very weak interaction Sn$\cdots$Cl(1)^{ii} (ii $= x, 0.5 - y, 0.5 + z$, Sn$\cdots$Cl(1)^{ii} = 3.94 Å) connects the dimers as shown in Fig. 2. If these two weak Sn$\cdots$Cl(1) interactions are taken into account then the metal atom may be described as having a very distorted octahedral environment with Cl(1), Cl(2), Cl(1) and Cl(1)^{ii} in the equatorial plane (RMS for SnCl(1)Cl(2)Cl(1)^{i}Cl(1)^{ii}: 0.0749) and the phenyl and ethyl groups axial (though far from their ideal positions; see above). The molecular structure of this dichlorodiorganotin(IV) compound does not differ greatly from those previously described,[16] although certain differences in supramolecular structure arise from differences as regards the weak intermolecular Sn$\cdots$Cl interactions. The previously reported structurally characterized members of this class that include Et or Ph groups are Et$_2$SnCl$_2$,[17] Ph(Me)SnCl$_2$,[18] and Ph$_2$SnCl$_2$.[19] Et$_2$SnCl$_2$ forms polymeric chains in which each chlorine atom is weakly bound to the tin atom of a neighbouring molecule;[17] the asymmetric unit of Ph(Me)SnCl$_2$ consists of two different molecules (1 and 2) that are associated with two others (1′ and 2′) in a linear tetramer in which 1 and 1′ are central and 2 and 2′ terminal [in molecule 1, one chlorine atom bridges between Sn(1) and Sn(2) and the other between Sn(1) and Sn(1)′; in molecule 2, only one chlorine atom acts as a bridge];[18] Ph$_2$SnCl$_2$, though described as a discrete molecule,[19] is similar to Ph(Me)SnCl$_2$, but with weaker bridges. In Ph(Et)SnCl$_2$, Cl(2) is not involved in any weak intermolecular interaction, whereas Cl(1) interacts with two different tin atoms, Sn^i (i $= 2 - x, -y, 1 - z$) and Sn^{ii} (ii $= x, 0.5 - y, -0.5 + z$). These two interactions give rise to a polymeric layer parallel to the *bc* plane (see Fig. 2).

As in similar compounds, there are also several very weak intra- and inter-molecular C–H···Cl interactions.

Crystal structure of [Ph(Et)$SnCl_2$(phen)]

Figure 3 shows the molecular structure of [Ph(Et)$SnCl_2$(phen)]. Selected bond distances and angles are listed in Table 2.

The tin atom coordinates to two carbon, two chlorine and two nitrogen atoms in a distorted octahedral arrangement. The Sn–C, Sn–Cl and Sn–N bond lengths are within the ranges found in [R_2SnCl_2(phen)] derivatives.[1,20] As expected, the Sn–C and Sn–Cl bonds are longer than those of the free acceptor Ph(Et)$SnCl_2$. As in most adducts of this type, the phenanthroline ligand and the two chlorine ligands are in the equatorial plane, and the aryl and alkyl groups are in axial positions. The C–Sn–C unit is slightly bent (6°) towards the phenanthroline ligand. The phen bite angle, N–Sn–N [70.12(17)°], is 20° narrower than the ideal octahedral value (90°), whereas Cl–Sn–Cl at 103.3(8)° is 13° wider.

No additional Sn···Cl interactions were detected, but several weak C–H···Cl interactions were. The latter, which are probably imposed by the stereochemistry or crystal packing, are analogous to those previously observed in [Ph(Me)$SnCl_2$(phen)][20] and include both intra- and inter-molecular interactions. The asymmetric orientation of the phenyl ring with respect to the ligands in the equatorial plane places H(6) close enough to Cl(1) to establish a weak intramolecular C(6)–H(6)···Cl(1) interaction [C(6)–H(6)···Cl(1): 0.93, 2.79, 3.373(10) Å, 122°] and there may also be a C(20)–H(20)···Cl(1) interaction [C(20)–H(20)···Cl(1): 0.93, 3.00, 3.637(7) Å, 127°]. The strongest intermolecular interaction (see Fig. 4), which involves Cl(2) and $H(18)^i$ [$i = 0.5 + x, 0.5 - y, 0.5 + z$, $C(18)^i$–$H(18)^i$···Cl(2): 0.93, 2.81, 3.479(7) Å, 129.5°], gives rise to polymeric chains that are linked in a three-dimensional lattice by weak Cl(1)···$H(19)^{ii}$ interactions [$ii = 1 - x, 1 - y, -z$, $C(19)^{ii}$–$H(19)^{ii}$···Cl(1): 0.93, 2.96, 3.600(8) Å, 127.5°].

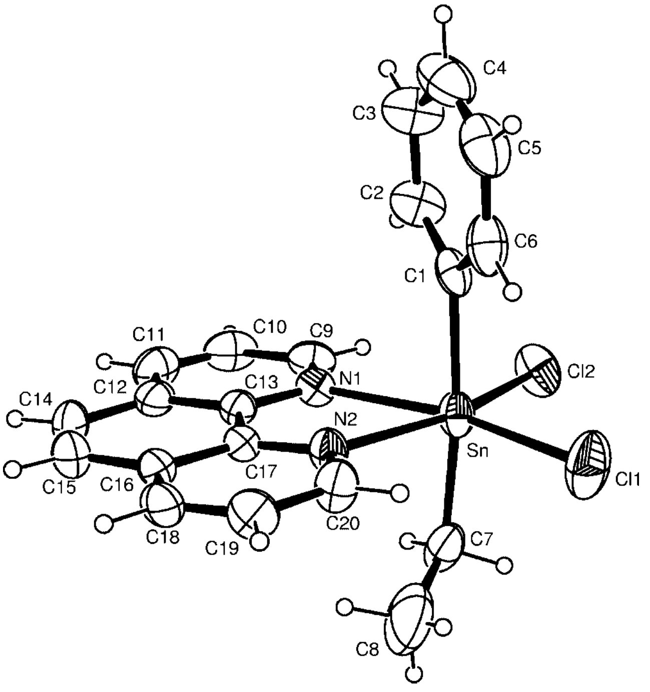

Figure 3. ORTEP drawing showing the molecular structure of [Ph(Et)$SnCl_2$(phen)], with the numbering scheme used. The ellipsoids correspond to 30% probability.

NMR studies

The ^{119}Sn chemical shift and ^nJ values for [Ph(Et)$SnCl_2$(phen)] in DMSO (see Experimental) are close to those obtained for Ph(Et)$SnCl_2$ in the same solvent. Since Ph(Et)$SnCl_2$ probably forms the complex [Ph(Et)$SnCl_2(DMSO)_2$] in DMSO, this suggests that either [Ph(Et)$SnCl_2$(phen)] dissociates in this solvent, phen being replaced by DMSO molecules, or that phen and DMSO have similar effects on the above-mentioned NMR parameters. The latter is very possible, since, for example, the $^2J(^1H-^{119}Sn)$ value for Me_2SnCl_2 in DMSO (114.8 Hz)[21] is almost the same as the 115.6 Hz reported for [Me_2SnCl_2(phen)] in dichloromethane,[21] a solvent in which the latter complex is probably undissociated. Furthermore, the ^{119}Sn chemical shift of [Ph(Et)$SnCl_2$(phen)] is practically the same in DMSO (−323.0 ppm) as in CD_2Cl_2(−320.2 ppm).

In the ^1H NMR spectrum of [Ph(Et)$SnCl_2$(Phen)] the H9,20, H10,19 and H11,18 signals are shifted about 0.4 ppm upfield from their positions in that of the free ligand.[22] In the ^{13}C NMR spectrum the C13,17 signal lies about 5 ppm downfield from its position in the spectrum of the free ligand, 145.5 ppm. The ^{15}N NMR signal of phen, which for the free ligand lies at −69.3 ppm in DMSO,[23] does not appear in the spectrum of the complex, suggesting that the metal may afford a more effective relaxation mechanism for the ^{15}N nucleus.

In conclusion, although the NMR data of the organometallic moiety are not conclusive, the data for the phenanthroline ligand suggest that, in DMSO, the complex is at least partially undissociated.

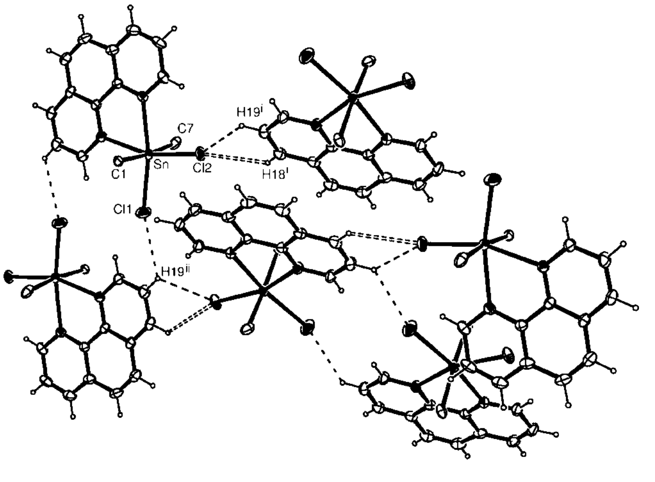

Figure 4. ORTEP plot showing weak intermolecular C–H···Cl interactions in [Ph(Et)$SnCl_2$(phen)].

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