APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 555–562
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.818

Structure and *in vitro* antibacterial activity of $BuSnCl_{3-n}[(OPPh_2)(SPPh_2)N]_n$ ($n = 1, 2$)†

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Received 25 June 2004; Revised 9 August 2004; Accepted 10 September 2004

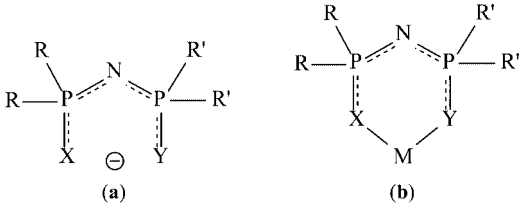
$BuSnCl_2[(OPPh_2)(SPPh_2)N]$ (1) and $BuSnCl[(OPPh_2)(SPPh_2)N]_2$ (2) were prepared by reacting $BuSnCl_3$ and $K[(OPPh_2)(SPPh_2)N]$, in 1:1 and 1:2 molar ratios. The compounds were investigated in solution by multinuclear (^1H, ^{13}C, ^{31}P, ^{119}Sn) NMR spectroscopy. Variable-temperature ^{31}P NMR studies indicate dynamic behaviour in solution. The solid-state molecular structure was established by single-crystal X-ray diffraction revealing 5- and 6-coordinated metal atoms in 1 and 2, respectively, as a result of the monometallic biconnective behaviour of the monothioimidodiphosphinato moieties. Preliminary results on the *in vitro* biological activity are reported. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: organotin (IV); monothioimidodiphosphinates; X-ray structure; antibacterial activity

INTRODUCTION

Tetraorganodichalcogenoimidodiphosphinato anions, $[(XPR_2)(YPR'_2)N]^-$ (**a**) (X, Y = O, S, Se), are well known versatile ligands able to adjust to various coordination geometries required by metal centres.[1] The most common coordination pattern exhibited by such ligands is *X,Y*-monometallic biconnective (**b**), the flexibility of the XPNPY skeleton allowing a considerably wider range of the ligand 'bite' in comparison with the restrictive one in 1,1-dichalcogenophosphorus ligands (e.g. dithiophosphates, $[(RO)_2PS_2]^-$, dithiophosphinates, $[R_2PS_2]^-$).

We have previously reported on the synthesis and characterization of several organotin(IV) derivatives containing tetraorganodichalcogenoimidodiphosphinato ligands.[2–9] Although solution NMR indicated that angular C–Sn–C angles were also obtained in some cases, in the solid state most of the $R''_2Sn[(XPR_2)(YPR'_2)N]_2$ derivatives were found



to be monomeric, with an almost perfect all-*trans*-$C_2SnX_2Y_2$ octahedral core (**c**, *trans*-C-Sn-C, X-Sn-X and Y-Sn-Y angles of 180°). Only in one case, i.e. $Bu_2Sn[(OPPh_2)(SPPh_2)N]_2$, could both all-*trans* (**c**) and *cis* (**d**, C–Sn–C 160.73°, X *trans* Y) isomers be isolated and characterized by single crystal X-ray diffraction.[9]

So far only one diorganotin(IV) halo derivative, $Ph_2SnCl[(SePPh_2)_2N] \cdot H_2O$ ($C_2SnClSe_2$ trigonal bipyramidal core), has been characterized,[10] but no monoorganotin (IV) compounds containing $[(XPR_2)(YPR'_2)N]^-$ ligands were reported. Some mixed chloro-dithiocarbamato complexes of the type $BuSnCl_2[S_2CNEt_2]$,[11] and $RSnCl[S_2CNR'_2]_2$ [R = Bu, R′ = Et;[11] ^{i}Pr,[12] ^{i}Bu;[13] R = Ph, R′ = Et,[14] ^{i}Bu,[15] *cyclo*-C_4H_4;[16] R = CH≡CH_2, Et;[17] R = CH_2CH_2C(=O)OMe, R′=Me[18]] were investigated by X-ray diffraction; in all cases the dithioligand units chelate the metal atom, resulting in

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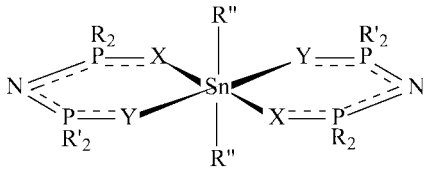
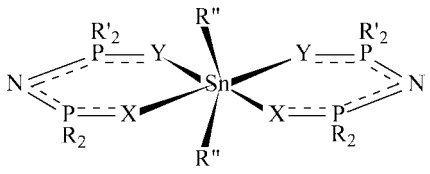
†Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.
Contract/grant sponsor: Natural Sciences and Engineering Research Council of Canada.



(**c**)



(**d**)

significantly distorted trigonal bipyramidal ($CSnCl_2S_2$ core) and octahedral ($CSnClS_4$ core) coordination environments. In order to explore structural changes produced in the absence of a restrictive ligand 'bite' we have decided to investigate monoorganotin (IV) derivatives containing ligands of general formula $[(XPR_2)(YPR'_2)N]^-$.

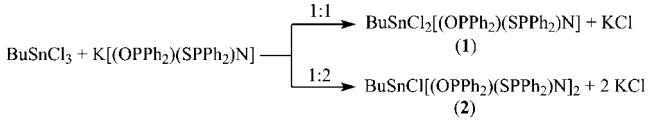
On the other hand, the biological activity of organotin(IV) compounds has been studied intensively and many of them were found to exhibit a broad range of both *in vitro* and *in vivo* activity (antitumor, antifungal, etc).[19–24]

We report here on the synthesis, spectroscopic characterization in solution as well as the crystal and molecular structures of $BuSnCl_2[(OPPh_2)(SPPh_2)N]$ (**1**) and $BuSnCl[(OPPh_2)(SPPh_2)N]_2$ (**2**). Preliminary results on the *in vitro* antibacterial activity are also reported.

RESULTS AND DISCUSSION

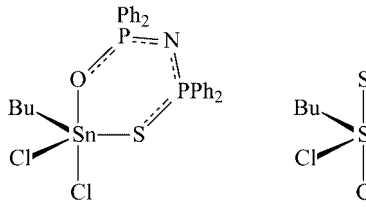
Syntheses and characterization

The title compounds were obtained by reacting the potassium salt of the monothioimidodiphosphinic acid with butyltin(IV) trichloride, in benzene, at room temperature:

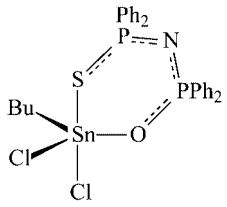


They were isolated as air-stable, colourless crystalline solids after recrystallization of the crude products from chloroform–hexane. The compounds were characterized by multinuclear (^1H, ^{13}C, ^{31}P, ^{119}Sn) NMR spectroscopy in solution and the molecular structures were determined by single crystal X-ray diffraction.

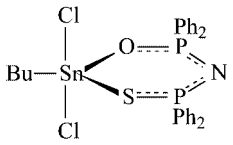
The room temperature (r.t.) ^1H and ^{13}C spectra of **1** in $CDCl_3$ solution showed the expected pattern for the organic groups attached to the metal (proton–proton couplings and tin satellites for the *alpha*-CH_2 protons) and phosphorus atoms (doublet due to phosphorus–proton and phosphorus–carbon couplings), respectively. The r.t. ^{31}P NMR spectrum of **1** exhibited two singlet resonances at 28.8 (Ph_2PO) and 32.5 (Ph_2PS) ppm (the splitting due to phosphorus–phosphorus coupling not being observed) and was consistent with the bidentate coordination of the ligand. The shift of the resonance assigned to the phosphorus atom in the Ph_2PO group with respect to that in the free $(OPPh_2)(SPPh_2)NH$ ligand (23.1 ppm) and its potassium salt, $K[(OPPh_2)(SPPh_2)N]$ (16.1 ppm)[6] is indicative of the coordination of the deprotonated ligand with the oxygen *trans* to a Cl atom. The r.t. ^{119}Sn NMR resonance (−263 ppm) for **1** suggests that it possesses a five-coordinate structure in solution (cf. $BuSnCl_2[S_2CNEt_2]$: δ, −285.7 ppm, in C_6D_6).[11] A variable temperature ^{31}P NMR study, however, suggests a dynamic behaviour in solution. At −60 °C, in addition to the main resonances [30.2 (Ph_2PO, $^1J_{PC}$ 134.3 Hz) and 33.7 (s, Ph_2PS)] assigned to isomer **1a** (also found in solid state, see subsequent discussion), new ^{31}P signals of lower intensity [35.0 (s, br), 37.1 (d, $^2J_{PP}$ 6.2 Hz) and 55.4 (s, br) ppm; relative intensity ratio 3 : 3 : 0.5 : 0.1 : 1] are observed. The presence of solution equilibria between **1a** and other isomers, e.g. **1b** (S *trans* Cl) and **1c** (Cl *trans* Cl), might account for this behaviour. In the ^{119}Sn NMR spectrum of **1** recorded at −60 °C, only one resonance at −262 ppm [dd, $^2J_{SnP(O)}$ 134, $^2J_{SnS}$ 32 Hz] could, however, be observed.



1a



1b



1c

For compound **2** several isomers are possible of which the most probable are those containing the butyl and the Cl atom in *cis* positions of a $CSnCl(O,S)_2$ octahedral arrangement around the metal centre (isomers **2a**–**2d**). At room temperature the NMR spectra of **2** in CD_2Cl_2 solution suggest a fast fluxional behaviour. Indeed, the two broad ^{31}P resonances observed at 18 °C [δ, 25.5 (Ph_2PO), 33.7 (Ph_2PS)] are each split into six signals when the ^{31}P spectrum is recorded at −80 °C (Fig. 1). This behaviour suggests that the interconversion between the several isomers present in solutions is frozen at this temperature. Unfortunately, we were not able to assign the observed ^{31}P resonances to particular isomers.

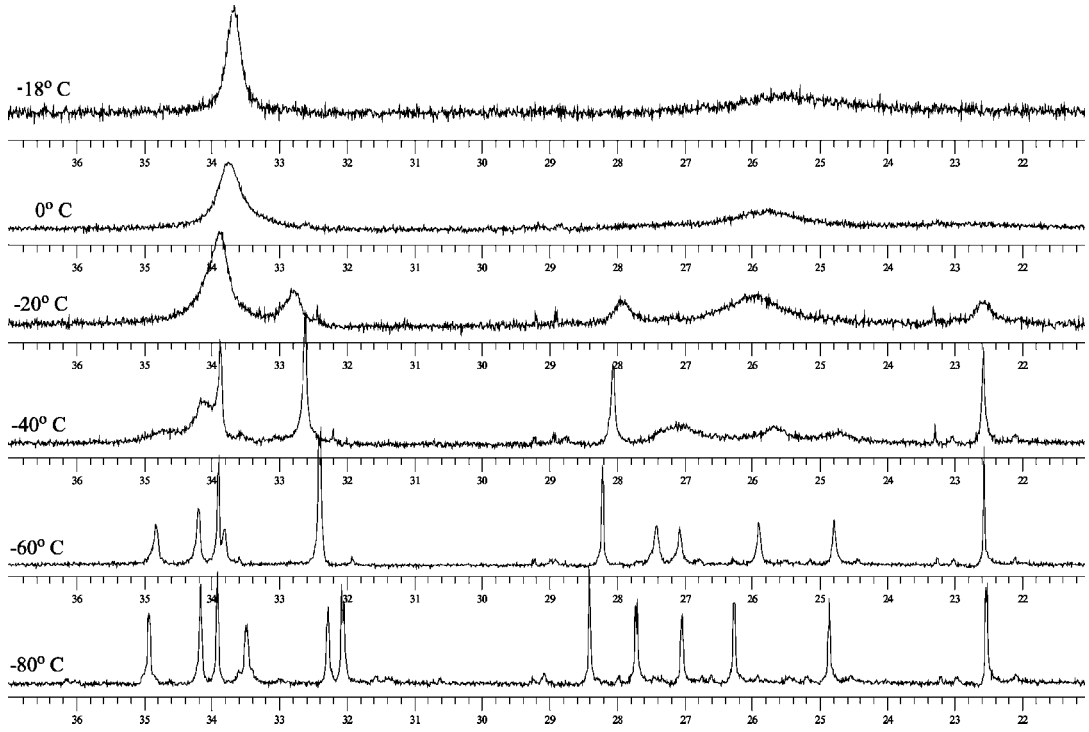
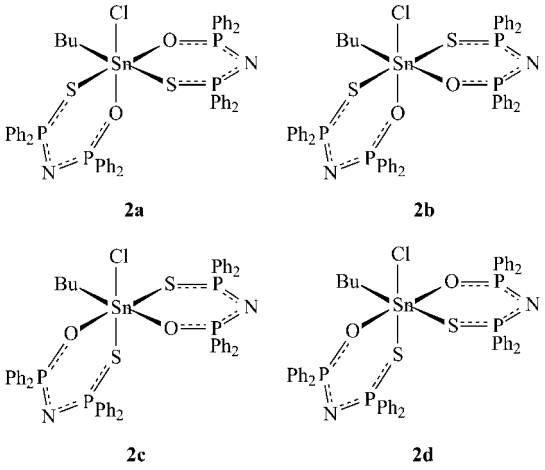


Figure 1. Variable temperature ^{31}P NMR spectra of compound **2** in CD_2Cl_2 solution.



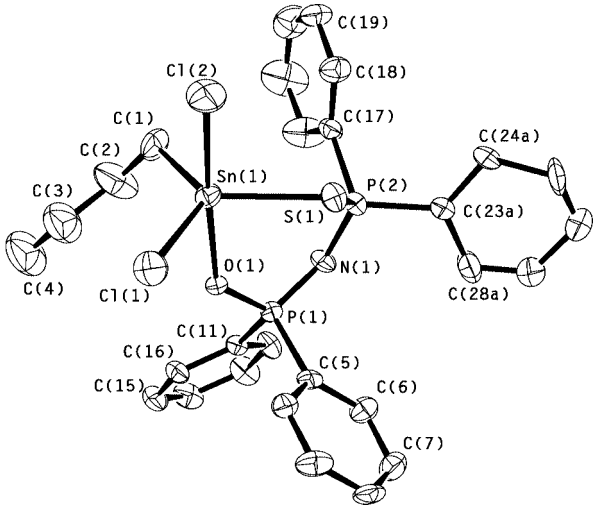


Figure 2. ORTEP diagram for *n*-$BuSnCl_2[(OPPh_2)(SPPh_2)N]$ (**1**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The solid-state molecular structures of **1** and **2**, as established by single-crystal X-ray diffraction, are shown as ORTEP plots in Figs 2, and 3, respectively, and selected interatomic distances and angles are listed in Table 1. The crystals of both compounds contain discrete molecular units, separated by normal van der Waals distances. In the case of compound **1** the crystal contains the isomer **1a**, as is also suggested by solution NMR data too, while in the case of compound **2** of several possible isomers, only **2a** is observed in the solid state.

In both compounds the monothioimidodiphosphinato units are coordinated through the chalcogen atoms to the metal centre, resulting in slightly distorted trigonal bipyramidal (in **1**) and octahedral (in **2**) coordination environments. One Cl and the oxygen atom occupy the axial positions of the $CSnCl_2(O,S)$ core in **1** [Cl(2)–Sn(1)–O(1) 172.2(2)°], while the S(1), Cl(1) and C(1) of the butyl group are in the equatorial positions [almost planar CSnClS system, with the metal atom deviated 0.036 Å towards the axial

Table 1. Important interatomic distances (Å) and angles (deg) for $BuSnCl_2[(OPPh_2)(SPPh_2)N]$ (**1**) and $BuSnCl[(OPPh_2)(SPPh_2)N]_2$ (**2**)

1		**2**			
Sn(1)–C(1)	2.12(1)	Sn(1)–C(1)	2.146(3)		
Sn(1)–Cl(1)	2.336(3)	Sn(1)–Cl(1)	2.485(1)		
Sn(1)–Cl(2)	2.453(3)				
Sn(1)–O(1)	2.164(6)	Sn(1)–O(1)	2.099(2)	Sn(1)–O(2)	2.147(2)
Sn(1)–S(1)	2.468(3)	Sn(1)–S(1)	2.534(1)	Sn(1)–S(2)	2.636(1)
P(1)–O(1)	1.525(6)	P(1)–O(1)	1.529(2)	P(3)–O(2)	1.533(2)
P(2)–S(1)	2.071(4)	P(2)–S(1)	2.034(1)	P(4)–S(2)	2.036(1)
P(1)–N(1)	1.593(8)	P(1)–N(1)	1.583(3)	P(3)–N(2)	1.584(3)
P(2)–N(1)	1.577(7)	P(2)–N(1)	1.583(3)	P(4)–N(2)	1.587(3)
O(1)···S(1)[a]	3.239(6)	O(1)···S(1)[a]	3.28(4)	O(2)···S(2)[a]	3.49(4)
Cl(2)–Sn(1)–O(1)	172.2(2)	Cl(1)–Sn(1)–O(2)	171.41(7)		
C(1)–Sn(1)–Cl(1)	121.4(4)	O(1)–Sn(1)–S(2)	175.50(6)		
C(1)–Sn(1)–S(1)	126.2(4)	C(1)–Sn(1)–S(1)	175.6(1)		
Cl(1)–Sn(1)–S(1)	112.3(1)				
		Cl(1)–Sn(1)–C(1)	93.2(1)	O(2)–Sn(1)–C(1)	95.3(1)
Cl(2)–Sn(1)–C(1)	94.5(4)	Cl(1)–Sn(1)–O(1)	91.29(7)	O(2)–Sn(1)–O(1)	86.60(9)
Cl(2)–Sn(1)–Cl(1)	90.6(1)	Cl(1)–Sn(1)–S(1)	84.55(3)	O(2)–Sn(1)–S(1)	87.12(7)
Cl(2)–Sn(1)–S(1)	87.3(1)	Cl(1)–Sn(1)–S(2)	88.22(3)	S(1)–Sn(1)–S(2)	85.72(4)
		C(1)–Sn(1)–O(1)	94.1(1)	C(1)–Sn(1)–S(2)	90.4(1)
O(1)–Sn(1)–S(1)	88.5(2)	S(1)–Sn(1)–O(1)	89.78(7)	O(2)–Sn(1)–S(2)	93.24(7)
O(1)–Sn(1)–Cl(1)	85.0(2)				
O(1)–Sn(1)–C(1)	93.3(4)				
Sn(1)–O(1)–P(1)	132.6(3)	Sn(1)–O(1)–P(1)	135.9(1)	Sn(1)–O(2)–P(3)	132.6(1)
Sn(1)–S(1)–P(2)	99.6(1)	Sn(1)–S(1)–P(2)	109.41(4)	Sn(1)–S(2)–P(4)	109.18(5)
O(1)–P(1)–N(1)	116.1(4)	O(1)–P(1)–N(1)	117.4(1)	O(2)–P(3)–N(2)	117.9(1)
P(1)–N(1)–P(2)	126.5(5)	P(1)–N(1)–P(2)	133.4(2)	P(3)–N(2)–P(4)	135.3(2)
S(1)–P(2)–N(1)	115.9(3)	S(1)–P(2)–N(1)	117.2(1)	S(2)–P(4)–N(2)	118.3(1)

[a] Non-bonding distances.

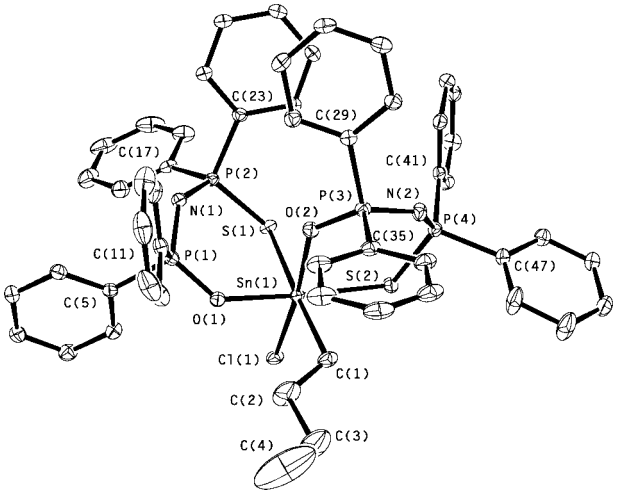


Figure 3. ORTEP diagram for *n*-$BuSnCl[(OPPh_2)(SPPh_2)N]_2$ (**2**). The atoms are drawn with 30% probability ellipsoids. Four carbon atoms in one of the disordered phenyl rings and hydrogen atoms are omitted for clarity.

Cl(2) atom]. In the case of compound **2** the $CSnCl(O,S)_2$ core exhibits different atoms in *trans* positions describing angles at Sn close to 180° [Cl(1)–Sn(1)–O(2) 171.41(7), O(1)–Sn(1)–S(2) 175.50(6), C(1)–Sn(1)–S(1) 175.6(1)°] and *cis* angles in the range 84.55(3)–95.3(1)°. It is obvious that the large bite of the phosphorus ligand [O(1)···S(1) 3.239(6) Å in **1**; O(1)···S(1) 3.28(4), O(2)···S(2) 3.49(4) Å in **2**] accounts for the much less distorted coordination cores from an ideal polyhedron as compared with the $CSnCl_2(S,S)$ core in $BuSnCl_2[S_2CNEt_2]$ [Cl_{ax}–Sn–S_{ax} 156.5(1)°, and deviation of the tin from the equatorial plane: 0.150(5) Å] or the $CSnCl(S,S)_2$ core in $BuSnCl[S_2CNEt_2]_2$ [*trans* angles: Cl–Sn–S 160.9(1), S–Sn–S 153.8(1), C–Sn–S 166.9(5)°; *cis* angles (range): 69.3(1)–104.1(1)°].[11]

The Sn–Cl distances in **1** are different [2.336(3), 2.453(3) Å], as they are in $BuSnCl_2[S_2CNEt_2]$ [2.361(3), 2.449(3) Å],[11] with the shorter one *trans* to the oxygen atom. The vector of the Sn–Cl bond in **2** is also *trans* to an oxygen atom, but this bond is considerable longer [2.485(1) Å] than in **1** and compares well with that observed in $BuSnCl[S_2CNEt_2]_2$ [2.464(3) Å], which however is *trans* to a sulphur atom.[11]

Table 2. Torsion angles (°) for the $SnOSP_2N$ rings in $BuSnCl_2[(OPPh_2)(SPPh_2)N]$ (**1**) and $BuSnCl[(OPPh_2)(SPPh_2)N]_2$ (**2**)

1		**2**			
Sn(1)O(1)P(1)N(1)	−23.6	Sn(1)O(1)P(1)N(1)	15.4	Sn(1)O(2)P(3)N(2)	38.7
O(1)P(1)N(1)P(2)	40.7	P(2)N(1)P(1)O(1)	24.7	O(2)P(3)N(2)P(4)	2.9
P(1)N(1)P(2)S(1)	6.0	S(1)P(2)N(1)P(1)	−15.9	P(3)N(2)P(4)S(2)	−29.9
Sn(1)S(1)P(2)N(1)	−55.1	Sn(1)S(1)P(2)N(1)	−19.5	Sn(1)S(2)P(4)N(2)	18.5
O(1)Sn(1)S(1)P(2)	52.8	P(2)S(1)Sn(1)O(1)	34.8	O(2)Sn(1)S(2)P(4)	5.1
P(1)O(1)Sn(1)S(1)	−24.6	S(1)Sn(1)O(1)P(1)	−40.0	P(3)O(2)Sn(1)S(2)	3.0

The tin–oxygen distances [2.164(6) Å in **1**, and 2.099(2), 2.147(2) Å in **2**] are similar to those observed in diorganotin(IV) derivatives containing the same ligand units, *trans*-$R_2Sn[(OPPh_2)(SPPh_2)N]_2$ [R/Sn–O: Me/2.199(2) Å; Ph/2.189(5) Å;[6] Bz/2.217(9) Å;[8] Bu/2.292(4) Å[9]]. By contrast, the tin-sulfur distances are considerably shorter [2.468(3) in **1**, and 2.534(1), 2.636(1) Å in **2**] than those observed in *trans*-$R_2Sn[(OPPh_2)(SPPh_2)N]_2$ [R/Sn–S: Me/2.758(1) Å; Ph/2.680(4) Å;[6] Bz/Sn–S 2.719(4) Å;[8] Bu/2.720(1) Å[9]].

The differences in the coordination environment of the tin atom in **1** and **2** are not dramatically reflected in the bond lengths within the OPNPS skeleton of the monothioimidodiphosphinato units. The phosphorus–oxygen bond distances [P(1)–O(1) 1.525(6) Å in **1**; P(1)–O(1) 1.529(2), P(3)–O(2) 1.533(2) Å in **2**] are similar to the single P–O bond in $Ph_2P(=O)OH$ [P–O 1.526(6), P=O 1.486(6) Å].[25] The magnitude of phosphorus–sulfur distances [P(2)–S(1) 2.071(4) Å in **1**; P(2)–S(1) 2.034(1), P(4)–S(2) 2.036(1) Å in **2**] indicates a considerable double bond character [cf. the methyl ester, $MeS–PPh_2=N–Ph_2P=S$:[26] P–S 2.071(1), P = S 1.954(1) Å], thus suggesting the ligands are primarily (covalently) bound to the metal centre through the oxygen atoms while the sulphur atoms are involved in intramolecular coordinative bonds. However, the two phosphorus–nitrogen bonds within a ligand unit (Table 1) are equivalent within experimental error and intermediate between single P–N and double P=N bonds [cf. $MeS–PPh_2=N–Ph_2P=S$:[26] P–N 1.610(2), P=N 1.562(2); $[(Me_3Si)_2N–P(=NBu^t)S]_2$:[27] P–N 1.662(2), P=N 1.529(2) Å)].

The main differences in the molecular parameters of the ligand moieties in the title compounds reside in the magnitude of some angles within the chelate six-membered $SnOSP_2N$ rings. While the Sn–O–P, O–P–N and S–P–N angles are almost similar in the two compounds (Table 1), the Sn–S–P and P–N–P angles are considerably increased in the monochloro derivative **2** [Sn(1)–S(1)–P(2) 109.41(4)°, Sn(1)–S(2)–P(4) 109.18(5)°, and P(1)–N(1)–P(2) 133.4(2)°, P(3)–N(2)–P(4) 135.3(2)°] in comparison with those found in the dichloro compound **1** [Sn(1)–S(1)–P(2) 99.6(1)° and P(1)–N(1)–P(2) 126.5(5)°]. The differences observed in the O···S bite and the bond angles in compounds **1** and **2** reflect the flexibility of the OPNPS skeleton and the ability of this type of ligand to accommodate to different coordination requirements.

Although some delocalization of the π-electrons over the OPNPS systems is suggested by the magnitude of the bonds, the six-membered SnO_2P_2N rings are not planar as reflected by the torsion angles (Table 2). They exhibit twisted boat conformation of variable distortion and with different atom types in the apices: the P(1) and S(1) atoms [S(1)Sn(1)O(1)P(1)/S(1)P(2)N(1)P(1) dihedral angle of 54.5°] in **1**, and the metal and N(1) atoms [Sn(1)O(1)P(1)N(1)/Sn(1)S(1)P(2)N(1) dihedral angle of 34.5°] and the P(4) and O(2) atoms [O(2)Sn(1)S(2)P(4)/O(2)P(3)N(2)P(4) dihedral angle of 27.2°] in **2**, respectively.

Biological screening

In vitro antibacterial results against *Escherichia coli* and *Staphylococcus aureus* are summarized in Table 3 for compounds $BuSnCl_2[(OPPh_2)(SPPh_2)N]$ (**1**) and $BuSnCl[(OPPh_2)(SPPh_2)N]_2$ (**2**). It may be observed that after 7 days the germs are still present for a 10^{-4}–10^{-7} dilution in the case of *E. coli* and 10^{-2}–10^{-4} for *S. aureus*, respectively, while they completely disappeared after 14 days. The results suggest a higher antibacterial activity for compound **1** than for compound **2**, obviously stronger against *S. aureus*, and the activity is dependent on the contact time and the germ concentration. Both compounds have some activity against these pathogen germs, but only at low bacteria concentrations, so that after 14 days the tested media become sterile again.

EXPERIMENTAL

The potassium salt, $K[(OPPh_2)(SPPh_2)N]$, was prepared according to a published method,[6] while $BuSnCl_3$ was a commercial product. Solvents were dried and distilled prior to use. Solutions in dried $CDCl_3$ (for **1**) and CD_2Cl_2 (for **2**) were used for NMR studies. Room-temperature ^1H, ^{13}C and ^{31}P NMR spectra were recorded for **1** on a Bruker AV 400 instrument operating at 400.16, 100.62 and 161.99 MHz, respectively. The ^1H and ^{13}C chemical shifts for **1** were assigned based on H,H-COSY, H,C-HSQC and H,C-HMBC experiments. NMR spectra for **2**, including variable-temperature ^{31}P NMR, were recorded on a Varian Mercury 300BB apparatus (^1H, 299.98 and ^{31}P NMR, 121.44 MHz). The chemical shifts are reported in ppm relative to TMS (ref. $CHCl_3$ ^1H 7.26, ^{13}C 77.0 ppm; CH_2Cl_2 = 5.32 ppm) and

Table 3. *In vitro* antibacterial activity of compounds **1** and **2** (in TNG/ml)[a]

	E. coli						*S. aureus*								
	10 ml 0.5% **1** + 1 ml 10^5CFU/ml			1 ml 0.5% **1** + 1 ml 10^5CFU/ml			10 ml 0.5% **1** + 1 ml 10^5CFU/ml			1 ml 0.5% **1** + 1 ml 10^5CFU/ml			1 ml 0.5% **2** + 1 ml 10^5CFU/ml		
Dilution	1 day	7 days	14 days	1 day	7 days	14 days	1 day	7 days	14 days	1 day	7 days	14 days	1 day	7 days	14 days
10^{-2}							X	66	0	X	X	0			
10^{-3}							12	3	0	48	26	0	X	X	0
10^{-4}	X	X	0	X	X	0	1	0	0	6	4	0	X	130	0
10^{-5}	X	X	0	X	X	0	0	0	0	0	0	0	104	8	0
10^{-6}	39	34	0	55	3	0	0	0	0	0	0	0	11	0	0
10^{-7}	3	2	0	6	0	0									

[a] TNG = total number of germs; X = cannot be counted.

H_3PO_4 85%, respectively. Abbreviations used in multiplicities are: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; tt, triplet of triplets; tq, triplet of quartets; m, multiplet. The ^{119}Sn NMR spectra (at 111.81 MHz; chemical shifts reported in ppm relative to neat $SnMe_4$), as well as low temperature ^{31}P NMR for **1**, were recorded on a VARIAN UNITY 300 instrument.

Preparation of $BuSnCl_2[(OPPh_2)(SPPh_2)]$ (1)

$K[(SPPh_2)(OPPh_2)N]$ (1.216 g, 2.58 mmol) was added to a solution of $BuSnCl_3$ (0.727 g, 2.58 mmol) in 20 ml anhydrous benzene. The reaction mixture was stirred for 18 h, then filtered to remove the resulting KCl. The clear filtrate was concentrated under reduced pressure to minimum volume and then kept at low temperature (−20 °C) when the title compound deposited as a solid. The compound was filtered off and recrystallized from $CHCl_3$/*n*-hexane (1 : 4 by volume) to yield colourless crystals (1.67 g, 95%) (m.p. 201–203 °C). Analyses: found, C 49.52, H 4.30, N 2.06; calcd, for $C_{28}H_{29}Cl_2NOP_2SSn$: C 49.34, H 4.18, N 2.12%. ^{1}H-NMR: δ, 0.76 [t, 3H, Sn–$(CH_2)_3CH_3$, $^3J_{HH}$ 7.3 Hz], 1.26 [tq, 2H, Sn–$(CH_2)_2CH_2CH_3$, $^3J_{HH}$ 7.3 Hz], 1.63 [tt, 2H, Sn–$CH_2CH_2CH_2CH_3$, $^3J_{HH}$ 7.6 Hz], 1.90 [t, 2H, Sn–$CH_2CH_2CH_2CH_3$, $^3J_{HH}$ 7.6, $^2J_{SnH}$ 100.5 Hz], 7.39 (m, 8H, P–C_6H_5-*meta*), 7.49 (m, 4H, P–C_6H_5-*para*), 7.74 (dd, 4H, P–C_6H_5-*ortho*, $^3J_{PH}$ 13.1, $^3J_{HH}$ 7.3 Hz), 7.82 (dd, 4H, P–C_6H_5-*ortho*, $^3J_{PH}$ 14.7, $^3J_{HH}$ 7.3 Hz). ^{13}C-NMR: δ, 13.43 (s, C_δ), 25.49 (s, C_γ), 27.24 (s, C_β), 37.79 (s,br, C_α), 128.30 (d, P–C_6H_5-*meta*, $^3J_{PC}$ 13.9 Hz), 128.66 (d, P–C_6H_5-*meta*, $^3J_{PC}$ 13.9 Hz), 130.99 (d, P–C_6H_5-*ortho*, $^2J_{PC}$ 12.4 Hz), 131.08 (d, P–C_6H_5-*ortho*, $^2J_{PC}$ 11.7 Hz), 131.73 (s, P–C_6H_5-*para*), 132.46 (d, P–C_6H_5-*para*, $^4J_{PC}$ 2.9 Hz), 133.91 (d, P–C_6H_5-*ipso*, $^1J_{PC}$ 112.0 Hz), 134.16 (d, P–C_6H_5-*ipso*, $^1J_{PC}$ 136.1 Hz). ^{31}P-NMR (r.t.): δ, 28.8 (s, Ph_2PO, $^1J_{PC}$ 136 Hz), 32.5 (s, Ph_2PS). ^{31}P-NMR (−60 °C): δ, 30.2 (s, Ph_2PO, $^1J_{PC}$ 134.3 Hz), 33.7 (s, Ph_2PS) (see Results and Discussion section). ^{119}Sn-NMR (r.t.): δ, −263 (s, br, $w_{1/2}$ 8.2 Hz). ^{119}Sn-NMR (−60 °C): δ, −262 [dd, $^2J_{SnP(O)}$ 134, $^2J_{SnP(S)}$ 32 Hz].

Preparation of $BuSnCl[(OPPh_2)(SPPh_2)]_2$ (2)

The procedure to obtain compound **2** was the same as above, but using a 2 : 1 molar ratio of $K[(SPPh_2)(OPPh_2)N]$ (1.50 g, 3.18 mmol) and $BuSnCl_3$ (0.449 g, 1.59 mmol). The compound was recrystallized from $CHCl_3$/n-hexane (1 : 4 by volume) to yield colourless crystals (1.35 g, 79%) (m.p. 232–233 °C). Analyses: found, C 57.83, H 4.34, N 2.43; calcd, for $C_{52}H_{49}ClN_2O_2P_4S_2Sn$: C 58.04, H 4.59, N 2.60%. ^{1}H-NMR (r.t.): δ, 0.53 [t, 3H, Sn–$(CH_2)_3CH_3$, $^3J_{HH}$ 7.4 Hz], 0.89 [tq, 2H, Sn–$(CH_2)_2CH_2CH_3$, $^3J_{HH}$ 7.4 Hz], 1.46 [tt, 2H, Sn–$CH_2CH_2CH_2CH_3$, $^3J_{HH}$ 7.7 Hz], 1.67 [t, 2H, Sn–$CH_2CH_2CH_2CH_3$, $^3J_{HH}$ 7.7, $^2J_{SnH}$ 117.7 Hz], 7.30 (m, 24H, P–C_6H_5-*meta*+*para*), 7.65 (m, 8H, P–C_6H_5-*ortho*), 7.76 (dd, 8H, P–C_6H_5-*ortho*, $^3J_{PH}$ 13.7, $^3J_{HH}$ 7.2 Hz). ^{31}P-NMR (r.t.): δ, 25.5 (s,br Ph_2PO), 33.7 (s,br Ph_2PS); ^{31}P-NMR (−80 °C): δ, 22.5 (d, $^2J_{PP}$ 2.2 Hz), 24.9 (s), 26.2 (s), 27.0 (s), 27.7 (d, $^2J_{PP}$ 3.3 Hz), 28.4 (s) (Ph_2PO); 32.1 (d, $^2J_{PP}$ 4.5 Hz), 32.3 (s), 33.5 (s) (d, $^2J_{PP}$ 3.3 Hz), 33.9 (s), 34.2 (s), 34.9 (d, $^2J_{PP}$ 2.2 Hz) (Ph_2PS).

Crystallography

Colourless, block crystals of $BuSnCl_2[(OPPh_2)(SPPh_2)N]$ (**1**) and $BuSnCl[(OPPh_2)(SPPh_2)N]_2$ (**2**) were mounted on glass fibres. Data collection and processing for **1** was carried out by G. Yapp, at the University of Windsor, using a Siemens SMART/CCD system, while for **2** cell dimensions and intensity data were recorded on an Enraf Nonius KCCD diffractometer, with ϕ and ω scans chosen to give a complete asymmetric unit. Cell refinement (Denzo)[28] gave cell constants corresponding to orthorhombic (for **1**) and monoclinic (for **2**) cells, whose dimensions are given in Table 4 along with other experimental parameters.

An absorption correction was applied (SORTAV),[29,30] and the structures were solved by direct methods[31] and the structure was refined using the WinGX version[32] of SHELX-97.[33] All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. In

Table 4. Crystal data and structure refinement for $BuSnCl_2[(OPPh_2)(SPPh_2)N]$ (**1**) and $BuSnCl[(OPPh_2)(SPPh_2)N]_2$ (**2**)

Compound	**1**	**2**
Empirical formula	$C_{28}H_{29}Cl_2NOP_2SSn$	$C_{52}H_{49}ClN_2O_2P_4S_2Sn$
Formula weight	678.10	1076.07
Temperature (K)	299(2)	153(2)
Wavelength (Å)	0.71069	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/n$
Unit cell dimensions		
a (Å)	9.311(2)	11.082(2)
b (Å)	19.128(3)	20.956(4)
c (Å)	33.842(6)	21.532(4)
β (°)		97.61(3)
Volume (Å^3)	6028(2)	4956(2)
Z	8	4
D_c (g/cm^3)	1.494	1.442
Absorption coefficient (mm^{-1})	1.222	0.825
F(000)	2728	2200
Crystal size, mm	0.30 × 0.21 × 0.18	0.25 × 0.25 × 0.13
θ range for data collections (deg)	2.13–27.54	2.93–27.45
Reflections collected	41 649	33 303
Independent reflections	6900 [$R_{int} = 0.2616$]	11 185 [$R_{int} = 0.0508$]
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.02	1.04
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.095$	$R_1 = 0.045$
	$wR_2 = 0.161$	$wR_2 = 0.105$
R indices (all data)	$R_1 = 0.240$	$R_1 = 0.063$
	$wR_2 = 0.207$	$wR_2 = 0.114$
Extinction coefficient	0.00027(9)	
Largest difference peak and hole, e Å^{-3}	0.75 and −0.59	1.35 and −1.08

1, one of the phenyl groups was restrained and in **2**, two C–C distances in the butyl group were restrained because of disorder. The large residual peak in **2** at 1.07 e Å^{-3} from C(4) reflects the difficulty of modelling this badly disordered butyl group. The final cycle of full-matrix least-squares refinement[33] was based on 6900 (for **1**) and 11 185 (for **2**) observed reflections and 339 (for **1**) and 738 (for **2**) variable parameters and converged (largest parameter shift was 0.001 times its ESD). Unfortunately, the quality of the crystal and data for **1** were poor so that high R values are not unexpected.

Crystallographic data for the structural analysis of compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC nos 197 766, 197 765). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk; or www: www.ccdc.cam.ac.uk).

Biological screening

In vitro biological screenings against *Escherichia coli* (ATCC 8739) and *Staphilococus aureus* (ATCC 6538 P) were carried out for compounds **1** and **2** using the direct insemination method on a specific test medium. Each compound was dissolved in saline phosphate solution (PBS) to a concentration of 0.5% and the sterility of the stock solutions was checked. Specific test media for bacteria (pH 7.1) and fungi (pH 5.5) were inoculated with solutions of **1** and **2**, respectively, at a 1 : 10 compound/medium ratio. After 14 days of incubation at 35–37 °C for bacteria and 25 °C for fungi the test media remained sterile.[34]

Bacteria inocula of *E. coli* and *S. aureus* were obtained at a concentration of 1×10^8 and 20×10^8 CFU/ml, respectively. Mixtures of the stock solutions of the tested compounds and a suspension of either *E. coli* or *S. aureus* at a concentration of 10^5–10^6 CFU/ml were obtained in four variants for **1**, namely 1 : 1 and 10 : 1 (v/v) ratio with respect to both bacteria, and one variant for compound **2**, namely 1 : 1 (v/v) ratio, with respect to *S. aureus*, and used to obtain dilutions in the range 10^{-2}–10^{-7}. The test media were treated with 1 ml inoculum in this dilution range (Table 3) and incubated at 35–37 °C for 24 h. The total number of germs (TNG/ml) was determined after 1, 7 and 14 days, respectively. After 14 days no bacteria were anymore present in the tested media.

Acknowledgements

This work was supported by the National University Research Council of Romania (CNCSIS grant, AT-552/2003, and CERES Project, contract no. 32/12.11.2002). M.B.H. thanks the UK Engineering and Physical Sciences Council for support of the X-ray facilities at Southampton and J.E.D. thanks the Natural Sciences and Engineering Research Council of Canada for financial support.

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