

Synthesis and structure of 1 : 1 complex of dimethyltin dichloride with *meso*-1,2-bis(α -diethoxyphosphorylbenzylamino) ethane

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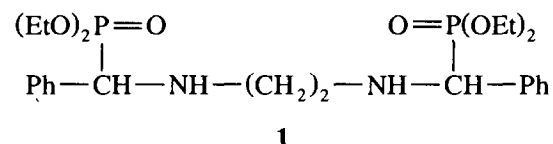
Abstract

The crystal and molecular structure of the title compound has been determined by single crystal X-ray analysis. The complex is polymeric, the ligand coordinating in a bridging mode via two phosphoryl groups. The coordination environment at tin is octahedral with two methyl groups, two chlorine and two oxygen atoms occupying trans positions.

Keywords: Tin; Phosphoryl ligand; Crystal structure

1. Introduction

Phosphoryl-containing compounds have been widely used as effective complexation agents in organotin coordination chemistry [1]. Nevertheless the complexation behaviour of ligand molecules containing other donor groups besides phosphoryl is not obvious and has not been investigated in detail so far. In this work we tried to use the aminoalkyl phosphonate ester **1** [2] in coordination with an organotin compound in order to estimate the ability of the amino group in the α position of the alkylphosphonate moiety to be engaged in coordination to tin together with a phosphoryl group:



Ligand **1** has a *meso* configuration according to X-ray diffraction data [3] and contains four donor sites which are available for the organotin moiety. The competition between phosphoryl and amino groups in **1** should lead to different possibilities of coordination in the complex

prepared from Me_2SnCl_2 and **1** in a 1:1 molar ratio, complexation either via both amino groups or via phosphoryl and amino groups giving two types of octahedral organotin chelates; also **1** can coordinate to tin via both phosphoryl units in either chelating or bridging mode.

2. Experimental section

A solution of ligand **1** (0.6 mmol) in dichloromethane was added to a solution of 0.6 mmol of Me_2SnCl_2 in the same solvent. After evaporation of the solvent a colourless viscous residue was obtained which crystallized on standing. The crystalline complex was washed with petroleum ether and dried in vacuo (melting point, 128–130°C; yield, 95%). Single crystals of the adduct were obtained by slow evaporation of the solution of the complex in chloroform. Elemental Anal. Found: C, 41.73; H, 6.04; N, 3.57. $\text{C}_{26}\text{H}_{44}\text{Cl}_2\text{N}_2\text{O}_6\text{P}_2\text{Sn}$ Calc.: C, 42.62; H, 6.01; N, 3.83%.

3. Crystal structure determination

Data for a crystal of the title complex were collected on a four-circle X-ray diffractometer. Crystal data and

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Table 1
Experimental data for the crystal structure determination of $\text{Me}_2\text{SnCl}_2 \cdot 1$

<i>Crystal data</i>	
Formula	$\text{C}_{26}\text{H}_{44}\text{Cl}_2\text{N}_2\text{O}_6\text{P}_2\text{Sn}$
Formula weight (g mol^{-1})	732.16
Absorption μ (cm^{-1})	10.8 (no correction)
Space group	$P2_1/n$
Lattice constants (Mo $\text{K}\alpha$)	
a (\AA)	9.216(1)
b (\AA)	17.516(2)
c (\AA)	10.781(2)
β ($^\circ$)	110.10(1)
Temperature (K)	233
Density d_c (g cm^{-3})	1.488
<i>Data collection</i>	
Diffractometer	4-circle, CAD4 (Enraf–Nonius)
Radiation	Mo $\text{K}\alpha$; graphite monochromator
Scan type	ω scans
Measuring ranges	
θ ($^\circ$)	2–25
hkl	$h, 0 \rightarrow 12; k, -20 \rightarrow 0; l, -12 \rightarrow +11$
Number of reflections	2713 total, 2552 unique, 2164 $> 2\sigma(I)$
<i>Computing</i>	
Programs	SHELXTL-PLUS [4], SHELXL-93 [5]
Atomic scattering factors for neutral atoms	$\Delta f', \Delta f''$ from [6]
Refinement	Full matrix least squares on F^2 ; 178 parameters
Residuals	
wR_2	0.1006 for all reflections
R	0.0348 for $F_o > 4\sigma(F)$
$\Delta\rho_{\text{max}}; \Delta\rho_{\text{min}}$ (e \AA^{-3})	1.18; -0.53

details of data collection as well as for the refinement are given in Table 1. The structure was solved by Patterson and difference Fourier methods and refined

with the full matrix against the F_o^2 data. All heavier atoms were refined using anisotropic temperature factors. The H atoms were included riding on calculated

Table 2
Fractional coordinates and equivalent isotropic temperature factors for $\text{Me}_2\text{SnCl}_2 \cdot 1$, where U_{eq} is one third of the trace of the orthogonalized U_{ij} matrix

Atom	x	y	z	U_{eq} (\AA^2)
Sn	0.0000	0.0000	0.0000	0.0265(2)
Cl	0.22880(12)	$-0.01278(6)$	$-0.08453(11)$	0.0375(3)
C(20)	0.1044(5)	$-0.0806(2)$	0.1492(4)	0.0370(9)
P	0.21605(11)	0.13055(5)	0.25792(10)	0.0279(2)
O(2)	0.3643(3)	0.0828(2)	0.3277(3)	0.0387(7)
C(3)	0.4717(5)	0.0620(3)	0.2611(4)	0.0452(11)
C(4)	0.5742(7)	0.0017(3)	0.3413(6)	0.065(2)
O(3)	0.2727(3)	0.2131(2)	0.2423(3)	0.0374(6)
C(5)	0.2447(7)	0.2519(3)	0.1182(5)	0.0620(14)
C(6)	0.0970(8)	0.2883(4)	0.0788(7)	0.092(2)
O(1)	0.1146(3)	0.09894(14)	0.1300(2)	0.0327(6)
C(1)	0.1255(4)	0.1346(2)	0.3831(4)	0.0308(8)
C(11)	0.0135(4)	0.2012(2)	0.3608(4)	0.0291(8)
C(12)	$-0.1417(5)$	0.1938(2)	0.2842(4)	0.0373(9)
C(13)	$-0.2416(5)$	0.2559(2)	0.2636(4)	0.0437(11)
C(14)	$-0.1871(5)$	0.3247(2)	0.3210(4)	0.0439(11)
C(15)	$-0.0333(5)$	0.3336(2)	0.3981(4)	0.0444(11)
C(16)	0.0655(5)	0.2720(2)	0.4176(4)	0.0370(9)
C(2)	0.0154(4)	0.0424(2)	0.4978(4)	0.0300(8)
N	0.0651(4)	0.0577(2)	0.3848(3)	0.0305(7)

Table 3
Selected bond lengths (Å) and angles (°) for Me₂SnCl₂ · 1

<i>Bond lengths</i>			
Sn–C(20)	2.108(4)	O(2)–C(3)	1.455(5)
Sn–O(1)	2.250(3)	C(3)–C(4)	1.481(7)
Sn–Cl	2.578(1)	O(3)–C(5)	1.443(5)
P–O(1)	1.482(3)	C(5)–C(6)	1.430(8)
P–O(2)	1.558(3)	C(1)–N	1.459(5)
P–O(3)	1.566(3)	C(1)–C(11)	1.521(5)
P–C(1)	1.816(4)	C(11)–C(12)	1.390(6)
C(14)–C(15)	1.384(6)	C(11)–C(16)	1.395(6)
C(15)–C(16)	1.379(6)	C(12)–C(13)	1.393(5)
C(2)–N	1.467(4)	C(13)–C(14)	1.369(6)
C(2)–C(2) ^a	1.515(8)		
<i>Bond angles</i>			
C(20) ^b –Sn–C(20)	180.0	O(1)–P–O(2)	114.6(2)
C(20)–Sn–O(1) ^b	87.28(14)	O(1)–P–O(3)	111.8(2)
C(20)–Sn–O(1)	92.72(14)	O(2)–P–O(3)	106.2(2)
O(1) ^b –Sn–O(1)	180.0	O(1)–P–C(1)	113.7(2)
C(20) ^b –Sn–Cl	90.14(11)	O(2)–P–C(1)	102.3(2)
C(20)–Sn–Cl	89.86(11)	O(3)–P–C(1)	107.4(2)
O(1) ^b –Sn–Cl	88.79(7)	C(3)–O(2)–P	121.9(3)
O(1)–Sn–Cl	91.21(7)	O(2)–C(3)–C(4)	107.2(4)
Cl–Sn–Cl ^b	180.0	C(5)–O(3)–P	125.0(3)
C(1)–N–C(2)	114.2(3)	C(6)–C(5)–O(3)	109.5(5)
		P–O(1)–Sn	151.4(2)
		N–C(1)–C(11)	117.9(3)
		N–C(1)–P	104.4(2)
		C(11)–C(1)–P	111.9(3)
		N–C(2)–C(2) ^a	108.7(4)

^a Symmetry transformation for the equivalent atoms: $-x, -y, -z + 1$.

^b Symmetry transformation for the equivalent atoms: $-x, -y, -z$.

positions with isotropic temperature factors taken as $1.2U_{eq}$ (phenyl H atoms) or $1.5U_{eq}$ (aliphatic H atoms) of the corresponding C atoms. The resulting atomic coordinates are listed in Table 2, and the bond lengths and bond angles in Table 3. The structure of the com-

plex, together with the atomic numbering scheme, is depicted in Fig. 1. Further details are obtainable from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, under specifica-

Table 4
Comparison of some bond distances (Å) and bond angles (°) in the title complex I and related adducts: Me₂SnCl₂ · 2HMPA (II), Bu₂SnCl₂ · [Ph₂P(O)CH₂]₂ (III), Ph₂SnCl₂ · [(EtO)₂P(O)CH₂]₂ (IV) and {Me₂SnCl₂ · [(EtO)₂P(O)]₂CHNMe₂]₂ (V)

	Value for the following structures				
	I this work	II [8]	III [9]	IV [10]	V [11]
<i>Bond distances</i>					
Sn–Cl	2.578(1)	2.525(1)	2.483(2)	2.459(4)	2.482(4)
		2.529(1)	2.468(3)	2.440(4)	2.482(4)
Sn–O	2.250(3)	2.231(3)	2.640(7)	2.377(9)	2.466(13)
			2.386(7)	2.328(10)	2.466(13)
Sn–C	2.108(4)	2.105(5)	2.126(9)	2.145(13)	2.08(2)
			2.112(8)	2.116(13)	2.15(2)
<i>Bond angles</i>					
Sn–O–P	151.4(2)	162.7(2)	167.8(4)	152.0(6)	150.1(7)
			163.9(4)	151.6(6)	150.1(7)
C–Sn–C	180	180	154.3(3)	161.8(6)	154.5(7)

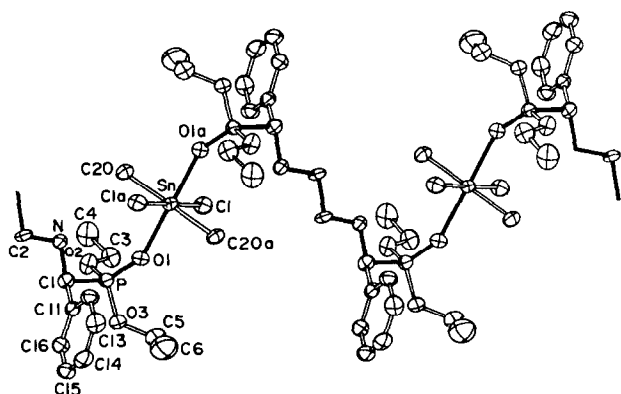


Fig. 1. Section of the infinite chain structure of $\text{Me}_2\text{SnCl}_2\text{-1}$ with labelling of the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level [4].

tion of deposit No. CSD-404390, authors and journal reference.

4. Discussion

The title complex has a polymeric crystal structure with centrosymmetric bridging molecules of the aminoalkylphosphonate ligand (Fig. 1). Only the phosphoryl groups of **1** are engaged in the coordination to tin in *trans* configuration. The two methyl substituents and the two chlorine atoms are also situated in *trans* positions, as the tin atom is placed in a centrosymmetrical octahedral environment. The main structural characteristics of **1** in the title adduct are the same as for the free ligand [3]. The Sn–O, Sn–C and Sn–Cl bond distances and the main bond angles in tin coordination octahedron of the title complex are similar to those in the Me_2SnCl_2 1:2 *trans* adduct with HMPA [7,8]. Comparison of these two *trans* adducts with related complexes with *cis*-situated donor groups (Table 4) displays that the Sn–O bonds in the *trans* adducts are significantly shorter than those in the *cis* complexes, while the Sn–Cl bond distances in these groups of adducts differ in the opposite mode, and the Sn–C bonds are approximately equal. These differences can be arise by redistribution of electron density in O–Sn–O and Cl–Sn–Cl fragments in *trans* adducts compared with O–Sn–Cl fragments in *cis* complexes. The Sn–O–P bond angles in the title adduct are similar to those in tin–phosphoryl complexes with open, dimeric and polymeric structures (Table 4).

5. NMR spectra

In order to establish the coordination mode of **1** to Me_2SnCl_2 in solution we tried to study the ^{119}Sn and ^{31}P NMR spectra of the title complex in dichloromethane at low temperatures as this is the most powerful tool for the investigation of organotin coordination compounds in the liquid phase [10,12,13]. Unfortunately, this complex appeared to be too labile in solution even at low temperatures like the other complexes of diorganotin halides with alkylphosphonic esters. At $+30^\circ\text{C}$ the ^{31}P NMR spectrum of the title adduct consists of a singlet at 18.6 ppm without tin satellites, and a broad signal centred at -80 ppm appeared in the ^{119}Sn NMR spectrum. Lowering the temperature to -90°C caused an extreme broadening of ^{31}P signal and the disappearance of the ^{119}Sn signal, so the lowering of the exchange process rate in solution of the title complex was not extended enough to provide any concrete information about the tin–phosphoryl coordination.

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