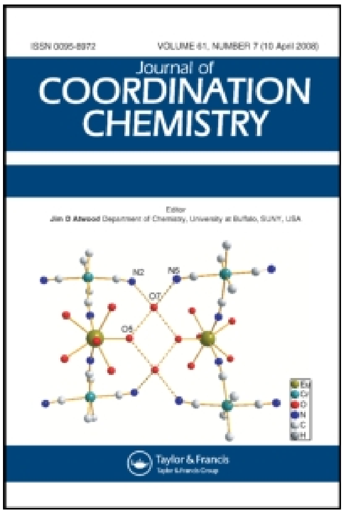

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Synthesis and characterization of chlorodiorganotin(IV) derivatives of O,O-alkylene dithiophosphates

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The O,O-alkylene dithiophosphates of chlorodiorganotin(IV), $\mathrm{ClR_2SnS_2}\overline{\mathrm{POGO}}$ (where R = Me, G = $-\mathrm{CMe_2CMe_2}-$; R = Me, Bu; G = $-\mathrm{CH_2CMe_2CH_2}-$, and R = Me, Bu, Ph; G = $-\mathrm{CHMeCH_2CMe_2}-$) have been synthesized by reactions of diorganotindichloride with the ammonium salts of O,O-alkylene dithiophosphates in 1 : 1 molar ratio in benzene. These compounds have been characterized by IR, ^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectroscopy. Unlike triorganotin derivatives, the ligand is bidentate in these derivatives.

Keywords: Organotin(IV); Alkylene dithiophosphates; Multinuclear NMR; Trigonal bipyramidal geometry

1. Introduction

O,O-Alkylene dithiophosphate anions $\overline{\mathrm{OGOP}}\mathrm{(S)S^-}$ are versatile 1,1-dithioato ligands capable of binding to metallic [1–4] and organometallic moieties [1–9]. Structures of organotindialkyl dithiophosphates which show remarkable biological activity have been studied. Trialkyltin derivatives [10] appear to be tetrahedral with unidentate dithiophosphate, whereas bis(dialkyldithiophosphates) as well as bis(alkylene dithiophosphate) have octahedral structures with bidentate dithiophosphate [11]. Triphenyltin derivatives of dithiophosphates are bidentate [10].

Surprisingly, halodiorganotin alkylene dithiophosphates have not been described. Parallel studies of organotin and organotin dithioxanthates indicate that the presence of halogen on tin modifies the structures [12–15]. The present study concerns with the synthesis and spectroscopic studies of chlorodiorganotin alkylene dithophosphates.

2. Experimental

Reagents were of analytical grade. Dimethyl tindichloride (Aldrich) was used as received. Tin was estimated as tin oxide [16]. Sulfur was estimated by Messenger's

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method [16]. Volhard method was used to estimate chlorine [16]. IR spectra were recorded on Perkin Elmer FT-IR spectrophotometer using a CsI cell. NMR (^{1}H, ^{13}C, ^{31}P, and ^{119}Sn) spectra were recorded on a Bruker DP 300 MHz spectrometer using $CDCl_3$ solution. TMS was used as internal reference for ^{1}H and ^{13}C NMR spectral studies, whereas H_3PO_4 and Me_4Sn were used as external references for ^{31}P and ^{119}Sn spectra. Molecular weights of these compounds were determined on a Knour vapor pressure osmometer as well as cryoscopically using Beckmann's thermometer. Since similar methods have been used to synthesize these compounds, one representative compound is given in detail. Synthetic and analytical data of the other analogous compounds are summarized in table 1.

2.1. *Synthesis of $ClMe_2SnSP(S)OCMe_2CMe_2O$: Reaction of dimethyltin dichloride with ammonium tetramethylethylene phosphorodithioate*

Dimethyltin dichloride (1.08 g) was added to the suspension of ammonium salt of tetramethylethylene phosphorodithioate (1.12 g) in benzene (~10 mL) and the contents were stirred at ambient temperature for 3 h. The white solid separated during the course of reaction was filtered out and benzene was evaporated from the filtrate under reduced pressure yielding a white solid (1.84 g) which was recrystallized (m.p. 183–185°C) using toluene/petroleum ether (b.p. 40–60°C) mixture (1 : 1).

3. Results and discussion

Chloro diorganotin(IV) alkylenedithiophosphates have been prepared in quantitative yield by reactions of diorganotin dichlorides with ammonium dithiophosphates in equimolar ratio:

$$\begin{aligned}&[R = Me, G = -CMe_2CMe_2- (\mathbf{1});\ R = Me, G = -CH_2CMe_2CH_2- (\mathbf{2});\\ &R = Me, G = -CHMeCH_2CMe_2- (\mathbf{3});\ R = Bu, G = -CH_2CMe_2CH_2- (\mathbf{4});\\ &R = Bu, G = -CHMeCH_2CMe_2- (\mathbf{5});\ R = Ph, G = -CHMeCH_2CMe_2- (\mathbf{6})].\end{aligned}$$

These reactions are exothermic and proceed to completion at ambient temperature in benzene. The molecular weight determination corresponds to monomers. These dithiophosphate derivatives are non-volatile even under reduced pressure.

3.1. *IR spectra*

Infrared spectra contain characteristic peaks assigned to νS–Sn and νP–SSn modes, the former is a weak absorption in the range 358–408 cm^{-1}. Two absorptions from 512–535 and 595–610 cm^{-1} have been assigned to ν(P–SSn) [17, 18]. The lower frequency mode is weaker than the other mode. Because of the presence of strong νP–S vibration in the region 512–535 and 595–610 cm^{-1}, ν(Sn–C) asymmetric and symmetric vibrations are not discernible. The $\nu P{=}S$ absorptions are found in the expected region of 660–700 cm^{-1}.

Table 1. Reactions of diorganotindichlorides with ammonium alkylene phosphorodithioates in 1 : 1 molar ratio.

Compound number	Reactants (g)		Physical state	Molecular weight found (Calcd)	m.p. (°C) ± 2	Analysis (%): Found and (Calcd)		
	R_2SnCl_2R	$\overline{OGO}P(S)SNH_4G$				Tin	Sulfur	Chlorine
1	Me 1.08	$-CMe_2 \cdot CMe_2-1.12$	(95%) White solid	402 (395)	183	29.90 (30.04)	16.04 (16.20)	8.80 (8.97)
2	Me 1.44	$-CH_2CMe_2CH_2-1.41$	(96%) White solid	375 (381)	156	31.05 (31.15)	16.64 (16.78)	9.20 (9.30)
3	Me 1.03	$-CHMeCH_2CMe_2-1.07$		–	128	30.11 (30.04)	16.10 (16.20)	8.70 (8.97)
4	Bu 1.35	$-CH_2CMe_2CH_2-0.95$	(94%) White solid	477 (465)	154	25.48 (25.52)	13.70 (13.76)	7.60 (7.62)
5	Bu 1.46	$-CHMeCH_2CMe_2-1.14$	(96%) Viscous liquid	–	–	24.60 (24.77)	13.22 (13.36)	7.40 (7.57)
6	Ph 1.65	$-CHMeCH_2CMe_2-1.11$	(96%) White solid	530 (519)	119	22.69 (22.86)	12.18 (12.32)	6.72 (6.83)

Contents were stirred for 3 h at room temperature.

The νSn–Cl modes are observed as medium intensity peaks in the narrow range of 308–315 cm^{-1} [18]. Bands at 1037–1130 and 790–885 cm^{-1} are due to C–OP and CO–P linkages, respectively. Very strong absorption bands (925–982 cm^{-1}) are assigned to dioxaphosphalane and dioxaphosphorinane ring [18, 19].

3.2. *^{1}H NMR spectra*

The ^{1}H NMR spectra (table 2), particularly those of chlorodimethyltin(IV) alkylenedithiophosphate derivatives provide valuable information regarding the structures. Phenyl and butyl–tin protons are observed in their usual pattern and in expected region, i.e. δ 7.05–8.15 and δ 0.75–2.10 ppm, respectively.

The tin–methyl protons in chlorodimethyltin(IV) alkylene phosphorodithioates appear as singlets in the region δ 1.05–1.45 ppm. Coupling constant values of δ 72–78 Hz for $^2J(^1H,^{119}Sn)$ in these derivatives are larger in comparison to four-coordinate trimethyl tin esters [20, 21] suggesting five-coordinate tin in these complexes. Signals due to protons at α-carbons of the glycoxy groups are doublets due to coupling with phosphorous. Thus, a doublet ($J = 16.0$ Hz) and a multiplet are observed at δ 4.00 and δ 4.45–5.05 ppm for $-OCH_2$ and –OCH– protons of 2,2-dimethylpropane-1,3-diol and 2,3-dimethylbutane-2,3-diol (compounds **2**, **4**) derivatives, respectively. All other signals are present at their expected positions; the details are given in table 2.

3.3. *^{13}C NMR spectra*

^{13}C NMR spectra have been recorded for a few derivatives (table 3), but satellites arising from the coupling of α-C with ^{119}Sn could be located for only one compound, $\mathrm{ClMe_2SnS_2\overline{POC(Me)_2C(Me)_2O}}$. The $^1J(^{13}C, ^{119}Sn)$ coupling constant of 552.0 Hz in this case matches well with the values suggested for five-coordinate tin [22].

3.4. *^{119}Sn NMR spectra*

The ^{119}Sn NMR data for some representatives are given in table 2. The chemical sifts δ (–) 41.79 to (–) 65.91 ppm of these complexes are about δ 155 ppm upfield of the chemical shifts reported for their triorganotin counterparts in which tin was four-coordinate [10]. Our results can be best interpreted in terms of five-coordinate tin in these chlorodiorganotin derivatives. Singlets (–240.24 ppm) in ^{119}Sn NMR spectrum of chlorodiphenyltin hexylene phosphorodithioates, as expected, lie very much upfield of the signals observed for the chlorodialkyltin alkylene phosphorodithioates.

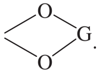
3.5. *^{31}P NMR spectra*

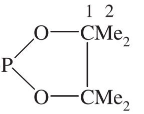
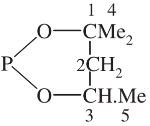
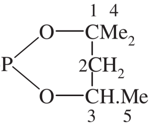
^{31}P NMR signals of these complexes occur at $\delta\, 84 \pm 4$ ppm for six-membered phosphorinane complexes and at δ 102.61 ppm for the five-membered phospholane complexes [23] (table 2). The chemical shift differences between the ligand acids and the organotin complexes are ~10.0 ppm. These changes can be attributed to bidentate phosphorodithioate; other factors such as bond polarity and electron releasing alkyl groups on tin which could affect π-bonding with phosphorus [9].

Table 2. ^{1}H, ^{31}P, and ^{119}Sn NMR spectral data for chlorodiorganotin (IV) O,O-alkylene phosphorodithioates and, $\mathrm{ClR_2SnS_2\overline{POGO}}$.

	Sn–R protons	$\mathrm{\overline{POGO}}$ protons				
Compound	Chemical shift (ppm)	^2J (^{1}H, ^{119}Sn) (Hz)	Chemical shift (ppm)	J (Hz)	^{31}P (ppm)	^{119}Sn (ppm)
1	1.40, s 6H(Me)	76.0	1.45, s 18H(Me)	–	102.61	–
2	1.34, s, 6H(Me)	72.0	1.05, s, 6H(Me) 4.04, d, 4H($\mathrm{OCH_2}$)	$J^* = 16.0$	88.17	−60.79
3	1.37, s 6H(Me) [overlapping with $\mathrm{Me_2CH_2}$(OGO) protons]	78.0	1.37, s 6H($\mathrm{Me_2C}$) 1.54, d, 3H(MeC) 1.94, d, 2H($\mathrm{CH_2}$) 4.45–5.05, m, 1H(OCH)	$J^* = 7.0$ $J^* = 10.0$	83.46	−65.91
4	0.75–2.30, m 18H(Bu) [overlapping with Me(OGO) protons]		1.37, s 6H($\mathrm{Me_2C}$) 4.05, d, 4H($\mathrm{OCH_2}$)	$J^{**} = 16.0$	–	−41.79
5	0.75–2.10, m 18H(Bu) [overlapping with Me, $\mathrm{CH_2}$(OGO) protons]		0.75–2.10, m ($\mathrm{MeCH_2}$) 4.45–5.05, m, 1H(OCH)		84.61	–
6	7.05–8.15, m, (Ph, 10H)		1.46, s 6H($\mathrm{Me_2C}$) 1.50, d, 3H(Me–C) 1.90, d, 2H($\mathrm{CH_2}$) 4.45–5.05, m, 1H(OCH)	$J^* = 11.0$ $J^* = 11.0$	80.35	−240.24

$J^* = {}^3J(^1\mathrm{H}, {}^{119}\mathrm{Sn})$; $J^{**} = 3J(^1\mathrm{H}, {}^{31}\mathrm{P})$. Bond angle C–Sn–C ($\theta$) from the equation $\theta = 0.016J^2 - 1.32J + 133.4$ comes to be 125.5, 121.3, and 127.8 for the compounds **1**, **2**, and **3**, respectively; $J = {}^2J$ (^{1}H, ^{119}Sn).

Table 3. ^{13}C NMR spectral data for some chlorodiorganotin O,O-alkylene phosphorodithioates, ClR$_2$SnS(S)P .

Compound	Sn–C(1)–C(2)–C(3)–C(4) carbons				P–O–G–O carbons				
	Chemical shift (ppm) [$J(^{13}C, ^{119}Sn)$, Hz]				Chemical shift (ppm) [$J(^{13}C, ^{31}P)$, Hz]				
	C1	C2	C3	C4	C1	C2	C3	C4	C5
ClMe$_2$SnS(S)P 	11.95 (552.0)	–	–	–	91.08, d (2.8)	23.81, d (5.2)	–	–	–
ClBu$_2$SnS(S)P 	27.84[a]	26.65[a]	26.32 (97.64)	13.87	85.65, d (12.2)	43.77, d (4.9)	72.43, d (7.3)	31.69 (7.3)	22.21 (9.7)
ClPh$_2$SnS(S)P 	142.12[a]	135.26 (64.5)	128.72 (92.38)	130.24	86.75, d (8.84)	43.60, d (8.0)	73.33, d (7.3)	31.37, d (6.7)	21.97, d (9.34)

∠C–Sn–C (θ) for compound **1** comes to be 125° from the equation $11.4\ \theta = J + 875$ ($J = 552.0$ Hz).

[a] Not discernible.

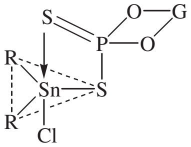


Figure 1. Proposed structure for chlorodiorganotin(IV) O,O-alkylenedithiophosphates, where R = Me, G = –CMe$_2$CMe$_2$– (**1**); R = Me, G = –CH$_2$CMe$_2$CH$_2$– (**2**), R = Me, G = –CHMeCH$_2$CMe$_2$– (**3**); R = Bu, G = –CH$_2$CMe$_2$CH$_2$– (**4**), R = Bu, G = –CHMeCH$_2$CMe$_2$– (**5**), and R = Ph, G = –CHMeCH$_2$CMe$_2$– (**6**).

3.6. *Structure*

The ^{1}H, ^{13}C, and ^{119}Sn NMR spectral data for the chlorodiorganotin derivatives discussed above correspond to five-coordinate tin, suggesting bidentate phosphorodithioate. Monomeric nature of these derivatives and chelating nature of the dithioato group rule out the possibility of intermolecular association.

In a trigonal bipyramid chelated structure involving a four-membered SnS$_2$P ring, the two sulfurs should occupy axial–equatorial positions [24]. Keeping in mind that only one set of satellites, arising due to ^{1}H–C–^{119}Sn coupling, is observed in the ^{1}H NMR spectra of the chlorodimethyltin(IV) derivatives, structures given in figure 1 can be assigned for these alkylene phosphorodithioate in which chloride occupies the axial position.

A survey of literature indicates that there is remarkable similarity in the bonding patterns of dithiocarbamate [14], xanthate [13], and phosphorodithioate moietis [17]. The structures of ClMe$_2$SnS$_2$CNMe$_2$ [24] and ClPh$_2$SnS$_2$COPr^i [13] have been determined crystallographically and support the above conclusion about the structure of chlorodiorganotin alkylene phosphorodithioate.

The calculation of C–Sn–C bond angle, on the basis of the observed values of $^2J(^1\text{H}, {}^{119}\text{Sn})$ and $^1J(^1\text{H}, {}^{119}\text{Sn})$, according to the correlation given by Lockhart *et al.* [20] show the values of $\sim$125° for the chlorodimethyltin derivatives. This bond angle is very close to the theoretical value expected for a regular trigonal bipyramid structure.

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