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Tin(IV) complexes with *O*-ethyl(*N*-ethyl-*N*,*N*-dimethylammoniomethyl)phosphonate

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Abstract

O,*O*-Diethyl-(*N*,*N*-dimethylaminomethyl)phosphonate undergoes ethyl migration leading to *O*-ethyl-(*N*-ethyl-*N*,*N*-dimethylammoniomethyl)phosphonate (L). Several new complexes of tin(IV) and organotin(IV) chlorides with the title ligand have been synthesized. The stoichiometry of the obtained complexes is as follows: $(R_3SnCl)_2 \cdot L$ (R = Me, Bu, Ph), $R_2SnCl_2 \cdot L$ (R = Me, Bu, Ph), $RSnCl_3 \cdot L$ (R = Me, Ph) and $SnCl_4 \cdot L$. All the complexes have been studied in solution by means of ^{1}H-, ^{13}C-, ^{31}P- and ^{119}Sn-NMR spectroscopy. Their solid state structures have been investigated by means of Mössbauer spectroscopy and the molecular structure of the complex $(Ph_3SnCl)_2 \cdot L$ has been determined by X-ray crystallography. The ligand behaves as a bidentate ligand, bridging two pentacoordinate trigonal bipyramidal organotin moieties through an O–P–O fragment. The spectroscopic data for $R_2SnCl_2 \cdot L$, $RSnCl_3 \cdot L$ and $SnCl_4 \cdot L$ suggest hexacoordinate structures with an octahedral tin environment, the complexes probably being polymeric according to the bridging ligand behavior.

Keywords: Tin; X-ray diffraction; Mössbauer spectroscopy; Phosphonic acid monoester ligand; Inner salt

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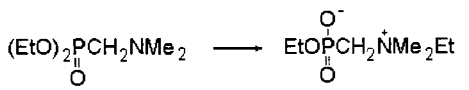
1. Introduction

Aminoalkylphosphonic acid diesters usually undergo alkyl migration to nitrogen leading to inner salts—aminoalkylphosphonic monoesters [1]. For instance, during the storage of liquid *O*,*O*-diethyl(*N*,*N*-dimethylaminomethyl)phosphonate the colorless crystals of the inner salt (L) are formed:



$$(EtO)_2\overset{}{\underset{\underset{O}{\|}}{P}}CH_2NMe_2 \longrightarrow EtO\overset{\overset{O^-}{|}}{\underset{\underset{O}{\|}}{P}}CH_2\overset{+}{N}Me_2Et$$

L

The product containing anionic phosphonate moiety is considered to have a stronger donor ability towards Lewis acids than the parent *O*,*O*-dialkylphosphonate and related ligands widely used in organotin coordination chemistry [2]. The complexation of the ligand (L) with tin(IV) and organotin(IV) chlorides illustrates its electron donor properties and the syntheses together with spectroscopic and crystallographic studies of the complexes are presented in this paper.

On the other hand, the title ligand should be considered, with certain restrictions, as the synthetic analogue of phosphono- and phospholipid molecules, especially their phosphono- and phosphocholine moieties [3]. Consequently, the complexation studies of organotin compounds with the title ligand can provide information concerning the interaction of organotin derivatives with phosphorus-containing, biologically important molecules being the key step in organotin compounds metabolism in living organisms.

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2. Experimental section

2.1. Syntheses

2.1.1. Isolation of O-ethyl(N-ethyl-N,N-dimethylammoniomethyl)phosphonate (L)

Colourless crystals of the product precipitated from parent *O,O*-diethyl-(*N,N*-dimethylaminomethyl)phosphonate (prepared as described previously [4]) were separated, washed with petroleum ether and vacuum dried. The compound is highly hygroscopic and should be stored in an inert atmosphere. M.p.: 115–120°C. ^{1}H-NMR (CDCl$_3$, δ, ppm): 1.26 (3H, t, ^3J(HH) = 7.2 Hz, CH_3CH$_2$O); 1.42 (3H, t, ^3J(HH) = 7.2 Hz, CH_3CH$_2$N); 3.37 (6H, s, Me$_2$N); 3.43 (2H, d, ^2J(HP) = 12.0 Hz, CH$_2$P); 3.74 (2H, q, ^3J(HH) = 7.2 Hz, CH$_2$N); 3.97 (2H, dq, ^3J(HH) = ^3J(HP) = 7.2 Hz, CH$_2$O). ^{13}C-NMR (CDCl$_3$, δ, ppm): 8.74 (CH$_3$CH$_2$N); 17.01 (d, ^3J(CP) = 6.4 Hz, CH$_3$CH$_2$O); 52.13 (Me$_2$N); 60.18 (d, ^2J(CP) = 5.7 Hz, CH$_2$O); 60 26 (d, ^1J(CP) = 126.4 Hz, CH$_2$P); 61.95 (CH$_2$N). ^{31}P-NMR (CDCl$_3$, δ): + 1.0 ppm.

2.1.2. Preparation of the complexes

General procedure. A solution of L in dry dichloromethane was added to a calculated amount of tin(IV) solution in the same solvent. Isolation of the complexes was performed in different ways according to their properties.

Method A: the complexes that were soluble in dichloromethane were obtained by evaporation of the solvent, washed with petroleum ether and vacuum dried.

Method B: insoluble complexes which precipitated upon mixing of the components were filtered off, washed with dichloromethane and vacuum dried. The analytical and spectroscopic data are as follows:

$(Me_3SnCl)_2\cdot L$ (**1a**). Isolation: method A. The complex appeared as a viscous mass which crystallized upon standing. M.p.: 73–75°C. Analysis (%), found: C 25.42; H 6.00; N 2.28. C$_{13}$H$_{36}$Cl$_2$NO$_3$PSn$_2$. Calc.: C 26.28; H 6.07; N 2.36. ^{31}P-NMR (CDCl$_3$. δ): − 1.9 ppm. ^{119}Sn-NMR (CDCl$_3$, δ): + 6.3 ppm (br s).

$(Bu_3SnCl)_2\cdot L$ (**1b**). Isolation: method A. The complex appeared as an oily residue. Analysis (%), found: C 42.30; H 7.61. C$_{31}$H$_{72}$Cl$_2$NO$_3$PSn$_2$. Calc.: C 43.97; H 8.51.^{31}P-NMR (CDCl$_3$, δ): − 1.4 ppm. ^{119}Sn-NMR (CDCl$_3$, δ): + 63.5 ppm (br s).

$(Ph_3SnCl)_2\cdot L$ (**1c**). Isolation: method B. The product precipitated upon standing as a white crystalline solid. M.p.: 193–195°C. Analysis (%), found: C 53.68; H 5.00; N 1.62. C$_{43}$H$_{48}$Cl$_2$NO$_3$PSn$_2$. Calc.: C 53.42; H 4.97; N 1.45. ^{31}P-NMR (DMSO-d$_6$, δ): − 0.5 ppm. ^{119}Sn-NMR (DMSO-d$_6$, δ): − 230 ppm (br s). The single crystal for X-ray diffraction study was obtained by slow evaporation of a saturated methanolic solution of **1c**.

$Me_2SnCl_2\cdot L$ (**2a**) Isolation: method B. The product separated immediately as a colorless, viscous mass which crystallized upon standing. M.p.: 125–127°C. Analysis (%), found: C 25.83; H 5.83; N 3.30. C$_9$H$_{24}$Cl$_2$NO$_3$PSn. Calc.: C 26.05; H 5.79; N 3.38. ^{31}P-NMR (CD$_3$OD, δ): + 1.3 ppm. ^{119}Sn-NMR (CD$_3$OD, δ): − 180 ppm (s).

$Bu_2SnCl_2\cdot L$ (**2b**). Isolation: method A. The product appeared as a highly viscous colorless residue. Analysis (%), found: C 35.21; H 7.25; C$_{15}$H$_{36}$Cl$_2$NO$_3$PSn. Calc.: C 36.08; H 7.22. ^{31}P-NMR (CDCl$_3$, δ): − 1.6 ppm. ^{119}Sn-NMR (CDCl$_3$, δ): − 145 ppm (br s).

$Ph_2SnCl_2\cdot L$ (**2c**). Isolation: method B. The white microcrystalline complex precipitated immediately. M.p.: 195–200°C. Analysis (%), found: C 41.85; H 5.13; N 2.69. C$_{19}$H$_{28}$Cl$_2$NO$_3$PSn. Calc.: C 42.30; H 5.19; N 2.60. ^{31}P-NMR (DMSO-d_6, δ): − 1.0 ppm. ^{119}Sn-NMR (DMSO-d$_6$, δ): − 420 ppm (br s).

$MeSnCl_3\cdot L$ (**3a**). Isolation: method B. The oily product separated immediately and became solid upon standing overnight. M.p.: 163–165°C. Analysis (%), found: C 21.04; H 4.89; N 3.07. C$_8$H$_{21}$Cl$_3$NO$_3$PSn. Calc.: C 22.04: H 4.82; N 3.21. ^{31}P-NMR (CD$_3$OD, δ): + 3.1 ppm. ^{119}Sn-NMR (CD$_3$OD, δ): − 430 ppm (br s).

$PhSnCl_3\cdot L$ (**3c**). Isolation: method B. The solid complex precipitated immediately. M.p.: 182–186°C. Analysis (%), found: C 31.17; H 4.62; N 2.81. C$_{13}$H$_{23}$Cl$_3$NO$_3$PSn. Calc.: C 31.36; H 4.62, N 2.81. ^{31}P-NMR (CD$_3$OD, δ): + 5.2 ppm. ^{119}Sn-NMR: δ not determined, the signal is extremely broadened.

$SnCl_4\cdot L$ (**4**). Isolation: method B. The white solid complex precipitated immediately. M.p.: > 250°C. Analysis (%), found: C 19.63; H 4.18; N 3.01. C$_7$H$_{18}$Cl$_4$NO$_3$PSn. Calc.: C 18.42; H 3.95; N 3.07. ^{31}P- and ^{119}Sn-NMR spectra are discussed below.

2.2. Spectroscopic studies and crystal structure determination

NMR spectra (^{1}H, ^{13}C, ^{31}P, ^{119}Sn) were recorded at 300 K using Varian VXR-400 equipment operating at 400.0, 100.6, 161.9 and 149.1 MHz, respectively. ^{1}H-NMR spectra were referenced against internal TMS or the residual proton signal of DMSO-d_6 (2.49 ppm); ^{13}C-NMR spectra were referenced against internal TMS or DMSO-d_6 carbon signal (39.5 ppm); ^{31}P-NMR spectra were referenced against external 85% H$_3$PO$_4$ and ^{119}Sn-NMR spectra were referenced against external Me$_4$Sn. ^{119m}Sn Mössbauer spectra of compounds **1c, 2a** and **2c** were recorded using a Laben 8001 multichannel analyzer, an MWE velocity transducer generator, an FG2 digital function generator and MA 250 velocity

Table 1
Crystal structure data of **1c**

Crystal data	
Habitus, color	Nugget, colorless
Crystal size	$0.30 \times 0.20 \times 0.10$ mm
Crystal system	Triclinic
Space group	$P\bar{1}$, $Z = 2$
Unit cell dimensions	$a = 1039.4$ (1) pm
	$b = 1121.5$ (1) pm
	$c = 1944.9$ (2) pm
	$\alpha = 106.942$ (11)°
	$\beta = 103.943$ (12)°
	$\gamma = 95.087(9)$°
Volume	2073.9 (4)$*10^{-30}$ m^3
Cell determination	25 reflections, 35.2–41.5°, 2θ
Chemical formula	$C_{43}H_{48}Cl_2NO_3PSn_2$
Formula weight	966.07 g mol^{-1}
F(000)	972
$D_{calc.}$	1.547 Mg m^{-3}
Absorption coefficient	1.411 mm^{-1}
Data collection	
Diffractometer type	Enraf Nonius CAD4
Wavelength	Mo–K$_\alpha$ (71.073 pm)
Temperature	193 (2) K
θ range for data collection	2.46–25.00°
Index ranges	$-12 \leq h \leq 12$, $-13 \leq k \leq 0$, $-22 \leq l \leq 23$
Scan method	ω-scans
Scan angle	$(0.87 + 0.45 \text{ tg } \theta)$°
Scan time	Max. 30 s
Control reflections and decay	Three reflections, all 120 min., 0%
Data collection software	CAD4 EXPRESS
Cell refinement software	CAD4 EXPRESS
Data reduction software	XCAD4 (Harms, 1993)
Solution and refinement	
Reflections collected	7633
Independent reflections	7229 [$R_{int} = 0.0222$]
Observed reflections	5688 [$I > 2\sigma(I)$]
Reflections used for refinement	7046
Extinction coefficient	$X = 0.0007$ (3)
Extinction correction formula	$F_c^* = F_c \times k[(1 + 0.001X \times F_c^2 \times \lambda^3)/\sin 2\theta]^{-1/4}$ (k = overall scale factor)
Largest difference peak and hole	1.239 and $-1.471*10^{30}$ e m^{-3}
Solution	Patterson/difmap
Refinement	Full-matrix refinement at F^2
Treatment of hydrogen atoms	geom, refxyz
Programs used	SHELXS-86 (Sheldrick, 1990), SHELXS-93 (Sheldrick, 1993)
Data/restraints/parameters	7046/0/614
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0201P)^2 + 26.9378P]$; $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2	1.199
R index (all data)	$wR_2 = 0.1687$
R index conventional [$I > 2\sigma(I)$]	$R = 0.0425$

transducer (Wissenschaftliche Elektronik GmbH, Munich). A DN 700 Oxford cryostat with a DTC 2 temperature controller was used to maintain the absorber samples (absorber concentration, 0.5–0.6 mg ^{119}Sn cm^{-2}) at the liquid nitrogen temperature (77 K). ^{119m}Sn Mössbauer spectra of compounds **1a, 1b** and **2b** were obtained using an Express Mössbauer spectrometer MS-1101 E (Rostov-on-Don).

Crystal structure determination of $(Ph_3SnCl)_2 \cdot L$ (**1c**) was performed using Enraf-Nonius CAD 4 equipment. Experimental details, data collection, structure solution and refinement parameters together with crystallographic data for **1c** are shown in Table 1. The structure was solved by Patterson and difference Fourier methods. Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft fur wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, with quotation of the deposit number CSD-406546, the names of the authors and the journal citation.

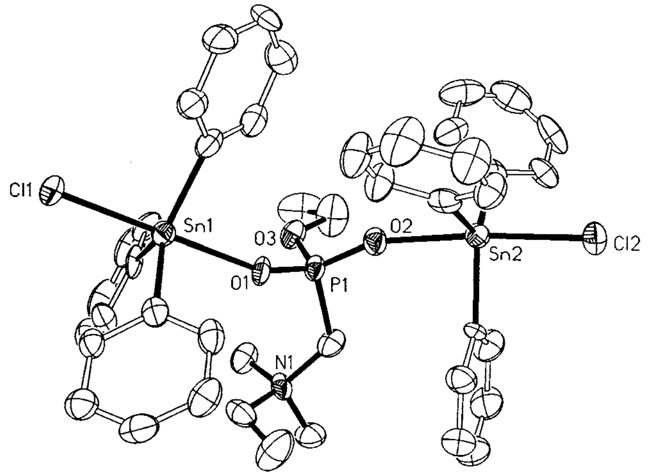


Fig. 1. Molecular structure of $(Ph_3SnCl)_2 \cdot EtOPO_2^- CH_2N^+Me_2Et$ (**1c**).

3. Results and discussion

3.1. Preparation of the complexes

The zwitterionic nature of *O*-ethyl(*N*-ethyl-*N*,*N*-dimethylammoniomethyl)phosphonate (L) and, therefore, its organotin complexes, leads to their insolubility in common non-solvating solvents. Only trimethyl-, tributyl- and dibutyltin derivatives bearing bulky and long-chain hydrocarbon substituents at tin are readily soluble in, for instance, dichloromethane and chloroform.

The other complexes separate from dichloromethane solution upon mixing of the components and thus are very convenient for isolation. Triorganotin chlorides and L form 2:1 complexes of the composition $(R_3SnCl)_2 \cdot L$ in all cases. The 1:1 component reaction resulted in the mixture of 2:1 complex and excess of free ligand, displaying the strong donor ability of the both oxygen atoms in anionic phosphonate group leading to its bridging coordination mode and ability to coordinate simultaneously with two molecules of weak

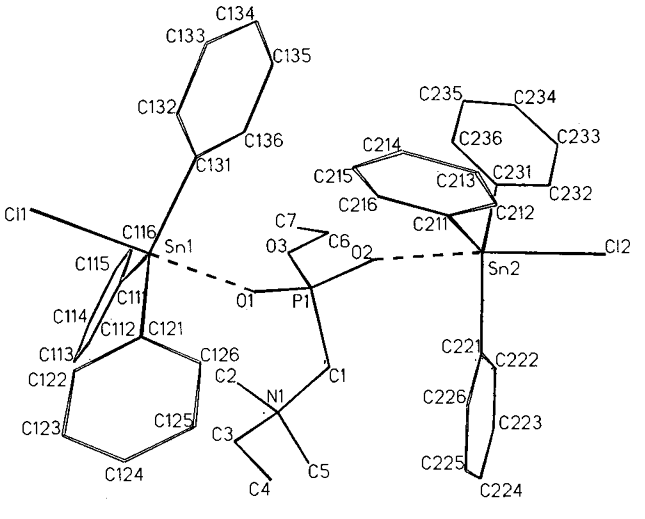


Fig. 2. Atomic numbering scheme for $(Ph_3SnCl)_2 \cdot EtOPO_2^- CH_2$-$N^+Me_2Et$ (**1c**).

Table 2
Atomic coordinates and equivalent isotropic displacement parameters [Å^2] for **1c**

Atom	x	y	z	U_{eq} [a]
Sn(1)	0.03521(5)	0.14557(5)	0.19774(3)	0.0274(2)
Cl(1)	−0.2058(2)	0.0488(2)	0.14972(14)	0.0416(6)
C(111)	0.1040(8)	−0.0146(7)	0.1354(5)	0.032(2)
C(112)	0.1216(10)	−0.1126(10)	0.1652(6)	0.045(2)
C(113)	0.1719(11)	−0.2182(10)	0.1298(8)	0.057(3)
C(114)	0.2025(12)	−0.2248(12)	0.0636(8)	0.068(4)
C(115)	0.1850(11)	−0.1294(13)	0.0316(7)	0.062(4)
C(116)	0.1362(9)	−0.0235(10)	0.0681(5)	0.039(2)
C(121)	0.0363(8)	0.1453(8)	0.3075(5)	0.032(2)
C(122)	−0.0382(8)	0.0459(9)	0.3173(6)	0.034(2)
C(123)	−0.0368(9)	0.0384(10)	0.3894(5)	0.038(2)
C(124)	0.0382(10)	0.1303(11)	0.4469(6)	0.045(3)
C(125)	0.1146(10)	0.2315(10)	0.4410(5)	0.044(2)
C(126)	0.1120(9)	0.2372(9)	0.3688(6)	0.038(2)
C(131)	−0.0023(9)	0.2984(9)	0.1575(5)	0.035(2)
C(132)	−0.1162(10)	0.3529(9)	0.1661(5)	0.039(2)
C(133)	−0.1463(11)	0.4504(10)	0.1377(6)	0.051(3)
C(134)	−0.0605(12)	0.4987(10)	0.1025(7)	0.056(3)
C(135)	0.0514(12)	0.4472(11)	0.0924(7)	0.053(3)
C(136)	0.0826(10)	0.3477(10)	0.1225(6)	0.044(2)
Sn(2)	0.52702(6)	0.62918(5)	0.32544(3)	0.0281(2)
Cl(2)	0.6545(2)	0.8393(2)	0.40718(14)	0.0426(6)
C(211)	0.3394(9)	0.6680(9)	0.3479(5)	0.033(2)
C(212)	0.3287(10)	0.7801(9)	0.3992(6)	0.040(2)
C(213)	0.2082(12)	0.8107(12)	0.4118(7)	0.060(3)
C(214)	0.0940(12)	0.7289(13)	0.3734(8)	0.067(4)
C(215)	0.1025(11)	0.6142(12)	0.3235(7)	0.061(3)
C(216)	0.2228(9)	0.5847(9)	0.3094(6)	0.044(2)
C(221)	0.6537(8)	0.5350(7)	0.3835(4)	0.026(2)
C(222)	0.7677(10)	0.4995(10)	0.3609(6)	0.043(2)
C(223)	0.8504(11)	0.4352(11)	0.3961(7)	0.055(3)
C(224)	0.8219(12)	0.4071(11)	0.4561(8)	0.060(3)
C(225)	0.7114(13)	0.4412(11)	0.4792(7)	0.055(3)
C(226)	0.6284(10)	0.5080(10)	0.4430(6)	0.040(2)
C(231)	0.5707(9)	0.6537(8)	0.2280(6)	0.039(2)
C(232)	0.6900(11)	0.7198(9)	0.2291(6)	0.042(2)
C(233)	0.7213(16)	0.7372(10)	0.1654(9)	0.063(4)
C(234)	0.6285(17)	0.6857(13)	0.1005(8)	0.065(4)
C(235)	0.5104(16)	0.6241(15)	0.0957(7)	0.069(4)
C(236)	0.4800(12)	0.6059(11)	0.1614(7)	0.052(3)
P(1)	0.3855(2)	0.2869(2)	0.23106(12)	0.0257(5)
O(1)	0.2561(5)	0.2385(5)	0.2436(3)	0.0294(13)
O(2)	0.4271(6)	0.4238(5)	0.2523(3)	0.0329(14)
O(3)	0.3808(6)	0.2232(6)	0.1462(3)	0.0340(14)
C(1)	0.5224(9)	0.2292(9)	0.2806(6)	0.036(2)
N(1)	0.5096(7)	0.0954(6)	0.2815(4)	0.031(2)
C(2)	0.4712(11)	0.0057(10)	0.2048(6)	0.041(2)
C(3)	0.4097(10)	0.0647(10)	0.3247(6)	0.042(2)
C(4)	0.4400(14)	0.1420(16)	0.4041(8)	0.069(4)
C(5)	0.6452(10)	0.0753(11)	0.3159(6)	0.043(2)
C(6)	0.4757(15)	0.2635(14)	0.1090(8)	0.066(4)
C(7)	0.4835(18)	0.1612(18)	0.0444(9)	0.082(5)

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

Table 3
Selected bond lengths [Å] and angles [°] for **1c**

Bond length (Å)			
Sn(1)–C(131)	2.111(9)	Sn(1)–C(121)	2.132(10)
Sn(1)–C(111)	2.142(8)	Sn(1)–O(1)	2.280(5)
Sn(1)–Cl(1)	2.475(2)	Sn(2)–Cl(2)	2.466(2)
Sn(2)–C(231)	2.137(10)	Sn(2)–C(211)	2.153(9)
Sn(2)–O(2)	2.316(6)	Sn(2)–C(221)	2.085(7)
P(1)–O(2)	1.463(6)	P(1)–O(1)	1.506(6)
P(1)–O(3)	1.583(6)	P(1)–C(1)	1.799(9)
O(3)–C(6)	1.467(13)	C(1)–N(1)	1.501(11)
N(1)–C(2)	1.472(12)	N(1)–C(5)	1.474(11)
C(6)–C(7)	1.46(2)	C(3)–C(4)	1.47(2)
Bond angle (°)			
C(131)–Sn(1)–C(121)	124.4(3)	C(131)–Sn(1)–C(111)	121.5(4)
C(121)–Sn(1)–C(111)	113.5(3)	C(131)–Sn(1)–O(1)	87.7(3)
C(121)–Sn(1)–O(1)	88.9(3)	C(111)–Sn(1)–O(1)	86.0(3)
C(131)–Sn(1)–Cl(1)	91.6(2)	C(121)–Sn(1)–Cl(1)	90.6(2)
C(111)–Sn(1)–Cl(1)	95.2(2)	O(1)–Sn(1)–Cl(1)	178.8(2)
C(221)–Sn(2)–C(231)	116.9(3)	C(221)–Sn(2)–C(211)	122.1(3)
C(231)–Sn(2)–C(211)	120.0(3)	C(221)–Sn(2)–O(2)	81.8(3)
C(231)–Sn(2)–O(2)	87.3(3)	C(211)–Sn(2)–O(2)	90.5(3)
C(221)–Sn(2)–Cl(2)	92.8(2)	C(231)–Sn(2)–Cl(2)	93.1(3)
C(211)–Sn(2)–Cl(2)	94.3(3)	O(2)–Sn(2)–Cl(2)	174.2(2)
O(2)–P(1)–O(1)	118.3(3)	O(2)–P(1)–O(3)	109.2(4)
O(1)–P(1)–O(3)	109.1(3)	O(2)–P(1)–C(1)	106.4(4)
O(1)–P(1)–C(1)	109.6(4)	O(3)–P(1)–C(1)	103.1(4)
P(1)–O(1)–Sn(1)	150.2(4)	P(1)–O(2)–Sn(2)	159.7(4)
C(6)–O(3)–P(1)	125.2(7)	N(1)–C(1)–P(1)	122.0(6)
C(2)–N(1)–C(5)	104.6(8)	C(2)–N(1)–C(1)	110.6(8)
C(5)–N(1)–C(1)	107.3(7)	C(2)–N(1)–C(3)	110.3(7)
C(5)–N(1)–C(3)	110.3(7)	C(1)–N(1)–C(3)	113.4(7)
C(4)–C(3)–N(1)	116.6(9)	C(7)–C(6)–O(3)	112.1(12)

Lewis acids, such as R_3SnCl, as in the complex $(Ph_3SnCl)_2 \cdot L$ (**1c**) according to X-ray diffraction data (see below).

Di- and monoorganotin chlorides and $SnCl_4$ form 1:1 complexes with L. The attempts to obtain 2:1 pentacoordinate complexes of Me_2SnCl_2 and Ph_2SnCl_2 with possible binuclear structure similar to that described [5] for methylenediphosphonate 1:2 adducts with Me_2SnHal_2 were performed, but in all cases the 1:1 complexes **2a** and **2c** precipitated.

*3.2. Molecular structure of $(Ph_3SnCl)_2 \cdot L$ (**1c**)*

The structure of **1c** and atomic numbering scheme are depicted in Figs. 1 and 2. The atomic coordinates are listed in Table 2, and selected bond lengths and bond angles are listed in Table 3. Complex **1c** is a monomeric dinuclear complex with a bridging bidentate ligand. Both the tin environments are trigonal bipyramidal with equatorial phenyl groups and axial positions occupied by chlorine and oxygen atoms, the bond angles Cl–Sn–O being 178.8 and 174.2°. The two P–O bonds differ by 0.05 Å: 1.506 Å (P–O1) and 1.463 Å (P–O2), and the corresponding Sn–O bonds (Sn–O1 and Sn–O2) differ in the opposite mode: 2.280 and 2.316 Å, respectively. The Sn–O–P bond angles differ by ca. 10°: 150.2 and 159.7°. Thus the Sn–O–P fragments in **1c** are unequal probably due to intermolecular contacts. The donor–acceptor Sn–phosphoryl bonds in **1c** are much stronger than those in triphenyltin chloride adducts with phosphine oxides, but weaker than both covalent and coordinating Sn–O bonds in triphenyltin phosphates and phosphonates (Table 4) with the other structural characteristics of tin coordination polyhedra remaining almost unchanged.

Both the tin coordination polyhedra are slightly distorted from idealized trigonal bipyramidal geometry. The Sn–C bonds are bent towards the ligand molecule: the C–Sn–O bond angles lie in the range 81.8–90.5° and the C–Sn–Cl bond angles are between 90.6 and 95.2°. The equatorial planar C–Sn–C bond angles are in the range 113.5–124.4°.

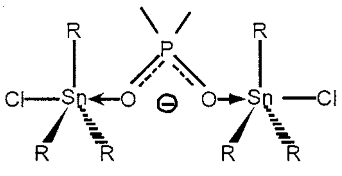
3.3. Mössbauer spectra

The ^{119m}Sn Mössbauer parameters (IS, isomer shifts; QS, quadrupole splittings) of the compounds $(R_3SnCl)_2 \cdot L$ (**1a–c**) and $R_2SnCl_2 \cdot L$ (**2a–c**) are given in Table 5. The QS values for **1a–c** are consistent with trigonal bipyramidal tin environment with equatorial

Table 4
Comparison of the complex **1c** with related molecules: $Ph_3SnCl \cdot Ph_3PO$ (**5**), $(Ph_3SnCl)_2 \cdot [Ph_2P(O)CH_2]_2$ (**6**), $Ph_3SnOP(O)Me(OMe)$ (**7**) and $Ph_3SnOP(O)(OPh)_2$ (**8**)

Compound/Ref.	**1c**/This work	**5** [6]	**6** [7]	**7** [8]	**8** [9]
Bond distance (Å)					
Sn–O	2.280(5)	2.374(6)	2.357(3)	2.201(3)	2.241(8)
	2.316(6)			2.209(3)	2.228(8)
P–O	1.506(6)	1.494(6)	1.487(3)	1.489(3)	1.486(8)
	1.463(6)			1.485(4)	1.488(8)
Sn–Cl	2.475(2)	2.510(2)	2.475(2)	–	–
	2.466(2)				–
Bond angle (°)					
O–Sn–Cl or O–Sn–O	178.8(2)	177.8	174.4(1)	177.1(2)	177.0(3)
	174.2(2)				
Sn–O–P	150.2(4)	147.4(3)	161.8(2)	147.8(2)	151.8(5)
	159.7(4)			177.3(2)	148.8(5)
O–P–O′	118.3(3)			117.1(2)	118.5(5)

R_3Sn fragment (structure **I**) as for complex $(Ph_3SnCl)_2 \cdot L$ (**1c**), and these data are typical for pentacoordinated triorganotin chloride complexes with phosphoryl ligands [10]. The partial quadrupole splitting value (PQS) for the ligand L (-0.062 mm s^{-1}, trigonal bipyramidal structure, axial position) was calculated using experimental geometry for **1c** and its Mössbauer spectral parameters according to the point charge model formalism [10]. The PQS values for Ph_3PO and HMPA were $+0.12$ and $+0.13$ mm s^{-1}, respectively [10].



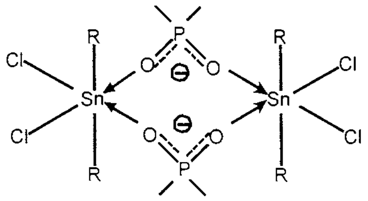
I

The Mössbauer parameters for **2a–c** suggest an octahedral structure with *trans*-situated organic substituents for these adducts according to the point charge model predictions [11]. The coordination octahedron at tin is constructed by two alkyl or phenyl groups, two chlorine and two phosphoryl oxygen atoms which presumably originate from two different ligand molecules, leading to at least dimeric structure of complexes **2a–c** with bridging ligand molecules (structure **II**).

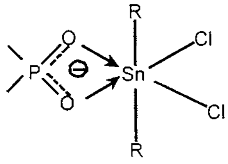
Table 5
Mössbauer parameters of tri- and diorganotin chloride adducts $(R_3SnCl)_2 \cdot L$ (R = Me, Bu, Ph) (**1a–c**) and $R_2SnCl_2 \cdot L$ (R = Me, Bu, Ph) (**2a–c**)

Compound	IS[a] (mm s^{-1})	QS[b] (mm s^{-1})	Γ_1[c](mm s^{-1})	Γ_2[c] (mm s^{-1})
1a	1.33	3.61	0.88	0.92
1b	1.45	3.53	0.96	1.03
1c	1.30	3.27	0.89	0.90
2a	1.40	4.23	0.98	1.00
2b	1.50	3.99	1.07	1.18
2c	1.24	3.77	1.09	1.11

[a] Isomer shifts with respect to $CaSnO_3$, ± 0.03 mm s^{-1}.
[b] Nuclear quadrupole splitting, $+0.03$ mm s^{-1}.
[c] Full width at half-height of the resonant peaks, $+0.08$ mm s^{-1}.



II



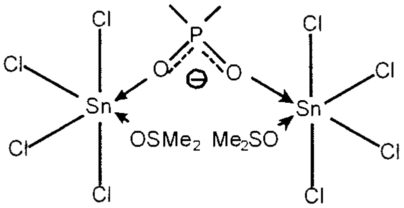
III

The bidentate chelating behavior of the ligand leading to formation of the four-membered chelate ring **III** is considered to be significantly less common for oxophosphorylic systems taking into account the prevailing σ-mode of coordination of oxophosphorylic unit through the axial sp-hybridized electron pair on oxygen [12]. From this point of view, the formation of chelate **III** would face strong stereoelectronic restrictions, though the structures with fragments of the type **III** in general are not excluded [13].

3.4. NMR spectra

The room temperature ^1H- and ^{13}C-NMR spectra of chloroform solutions of $(R_3SnCl)_2 \cdot L$ (R = Me, Bu) (**1a,b**) and $Bu_2SnCl_2 \cdot L$ (**2b**) display the significant increase of the $^2J(Sn-H)$ and $^1J(Sn-C)$ values compared with the free Lewis acids indicating the strong interaction of the ligand and acceptors in solution. This effect is enhanced for the methanolic and DMSO solutions of the complexes $(Ph_3SnCl)_2 \cdot L$ (**1c**), $Me_2SnCl_2 \cdot L$ (**2a**), and $MeSnCl_3 \cdot L$ (**3a**) as a consequence of the involvement of donor solvent molecules in the exchange equilibria leading to the increased population of penta- and hexacoordinated tin species.

The ^{31}P- and ^{119}Sn-NMR spectra of the complexes $(R_3SnCl)_2\cdot L$ (R = Me, Bu, Ph) (**1a–c**), $R_2SnCl_2\cdot L$ (R = Me, Bu, Ph) (**2a–c**), $RSnCl_3\cdot L$ (R = Me, Ph) (**3a,c**) exhibit no Sn–P spin couplings, the ^{119}Sn signals being broadened and significantly shifted to high field compared with those for corresponding free Lewis acids. This indicates rapid exchange between species with different tin coordination numbers in solution at room temperature. The Sn–P coupling did not appear at low temperatures even for methanolic solutions of monoorganotin chloride complexes **3a** and **3c** due to the high lability of these adducts and/or fast exchange interaction with methanol. The tin tetrachloride complex $SnCl_4\cdot L$ (**4**) is soluble only in DMSO and its ^{31}P-NMR spectrum consists of two signals: a broad singlet at + 1.7 ppm which was attributed to the free ligand L and a sharp singlet at − 2.6 ppm with $^{119/117}$Sn satellites with corresponding ^2J(Sn–P) couplings of 164 and 157 Hz. The ^{119}Sn-NMR signals of **4** are shifted to the hexacoordinated $SnCl_4$ region: a singlet at − 670 ppm which can be attributed to the complex $SnCl_4(DMSO)_2$ and a doublet at − 677 ppm with ^2J(SnP) = 164 Hz. The latter signal probably arises from the complex **4** with a phosphoryl ligand partly substituted by DMSO (structure **IV**):



IV

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