The crystal structure of tetraethylammonium trichlorodiphenylstannate(IV)

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Abstract

The structure of tetraethylammonium trichlorodiphenylstannate(IV) has been determined by X-ray diffraction. Its crystals are monoclinic (space group, $P2_1/n$) and consist of tetraethylammonium cations and slightly distorted trigonal bipyramidal $[SnPh_2Cl_3]^-$ anions, with both phenyl groups equatorial.

Key words: Tin; X-ray diffraction

1. Introduction

Structural studies of pentacoordinate tin(IV) compounds have multiplied in recent years [1], partly because of the probable role of species with this coordination number in the nucleophilic substitution reactions of organotin derivatives, and partly because of interest in the nature of their bonding, the applicability of stereochemical models, or the influence of structural parameters on hydrogen bonding or cation–anion interactions.

The structures of anionic diorganotrihaloderivatives of tin have been studied by spectroscopic methods (in particular via their vibrational, Mössbauer and nuclear magnetic resonance (NMR) spectra) and by X-ray diffraction techniques. Although the structures of $[SnMe_2Cl_3]^-$ and $[SnEt_2Cl_3]^-$ have been determined by X-ray diffraction [2–9], the proposed trigonal bipyramidal structure of $[SnPh_2Cl_3]^-$ is based solely on vibrational [10–12] and Mössbauer [13–15] data. This paper describes the crystal structure of the tetraethylammonium salt of this anion [10], which was isolated when we tried to obtain a crystal of the salt $(Et_4N)[SnPh_2Cl_3(Hmimt)]$ (Hmimt = 1-methyl-2(3*H*)-imidazolinethione) [16].

2. Experimental details

2.1. Synthesis

A solution of $[SnPh_2Cl_2]$ (1.25 mmol) in dry acetone was slowly added to a solution of Hmimt (1.25 mmol) in the same solvent. The mixture was stirred for 3 days, a solution of $Et_4NCl \cdot H_2O$ (1.25 mmol) in dry CH_3OH was added dropwise, and after stirring for 1 day the solvent was evaporated off very slowly. The first batch of crystals obtained proved to be X-ray quality $[Et_4N][SnPh_2Cl_3]$.

2.2. Crystal structure determination

A colourless transparent crystal of $[Et_4N][SnPh_2Cl_3]$ approximately 0.10 mm × 0.20 mm × 0.25 mm was mounted on a glass rod and used for all X-ray experiments, which were carried out with an Enraf–Nonius CAD4 diffractometer at room temperature using Mo Kα radiation. The lattice parameters (Table 1) of the monoclinic crystal [space group, $P2_1/n$ (non-standard No. 14)] were refined using 25 reflections in the range $\theta = 8.46\text{–}13.61°$. Scanning between $\theta = 3°$ and $\theta = 31°$ in $\omega\text{–}2\theta$ mode afforded 6705 intensity values, 5203 of which with $I > 3\sigma(I)$ were used for structure determination. Three control reflections monitored every 2 h during data collection showed no loss of intensity.

The structure was solved by direct methods [17]. Refinement by the full-matrix least-squares method

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based on F with the weighting scheme $w = 1/\sigma^2(F)$ [18] (including all non-H atoms with isotropic displacement parameters) converged at $R = 0.087$. An empirical absorption correction applied with the program DIFABS [19] and merging improved the R value to 0.068, after which anisotropic displacement parameters were assigned to all non-H atoms, reducing R to 0.035. The positions of the hydrogen atoms were obtained by difference Fourier synthesis. Refinement with anisotropic displacement factors for all non-hydrogen atoms, with H positions included with $B_{iso} = 4.0$ Å^2 fixed but not refined, and with application of a secondary extinction correction [20] in the last cycle of the refinement, converged to the final R value of 0.025 ($R_w = 0.025$). All calculations were carried out on a DECMicroVAXII. Atomic scattering factors were taken from ref. 21. Molecular graphics were obtained with SCHAKAL [22]. The final atomic coordinates, with standard deviations, are given in Table 2. Full lists of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

3. Results and discussion

The crystal structure (see Fig. 1 for atom numbering) consists of isolated $[Et_4N]^+$ cations and $[SnPh_2Cl_3]^-$ anions (there are no interanionic Sn–Cl distances less than 6 Å). The cationic N has a tetrahedral environment. In the anion, the environment of the tin atom is trigonal bipyramidal, with both phenyl groups occupying equatorial positions. Isolated $[SnR_2Cl_3]^-$ anions such as founed here seem to be present in $[SnMe_2Cl(terpiridyl)][SnMe_2Cl_3]$ [2] $[IrH\{P(OMe)_3\}_4\{P(OMe)_2OSnMe_2Cl_2\}][SnMe_2Cl_3]$ [4] and $[SnEt_2(H_2dapin')]_2[SnEt_2Cl_3]Cl_3 \cdot H_2O$ [H_2dapin' = 2,6-diacetylpyridinebis(isonicotinoylhidrazone)] [9] whereas in all other cases where such a structure might be possible the anions dimerize through weak Sn ··· Cl interactions.

Interatomic bond lengths and angles are listed in Table 3. For the tetraethylammonium cation these values are unremarkable [23]. In the anion, the mean length of the axial Sn–Cl bonds (2.5241(7) Å) is greater than that of the equatorial Sn–Cl bond (2.3776(7) Å), although the difference between the two values is less than that in the isolated $[SnMe_2Cl_3]^-$ anion [2]. The Sn–C bond lengths are close to those found in other pentacoordinate diphenyltin systems [23]. The bond angles in Table 3 show slight distortion of the trigonal bipyramidal geometry: the C(11)–Sn–C(21) (127.51(8)°), Cl(3)–Sn–C(21) (116.91(6)°) and Cl(3)–Sn–C(11) (115.58(6)°) angles reflect the greater bulk of the phenyl rings compared with the equatorial chloride ligand, and the axial bonds are not collinear (Cl(1)–Sn–Cl(2), 174.02(2)°). In $[SnMe_2Cl_3]^-$ there is distortion in

TABLE 1. Crystal data for $(Et_4N)[SnPh_2Cl_3]$, with data collection and structure refinement details

Chemical formula	$C_{20}H_{30}Cl_3NSn$
Formula weight	509.52
Unit-cell dimensions	
a (Å)	9.725(1)
b (Å)	13.648(1)
c (Å)	17.749(2)
β (°)	101.491(1)
Volume of unit cell (Å^3)	2308.5(5)
Z	4
D_x (g cm^{-3})	1.466
$F(000)$	1032
Linear absorption coefficient (cm^{-1})	14.64
Minimum absorption correction	0.85
Maximum absorption correction	1.14
Average absorption correction	0.99
Maximum value of $(\sin\theta)/\lambda$ reached (Å^{-1}) in intensity measurement	0.682
Ranges of h, k, l	$0 \rightarrow 13, 0 \rightarrow 18, -24 \rightarrow 24$
Standard reflections	$0, -5, -6; -3, -5, 1; -4, 4, -6$
Parameters refined	227
Value of R	0.025
Value of wR	0.025
Ratio Δ/σ of maximum LS shift to estimated standard deviation	0.001
Maximum $\Delta\rho$ in final difference electron density map (electrons Å^{-3})	0.325
Error in an observation of unit weight	0.985
Secondary-extinction coefficient	8.85×10^{-8}

TABLE 2. Positional parameters and their estimated standard deviations in parentheses

Atom	x	y	z	B_{iso} (Å^2)
Sn	0.19598(2)	0.23762(1)	0.51844(1)	2.960(3)
Cl(1)	0.24347(8)	0.07349(5)	0.58494(4)	4.38(1)
Cl(2)	0.16444(7)	0.40859(5)	0.46461(4)	4.51(1)
Cl(3)	0.36741(7)	0.30366(6)	0.62017(4)	4.65(1)
N(1)	0.6513(2)	0.3763(2)	0.3144(1)	3.62(4)
C(11)	−0.0136(2)	0.2365(2)	0.5372(1)	3.16(4)
C(12)	−0.0733(3)	03198(2)	0.5627(2)	3.90(5)
C(13)	−0.2099(3)	0.3171(2)	0.5753(2)	4.54(6)
C(14)	−0.2873(3)	0.2324(3)	0.5613(2)	4.83(6)
C(15)	−0.2316(3)	0.1507(2)	0.5345(2)	4.68(6)
C(16)	−0.0942(3)	0.1518(2)	0.5232(2)	3.98(5)
C(21)	0.2686(2)	0.1850(2)	0.4201(1)	3.23(4)
C(22)	0.2059(3)	0.2190(2)	0.3472(2)	4.17(5)
C(23)	0.2469(3)	0.1823(3)	0.2820(2)	5.02(7)
C(24)	0.3528(3)	0.1145(2)	0.2887(2)	5.08(6)
C(25)	0.4173(3)	0.0812(2)	0.3600(2)	4.74(6)
C(26)	0.3748(3)	0.1159(2)	0.4260(2)	3.83(5)
C(31)	0.5737(3)	0.3447(2)	0.3767(2)	4.34(6)
C(32)	0.5692(3)	0.4512(2)	0.2603(2)	4.42(6)
C(33)	0.7898(3)	0.4218(2)	0.3526(2)	4.60(6)
C(34)	0.6750(3)	0.2866(2)	0.2681(2)	4.42(6)
C(35)	0.5290(3)	0.4278(3)	0.4225(2)	5.51(7)
C(36)	0.4199(4)	0.4209(3)	0.2260(2)	6.68(9)
C(37)	0.8865(3)	0.4489(3)	0.2983(2)	5.73(8)
C(38)	0.7650(4)	0.2071(3)	0.3128(2)	6.34(8)

the equatorial plane, but Cl_{ax}–Sn–Cl_{ax} is 180°. The axial bending in $[SnPh_2Cl_3]^-$ appears to be due to the non-coplanarity of the two quasi-planar phenyl rings [C(11)–C(16), $\chi^2 = 45.1$; C(21)–C(26), $\chi^2 = 32.7$, Cl(1)–Sn–C(11)–C(12) = 135.92(0.19)°; Cl(1)–Sn–C(21)–C(22) = 145.84 (0.20)°].

TABLE 3. Bond distances and angles with estimated standard deviations in parentheses

	Bond distance (Å)		Bond distance (Å)
Sn–Cl(1)	2.5312(7)	C(14)–C(15)	1.366(5)
Sn–Cl(2)	2.5170(7)	C(15)–C(16)	1.390(5)
Sn–Cl(3)	2.3776(7)	C(21)–C(22)	1.395(3)
Sn–C(11)	2.131(2)	C(21)–C(26)	1.387(3)
Sn–C(21)	2.134(2)	C(22)–C(23)	1.390(4)
N(1)–C(31)	1.520(4)	C(23)–C(24)	1.372(5)
N(1)–C(32)	1.516(3)	C(24)–C(25)	1.373(4)
N(1)–C(33)	1.516(3)	C(25)–C(26)	1.400(4)
N(1)–C(34)	1.518(3)	C(31)–C(35)	1.509(4)
C(11)–C(12)	1.392(4)	C(32)–C(36)	1.516(4)
C(11)–C(16)	1.392(4)	C(33)–C(37)	1.522(5)
C(12)–C(13)	1.391(4)	C(34)–C(38)	1.515(4)
C(13)–C(14)	1.375(4)		

	Bond angle (°)		Bond angle (°)
Cl(1)–Sn–Cl(2)	174.02(2)	C(32)–N(1)–C(34)	108.6(2)
Cl(1)–Sn–Cl(3)	86.91(2)	C(33)–N(1)–C(34)	110.8(3)
Cl(1)–Sn–C(11)	90.70(6)	C(12)–C(11)–C(16)	118.7(2)
Cl(1)–Sn–C(21)	91.39(7)	C(11)–C(12)–C(13)	120.3(2)
Cl(2)–Sn–Cl(3)	87.18(2)	C(12)–C(13)–C(14)	120.1(3)
Cl(2)–Sn–C(11)	91.02(7)	C(13)–C(14)–C(15)	120.5(3)
Cl(2)–Sn–C(21)	92.11(7)	C(14)–C(15)–C(16)	120.1(3)
Cl(3)–Sn–C(11)	115.58(6)	C(11)–C(16)–C(15)	120.4(3)
Cl(3)–Sn–C(21)	116.91(6)	C(22)–C(21)–C(26)	118.6(2)
C(11)–Sn–C(21)	127.51(8)	C(21)–C(22)–C(23)	120.4(3)
Sn–C(11)–C(12)	121.3(2)	C(22)–C(23)–C(24)	120.4(3)
Sn–C(11)–C(16)	120.0(2)	C(23)–C(24)–C(25)	120.1(3)
Sn–C(21)–C(22)	119.4(2)	C(24)–C(25)–C(26)	120.2(3)
Sn–C(21)–C(26)	122.0(2)	C(21)–C(26)–C(25)	120.5(2)
C(31)–N(1)–C(32)	112.2(3)	N(1)–C(31)–C(35)	114.6(2)
C(31)–N(1)–C(33)	108.5(2)	N(1)–C(32)–C(36)	114.3(3)
C(31)–N(1)–C(34)	108.4(3)	N(1)–C(33)–C(37)	115.0(2)
C(32)–N(1)–C(33)	108.4(3)	N(1)–C(34)–C(38)	115.3(2)

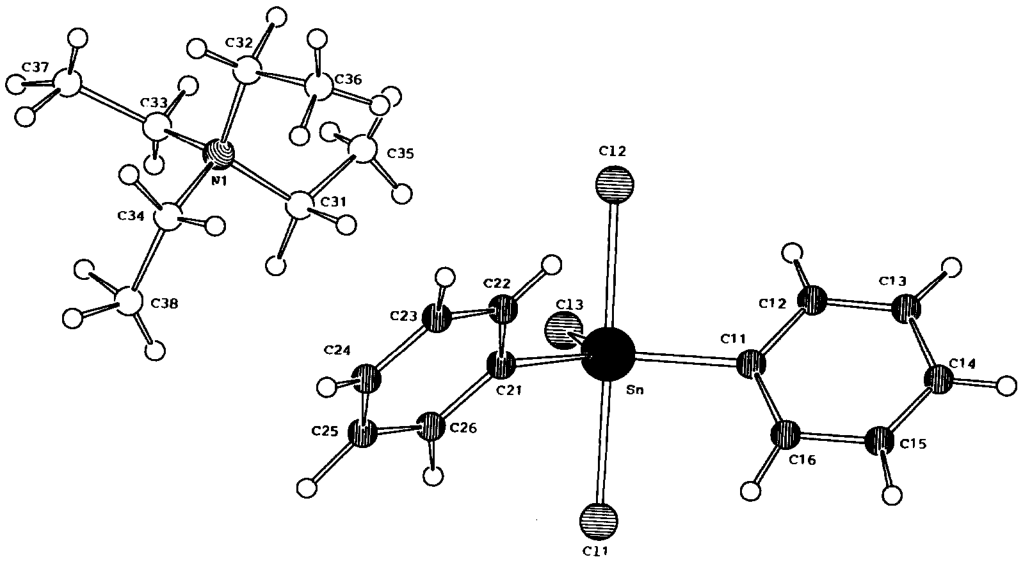

Fig. 1. Crystal structure of $(Et_4N)[SnPh_2Cl_3]$, with numbering scheme.

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