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Organotin(IV) Complexes with Tetraethyl Ethylene- and Propylene-diphosphonates

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The series of organotin halide complexes with tetraethyl ethylene- and propylene-diphosphonates $R_nSnX_{4-n}\cdot L$ [$n=0$, X=Cl; $n=1$, R=Me, X=Cl, Br; $n=1$, R=Ph, X=Cl; $n=2$, R=Me, Et, Bu, X=Cl, Br; $n=2$, R=Ph, X=Cl; $L=(EtO)_2P(O)CH_2CHR'P(O)(OEt)_2$, R′=H, Me] were synthesized and characterized by means of NMR and Mössbauer spectroscopy. The crystal structure of the complex of diphenyltin dichloride with propylenediphosphonate was determined. The complex consists of polymer chains with bridging bidentate ligands and an octahedral tin environment containing two types of phosphoryl fragments. All of the R_2SnX_2 adducts have *trans*-R_2SnX_4 geometries of tin coordination octahedra according to the quadrupole splitting values in the Mössbauer spectra. The ^{31}P and ^{119}Sn NMR studies at low temperatures revealed that $RSnHal_3$ complexes in solution form isomers with different mutual orientations of phosphoryl ligands and organic groups in the coordination sphere. The diethyltin dichloride adduct with ethylenediphosphonate appeared to be active against lung cancer NCI-H522 cells.

Keywords: organotin(IV) complexes; diphosphoryl ligands; NMR; Mössbauer spectroscopy; X-ray analysis; antitumour activity

INTRODUCTION

Organotin(IV) complexes with electron-donating molecules are potentially antitumour agents and a number of them have been shown to be active.[1] The understanding of the activity mechanism requires investigation of their structure and isomerism both in solid state and in solution.

The previous spectroscopic and X-ray structural studies of diphosphoryl adducts of mono- and di-organotin(IV) halides revealed that these compounds possess different structures depending on the nature of organotin(IV) halide and diphosphoryl ligand.[2–6] Thus, methylenediphosphonates and -diphosphinates usually serve as bidentate chelating ligands providing monomeric octahedral complexes, preferably with the *trans*-R_2-configuration for diorganotin adducts.[2,3] In the case of mono-organotin compounds two isomers of chelate complexes can exist in solution and in the solid state.[4,5] Bridging by methylenediphosphoryl ligands appeared to be rare.[3,6]

The present paper deals with the synthesis and investigation of several complexes of mono- and di-organotin(IV) halides with tetraethyl ethylene- and propylene-diphosphonates $(EtO)_2P(O)CH_2CHRP(O)(OEt)_2$ (L^1: R=H; L^2: R=Me).

The $Ph_2SnCl_2\cdot L^2$ adduct has been studied by means of X-ray diffraction crystallography and its molecular structure is reported. The structure and isomerism of mono-organotin(IV) complexes in solution have been studied by means of ^{31}P and ^{119}Sn NMR spectroscopy at low temperatures in order to slow down the rapid exchange processes. The complexes of diorganotin halides with the same ligands appeared to be too labile, having averaged NMR signals even at low temperatures. Complexes of diorganotin dihalides have been studied in the solid state by means of Mössbauer spectroscopy. Two $SnCl_4$ adducts have also been synthesized and characterized by means of NMR spectroscopy. The complex $Et_2SnCl_2\cdot L^1$ has been subjected to NCI (Bethesda, MD, USA) antitumour drug tests.

EXPERIMENTAL

Syntheses

Mono- and di-organotin(IV) halides either were commercial products or were obtained by known procedures. The ligands were prepared by des-

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Table 1 Elemental analysis and melting points of the organotin(IV) halide complexes with L^1 and L^2

		Analysis: Found (Calcd) (%)	
Complex	M.p. (°C)	C	H
1 $MeSnCl_3 \cdot L^1$	95–97	24.18 (24.33)	5.13 (4.98)
2 $MeSnBr_3 \cdot L^1$	73–75	19.00 (19.53)	4.10 (3.99)
3 $PhSnCl_3 \cdot L^1$	114–116	31.65 (31.76)	4.75 (4.80)
4 $Bu_2SnCl_2 \cdot L^1$	36–40	35.23 (35.64)	6.99 (6.93)
5 $Bu_2SnBr_2 \cdot L^1$	Oil	30.82 (31.08)	6.35 (6.04)
6 $Ph_2SnCl_2 \cdot L^1$	141–142	40.70 (40.87)	5.31 (5.26)
7 $MeSnCl_3 \cdot L^2$	50–52	25.81 (25.88)	5.33 (5.21)
8 $MeSnBr_3 \cdot L^2$	67–68	21.41 (20.87)	4.94 (4.20)
9 $PhSnCl_3 \cdot L^2$	93–96	32.56 (32.98)	5.39 (5.01)
10 $Me_2SnCl_2 \cdot L^2$	64–65	28.72 (29.10)	5.93 (5.97)
11 $Me_2SnBr_2 \cdot L^2$	79–80	25.15 (24.98)	5.31 (5.12)
12 $Et_2SnCl_2 \cdot L^2$	66	33.30 (31.91)	6.71 (6.38)
13 $Et_2SnBr_2 \cdot L^2$	63	27.75 (27.57)	5.59 (5.51)
14 $Bu_2SnCl_2 \cdot L^2$	Oil	37.51 (36.77)	7.18 (7.10)
15 $Bu_2SnBr_2 \cdot L^2$	Oil	32.56 (32.16)	6.10 (6.21)
16 $Ph_2SnCl_2 \cdot L^2$	72–73	41.60 (41.82)	5.45 (5.45)
17 $SnCl_4 \cdot L^1$	168–170	22.08 (21.31)	4.18 (4.26)
18 $SnCl_4 \cdot L^2$	152–154	22.93 (22.88)	4.50 (4.51)

Table 2 Crystal data and structure refinement for **16**

Identification code	ja_2
Empirical formula	$C_{23}H_{36}Cl_2O_6P_2Sn$
Formula weight	660.05
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	$a = 12.780(4)$ Å $\alpha = 90°$ $b = 13.900(3)$ Å $\beta = 90°$ $c = 16.427(5)$ Å $\gamma = 90°$
Volume	2918.1(14) Å^3
Z	4
Density (calculated)	1.502 Mg m^{-3}
Absorption coefficient	1.202 mm^{-1}
$F(000)$	1344
Crystal size	0.225 mm × 0.15 mm × 0.113 mm
θ range for data collection	1.92–25.00°
Index ranges	$-1 \leq h \leq 15$, $-1 \leq k \leq 16$, $-1 \leq l \leq 19$
Reflections collected	3673
Independent reflections	3456 ($R_{int} = 0.0628$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3451/0/307
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0784$, $wR2 = 0.2001$
R indices (all data)	$R1 = 0.0999$, $wR2 = 0.2198$
Absolute structure parameter	0.06(9)
Largest diff. peak and hole	0.785 and −1.951 e Å^{-3}
Data collection	
Diffractometer	Siemens P4
Radiation	MoKα ($\lambda = 0.71073$ Å)
Temperature	173 K
Monochromator	Highly oriented graphite crystal
2θ range	4.0–50.0°
Scan type	ω
Scan speed	Constant; 7.00° min^{-1}, in ω
Scan range (ω)	2.02°
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	3 measured every 100 reflections

cribed methods.[7,8] Complexes of organotin(IV) halides with diphosphoryl compounds were obtained according to the standard procedure.[3] All of them have a 1:1 composition. Melting points and elemental analyses data are listed in Table 1. A single crystal of $Ph_2SnCl_2 \cdot L^2$ (**16**) was obtained by recrystallization from CH_2Cl_2–petroleum ether. Complexes of L^1 and L^2 with tin tetrachloride were prepared using the reaction of $PhSnCl_3$ with diphosphoryl ligand in 2:1 molar ratio:

$$2PhSnCl_3 + L \rightarrow SnCl_4 \cdot L + Ph_2SnCl_2 \qquad [1]$$

The solution of *ca* 1 mmol of the ligand in 5 cm^3 of dry CH_2Cl_2 was treated with two equivalents of $PhSnCl_3$. After two days the reaction was completed; the solvent was evaporated, and the residue was washed several times with hot hexane in order to remove Ph_2SnCl_2 and dried *in vacuo*. Melting points and elemental analyses data are included in Table 1.

Instruments

An X-ray structure analysis of **16** has been performed with a Siemens P4 diffractometer. Crystallographic data are collected in Table 2.

^{119m}Sn Mössbauer spectra were measured with a Laben 8001 multichannel analyzer, an MWE velocity transducer generator (Wissenschaftliche Elektronik GmbH, Munich), an FG2 digital function generator (Wissenschaftliche Elektronik GmbH, Munich) and an MA250 velocity transducer (Wissenschaftliche Elektronik GmbH, Munich), with linear velocity and constant acceleration in a triangular waveform. A DN700 Oxford cryostat with a DTC2 temperature controller was used to maintain the absorber samples

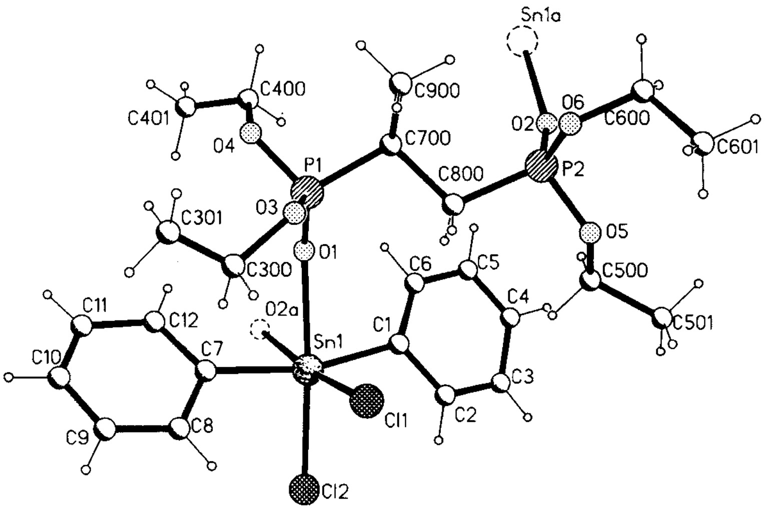


Figure 1 Crystal structure and atomic numbering in complex **16**.

(absorber concentration, 0.5–0.6 mg ^{119}Sn cm^{-2}) at the temperature of liquid nitrogen (77 K).

Proton-decoupled ^{31}P and ^{119}Sn NMR spectra were obtained with a Varian VXR-400 spectrometer at 161.9 and 149.2 MHz respectively. ^{31}P NMR spectra were referenced against external 85% H_3PO_4 and ^{119}Sn NMR spectra were referenced against external Me_4Sn.

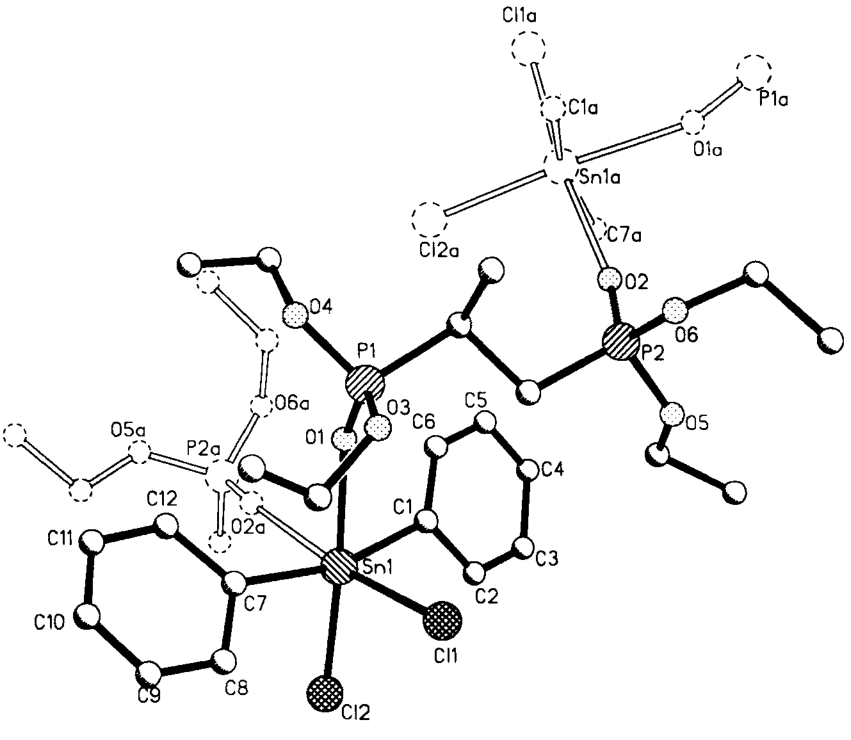


Figure 2 Polymer chain of **16**.

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathrm{Å}^2 \times 10^3$) for **16**

	x	*y*	*z*	*U*(eq)[a]
Sn(1)	885(1)	2547(1)	8390(1)	39(1)
Cl(2)	132(4)	4074(3)	8896(3)	52(1)
Cl(1)	1149(3)	1855(3)	9754(3)	54(1)
C(1)	−566(11)	1852(12)	8188(10)	45(4)
C(2)	−1421(12)	2116(12)	8678(14)	64(6)
C(3)	−2458(14)	1744(13)	8532(11)	65(6)
C(4)	−2528(15)	1016(14)	7937(12)	64(5)
C(5)	−1699(14)	758(13)	7486(11)	53(5)
C(6)	−754(14)	1177(11)	7626(9)	46(4)
C(7)	2382(12)	3102(12)	8260(9)	47(4)
C(8)	2888(15)	3566(16)	8957(12)	64(5)
C(9)	3885(23)	3923(19)	8871(17)	99(10)
C(10)	4418(20)	3844(20)	8193(20)	100(9)
C(11)	3972(15)	3479(15)	7480(15)	71(6)
C(12)	2946(14)	3093(14)	7500(12)	61(5)
P(1)	2299(3)	283(3)	7941(3)	45(1)
O(1)	1650(8)	1154(8)	7841(7)	46(3)
P(2)	−174(4)	−1654(3)	8767(3)	53(1)
O(2)	−664(9)	−1961(9)	8011(6)	54(3)
O(3)	3020(9)	249(8)	8696(8)	56(3)
C(300)	3730(16)	1045(16)	9014(15)	72(7)
C(301)	4675(17)	1039(18)	8739(16)	86(8)
O(4)	3057(10)	120(10)	7228(9)	67(4)
C(401)	3185(31)	693(24)	5926(16)	142(15)
C(400)	2676(20)	65(22)	6368(15)	97(9)
O(5)	−977(14)	−1295(10)	9391(10)	89(5)
C(500)	−1679(26)	−634(20)	9306(19)	117(11)
C(501)	−2564(25)	−787(18)	9925(20)	134(14)
O(6)	394(9)	−2488(11)	9227(6)	61(3)
C(600)	−134(20)	−3335(13)	9423(10)	68(6)
C(601)	−483(30)	−3334(22)	10 330(17)	159(16)
C(700)	1584(15)	−808(13)	8004(13)	56(5)
C(800)	715(19)	−645(13)	8697(14)	74(6)
C(900)	2273(18)	−1710(13)	8232(16)	86(7)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

RESULTS AND DISCUSSION

X-ray study of compound 16

The structure and atomic numbering scheme for **16** are depicted in Fig. 1. Fractional atomic coordinates, isotropic displacement parameters, selected bond distances, bond angles and torsional angles are reported in Tables 3–7. As shown by the results of X-ray analysis, complex **16** consists of polymeric chains, with propylenediphosphonate acting as a bridging bidentate ligand connecting adjacent tin atoms. The ligand contains two types of different phosphoryl units. $\cdots P^1(O)CH_2\cdots$ and $\cdots P^2(O)CHMe\cdots$ so there are three possible tin coordination fragments in the polymeric complex: P^1OSnOP^2, P^1OSnOP^1 and P^2OSnOP^2. The extended drawing of the coordination fragment depicted in Fig. 2 shows that only the first type of coordination octahedra exist in the complex: every tin atom is bound to both types of phosphoryl groups. Thus the monomeric unit can be described as $CH_2(EtO)_2PO(Ph_2)Sn(Cl_2)OP(OEt)_2CHMe$. The chain has the symmetry of 2_1 screw axis. The tin environment can be viewed as a distorted octahedron with two phenyl groups occupying axial positions, while the pairs of chlorine and oxygen atoms are situated in *cis*-equatorial positions of the octahedron. The C—Sn—C fragment is distorted from linearity (C—Sn—C angle 164.1°) and Sn—C bonds are bent towards phosphoryl ligands: the C—Sn—O angles (83.0–85.9°) are smaller than the C—Sn—Cl angles (94.3–96.5°).

The main bond distances and bond angles in coordination octahedra of **16** are comparable with those in related compounds such as analogous polymeric ethylenediphosphoryl adducts (**6**)[9] and Bu_2SnCl_2 dppoe $(Ph_2P(O)CH_2)_2$ (**19**),[10] monomeric chelate methylenediphosphonate adduct $Ph_2SnCl_2\cdot[(EtO)_2P(O)]_2CH_2$ (**20**)[2] and cyclic dimer $\{Me_2SnCl_2\cdot[(EtO)_2P(O)]_2CHNMe_2\}_2$ (**21**)[6] (Table 8). Polymeric diphosphoryl complexes of organotin(IV) halides possess Sn—O—P angles significantly bigger [150–168°) than those of the closed chelate adducts (133–138°). The propylenediphosphonate ligand in **16** adopts an antiperiplanar conformation, as indicated by torsional angle P—C—C—P = 174.1° (Table 5). The C—C bond distances in the propane fragment (1.61 and 1.58 Å), resemble that in the ethane fragment of the dppoe ligand in **19**[10] while this bond is significantly shorter in adduct **6**, (1.43 Å).[9]

Mössbauer spectra

^{119m}Sn Mössbauer data of the diorganotin adducts are given in Table 9. The isomer shifts (δ) and quadrupole splittings (ΔE) are typical for octahedral dialkyl- and diaryl-tin(IV) complexes having a *trans*-R_2Sn configuration with slight distortion from linearity in C—Sn—C fragments.[11,12] This conclusion is confirmed for $Ph_2SnCl_2\cdot L^2$ by the X-ray analysis (C—Sn—C angle is 164.1°). The full width at half-height parameters (Γ) not exceeding 1.3 mm s^{-1} indicate the occurrence of

Table 4 Bond lengths (Å) and angles (°) for **16**

Sn(1)-C(7)	2.07(2)	Sn(1)-C(1)	2.118(14)
Sn(1)-O(1)	2.349(12)	Sn(1)-O(2) [1][a]	2.417(10)
Sn(1)-Cl(1)	2.463(4)	Sn(1)-Cl(2)	2.474(4)
C(1)-C(6)	1.34(2)	C(1)-C(2)	1.40(2)
C(2)-C(3)	1.44(2)	C(2)-H(2)	0.95
C(3)-C(4)	1.41(2)	C(3)-H(3)	0.95
C(4)-C(5)	1.34(3)	C(4)-H(4)	0.95
C(5)-C(6)	1.36(2)	C(5)-H(5)	0.95
C(6)-H(6)	0.95	C(7)-C(12)	1.44(2)
C(7)-C(8)	1.46(3)	C(8)-C(9)	1.37(3)
C(8)-H(8)	0.95	C(9)-C(10)	1.31(4)
C(9)-H(9)	0.95	C(10)-C(11)	1.40(4)
C(10)-H(10)	0.95	C(11)-C(12)	1.42(3)
C(11)-H(11)	0.95	C(12)-H(12)	0.95
P(1)-O(1)	1.476(11)	P(1)-O(4)	1.536(14)
P(1)-O(3)	1.546(12)	P(1)-C(700)	1.77(2)
P(2)-O(2)	1.454(11)	P(2)-O(5)	1.53(2)
P(2)-O(6)	1.563(14)	P(2)-C(800)	1.81(2)
O(2)-Sn(1) [2][a]	2.417(10)	O(3)-C(300)	1.52(2)
C(300)-C(301)	1.29(3)	C(300)-H(30a)	0.99
C(300)-H(30b)	0.99	C(301)-H(30c)	0.98
C(301)-H(30d)	0.98	C(301)-H(30e)	0.98
O(4)-C(400)	1.50(3)	C(401)-C(400)	1.31(4)
C(401)-H(40a)	0.98	C(401)-H(40b)	0.98
C(401)-H(40c)	0.98	C(400)-H(40d)	0.99
C(400)-H(40e)	0.99	O(5)-C(500)	1.29(3)
C(500)-C(501)	1.54(3)	C(500)-H(50a)	0.99
C(500)-H(50b)	0.99	C(501)-H(50c)	0.98
C(501)-H(50d)	0.98	C(501)-H(50e)	0.98
O(6)-C(600)	1.39(2)	C(600)-C(601)	1.56(3)
C(600)-H(60a)	0.99	C(600)-H(60b)	0.99
C(601)-H(60c)	0.98	C(601)-H(60d)	0.98
C(601)-H(60e)	0.98	C(700)-C(900)	1.58(2)
C(700)-C(800)	1.61(3)	C(700)-H(700)	1.00
C(800)-H(80a)	0.99	C(800)-H(80b)	0.99
C(900)-H(90c)	0.98	C(900)-H(90d)	0.98
C(900)-H(90e)	0.98		
C(7)—Sn(1)—C(1)	164.1(7)	C(7)—Sn(1)—O(1)	83.3(5)
C(1)—Sn(1)—O(1)	85.9(5)	C(7)—Sn(1)—O(2) [1]	84.5(5)
C(1)—Sn(1)—O(2) [1]	83.0(5)	O(1)—Sn(1)—O(2) [1]	85.2 (4)
C(7)—Sn(1)—Cl(1)	96.5(4)	C(1)—Sn(1)—Cl(1)	94.8(4)
O(1)—Sn(1)—Cl(1)	88.3(3)	O(2) [1]—Sn(1)—Cl(1)	173.3(3)
C(7)—Sn(1)—Cl(2)	94.3(5)	C(1)—Sn(1)—Cl(2)	95.9(5)
O(1)—Sn(1)—Cl(2)	176.4(3)	O(2) [1]—Sn(1)—Cl(2)	91.9(3)
Cl(1)—Sn(1)—Cl(2)	94.7(2)	C(6)—C(1)—C(2)	116.1(14)
C(6)—C(1)—Sn(1)	125.8(13)	C(2)—C(1)—Sn(1)	118.2(11)
C(1)—C(2)—C(3)	122(2)	C(1)—C(2)—H(2)	119.2(9)
C(3)—C(2)—H(2)	119.1(10)	C(4)—C(3)—C(2)	116(2)
C(4)—C(3)—H(3)	122.3(11)	C(2)—C(3)—H(3)	122.3(9)
C(5)—C(4)—C(3)	122(2)	C(5)—C(4)—H(4)	119.2(10)
C(3)—C(4)—H(4)	119.2(11)	C(4)—C(5)—C(6)	119.6(14)
C(4)—C(5)—H(5)	120.2(10)	C(6)—C(5)—H(5)	120.2(9)
C(1)—C(6)—C(5)	125(2)	C(1)—C(6)—H(6)	117.4(10)

Table 4 *contd.*

C(5)—C(6)—H(6)	117.4(9)	C(12)—C(7)—C(8)	117(2)
C(12)—C(7)—Sn(1)	123.2(13)	C(8)—C(7)—Sn(1)	119.4(11)
C(9)—C(8)—C(7)	119(2)	C(9)—C(8)—H(8)	120(2)
C(7)—C(8)—H(8)	120.4(10)	C(10)—C(9)—C(8)	123(2)
C(10)—C(9)—H(9)	119(2)	C(8)—C(9)—H(9)	119(2)
C(9)—C(10)—C(11)	122(2)	C(9)—C(10)—H(10)	119(2)
C(11)—C(10)—H(10)	119.0(14)	C(10)—C(11)—C(12)	120(2)
C(10)—C(11)—H(11)	120.2(14)	C(12)—C(11)—H(11)	120.2(13)
C(11)—C(12)—C(7)	119(2)	C(11)—C(12)—H(12)	120.6(13)
C(7)—C(12)—H(12)	120.7(11)	O(1)—P(1)—O(4)	113.0(7)
O(1)—P(1)—O(3)	116.6(7)	O(4)—P(1)—O(3)	103.3(7)
O(1)-P(1)-C(700)	114.7(7)	O(4)-P(1)-C(700)	104.1(9)
O(3)—P(1)—C(700)	103.5(8)	P(1)—O(1)—Sn(1)	150.1(7)
O(2)—P(2)—O(5)	112.2(9)	O(2)—P(2)—O(6)	113.3(7)
O(5)—P(2)—O(6)	103.2(8)	O(2)—P(2)—C(800)	116.4(9)
O(5)—P(2)—C(800)	102.1(10)	O(6)—P(2)—C(800)	108.3(9)
P(2)—O(2)—Sn(1) [2]	161.1(8)	C(300)—O(3)—P(1)	127.5(13)
C(301)—C(300)—O(3)	116(2)	C(301)—C(300)—H(30a)	108(2)
O(3)—C(300)—H(30a)	108.4(10)	C(301)—C(300)—H(30b)	108(2)
O(3)—C(300)—H(30b)	108.4(11)	H(30a)—C(300)—H(30b)	107.4
C(300)—C(301)—H(30c)	110(2)	C(300)—C(301)—H(30d)	110(2)
H(30c)—C(301)—H(30d)	109.5	C(300)—C(301)—H(30e)	109(2)
H(30c)—C(301)—H(30e)	109.5	H(30d)—C(301)—H(30e)	109.5
C(400)—O(4)—P(1)	121.4(12)	C(400)—C(401)—H(40a)	110(2)
C(400)—C(401)—H(40b)	110(2)	H(40a)—C(401)—H(40b)	109.5
C(400)—C(401)—H(40c)	109(2)	H(40a)—C(401)—H(40c)	109.5
H(40b)—C(401)—H(40c)	109.5	C(401)—C(400)—O(4)	109(3)
C(401)—C(400)—H(40d)	110(2)	O(4)—C(400)—H(40d)	109.8(12)
C(401)—C(400)—H(40e)	110(2)	O(4)—C(400)—H(40e)	109.9(10)
H(40d)—C(400)—H(40e)	108.3	C(500)—O(5)—P(2)	129(2)
O(5)—C(500)—C(501)	110(2)	O(5)—C(500)—H(50a)	110(2)
C(501)—C(500)—H(50a)	110(2)	O(5)—C(500)—H(50b)	110(2)
C(501)—C(500)—H(50b)	110(2)	H(50a)—C(500)—H(50b)	108.2
C(500)—C(501)—H(50c)	109.5(14)	C(500)—C(501)—H(50d)	109(2)
H(50c)—C(501)—H(50d)	109.5	C(500)—C(501)—H(50e)	110(2)
H(50c)—C(501)—H(50e)	109.5	H(50D)—C(501)—H(50e)	109.5
C(600)—O(6)—P(2)	120.8(13)	O(6)—C(600)—C(601)	111(2)
O(6)—C(600)—H(60a)	109.4(11)	C(601)—C(600)—H(60a)	109(2)
O(6)—C(600)—H(60b)	109.4(10)	C(601)—C(600)—H(60b)	109(2)
H(60a)—C(600)—H(60b)	108.0	C(600)—C(601)—H(60c)	110(2)
C(600)—C(601)—H(60d)	110(2)	H(60c)—C(601)—H(60d)	109.5
C(600)—C(601)—H(60e)	110(2)	H(60c)—C(601)—H(60e)	109.5
H(60d)—C(601)—H(60e)	109.5	C(900)—C(700)—C(800)	109(2)
C(900)—C(700)—P(1)	114.0(13)	C(800)—C(700)—P(1)	106.1(12)
C(900)—C(700)—H(700)	109.1(11)	C(800)—C(700)—H(700)	109.1(10)
P(1)—C(700)—H(700)	109.1(7)	C(700)—C(800)—P(2)	111.7(13)
C(700)—C(800)—H(80a)	109.3(10)	P(2)—C(800)—H(80a)	109.3(7)
C(700)—C(800)—H(80b)	109.3(10)	P(2)—C(800)—H(80b)	109.3(7)
H(80a)—C(800)—H(80b)	107.9	C(700)—C(900)—H(90c)	109.5(13)
C(700)—C(900)—H(90d)	109.5(11)	H(90c)—C(900)—H(90d)	109.5
C(700)—C(900)—H(90e)	109.5(11)	H(90c)—C(900)—H(90e)	109.5
H(90d)—C(900)—H(90e)	109.5		

[a] Symmetry transformations used to generate equivalent atoms: [1] $-x$, $y+1/2$, $-z+3/2$; [2] $-x$, $y-1/2$, $-z+3/2$.

Table 5 Torsional angles (°) for **16**

C(7)—Sn(1)—C(1)—C(6)	21(3)	O(1)—Sn(1)—C(1)—C(6)	−26.1(14)
O(2) [1]—Sn(1)—C(1)—C(6)[a]	59.5(14)	Cl(1)—Sn(1)—C(1)—C(6)	−114.1(14)
Cl(2)—Sn(1)—C(1)—C(6)	150.7(14)	C(7)—Sn(1)—C(1)—C(2)	−159(2)
O(1)—Sn(1)—C(1)—C(2)	154(2)	O(2) [1]—Sn(1)—C(1)—C(2)	−120(2)
Cl(1)—Sn(1)—C(1)—C(2)	66.4(14)	Cl(2)—Sn(1)—C(1)—C(2)	−28.9(14)
C(6)—C(1)—C(2)—C(3)	−5(3)	Sn(1)—C(1)—C(2)—C(3)	174(2)
C(1)—C(2)—C(3)—C(4)	8(3)	C(2)—C(3)—C(4)—C(5)	−6(3)
C(3)—C(4)—C(5)—C(6)	3(3)	C(2)—C(1)—C(6)—C(5)	2(3)
Sn(1)—C(1)—C(6)—C(5)	−178(2)	C(4)—C(5)—C(6)—C(1)	−1(3)
C(1)—Sn(1)—C(7)—C(12)	7(3)	O(1)—Sn(1)—C(7)—C(12)	54.4(14)
O(2) [1]—Sn(1)—C(7)—C(12)	−31.4(14)	Cl(1)—Sn(1)—C(7)—C(12)	141.9(14)
Cl(2)—Sn(1)—C(7)—C(12)	−122.8(14)	C(1)—Sn(1)—C(7)—C(8)	−176(2)
O(1)—Sn(1)—C(7)—C(8)	−128(2)	O(2) [1]—Sn(1)—C(7)—C(8)	146(2)
Cl(1)—Sn(1)—C(7)—C(8)	−41(2)	Cl(2)—Sn(1)—C(7)—C(8)	54.5(14)
C(12)—C(7)—C(8)—C(9)	−3(3)	Sn(1)—C(7)—C(8)—C(9)	179(2)
C(7)—C(8)—C(9)—C(10)	−2(4)	C(8)—C(9)—C(10)—C(11)	7(5)
C(9)—C(10)—C(11)—C(12)	−6(4)	C(10)—C(11)—C(12)—C(7)	1(3)
C(8)—C(7)—C(12)—C(11)	4(3)	Sn(1)—C(7)—C(12)—C(11)	−179.2(14)
O(4)—P(1)—O(1)—Sn(1)	−137.4(13)	O(3)—P(1)—O(1)—Sn(1)	−18(2)
C(700)—P(1)—O(1)—Sn(1)	103.4(14)	C(7)—Sn(1)—O(1)—P(1)	78.3(14)
C(1)—Sn(1)—O(1)—P(1)	−113.4(14)	O(2) [1]—Sn(1)—O(1)—P(1)	163.3(13)
Cl(1)—Sn(1)—O(1)—P(1)	−18.4(13)	Cl(2)—Sn(1)—O(1)—P(1)	127(4)
O(5)—P(2)—O(2)—Sn(1) [2][a]	167(2)	O(6)—P(2)—O(2)—Sn(1) [2]	−77(3)
C(800)—P(2)—O(2)—Sn(1) [2]	50(3)	O(1)—P(1)—O(3)—C(300)	−46(2)
O(4)—P(1)—O(3)—C(300)	79(2)	C(700)—P(1)—O(3)—C(300)	−173(2)
P(1)—O(3)—C(300)—C(301)	−91(3)	O(1)—P(1)—O(4)—C(400)	−55(2)
O(3)—P(1)—O(4)—C(400)	178(2)	C(700)—P(1)—O(4)—C(400)	70(2)
P(1)—O(4)—C(400)—C(401)	125(2)	O(2)—P(2)—O(5)—C(500)	−55(3)
O(6)—P(2)—O(5)—C(500)	−177(2)	C(800)—P(2)—O(5)—C(500)	71(3)
P(2)—O(5)—C(500)—C(501)	157(2)	O(2)—P(2)—O(6)—C(600)	−54.2(14)
O(5)—P(2)—O(6)—C(600)	67.4(14)	C(800)—P(2)—O(6)—C(600)	175.2(13)
P(2)—O(6)—C(600)—C(601)	−100(2)	O(1)—P(1)—C(700)—C(900)	−172(2)
O(4)—P(1)—C(700)—C(900)	64(2)	O(3)—P(1)—C(700)—C(900)	−44(2)
O(1)—P(1)—C(700)—C(800)	−52(2)	O(4)—P(1)—C(700)—C(800)	−175.7(12)
O(3)—P(1)—C(700)—C(800)	76.6(13)	C(900)—C(700)—C(800)—P(2)	−63(2)
P(1)—C(700)—C(800)—P(2)	174.1(11)	O(2)—P(2)—C(800)—C(700)	−52(2)
O(5)—P(2)—C(800)—C(700)	−174.6(14)	O(6)—P(2)—C(800)—C(700)	77(2)

[a] Symmetry transformations used to generate equivalent atoms: [1] $-x, y+1/2, -z+3/2$; [2] $-x, y-1/2, -z+3/2$.

the single tin site in all cases without formation of the other isomers.

NMR spectra

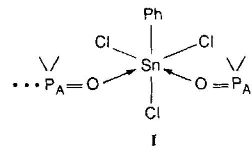
Organotin(IV) trihalide and tin tetrachloride complexes of L^1 and L^2 have been studied by means of ^{31}P and ^{119}Sn NMR spectroscopy. Compounds **1** and **2** had very broadened NMR signals even at low temperatures and no conclusion could be made concerning their structures in solution.

The ^{119}Sn NMR spectrum of adduct **3** at −90 °C consists of the triplet at −557 ppm and the doublet of doublets at −551 ppm with approximately 5:1 relative intensities. The triplet of small intensity at −689 ppm also exists in the spectrum. The respective singlets with $^{117/119}Sn$ satellites appear in the ^{31}P NMR spectrum. The NMR parameters are collected in Table 10. The ^{119}Sn NMR resonances in the region of −550 ppm are attributed to the isomers of the hexacoordinate $PhSnCl_3 \cdot L^1$ complex.[5, 13] The first isomer has two equivalent phosphorus atoms in the tin coordination sphere and consists of type-**I** tin octahedra in accordance with the preferred *cis*-bridging behaviour of the ethylenediphosphonate ligand.

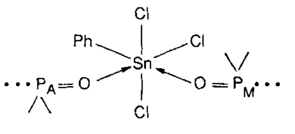
Table 6 Anisotropic displacement parameters[a] (Å$^2 \times 10^3$) for **16**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	34(1)	36(1)	47(1)	1(1)	−6(1)	−2(1)
Cl(2)	55(2)	45(2)	56(2)	−7(2)	−4(2)	−3(2)
Cl(1)	55(3)	60(2)	48(2)	9(2)	−8(2)	−12(2)
C(1)	21(7)	58(9)	55(10)	1(9)	−20(7)	−1(7)
C(2)	25(8)	49(9)	117(17)	−48(10)	−8(10)	6(7)
C(3)	53(11)	67(11)	75(13)	−49(11)	27(10)	−29(10)
C(4)	54(12)	59(11)	79(13)	−17(11)	−28(11)	−15(10)
C(5)	47(10)	64(11)	49(10)	−44(9)	3(9)	5(9)
C(6)	52(10)	46(8)	40(8)	−13(8)	8(9)	1(9)
C(7)	30(7)	67(10)	46(9)	30(9)	15(7)	7(8)
C(8)	42(10)	90(14)	59(11)	−10(11)	−7(9)	−2(11)
C(9)	113(24)	99(18)	84(18)	−24(16)	−32(18)	−65(18)
C(10)	61(15)	104(19)	135(24)	23(20)	−17(17)	−32(14)
C(11)	44(11)	76(13)	93(15)	−2(12)	25(11)	−13(11)
C(12)	52(10)	60(11)	70(12)	−7(10)	12(10)	12(10)
P(1)	33(2)	38(2)	64(3)	8(2)	1(2)	−4(2)
O(1)	31(5)	53(6)	56(7)	8(6)	−18(6)	−2(5)
P(2)	59(3)	48(2)	52(3)	6(2)	−5(2)	−17(2)
O(2)	61(7)	69(7)	33(5)	−12(6)	0(6)	14(7)
O(3)	46(7)	47(6)	75(8)	0(6)	−28(7)	−4(6)
C(300)	56(13)	69(13)	91(16)	−37(13)	14(13)	−10(11)
C(301)	57(14)	81(15)	120(20)	13(15)	29(14)	−9(12)
O(4)	52(8)	67(8)	81(10)	−18(8)	−11(7)	23(7)
C(401)	222(43)	134(27)	70(17)	11(19)	44(24)	0(31)
C(400)	72(16)	130(22)	87(19)	−44(17)	26(15)	18(16)
O(5)	105(13)	61(8)	100(11)	−27(8)	14(11)	6(10)
C(500)	159(30)	89(18)	102(20)	30(17)	40(23)	25(22)
C(501)	153(28)	57(14)	192(32)	57(18)	82(28)	17(1)7)
O(6)	63(7)	78(7)	42(5)	2(8)	−7(5)	−20(9)
C(600)	111(18)	55(11)	39(10)	−1(9)	2(11)	−27(13)
C(601)	240(42)	124(24)	114(21)	66(21)	98(26)	9(29)
C(700)	49(10)	52(10)	68(12)	−3(10)	−14(11)	5(9)
C(800)	90(16)	50(10)	83(14)	6(10)	−18(14)	−7(12)
C(900)	78(14)	44(10)	136(21)	−8(14)	−27(16)	20(10)

[a] The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$



I



II

The second isomer with non-equivalent phosphorus atoms consists of type-**II** coordination octahedra. The NMR parameters of this isomer were attributed to different types of phosphoryl groups according to the conclusion that nuclei in similar environments such as P$_A$ in structures **I** and **II** must have similar NMR parameters.

It has been established earlier for methylenediphosphonate complexes that substitution of a halogen atom by the more electropositive organic group in the *trans*-position relative to phosphoryl leads to the strengthening of the Sn—O bond together with significant lowering of the $^2J(^{119}Sn{-}^{31}P)$ magnitude.[4,5] This influence also exists in ethylenediphosphonate adducts (Table 10).

The $^2J(^{119}Sn{-}^{31}P)$ values in the polymeric complex **3** are slightly higher than those in the respective chelate methylenediphosphonate complexes (180–200 Hz),[5] probably due to an increase of the Sn—O—P bond angles in open-chain structures compared with six-membered chelate rings (see also Table 8).

The high-field triplet in the ^{119}Sn NMR spectrum of complex **3** appears in the region typical for hexacoordinate $SnCl_4$ adducts[14] and attributed

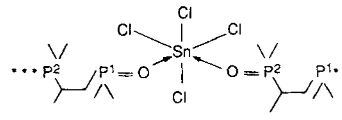
Table 7 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **16**

	x	y	z	U(eq)
H(2)	−1313(12)	2551(12)	9116(14)	77
H(3)	−3054(14)	1974(13)	8818(11)	78
H(4)	−3178(15)	700(14)	7853(12)	77
H(5)	−1771(14)	286(13)	7072(11)	64
H(6)	−182(14)	974(11)	7299(9)	55
H(8)	2532(15)	3619(16)	9462(12)	77
H(9)	4199(23)	4240(19)	9321(17)	118
H(10)	5130(20)	4041(20)	8185(20)	120
H(11)	4354(15)	3491(15)	6984(15)	85
H(12)	2637(14)	2833(14)	7023(12)	73
H(30a)	3408(16)	1673(16)	8878(15)	87
H(30b)	3758(16)	997(16)	9615(15)	87
H(30c)	5068(17)	1573(18)	8979(16)	129
H(30d)	4663(17)	1109(18)	8145(16)	129
H(30e)	5013(17)	429(18)	8882(16)	129
H(40a)	2939(31)	658(24)	5361(16)	213
H(40b)	3935(31)	551(24)	5945(16)	213
H(40c)	3060(31)	1341(24)	6140(16)	213
H(40d)	2792(20)	−591(22)	6150(15)	116
H(40e)	1917(20)	203(22)	6348(15)	116
H(50a)	−1966(26)	−655(20)	8746(19)	140
H(50b)	−1357(26)	6(20)	9391(19)	140
H(50c)	−3091(25)	−281(18)	9859(20)	201
H(50d)	−2277(25)	−762(18)	10 478(20)	201
H(50e)	−2888(25)	−1417(18)	9833(20)	201
H(60a)	330(20)	−3892(13)	9322(10)	82
H(60b)	−757(20)	−3402(13)	9069(10)	82
H(60c)	−850(30)	−3936(22)	10 453(17)	239
H(60d)	−954(30)	−2789(22)	10 428(17)	239
H(60e)	133(30)	−3276(22)	10 681(17)	239
H(700)	1227(15)	−929(13)	7472(13)	67
H(80a)	312(19)	−54(13)	8573(14)	89
H(80b)	1065(19)	−552(13)	9229(14)	89
H(90c)	2806(18)	−1810(13)	7811(16)	129
H(90d)	1826(18)	−2281(13)	8269(16)	129
H(90e)	2616(18)	−1600(13)	8758(16)	129

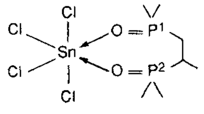
to the small amount of complex **17** formed in side-reaction [1] during the preparation of adduct **3**. This has been proved by independent NMR characterization of adduct **17** having the same NMR parameters. The $^2J(^{119}Sn-^{31}P)$ value in the tin tetrachloride complex is between the values for *trans*-Cl—Sn—O—P and *trans*-Ph—Sn—O—P fragments of the respective $PhSnCl_3$ adduct, probably indicating the intermediate strength of the Sn—O coordination bond in complex **17** compared with the two types of coordination bonds in unsymmetrical structure **II** of complex **3**.

The ^{31}P and ^{119}Sn resonances of complex **3** are greatly broadened at +30 °C showing no Sn–P spin coupling due to the rapid exchange processes. A single broad resonance appears in the ^{31}P NMR spectrum at 27.7 ppm having a half-width of about 25 Hz, while a very broad signal at −525 ppm appears in the ^{119}Sn NMR spectrum. The NMR signals and Sn–P coupling in the $SnCl_4$ complex **17** persists at room temperature indicating the high stability of this adduct in solution.

Propylenediphosphonate having two different phosphoryl units in the molecule can form tin complexes with a variety of coordination modes. In the simplest case of the $SnCl_4$ adduct **18** having a possibly polymeric structure, three different tin coordination complexes (discussed earlier in the section on X-ray structure) were expected to occur in solution and their signals were assumed to appear in the NMR spectra. However, the signals of only one type of tin octahedron appeared in the ^{31}P and ^{119}Sn NMR spectra of **18**, even at −90 °C. The NMR parameters are given in Table 11. The tin atom is bound to phosphoryl groups of both types as evidenced by the doublet of doublets in the ^{119}Sn NMR spectrum, with two respective singlets with $^{117/119}Sn$ satellites in the ^{31}P NMR spectrum. This result indicates that the polymer chain of **18** in solution consists of tin octahedra **III** similar to those of **16**, though the absence of coordination octahedra with equivalent phosphoryl groups in solution is not obvious. Another possible explanation is that the seven-membered chelate ring **IV** with a propylenediphosphonate ligand possessing *gauche* conformation is stabilized by chelating coordination with $SnCl_4$.



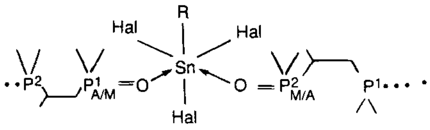
III



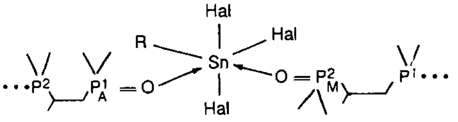
IV

Both structures **III** and **IV** would have similar NMR parameters as their main structural features — Sn—O—P bond angles, Sn—O and P—O bond distances — are almost the same.

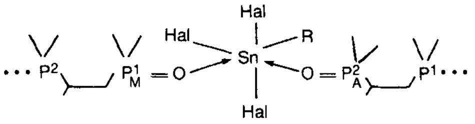
The respective $PhSnCl_3$ complex **9**, according to low-temperature NMR spectroscopy, has four types of octahedral isomers in solution; the ^{119}Sn NMR spectrum consists of three doublets of doublets and one triplet in the range from −550 to −560 ppm together with a small triplet at −689 ppm attributed to complex **18** formed in side-reaction [1]. The ^{31}P NMR spectrum of **9** is very complex and ten singlets, some of them overlapping, together with their $^{117/119}Sn$ satellites are situated in a narrow range of 7 ppm.



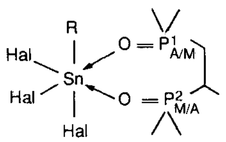
Va



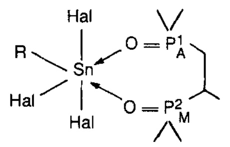
Vb



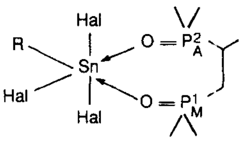
Vc



VIa



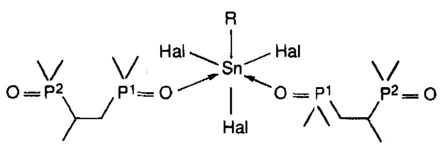
VIb



VIc

However, the ^{31}P NMR signals could be attributed almost completely to the respective ^{119}Sn NMR signals (Table 11). Three doublets of doublets in the ^{119}Sn NMR spectrum of **9** correspond to the three types of tin coordination octahedra, either **Va–Vc** (polymer structure with different types of phosphoryl groups in the tin coordination sphere in all cases) or **VIa–VIc** (chelate structures).

The intensive triplet at −559 ppm in the ^{119}Sn NMR spectrum of **9** corresponds to the intensive singlet with $^{117/119}Sn$ satellites together with the singlet without satellites (Table 11). The NMR parameters resemble those of complex **3** (Table 10). It can be postulated that this complex has the structure **VII** with two monodentate ligands.



VII

The corresponding $MeSnCl_3$ adduct **7** provides the ^{31}P and ^{119}Sn spectra at −90 °C similar to those of complex **9**, the NMR signals of **7** being broadened compared with **9**. The NMR parameters

Table 8 The main bond distances (Å) and bond angles (°) in complexes **16** and related species: $Ph_2SnCl_2\cdot[(EtO)_2P(O)CH_2]_2$ (**6**), $Bu_2SnCl_2\cdot$dppoe (**19**), $Ph_2SnCl_2\cdot[(EtO)_2P(O)]CH_2$ (**20**) and $\{Me_2SnCl_2\cdot[(EtO)_2P(O)]_2CHNMe_2\}_2$ (**21**)

Complex Ref.	**16** This work	**6** 9	**19** 10	**20** 2	**21** 6
Distances					
Sn-Cl(1)	2.463(4)	2.459(4)	2.483(2)	2.449(3)	2.482(4)
Sn-Cl(2)	2.474(4)	2.440(4)	2.468(3)	2.434(2)	2.482(4)
Sn-O(1)	2.349(12)	2.377(9)	2.640(7)	2.427(5)	2.466(13)
Sn-O(2)	2.417(10)	2.328(10)	2.386(7)	2.400(5)	2.466(13)
Sn-C(1)	2.118(14)	2.145(13)	2.126(9)	2.140(7)	2.08(2)
Sn-C(7)	2.07(2)	2.116(13)	2.112(8)	2.138(7)	2.15(2)
Angles					
Cl(1)—Sn—Cl(2)	94.7(2)	92.7(1)	90.1(1)	98.8(8)	90.7(2)
O(1)—Sn—O(2)	85.2(4)	89.9(3)	93.6(2)	82.1(2)	98.3(4)
C(1)—Sn—C(7)	164.1(7)	161.8(6)	154.3(3)	162.2(3)	154.5(7)
Sn—O(1)—P(1)	150.1(7)	152.0(6)	167.8(4)	133.9(3)	150.1(7)
Sn—O(2)—P(2)	161.1(8)	151.6(6)	163.9(4)	137.3(3)	150.1(7)

Table 9 Mössbauer data for some diorganotin dihalide complexes with L^1 and L^2

Complex	δ (mm s^{-1})[a]	ΔE (mm s^{-1})[b]	Γ_1[c]	Γ_2[c]
$Me_2SnCl_2 \cdot L^1$	1.44[d]	4.09[d]	0.95	0.98
$Me_2SnBr_2 \cdot L^1$	1.49	4.16	1.28	1.27
$Et_2SnCl_2 \cdot L^1$	1.56[d]	4.29[d]	0.97	0.97
$Et_2SnBr_2 \cdot L^1$	1.72	4.22	0.95	0.90
$Bu_2SnCl_2 \cdot L^1$	1.58[d]	4.14[d]	1.02	0.99
$Bu_2SnBr_2 \cdot L^1$	1.57	4.03	1.21	1.14
$Et_2SnCl_2 \cdot L^2$	1.62	4.14	1.01	1.07
$Et_2SnBr_2 \cdot L^2$	1.68	4.22	0.93	1.00
$Ph_2SnCl_2 \cdot L^2$	1.33	3.86	1.11	1.23

[a] Isomer shifts with respect to $BaSnO_3$ at room temperature, ±0.05 mm s^{-1}. [b] Nuclear quadrupole splitting, ±0.05 mm s^{-1}. [c] Full width at half-height of the resonant peaks, ±0.05 mm s^{-1}. [d] Data from Ref. 3.

Table 10 ^{31}P and ^{119}Sn NMR parameters for ethylenediphosphonate adducts with $PhSnCl_3$ (**3**) and $SnCl_4$ (**17**), CD_2Cl_2, −90 °C

Complex	Structure	$\delta(^{31}P)$ (ppm)	$\delta(^{119}Sn)$ (ppm)[a]	$^2J(^{119}Sn-^{31}P)$ (Hz)[b]
3	**I**	29.9	−557 t	253
	II	28.9(A) 27.0(M)	−551 dd	227(AX) 76(MX)
17		28.1	−689 t	139

[a] d, doublet; t, triplet. [b] $^3J(^{31}P-^{31}P) = 0$.

are collected in Table 11. ^{31}P and ^{119}Sn NMR spectra of the $MeSnBr_3$ complex **8** contain only two sets of sharp signals, attributed to the isomers of octahedral complexes. According to their NMR parameters (Table 11) the methyl group is situated *trans* to the phosphoryl ligand in both cases. In addition, the ^{31}P NMR spectrum contains extremely broad signals corresponding to the broad signal in the ^{119}Sn NMR spectrum at −770 ppm; they can be considered as average signals of the other isomers of **8** participating in rapid exchange processes in solution.

ANTITUMOUR ACTIVITY

The Et_2SnCl_2 complex with ethylenediphosphonate was subjected to National Cancer Institute (Bethesda, MD, USA) *in vitro* antitumour drug testing.[15] Its activity was tested in

Table 11 ^{31}P and ^{119}Sn NMR parameters of propylenediphosphonate complexes with $SnCl_4$ and organotin trihalides

Complex	Structure	$\delta(^{31}P)$ (ppm)	$\delta(^{119}Sn)$ (ppm)[a]	$^2J(^{119}Sn-^{31}P)$ (Hz)[b]
18	**III** or **IV**	25.3(A) 26.8(M)	−689 dd	128(AX) 160(MX)
9	**Va** or **VIa**	28.0(A) 27.7(M)	−557 dd	235(AX) 266(MX)
	Vb/c or **VIb/c**	26.3(A) 25.2(M)	−553 dd	216(AX) 98(MX)
	Vc/b or **VIc/b**	27.7(A) 24.3(M)	−552 dd	237(AX) 66(MX)
	VII	30.1(A) 26.1(M)	−559 t	253(AX)
7	**Va** or **VIa**	27.6(A) 25.6(M)	−496 dd	280(AX) 257(MX)
	Vb/c or **VIb/c**	25.3(A) [c](M)	−501 dd	248(AX) 84(MX)
	Vc/b or **VIc/b**	[c](A) 24.3(M)	−500 dd	262(AX) 52(MX)
	VII	29.3(A) 26.8(M)	−497 t	270(AX)
8	**Vb/c** or **VIb/c**	24.8(A) 23.4(M)	−719 dd	261(AX) 132(MX)
	Vc/b or **VIc/b**	26.3(A) 22.2(M)	−718 dd	270(AX) 102(MX)

[a] d, doublet; t, triplet. [b] $^3J(^{31}P-^{31}P) = 0$. [c] Not determined due to the overlapping of signals.

relation to 60 cell lines of different forms of human cancer. It was shown that this complex possesses selective activity against the lung cancer NCI-H522 cells. The concentrations of the complex in culture medium at which the percentage growth of cells is +50, 0 and −50 are 1.16, 2.66 and 6.12 μmol l^{-1} respectively.

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