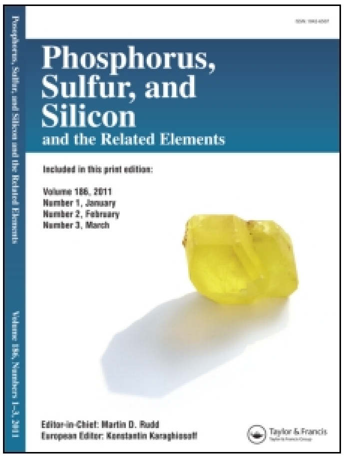

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Srivastava, S. K. , Tomar, Shailja , Rastogi, Rupali and Saxena, Richa(2010) 'Substituted Diorganotin(IV) *O,O'*-Alkylene Dithiophosphates: Synthesis and Spectral Aspects', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 3, 634 — 640

To link to this Article: DOI: 10.1080/10426500902894959

URL: http://dx.doi.org/10.1080/10426500902894959

Phosphorus, Sulfur, and Silicon, 185:634–640, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902894959

SUBSTITUTED DIORGANOTIN(IV) *O,O′*-ALKYLENE DITHIOPHOSPHATES: SYNTHESIS AND SPECTRAL ASPECTS

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Six new substituted diphenyltin(IV) O,O′-alkylene dithiophosphates, $(C_6H_5)_2Sn(X)S(S)\underline{POGO}$ [G = $-CH_2C(CH_3)_2CH_2-$, X = Cl (1), SCN (3), ClO_4 (5); G = $-CH_2C(C_4H_9)(C_2H_5)CH_2-$, X = Cl (2), SCN (4), ClO_4 (6)], were synthesized by the reaction of the corresponding ammonium salts of the O,O'-alkylene dithiophosphates with an appropriate organotin(IV) chloride. The compounds were characterized on the basis of elemental and spectral analyses (ESI mass spectrometry, IR, ^1H, ^{13}C, ^{31}P, and ^{119}Sn NMR). The presence of a four-coordinated Sn atom and monodentate O,O'-alkylene dithiophosphate moiety in compounds 1–4 as well as bidentate O,O'-alkylene dithiophosphate unit in compounds 5,6 is established.

Keywords *O*,*O*′-alkylene dithiophosphate; IR; NMR spectra; organotin(IV); synthesis

INTRODUCTION

Due to the wide applicability of sulfur-containing ligands in biological and industrial fields,[1–3] there is a large number of reports in the literature on dithiophosphate complexes of non-transition,[4–6] transition,[7,8] and post-transition[9,10] metals. However, compounds of substituted organotin(IV) derivatives with 2,2-dimethyl and 2-butyl-2-ethyl-propane-1,3-diol dithiophosphate esters have not been reported so far.

In continuation of our studies on organometal dithio complexes,[11,12] we report here the synthesis and spectral characterization of six new substituted organotin(IV) *O*,*O*′-alkylene dithiophosphates.

RESULTS AND DISCUSSION

All reactions proceeded under dry N_2 atmosphere. Substituted diphenyltin(IV) derivatives of *O*,*O*′-alkylene dithiophosphates were prepared by the reaction of a corresponding ammonium dithiophosphate salt with an appropriate organotin(IV) chloride (Scheme 1).

Received 30 October 2007; accepted 15 March 2009.

The authors are thankful to the Head, SOS in Chemistry, Jiwaji University, Gwalior, India, and the Chairman, CISC, Banaras Hindu University, Varanasi, India, for providing facilities for IR and ^{1}H, ^{13}C, ^{31}P, ^{119}Sn NMR spectra, respectively. Further, we are thankful to the Director, Central Drug Research Institute, Lucknow, India, for the C, H, N analysis and ESI mass spectra.

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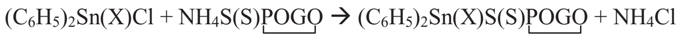

$$(C_6H_5)_2Sn(X)Cl + NH_4S(S)\underbracket{POGO} \rightarrow (C_6H_5)_2Sn(X)S(S)\underbracket{POGO} + NH_4Cl$$

1–6

1; X = Cl, G = $-CH_2C(CH_3)_2CH_2-$

2; X = Cl, G = $-CH_2C(C_4H_9)(C_2H_5)CH_2-$

3; X = SCN, G = $-CH_2C(CH_3)_2CH_2-$

4; X = SCN, G = $-CH_2C(C_4H_9)(C_2H_5)CH_2-$

5; X = ClO_4, G = $-CH_2C(CH_3)_2CH_2-$

6; X = ClO_4, G = $-CH_2C(C_4H_9)(C_2H_5)CH_2-$

Scheme 1

The analytical data collected in Table I indicate a 1:1 stoichiometry [$(C_6H_5)_2Sn(X)$: dtp; dtp = dithiophosphate] for the compounds **1–6**. The compounds are white solids and soluble in common organic solvents. They are not affected by atmospheric oxygen and moisture.

Molar conductivity of **1–4** (1.9–3.9 Ω^{-1} cm^2 mol^{-1}) has been found to be much lower than the expected value for any electrolyte, and hence these compounds may be considered to behave as non-electrolytes. Alternatively, the molar conductivity of compounds **5** and **6** (70.24–74.31 Ω^{-1} cm^2 mol^{-1}) suggests that they are 1:1 electrolytes.

The ESI mass spectrum of compound **1** confirms the monomeric character and the presence of a 1:1 metal:ligand stoichiometry in the compound. The molecular ion peak [M+H] is observed at m/z 506 with a very low intensity. The base peak at m/z 471 corresponds to (M-Cl). The peaks at m/z 429 [M-Ph] and m/z 275 [M-PhSnCl] are observed with low intensity. The isotopic clusters of tin are prominent in all these fragments except [M-PhSnCl].

Table I Analytical data of compounds **1–6**

Compound (empirical formula)	Color	Mp (°C)	Yield (%)	Elemental analysis (%) Found (Calcd.) Sn	S	C	H	N	Cl
1	White	89	78	23.56	12.80	40.28	3.94	–	7.08
$C_{17}H_{20}O_2PS_2ClSn$				(23.47)	(12.68)	(40.39)	(3.99)		(7.01)
2	White	112	84	21.21	11.26	44.99	5.38	–	6.26
$C_{21}H_{28}O_2S_2PClSn$				(21.13)	(11.41)	(44.91)	(5.46)		(6.31)
3	White	155	77	22.40	18.40	40.86	3.87	2.69	–
$C_{18}H_{20}O_2S_3PNSn$				(22.47)	(18.21)	(40.93)	(3.81)	(2.65)	
4	White	150	82	20.44	16.28	45.16	4.89	2.37	–
$C_{22}H_{28}O_2S_3PNSn$				(20.31)	(16.46)	(45.22)	(4.83)	(2.40)	
5	White	180	80	20.80	11.14	*	*	–	6.12
$C_{17}H_{20}O_6S_2PClSn$				(20.84)	(11.26)				(6.22)
6	White	144	84	18.86	10.36	*	*	–	5.54
$C_{21}H_{28}O_6S_2PClSn$				(18.97)	(10.25)				(5.67)

*Due to explosive nature, C and H analysis is not possible.

IR Spectra

The IR spectra of the compounds **1–6** have been recorded in KBr in the region 4000–340 cm^{-1}, and tentative assignments have been made on the basis of earlier reports.[13] In the compounds **1–4**, the bands present in the regions 1058–1037, 826–795, and 702–681 cm^{-1} have been assigned to ν (P)-O-C, ν P-O-(C) and ν (P=S), respectively. Another band of medium intensity in the region 524–518 cm^{-1} may be attributed to ν (P—S) vibration, which indicates the presence of monodentate dithiophosphate group having one of the two sulfur atoms bonded to the substituted organotin(IV) moiety. In compounds **5** and **6**, ν (P)-O-C, ν P-O-(C), and ν (P—S) appeared at 1060–1038, 828–799, and 522–518 cm^{-1}, respectively. The band for the ν (P=S) stretching vibration appears at 626 ± 1 cm^{-1}. The low value for ν (P=S) suggests that dithiophosphate moiety is linked to the tin atom in a bidentate manner. The IR spectra of **5** and **6** in chloroform solution are essentially similar to those of their solid-state spectra. These results are in good agreement with an earlier report on p-$MeOC_6H_4TeBr_2[S_2P(OMe)_2]$ having a bidentate dithiophosphate group, whose structure has been determined by single crystal X-ray diffraction.[14] The bands for the ν (Sn-S) and ν (Sn-Ph) stretching vibrations appear in the range 445 ± 5 and 562 ± 2 cm^{-1}, respectively.[15]

In the IR spectra of compounds **3** and **4**, ν (SCN), ν (C-S) and ν (NCS) appear at 2044 ± 4, 707 ± 3 and 418 ± 2 cm^{-1}, respectively. The data are consistent with a thiocyanate group, bonded to the metal via the sulfur atom.[16] Compounds **5** and **6** give rise to absorptions at 1098 ± 4 and 626 cm^{-1}, which are assigned to the ν_1 and ν_2 modes of vibration of an ionic perchlorate group.[12] This conclusion is supported by the conductivity data of **5** and **6** in DMSO, where they behave as a 1:1 electrolyte.

^{1}H, ^{13}C{^{1}H}, ^{31}P, and ^{119}Sn{^{1}H} NMR Spectra

The ^{1}H NMR spectroscopic data of compounds **1–3**, **5** are given in Table II. The phenyl protons show two multiplets at $\delta = 7.25$–8.04. The ^{1}H NMR spectra of the compounds also show characteristic signals due to CH_3, CH_2, and O—CH_2 protons. The O—CH_2 signals are shifted downfield (by 0.4 ppm) as compared to those of the ammonium salts of the *O,O′*-alkylene dithiophosphates and appear as a doublet due to coupling with the ^{31}P nucleus[13].

Table II ^{1}H NMR data of compounds **1–3**, **5**

Compound	Aryl protons (δ, ppm)	Alkyl/alkylene protons (δ, ppm)
1	7.94–7.46 m, 10H	3.73, d, $^3J_{PH} = 18$ Hz, 4H (OCH_2), 0.87, s, 6H (CH_3)
2	8.01–7.44, m, 10H	4.16, d, $^3J_{PH} = 15$ Hz, 4H (OCH_2), 1.52–1.14, m, 8H (all CH_2), 0.93–0.83, m, 6H (all CH_3)
3,	8.04–7.25, m, 10H	3.75, d, $^3J_{PH} = 15$ Hz, 4H (OCH_2), 0.87, s, 6H (CH_3)
5	8.07–7.29, m, 10H	3.70, d, $^3J_{PH} = 15$ Hz, 4H (OCH_2), 0.83, s, 6H (CH_3)

Table III ^{13}C, ^{31}P, and ^{119}Sn NMR data of compounds **1–3**, **5**

Compound	Alkylene/thiocyanate carbon atoms (δ, ppm)	Aryl carbons (δ, ppm)				$^{31}P(\delta$, ppm)	^{119}Sn (δ, ppm)
		C-*i*	C-*o*	C-*m*	C-*p*		
1	21.8, (CH_3) 31.8, $(\mathbf{C}\text{-}C_{alkylene})$ 73.1, (OCH_2), $^2J_{PC} = 36$ Hz	150.2	134.7	128.1	128.8	97.1 $^2J(^{31}P\text{-}^{13}C) = 39$ Hz $^2J(^{31}P\text{-}^{119}Sn) = 75$ Hz	−122.1
2	13.9, $(CH_2\mathbf{C}H_3)$ 30.0, $(\mathbf{C}H_2CH_3)$ 7.1, $(CH_2CH_2CH_2\mathbf{C}H_3)$ 23.2, $(CH_2CH_2\mathbf{C}H_2CH_3)$ 23.3, $(CH_2\mathbf{C}H_2CH_2CH_3)$ 24.6, $(\mathbf{C}H_2CH_2CH_2CH_3)$ 37.3, $(\mathbf{C}\text{-}C_{alkylene})$ 75.6, (OCH_2), $^2J_{PC} = 34$ Hz	141.2	135.5 $^2J(^{119}Sn\text{-}^{13}C)$ = 127 Hz	129.1 $^3J(^{119}Sn\text{-}^{13}C)$ = 177 Hz	130.7	–	–
3	21.9(CH_3) 31.9 $(\mathbf{C}\text{-}C_{alkylene})$, 73.2 (OCH_2), $^2J_{PC} = 30$ Hz 67.1 (SCN)	–	134.7 $^2J(^{119}Sn\text{-}^{13}C)$ = 141 Hz	127.5	128.3	–	–
5	–	–	–	–	–	111.6 $^2J(^{31}P\text{-}^{13}C) = 36$ Hz $^2J(^{31}P\text{-}^{119}Sn) = 74$ Hz	−182.3

In the $^{13}C\{^1H\}$ spectra of **1–3, 5** signals due to the phenyl carbon atoms, $O{-}CH_2$, all CH_3 and all CH_2 groups are found as expected (Table III). This is in good agreement with the results obtained by IR and ^1H NMR spectroscopy.

In the $^{31}P\{^1H\}$ NMR spectrum of **1**, the phosphorus signal is observed at $\delta = 97.1$, which is not very different from the signal of the free ligand, indicating monodentate coordination of the *O,O*′-alkylene dithiophosphate unit. However in compound **5,** the ^{31}P NMR signal is shifted to lower field (by 14 ppm) compared to that of free acid, which indicates a considerable drift of electron density from the phosphorus to the metal atom through both sulfur atoms, and thus confirms the formation of a chelated structure with a bidentate *O,O*′-alkylene dithiophosphate group.[13] These results are in agreement with the IR, ^1H, and ^{13}C NMR spectra.

In the $^{119}Sn\{^1H\}$ NMR spectrum of **1**, the ^{119}Sn signal is observed at –122.1 ppm, which may be interpreted in terms of a tetracoordinated Sn atom. The ^{119}Sn chemical shift for compound **5** is observed at higher field as compared to **1** at –182.3 ppm, which also indicates the presence of a tetracoordinated tin atom having a chelated *O,O*′-alkylene dithiophosphate group. These results are consistent with earlier reports on $\delta^{119}Sn$ of a tetracoordinated Sn atom.[17] We conclude that upon coordination of both sulfur atoms to the organotin moiety in **5**, the shift of electron density from phosphorus through sulfur causes shielding of the tin nucleus.

From the preceding discussion based on elemental analysis; conductivity; ESI mass spectrometry; IR, ^1H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectroscopy; and upon comparison with previous work, it becomes clear that all the new monomeric substituted diphenyltin(IV)

1, 2 X= Cl

3, 4 X= SCN

5-6

Figure 1 Proposed structures of substituted diphenyltin(IV) *O,O*′-alkylene dithiophosphates.

derivatives **1–4** have tetrahedral coordination around the tin atom resulting from two phenyl groups, one chlorine atom, and one sulfur atom.[18] In compounds **5** and **6**, the tin atom is also tetrahedrally coordinated by two phenyl groups and two sulfur atoms of the ligand acting as a chelate (Figure 1). A similarly bonded dithiophosphate moiety acting as a bidentate ligand is observed in $(C_6H_5)_2Sn\{S_2P(o\text{-}C_3H_7)_2\}_2$, the structure of which has been determined by single crystal X-ray diffraction.[19]

EXPERIMENTAL

Diphenyltin dichloride,[20] the ammonium salt of *O,O*′-alkylene dithiophosphate,[18] and substituted diphenyltin(IV) chloride[21,22] were prepared by reported methods. All solvents and other reagents were obtained commercially. Due to the high sensitivity of organotin halides to air and moisture, the solvents were freshly distilled after purification[23] before use. Metal, chlorine, and sulfur contents were determined by a reported procedure.[24] C, H, and N analyses were carried out with an Elementar Vario EL III analyzer.

Molar conductivities of 10^{-3} M solution were measured with a Decibel conductivity meter model DC 610 using a dip type conductivity cell in dry and purified DMSO. The electrospray mass spectra were recorded with a Micromass Quattro II triple quadrupole mass spectrometer. The sample (dissolved in acetonitrile) was introduced into the ESI source through a syringe pump at the rate of 5 μL per min. The ESI capillary was set at 3.5 kV, and the cone voltage was 40 V.

FT IR spectra were recorded with a Shimadzu Prestige 21 (340–4000 cm^{-1}, KBr) spectrophotometer. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR spectra were recorded of saturated $CDCl_3$ solutions at 300, 75.45, 121.5, and 111.95 MHz with a Bruker 300 FT and a JEOL AL 300 FT NMR spectrometer, respectively. Chemical shifts are given in ppm with respect to $(CH_3)_4Si$ for ^1H and $^{13}C\{^1H\}$ as internal standards. PCl_3 and $(CH_3)_2SnCl_2$ were used as external reference for the ^{31}P and $^{119}Sn\{^1H\}$ NMR spectra, respectively. The values of ^{119}Sn NMR chemical shifts are converted and given with respect to Me_4Sn.

Synthesis of $[(C_6H_5)_2Sn(Cl)S(S)\underline{POCH_2C(CH_3)_2CH_2O}]$ (1)

$(C_6H_5)_2SnCl_2$ (3.43 g, 0.01 mol) and $NH_4S(S)\underline{POCH_2C(CH_3)_2CH_2O}$ (2.15 g, 0.01 mol) in dry benzene (20 mL) were refluxed on a water bath for about 4 h and filtered. The solvent was distilled off under reduced pressure, and the product was precipitated by the addition of petroleum ether (60–80°C) (20 mL). The product was separated by filtration, washed with diethyl ether (10 mL), recrystallized from chloroform (20 mL), and dried in vacuo.

Similarly $[(C_6H_5)_2Sn(Cl)S(S)\underline{POCH_2C(C_4H_9)(C_2H_5)CH_2O}]$ (**2**) was prepared by the interaction of $(C_6H_5)_2SnCl_2$ with $NH_4S(S)\underline{POCH_2C(C_4H_9)(C_2H_5)CH_2O}$.

Synthesis of $[(C_6H_5)_2Sn(SCN)S(S)\underline{POCH_2C(C_4H_9)(C_2H_5)CH_2O}]$ (4)

A freshly prepared solution of $(C_6H_5)_2Sn(SCN)Cl$ (3.64 g, 0.01 mol) in absolute methanol (10 mL) was treated with $NH_4S(S)\underline{POCH_2C(C_4H_9)(C_2H_5)CH_2O}$ (2.71 g, 0.01 mol) in the same solvent (10 mL). The reaction mixture was stirred for 5 h, filtered, and concentrated under reduced pressure to give a viscous product. Compound **4** was precipitated by the addition of a petroleum ether:hexane mixture (7:3) (20 mL), washed with diethyl ether (15 mL), recrystallized from absolute methanol(10 mL), and dried in vacuo.

Similarly $[(C_6H_5)_2Sn(SCN)S(S)\underline{POCH_2C(CH_3)_2CH_2O}]$ (**3**) was prepared by the interaction of $(C_6H_5)_2Sn(SCN)Cl$ with $NH_4S(S)\underline{POCH_2C(CH_3)_2CH_2O}$.

Synthesis of $[(C_6H_5)_2SnS(S)\underline{POCH_2C(CH_3)_2CH_2O}]^+ [ClO_4]^-$ (5)

A freshly prepared solution of $(C_6H_5)_2Sn(ClO_4)Cl$ (4.06 g, 0.01 mol) in absolute methanol (10 mL) was treated with $NH_4S(S)\underline{POCH_2C(CH_3)_2CH_2O}$ (2.15 g, 0.01 mol) in methanol (10 mL). The mixture was stirred for 5 h and filtered. The filtrate was concentrated under reduced pressure, and the product was precipitated by the addition of warm petroleum ether (20 mL). It was washed with diethyl ether (15 mL), recrystallized from absolute methanol (12 mL), and dried in vacuo.

Similarly $[(C_6H_5)_2SnS(S)\underline{POCH_2C(C_4H_9)(C_2H_5)CH_2O}]^+[ClO_4]^-$ (**6**) was prepared by the interaction of $(C_6H_5)_2Sn(ClO_4)Cl$ with $NH_4S(S)\underline{POCH_2C(C_4H_9)(C_2H_5)CH_2O}$.

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