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Journal of Organometallic Chemistry 598 (2000) 160–166

Synthesis, characterization and X-ray structure of stannocanes substituted with a cyclic dithiophosphate ligand $X(CH_2CH_2S)_2Sn^nBu[S_2P(OCH_2C(Et_2)CH_2O)]$, (X = O, S): a study about the conformational tendencies and the relationship with the anomeric effect of the stannocane rings

Patricia García y García [a], Raymundo Cruz-Almanza [b], Rubén-Alfredo Toscano [b], Raymundo Cea-Olivares [b,*]

[a] *Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Chamilpa Cuernavaca, 62210, Morelos, Mexico*
[b] *Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Mexico City DF 04510, Mexico*

Received 9 September 1999; received in revised form 8 November 1999

Abstract

The preparation and conformational study of two stannocanes, 5-*n*-butyl-5-(5′,5′-diethyl-2′-thioxo-1′,3′,2′-dioxaphosphorinane-2′-thiolate)-1-oxa-4,6-dithia-5-stannocane, $O(CH_2CH_2S)_2Sn^nBu[S_2P(OCH_2CEt_2CH_2O)]$ (**1**) and 2-*n*-butyl-5-(5′5′-diethyl-2′-thioxo-1′,3′,2′-dioxaphosphorinane-2-thiolate)-1,3,6-trithia-2-stannocane $S(CH_2CH_2S)_2Sn^nBu[S_2P(OCH_2CEt_2CH_2O)]$ (**2**) is reported. These compounds were prepared from the corresponding chloro-oxa and -thia-stannocanes and the sodium salt of dithiophosphoric acid (2-mercapto-2-thiono-1,3,2-dioxaphosphorinane) in ethanol. Compounds **1** and **2** were characterized by IR, EI-MS and multinuclear NMR (^1H, ^{13}C, ^{31}P). The molecular structures were determined by X-ray analyses. The eight-membered ring in both compounds has a boat–chair conformation with a 1,5 transannular Sn···O (2.468 Å), Sn···S (2.94 Å) interaction. The 1,3,2-dioxaphosphorinane ring in **1** and **2** present a chair conformation with the stannocane in the axial position, in accordance with the anomeric effect. The coordination of the Sn-atoms is trigonal-bipyramidal in **1** and intermediate between trigonal-bipyramidal and a bicapped tetrahedral arrangement in **2**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Stannocanes; Dithiophosphates; Metallocane conformation; X-ray structure

1. Introduction

The 1-oxa-4,6-dithia and 1,3,6-trithia metallocanes (shown in Fig. 1) possess a strong 1,5 transannular interaction through an acceptor atom M = Ge, Sn, Pb, As, Sb, Bi and a donor X = O, S, NR atom. For stannocanes of the type $X(CH_2CH_2S)_2SnRR'$ (X = O, S, NMe) (RR′ = halogen, methyl) [1], Dräger has created a novel view about the bonding scheme of the long-known phenomenon of hypervalence at tin(IV). He has discussed this in terms of molecular orbitals, such that the path of the nucleophilic attack from a tetrahedron to a trigonal-bipyramid is controlled by four electronic factors [2,3]. The conformation adopted by the eight-membered ring in metallocanes has been investigated mainly by ^1H-NMR, in solution and by single crystal X-ray spectroscopy [1], showing that the

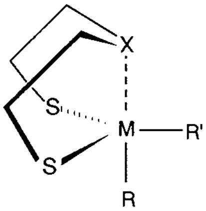

Fig. 1. Metallocanes of the type $X(CH_2CH_2S)_2MRR'$, X = S, O, NR; M = Ge, Sn, Pb, As, Sb; R,R′ = halogen, alkyl and aryl.

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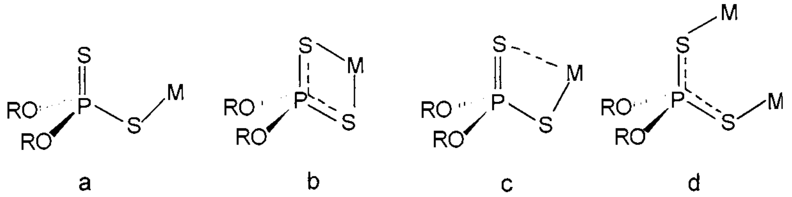
* Corresponding author.
E-mail address: cea@servidor.unam.mx (R. Cea-Olivares)

PII: S0022-328X(99)00694-4



Scheme 1.

eight-membered X(CH_2CH_2S)$_2$M ring is able to exhibit various conformations.

The stannocanes of the type O(CH_2CH_2S)$_2$SnHal$_2$/HalMe/Me$_2$ [2] exhibit a chair–chair conformation of the eight-membered ring, but the corresponding trithia compounds show the boat–chair. However, in O(CH_2CH_2S)$_2$SnMeCl the chair–chair and boat–chair conformations are present in the same crystal, while the diplanar transition state is observed in O(CH_2CH_2S)$_2$SnPhCl [4]. All of these are indicative of the transition between the two enantiomers of the boat–chair conformation. The O(CH_2CH_2S)$_2$SnPh$_2$ [5] shows a monoplanar transition conformation which corresponds to the path between the chair–chair and boat–chair conformations. Recently, in this journal, we have reported the synthesis and X-ray single crystal structure characterization of the stannocanes X(CH_2CH_2S)$_2$Sn(^{n}Bu)Cl (X = O, S) [6]. The eight-membered ring in both compounds shows the boat–chair conformations, in the trithia stannocane. This situation is in agreement with other stannocanes analogues, however the boat–chair conformation is observed in the oxa stannocane instead of the expected chair–chair. Now, we are interested in exploring the structural changes produced on the conformation of the metallocane ring by the replacement of the chlorine atom, in X(CH_2CH_2S)$_2$Sn(^{n}Bu)Cl (X = O, S), with a potentially dithia bidentate ligand, in this case a cyclic dithiophosphate.

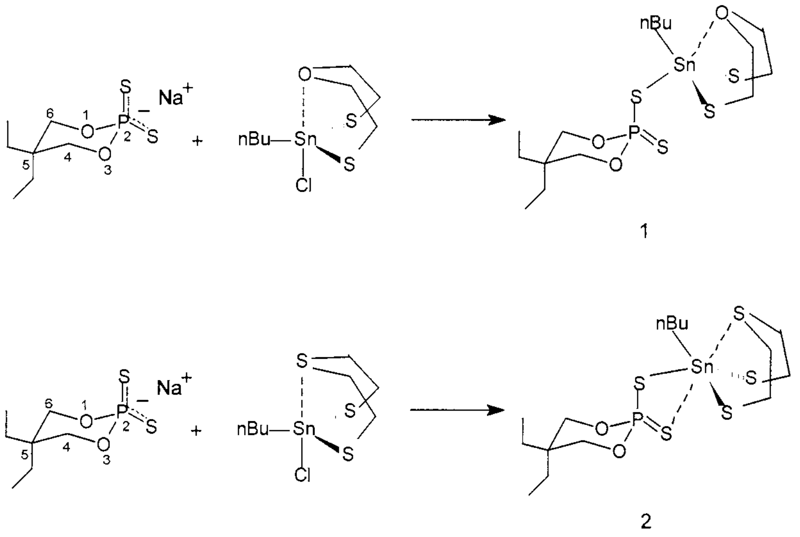
We have recently reported a study on the influence of some dithiolate ligands [7] on the bond strength and conformational preferences of the eight-membered ring of some arsocanes and stibocanes. We have observed a relationship between the strength of the transannular secondary bonding and the conformation of the metallocane ring. If the secondary bond is sufficiently strong, the conformation becomes boat–boat, but if the bond strength decreases, the preferred conformations become the boat–chair and then the chair–chair arrangement [8].

The structures of main group derivatives of dithiophosphates [(RO)$_2$PS$_2$]$^-$ ligands show a broad diversity of coordination patterns, basically due to their ability to involve the sulfur atoms in primary or secondary (intra or intermolecular) bonds with a monodentate (a), isobidentate (b), anisobidentate (c) or bridging (d) behavior [9]. The monodentate situation is rare, but it is known in Ph$_3$SnS$_2$P(OEt)$_2$ [10] whereas the iso- and anisobidentate coordination are found in some closely related organotin compounds (Scheme 1) [11–15].

Here, we report our studies of the synthesis and characterization of two stannocanes dithiophosphate derivatives, in order to characterize the hypervalence of the tin atom and the conformational preferences of the eight-membered ring of the stannocanes and the six-membered ring dioxaphosphorinane of the dithiophosphate ligand.

Table 1
Crystallographic data for compounds **1** and **2**

	1	**2**
Compound formula	$C_{15}H_{31}O_3PS_4Sn$	$C_{15}H_{31}O_2PS_5Sn$
Formula weight	537.3	553.3
Crystal size (mm)	0.28 × 0.16 × 0.16	0.60 × 0.40 × 0.40
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	16.799(2)	29.957(6)
b (Å)	7.828(2)	7.838(1)
c (Å)	18.827(2)	19.950(1)
β (°)	111.33(2)	94.38(1)
V (Å^3)	2306.3(5)	2335.3
Z	4	8
$D_{calc.}$ (mg m^{-3})	1.547	1.574
Absorption coefficient (mm^{-1})	1.550	1.616
F(000)	1096	1128
Scan mode	ω	ω
Temperature (K)	298	293(2)
θ Range for data collection (°)	3.0–55.0	1.50–25.00
Range of hkl	$0 \le h \le 21$ $0 \le k \le 10$ $-24 \le l \le 22$	$0 \le h \le 35$ $0 \le k \le 9$ $-23 \le l \le 23$
Reflections collected	5478	4210
No. of independent reflections	5301 ($R_{int} = 0.0413$)	4125 ($R_{int} = 0.0429$)
Max. and min. transmission		0.457 and 0.362
Data/restraints/parameters	5301/0/218	4125/0/217
Goodness-of-fit on F^2	1.010	1.043
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0608$, $wR_2 = 0.1174$	$R_1 = 0.0431$, $wR_2 = 0.0899$
Final indices (all data)	$R_1 = 0.1200$, $wR_2 = 0.1425$	$R_1 = 0.0704$, $wR_2 = 0.1032$
Largest difference peak and hole (e Å^{-3})	0.688 and −0.564	0.544 and −0.605



Scheme 2.

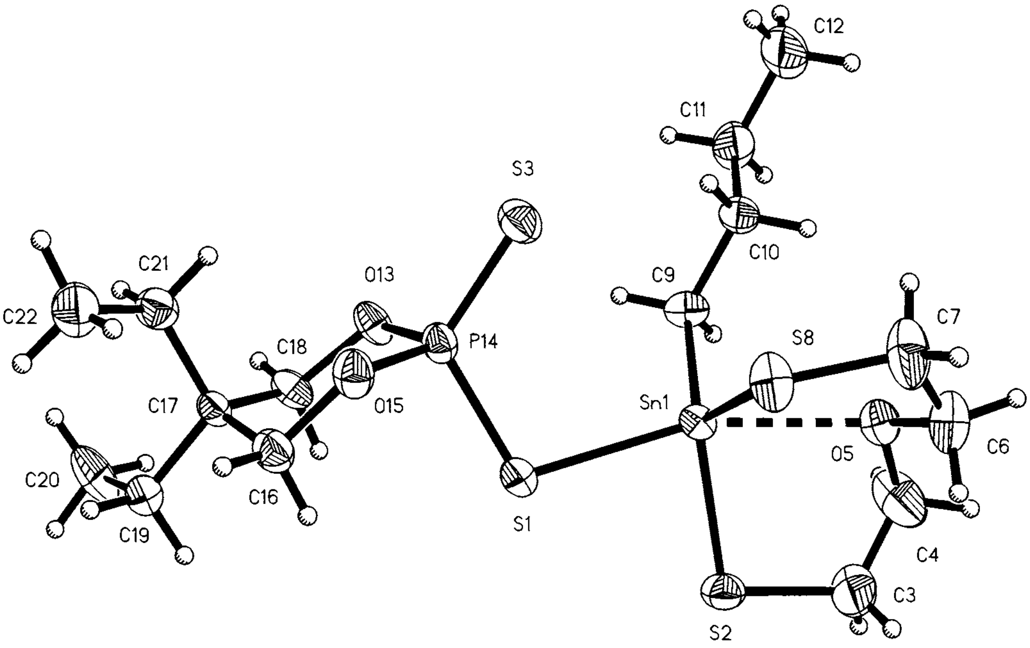


Fig. 2. ORTEP like drawing of O(CH$_2$CH$_2$S)$_2$Sn^{n}Bu[S$_2$P(OCH$_2$CEt$_2$CH$_2$O)] (**1**).

2. Experimental

Starting compounds O/S(CH$_2$CH$_2$SH)$_2$, ^{n}BuSnCl$_3$, HOCH$_2$C(CH$_2$CH$_3$)$_2$CH$_2$OH and P$_2$S$_5$ were Aldrich commercial samples, and were used as received. Solvents were dried by standard methods before use. The oxa and thia chloro stannocanes X(CH$_2$CH$_2$S)$_2$-Sn(^{n}Bu)Cl (X = O, S) and 2-mercapto, 2-thiono-1,3,2-dioxaphosphorinane were obtained using published procedures [6,16].

Elemental analyses (C, H) were performed by Galbraith Laboratories, Inc. (Knoxville, TN). IR spectra (4000–400 cm^{-1}) were recorded on KBr pellets using a MIDAC prospect spectrometer. 70 eV electron-impact mass spectra were recorded with a Hewlett–Packard MS/GS 598 instrument. ^{1}H-, ^{13}C-, ^{31}P- and ^{119}Sn-NMR spectra were obtained in a JEOL 300 spectrometer operating at 299.949, 75.57, 121.65 and 111.86 MHz, respectively, using CDCl$_3$ as solvent. The chemical shifts are relative to internal Me$_4$Si (^{1}H, ^{13}C), external H$_3$PO$_4$ (85%) (^{31}P) and Me$_4$Sn (^{119}Sn) for the indicated nuclei.

Single crystals of **1** and **2,** suitable for X-ray diffraction were obtained by diffusion using a dichloromethane–n-hexane mixture. The crystallographic and structure solution data are summarized in

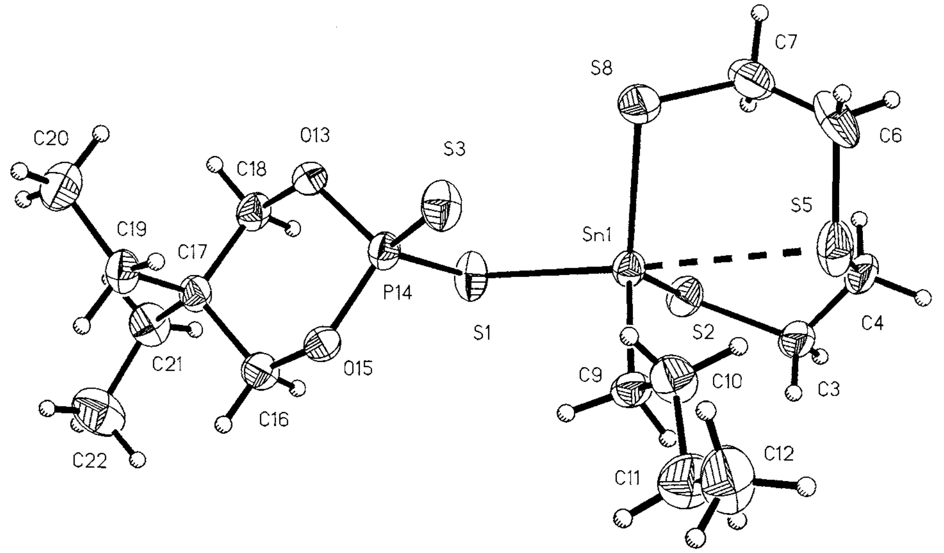


Fig. 3. ORTEP like drawing of $S(CH_2CH_2S)_2Sn^n Bu[S_2P(OCH_2CEt_2CH_2O)]$ (**2**).

Table 1. Data collections were carried out on a Siemens P4/PC diffractometer at room temperature, with graphite-monochromated Mo–K_α radiation (λ = 0.71073). In both cases, corrections were applied for background and Lorentz-polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares calculations using the SHELXTL-PLUS program [17]. All non-hydrogen atoms were refined anisotropically, the positions of the hydrogen atoms were calculated in idealized positions.

2.1. *Synthesis of 5-n-butyl-5-(5′,5′-diethyl-2′-thioxo-1′,3′,2′-dioxaphosphorinane-2′-thioato)-1-oxa-4,6-dithia-5-stannocane, $O(CH_2CH_2S)_2Sn^n Bu[S_2P(OCH_2CEt_2CH_2O)]$ (1)*

Stoichiometric amounts of $[(OCH_2CEt_2CH_2O)PS_2]$-Na (248 mg, 1 mmol), dissolved in 40 ml anhydrous ethanol, and a suspension of $O(CH_2CH_2S)_2Sn(^n Bu)Cl$ (347 mg, 1 mmol) also in ethanol (40 ml) were stirred overnight. The resulting solid was filtered and recrystallized from a dichloromethane–*n*-hexane solution. White crystals, stable on exposure to air, m.p. 103–105°C. Yield (317 mg, 59%), Anal. Calc. for $C_{15}H_{31}O_3PS_4Sn$: C, 32.52; H, 5.81%. Found C, 33.00; H, 5.74%. EI-MS (70 eV) *m*/*z* 481 (M + –^{n}Bu, 100%); 421 ($C_9H_{18}O_3S_3PSn$ +, < 10%), 344 ($C_7H_{14}O_2S_2PSn$+, 30%); 287 ($C_4H_8OS_3Sn$ +, 18%); 227 ($C_2H_4OS_2Sn$ +, 10%); 195 (C_2H_4OSSn +, 15%). IR (KBr) 2942 m, 2858 m, (νC–H); 1439 s, 1168 m (δ CH_2–S); 1056 s [ν(P)–O–C] and [νC–O–C]; 991 s, [ν(P–O–(C)], 926 m [dioxaphosphorinane ring] 674 s (ν_{sym} PS_2), 506 s cm^{-1} (ν_{asym} PS_2). ^{1}H-NMR ($CDCl_3$): δ 4.1 (d, $^3J(^{31}$P-O-C-^{1}H) = 15.9 Hz, 4H) (CH_2OP); 3.97 (ddd, ^2J = 2.8, 7.2 and 10 Hz, 2H) and 3.6 (ddd ^2J = 2.19, 6.03 and 9.9 Hz, 2H) CH_2–O; 2.98 (m, 4H) CH_2–SSn; 2.13 (m, 2H), 1.84 (m, 2H), 1.48 (sext, ^2J = 7.6 Hz, 2H), 0.93 (t,

Table 2
Relevant bond distances (Å) and bond angles (°) of $O(CH_2CH_2S)_2$-$Sn^n Bu[S_2P(OCH_2CEt_2CH_2O)]$ (**1**) and $S(CH_2CH_2S)_2Sn^n Bu[S_2P(OCH_2CEt_2CH_2O)]$ (**2**)

	1	**2**
Bond distances		
Sn(1)···X(5)	2.468(8)	2.940
Sn(1)···S(3)	3.710	3.457
Sn(1)–S(1)	2.509(3)	2.5379(16)
Sn(1)–S(2)	2.415(2)	2.4163(16)
Sn(1)–S(8)	2.410(4)	2.4017(19)
Sn(1)–C(9)[^{n}Bu]	2.132(9)	2.127(5)
S(1)–P(14)	2.050(4)	2.031(2)
S(3)–P(14)	1.917(3)	1.923(2)
O(13)–P(14)	1.585(8)	1.595(4)
O(15)–P(14)	1.594(7)	1.589(4)
Bond angles		
S(1)–Sn(1)···X(5)	163.0(2)	166.0
S(2)–Sn(1)–S(8)	115.0(1)	111.60(7)
S(2)–Sn(1)–C(9)	119.1(3)	115.15(18)
S(8)–Sn(1)–C(9)	119.2(3)	127.90(18)
S(1)–Sn(1)–S(2)	86.3(1)	86.71(6)
S(1)–Sn(1)–S(8)	100.9(1)	101.18(7)
S(1)–Sn(1)–C(9)	108.0(3)	103.11(18)
X(5)···Sn(1)–S(2)	78.7(2)	80.5
X(5)···Sn(1)–S(8)	78.5(2)	78.7
X(5)···Sn(1)–C(9)	86.6(6)	79.2
Sn(1)–S(1)–P(14)	105.0(1)	100.24(7)
S(1)–P(14)–S(3)	117.3(2)	116.69(10)
S(1)–P(14)–O(13)	108.1(3)	106.12(18)
S(1)–P(14)–O(15)	103.4(3)	107.97(18)
S(3)–P(14)–O(13)	111.0(2)	111.41(18)
S(3)–P(14)–O(15)	112.4(3)	110.57(17)
O(13)–P(14)–O(15)	103.5(4)	103.1(2)
C(16)–O(15)–P(14)	117.6(7)	118.8(3)
C(18)–O(13)–P(14)	119.9(6)	116.7(4)

Table 3
Bond distances in some tin compounds according to the type of bonding

Compounds	Sn–S	Sn···S	P=S	P–S	S–P–S	Sn–S–P	Coordination	Reference
$O(CH_2CH_2S)_2Sn^nBu[S_2P(OCH_2CEt_2CH_2O)]$ (**1**)	2.415		1.917	2.05	117.3	105.0	Monodentate	This work
$S(CH_2CH_2S)_2Sn^nBu[S_2P(OCH_2CEt_2CH_2O)]$ (**2**)	2.537	3.457	1.923	2.031	116.7	100.2	Anisobidentate	This work
$Ph_3Sn[S_2P(OEt)_2]$	2.458		1.931	2.054	112.3	103.8	Monodentate	[10]
$Bu_2Sn(OAc)[S_2P(OCH_2CMe_2CH_2O)]$	2.528	3.174	1.931	2.031	114.7	93.1	Anisobidentate	[11]
$Me_2Sn[S_2P(OCMe_2CMe_2O)]_2$	2.495	3.130	1.932	2.031	112.4	95.0	Anisobidentate	[12]
$Ph_3Sn[S_2P(OCMe_2CMe_2O)]$	2.436	3.411	1.903	2.039	114.8	102.1	Anisobidentate	[13]
$Ph_2Sn[S_2P(OEt)_2]_2$	2.490	3.23	1.942	2.029	112.4	97.5	Anisobidentate	[14]
	2.481	3.20	1.919	2.036	113.2	97.7		
$Ph_2Sn[S_2P(O^iPr)_2]_2$	2.678	2.689	1.998	2.006	111.3	85.4	Isobidentate	[15]

$^2J = 7.14$ Hz, 3H) ^{n}Bu; 1.44 (q, $^2J = 7.6$ Hz, 4H) CH_2CH_3, 0.83 (t, $^2J = 7.4$ Hz, 6H) CH_2CH_3. ^{13}C-NMR ($CDCl_3$) δ 74.49 [d, $^2J(^{31}P\text{-}O\text{-}^{13}C = 8.58$ Hz)] CH_2OP; 37.34 [d $^3J(^{31}P\text{-}O\text{–}CH_2\text{-}^{13}C) = 5.72$ Hz] CCH_2OP; 72.26, CH_2O; 27.95 CH_2SSn; 28.50, 28.07, 27.98 and 13.73 ^{n}Bu; 22.92 and 7.24 Et. ^{31}P-NMR ($CDCl_3$) δ 89.33. ^{119}Sn-NMR (CDCl3) δ −19.87.

2.2. *Synthesis of 2-n-butyl-2-(5′,5′-diethyl-2′-thioxo-2′,1′,3′-dioxaphosphorinane-2′-thiolate)-1,3,6-trithia-2-stannocane $S(CH_2CH_2S)_2Sn^nBu[S_2P(OCH_2CEt_2CH_2O)]$ (2)*

The compound was obtained as described for **1**, using $[(OCH_2CEt_2CH_2O)PS_2]Na$ (248 mg, 1 mmol) and $S(CH_2CH_2S)_2Sn(^nBu)Cl$ (263 mg, 1 mmol). Yield (171 mg, 31%), of white crystals, m.p. 130°C. Anal. Calc. for $C_{15}H_{31}O_2PS_5Sn$: C, 32.56; H, 5.64%. Found C, 33.18; H, 5.84%. EI-MS (70 eV) m/z 497 ($M+-^nBu$, 78%); 437 ($C_9H_{18}O_2S_4PSn+$, 15%), 344 ($C_7H_{14}O_2S_2PSn+$, 28%); 329 ($C_8H_{17}S_3Sn+$, 100%); 303 ($C_4H_8S_4Sn+$, 10%); 211 ($C_2H_4S_2Sn+$, 14%). IR (KBr) 2917 m, 2858 m, (νC–H); 1437 s, 1150 m (δ CH_2–S); 1070 s [ν(P)–O–C]; 1004 s, [ν(P–O–(C)], 665 s, 589 (ν_{sym} PS_2) and (νC–S–C), 504 s cm^{-1} (ν_{asym} PS_2). ^{1}H-NMR ($CDCl_3$): δ 4.08 (d, $^3J(^{31}P\text{-}O\text{-}C\text{-}^1H) = 15.93$ Hz, 4H) (CH_2OP); 3.09 (m, 4H), 2.93 (m, 2H) and 2.71 (m, 2H) CH_2S and CH_2–SSn; δ 2.34 (m, 2H), 1.87 (m, 2H), 1.47 (sext, $^2J = 7.4$ Hz, 2H), 0.92 (t, $^2J = 7.4$ Hz, 3H) ^{n}Bu; 1.42 (q, $^2J = 7.6$ Hz, 4H) CH_2CH_3, 0.81 (t, $^2J = 7.4$ Hz, 6H) CH_2CH_3. ^{13}C-NMR ($CDCl_3$) δ 74.18 [d, $^2J(^{31}P\text{-}O\text{-}^{13}C = 8.58$ Hz)] CH_2OP; 37.33 [d $^3J(^{31}P\text{-}O\text{–}CH_2\text{-}^{13}C) =$ 5.15 Hz] CCH_2OP; 40.42, CH_2S; 25.85 CH_2SSn; 33.54, 28.82, 28.47, and 13.73 ^{n}Bu; 23.01 and 7.15 Et. ^{31}P-NMR ($CDCl_3$) δ 93.04 ^{119}Sn-NMR ($CDCl_3$) δ −42.76.

3. Results and discussion

The 5-*n*-butyl-5-(5′,5′-diethyl-2′-thioxo-1′,3′,2′-dioxaphosphorinane-2′-thiolate)-1-oxa-4,6-dithia-5-stannocane $O(CH_2CH_2S)_2Sn^nBu[S_2P(OCH_2CEt_2CH_2O)]$ (**1**) and 2-*n*-*b*utyl-2-(5′,5′-diethyl-2′-thioxo-2′,1′,3′-dioxaphosphorinane-2-thiolate)-1,3,6-trithia-2-stannocane $S(CH_2CH_2S)_2Sn^nBu[S_2P(OCH_2CEt_2CH_2O)]$ (**2**) were prepared from the sodium salt of the dithiophosphoric acid, 5,5-diethyl-2-mercapto-2-thiono-1,3,2-dioxaphosphorinane and the stannocanes 5-chloro-5-*n*-butyl-1-oxa-4,6-dithia-5-stannocane and 2-chloro-2-*n*-butyl-1,3,6-trithia-2-stannocane, respectively in EtOH (Scheme 2).

The compounds **1** and **2** are air stable, colorless, crystalline solids, soluble in organic solvents (e.g. CH_2Cl_2, CH_3Cl, benzene, but not in hexane), were characterized by IR, EI-MS and multinuclear NMR (^{1}H, ^{13}C, ^{31}P, ^{119}Sn). The crystal and molecular structures of **1** and **2** were determined.

The IR spectra exhibit absorption bands characteristic for both the heterocyclic $O/S(CH_2CH_2S)_2M$ moiety and the phosphorodithioate ligand. The assignment of these bands was done by comparison with the spectra of the starting materials and literature data [10,15,18]. The ν[(P)O–C] and ν[P–O(C)] stretching modes have been observed in the region 1170–1095 and 1015–965 cm^{-1}, respectively. In **1** and **2** ν(P)O–C appear at 1056 and 1070 cm^{-1} and νP–O(C) at 991 and 1004 cm^{-1}. The medium bands at 926 and 935 cm^{-1} are due to the dioxaphosphorinane ring in **1** and **2**, respectively. The strong bands due to $\nu_{sym}(PS_2)$ and $\nu_{asym}(PS_2)$ are observed at 674 and 506 cm^{-1} for **1** and 665 and 504 cm^{-1} for **2**, while in the spectra of the free acid, a shift to lower frequencies (648 and 498 cm^{-1}) is observed. It is known that these data cannot, however, distinguish without uncertainty between the various structural possibilities, since it is not possible to assign with certainty the P–S and P=S stretching frequencies [10,15,18]. The spectra also exhibit absorption bands characteristic of the symmetrical and asymmetrical C–X–C group in the stannocanes.

The electron impact mass spectrum for **1** and **2** did not show the molecular ion, however the ion fragment, due to the loss of Bu from the molecular ion, corresponds to the base peak in **1**, while in **2** $S(CH_2CH_2S)_2Sn^nBu^+$ is the most intense. In both cases, ion fragments characteristic of stannocane eight-membered ring $X(CH_2CH_2S)_2Sn^+$ are found. The ion fragment assigned to the five membered heterocycle $C_2H_4SXSn^+$ seems to be the result of the elimination of a thiirane molecule from the original eight membered heterocycle. The spectra also show tin dithiophosphate fragments. No fragments were found at a higher mass than the $M–^nBu^+$ that is consistent with an essentially monomeric nature of **1** and **2**.

The ^{1}H-NMR spectrum of **1** and **2**, present the methylene signal for the 1,3,2-dioxaphosphorinane ring as a doublet arising from decoupling $[^3J(^{31}P\text{-}O\text{–}C\text{-}^1H)] = 15.9$ Hz. There is no evidence of the non-equivalence of the protons CH_2OP even though the spectra were recorded at low temperature (−90°C). This situation is in agreement with the free acid behavior.

It is interesting to note, that the ^{1}H-NMR spectra of the free acid methyl ester shows the non-equivalence of the methylene protons, which appear as two doublet of doublets at δ 4.09 and δ 4.15 $J_{gem} = 11.3$ and 11.8 Hz and $[^3J(^{31}P\text{-}O\text{–}C\text{-}^1H)] = 21.46$ and 1.9 Hz. The observed vicinal POCH couplings of such methyl ester is consistent with $^3J_{trans}$ and $^3J_{gauche}$ values, respectively, of a chair conformation of the dioxaphosphorinane ring with the CH_3S group on the axial position. Therefore the ethyl groups on C-5 are non-equivalent. The axial methylene protons appear at downfield shifts (δ 1.67) while the equatorial protons exhibit high field shifts (δ 1.29). The methyl groups lie δ 0.87 and 0.82, respectively [19].

The NMR equivalence of the methylene protons of the 1,3,2-dioxaphosphorinane ring in **1** and **2** is indicative of a rapid interchange between the two sulfur atoms, similar to that reported for other metal complexes where the linkage of the dithiophosphate group was assumed as isobidentate [11,20], while that in the free acid is due the tautomeric equilibrium of the proton acid, atoms as well as a conformational equilibrium of the phosphorinane ring atoms. The isobidentate coordination in solution is supported by the ^{31}P-NMR spectra. The downfield shift, in the range 10–14 in comparison with the free acid, is consistent with this type of coordination, according to that proposed by Glidewell [21]. The eight-membered ring of the stannocanes in **1** and **2** exhibits the anticipated resonance signals typical of an ABCD spin system. These signals are ascribed to the $–XCH_2CH_2S–$ fragments of the eight-membered ring. The equivalence of these two fragments supports the existence of an equilibrium between all the possible conformations. For the ^{13}C-NMR spectra, two group of resonances are present: two singlets due to the carbons of stannocane ring in agreement with the equilibrium conformational, and the signals attributable to dioxaphophorinane ring. The carbon atoms do not suffer significant shifts in comparison with the positions of the corresponding free acid. The values of the coupling constants (due to phosphorus–carbon coupling) $^2J(^{31}P\text{-}O\text{-}^{13}C)$ and $^3J(^{31}P\text{-}O\text{–}C\text{-}^{13}C)$ are averaged at 8.58 and 5.5 Hz, respectively. The values of the chemical shift of the ^{119}Sn-NMR spectra at −19.87 and −42.76 ppm for **1** and **2**, respectively, have no relationship with the proposed values related with the different coordination number around the Sn atom [22].

The molecular structures of **1** and **2** are shown in the ORTEP plots of Figs. 2 and 3, respectively with the corresponding atom numbering scheme. Selected bond lengths and angles are presented in Table 2.

There are no significant intermolecular interactions in both **1** and **2**. The Sn–S(3) distance in $O(CH_2CH_2S)_2Sn^nBu[S_2P(OCH_2CEt_2CH_2O)]$ (**1**) (3.71 Å) is close to the sum of the van der Waals radii (3.90 Å), but significantly longer than that found in organotin compounds, where the iso- and anisobidentate coordination is found (Table 3). However the Sn–S(3) distance is far from the corresponding value of the other monodentante example (5.326 Å) [10]. In addition, the bond angle Sn–S–P (105°) is slightly larger than in $Ph_3Sn[S_2P(OEt)_2]_2$ (103.8°) [10] and the bond distances P=S and P–S are in agreement with a monodentate coordination (Table 3). The monodentate character of the ligand is consistent with the transannular distance Sn···O in **1** (2.468 Å), that is slightly longer than in $O(CH_2CH_2S)_2Sn(^nBu)Cl$ (2.409 Å) [6], but shorter than in the two anisobidentate dithiocarbamates stannocanes $O(CH_2CH_2S)_2Sn(^nBu)S_2CNC_4H_8$ (2.763 Å) [23] and $O(CH_2CH_2S)_2Sn(CH_2CH_2CO_2CH_3)Cl$ [24] (2.615 Å), respectively. Therefore, the geometry around the tin atom can be described as a distorted trigonal-bipyramidal arrangement with S(1) and O(5) in the apical position and S(2), S(8) and C(9) in the equatorial ones. The axial S(1)–Sn···O(5) angle of 163° is similar to that found in $O(CH_2CH_2S)_2Sn(CH_3)_2$ (163.6°) [2] and smaller than in $O(CH_2CH_2S)_2Sn(^nBu)Cl$ (169.7°) [6], the equatorial angles are S(2)–Sn–S(8), S(8)–Sn–C(9) and S(2)–Sn–C(9), 115, 119.2 and 119.1°, respectively. The exocyclic angles are the largest of the equatorial angles at tin, in agreement with a boat–chair conformation.

The coordination geometry around the tin atom in **2** is difficult to describe. If the secondary interaction Sn···S(3) (3.457 Å) is taken into account, the tin atom becomes six-coordinate. Although the distance Sn···S(3) bond suggests a weak secondary interaction, the phosphorus–sulfur bond distances (2.031 and 1.923 Å) are indicative of an anisobidentate coordination, in agreement with the values reported for other organotin derivatives (Table 3). The transannular distance Sn···S(5) is longer than that found in $S(CH_2CH_2S)_2Sn(^nBu)Cl$ (2.785 Å) [6] and is due, may be, to the influence of the exocyclic interactions Sn···S. The same behavior is observed in $S(CH_2CH_2S)_2Sn^nBu[S_2P(O^iPr)_2]$ [25] Sn···S (3.027 Å) and a exocyclic interaction (3.489 Å). However the Sn···S(3) interaction is slightly longer than that present in $Ph_3Sn[S_2P(OCMe_2CMe_2O)]$ [13] [Sn···S, (3.411 Å)], where the coordination geometry is intermediate between tetrahedral and trigonal-bipyramidal. It is possible to suggest that **2** presents the same behavior, but with a coordination geometry intermediate between trigonal-bipyramidal and a bicapped tetrahedron.

The torsion angles of **1** and **2** are indicative of the boat–chair conformation for the eight-membered rings, as in the chloro stannocane $X(CH_2CH_2S)_2Sn(^{n}Bu)Cl$ (X = O, S). However in **1** the Sn(1)–S(2)–C(3)–C(4)–X(5) is the chair part while Sn(1)–S(8)–C(7)–C(6)–X(5) is the boat.

The six-membered 1,3,2-dioxaphosphorinane ring in **1** and **2** presents a chair conformation, with the P=S in the equatorial position and the sulfur atom bonded to the tin atom in the axial position of the 1,3,2-dioxaphosphorinane. The same conformational arrangement occurs in $Bi[S_2P(OCH_2CEt_2CH_2O)]_3$ [26] and $Me_2Te[S_2P(OCH_2CEt_2CH_2O)]_2$ [20] according to normal anomeric effect in these rings.

4. Conclusion

The most important feature of the molecular structure of **1** is the monodentate character of the dithiophosphate ligand, corresponding to the second reported example of this type of compound. Compound **2** is anisobidentate, but in solution both compounds present an isobidentate behavior.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CSD-133761 for compound **1** and CSD-133762 for compound **2**.

Acknowledgements

This work was supported by the Mexican National Council of Science and Technology CONACYT (Grant 1428P-N9507).

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