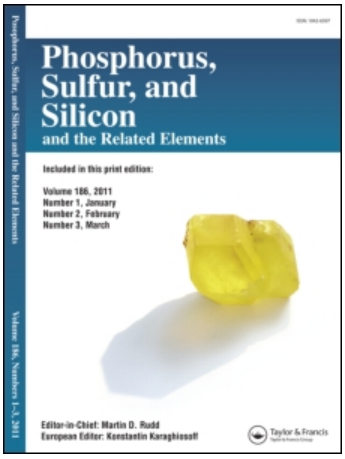

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MONOORGANOTIN(IV) *O,O*-ALKYLENEDITHIOPHOSPHATES

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MONOORGANOTIN(IV) *O,O*-ALKYLENEDITHIOPHOSPHATES

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Monoorganotin(IV) *O,O*-alkylenedithiophosphates, $RSn[S_2PO_2G]_nCl_{3-n}$ (here R=Ph, *n*-Bu, Et; G=CH_2—$C(CH_3)_2$—CH_2—, —$C(CH_3)_2$—$C(CH_3)_2$—and—$C(CH_3)_2$—CH_2—$CHCH_3$—; *n*=1–3) have been synthesized by the reactions of ammonium *O,O*-alkylenedithiophosphates with monoorganotin(IV) trichlorides in benzene. These products have been characterised by analytical, IR, and NMR (^1H, ^{31}P, ^{119}Sn) spectral data, on the bases of which plausible structures have been suggested.

INTRODUCTION

Organotin(IV) compounds having Sn—S linkages derive their importance from numerous industrial applications and their chemistry has been reviewed by a number of authors.[1-4] A considerable amount of work carried out on dithiophosphates of non-transition elements in our laboratories in recent years[5] has revealed interesting coordination modes of these dithio ligands, e.g., they have been shown to behave as monodentate species towards organo-silicon and -germanium (in general) and tri-organotin moieties, whereas these bind diorganotin as well as monoorganotin moieties in bidentate manner. In view of their interesting structural properties, we have extended these investigations to the corresponding alkylenedithiophosphates of organotin(IV) moieties. In continuation to our earlier publications,[6,7] we report the synthesis and structural investigations of some monoorganotin(IV) *O,O*-alkylene-dithiophosphates in this communication.

RESULTS AND DISCUSSION

Monoorganotin(IV) *O,O*-alkylenedithiophosphates have been synthesized by the reactions of ammonium *O,O*-alkylenedithiophosphates with monoorganotin(IV) chlorides in different stoichiometric ratios in benzene or by interaction of butyltin(IV) oxide with *O,O*-alkylenedithiophosphoric acids:

(i) $RSnCl_3 + nNH_4S_2P\langle^{O}_{O}\rangle G \rightarrow RSn\left[S_2P\langle^{O}_{O}\rangle G\right]_n Cl_{3-n} + nNH_4Cl\downarrow$

(R = Ph, *n*-Bu, Et

G = —$C(CH_3)_2C(CH_3)_2$—, —$C(CH_3)_2CH_2CHCH_3$—

and —$CH_2C(CH_3)_2CH_2$—

n = 1–3)

(ii) $(BuSnO)_2O + 6HS_2P\langle^{O}_{O}\rangle G \rightarrow 2BuSn\left[S_2P\langle^{O}_{O}\rangle G\right]_3 + 3H_2O$

$(G = -C(CH_3)_2C(CH_3)_2-$ and $-CH_2C(CH_3)_2CH_2-$

Similar to the corresponding reactions of tri- and di-organotin(IV) halides with ammonium *O,O*-alkylenedithiophosphates reported earlier,[6,7] the reactions of alkyltin trichlorides (equation i) are quite facile and can be completed at room temperature. In the route (ii), reactants are refluxed in benzene and the water formed in the reaction is removed azeotropically.

Monoorganotin(IV) *O,O*-alkylenedithiophosphates are powdery solids or liquids, which are soluble in common organic solvents. Similar to tri- and di-organotin *O,O*-alkylenedithiophosphates, these derivatives are resistant to atmospheric moisture and oxygen, but these could not be distilled under reduced pressure.

The solid samples were crystallised with the help of benzene-petroleum ether (40–60°) mixtures.

Ebulliometric molecular weight determination of these derivatives indicates their monomeric nature in refluxing benzene.

Infrared Spectra

The assignments of infrared spectral modes in these derivatives (Table I) have been made on lines similar to those adopted in tri- and di-organotin(IV) *O,O*-alkylenedithiophosphates earlier.[6,7] The bands in the region 1030–1100 and 770–860 cm^{-1} in the IR spectra of monoorganotin(IV) *O,O*-alkylenedithiophosphates may be ascribed to ν(P)—O—C and νP—O—(C) stretching modes respectively following earlier reports.[8]

The νP=S and νP—S stretching vibrations[9] are observed in the region 670–730 and 570–675 cm^{-1} respectively which are almost in the same range as in corresponding acids.[10] The bands present in the range 920–925 cm^{-1} may be assigned to dioxaphospholane and dioxaphosphorinane ring vibrations.[11,12] The Sn—S stretching bands are assigned in the region 350–410 cm^{-1} on the basis of earlier publications.[13,14]

Magnetic Resonance Spectra

The ^1H NMR Spectra of monoorganotin(IV) *O,O*-alkylenedithiophosphates show all the characteristic resonances of the ligands. The integration of protons in these spectra confirms their purity. The phenyl, butyl and ethyl protons attached to tin appear as multiplets and alkyltin proton signals are mixed with glyocxy proton signals (Table I).

The ^{31}P NMR chemical shifts of hexylene and neopentylenedithiophosphate complexes occur in the range 79.5–81.7 ppm and these are listed below:

Compound	$\delta(^{31}P)$ ppm
$EtSn[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_3$	80.69
$EtSn[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_3$	79.59
$EtSn(Cl)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	81.03

TABLE I

IR and PMR spectral data of monoorganotin(IV) *O,O*-Alkylenedithiophosphates, $RSn[S_2PO_2G]_nCl_{3-n}$

S. No.	Compound	IR (cm^{-1}) ν(P)—O—C	νP—O—(C)	Ring vibration	νP=S	νP—S	νSn—S	PMR Chemical shift δ, ppm
1	$BuSn[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_3$	1100	—	—	670	620	—	0.8–2.1, m, 27 H (C_4H_9Sn, CH_3) 4.1–4.3, d, 12 H (OCH_2)
2	$PhSn[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_3$	1120	850	990	670	565	—	—
3	$PhSn[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_3$	1040	770	970	720	590	—	1.0–2.4, m, 31 H (CH_3, CH_2) 4.6–5.2, m, 3 H (CHO) 7.2–8.2, m, 5 H (C_6H_5Sn)
4	$EtSn[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_3$	1030	860	940	710	570	350	4.6–5.2, m, 3 H (CHO) 1.1–2.2, m. 38 H (C_2H_5Sn, CH_3, CH_2)
5	$EtSn[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_3$	—	—	—	—	—	—	0.8–1.8, m, 23 H (C_2H_5Sn, CH_3) 3.8–4.3, d, 12 H (OCH_2)
6	$PhSnCl[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	1050	825	995	730	675	—	1.0, s, 12 H (CH_3) 4.1–4.3, d, 8 H (OCH_2) 7.5, s, 5 H (C_6H_5Sn)
7	$PhSnCl[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	1100	820	920	730	630	—	7.3–7.7, m, 5 H (C_6H_5Sn) 1.5, s, 24 H (CH_3)
8	$BuSnCl[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	—	—	—	—	—	—	0.8–2.0, m, 21 H (C_4H_9Sn, CH_3) 3.6–4.3, d, 8 H (OCH_2)
9	$BuSnCl[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	1100	810	920	680	—	360	—
10	$EtSnCl[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	1030	790	970	700	590	410	0.6–1.4, m, 17 H (C_2H_5Sn, CH_3) 3.6–4.4, m, 8 H (OCH_2)
11	$EtSnCl[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	—	—	—	—	—	—	1.1–1.8, m, 29 H (C_2H_5Sn, CH_3)
12	$PhSnCl_2[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]$	1100	820	930	700	630	—	7.3–7.5, m, 5 H (C_6H_5Sn) 1.4, s, 12 H (CH_3)

As observed in the cases of di- and tri-organotin(IV) *O,O*-alkylenedithiophosphates, the chemical shift differences between the ligand and its complexes are very small and these seem to be governed by several factors,[15] which are overlapping and can not be fully distinguished from one another. Therefore, the mode of bonding (mono or bidentate) of ligand moieties in these monoorganotin(IV) *O-O*-alkylene-dithiophosphates can not be clearly determined on the basis of above data.

The ^{119}Sn chemical shifts of only three representative compounds could be recorded and these are given below:

	Compound	$\delta(^{119}Sn)$ ppm
(i)	$PhSn[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_3$	−212.20 −213.09
(ii)	$EtSn[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_3$	−147.30 −147.59
(iii)	$EtSn(Cl)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	−204.73

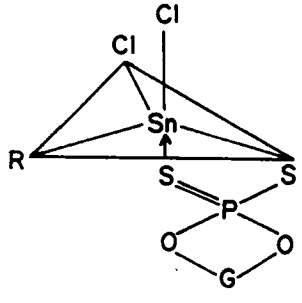
STRUCTURAL ELUCIDATION

The ^{119}Sn chemical shifts for monoorganotin(IV) tris(*O,O*-alkylenedithiophosphates) indicate that these compounds do not possess four coordinate tin with ester type linkage as observed in the simple thiolates $RSn(SR')_3$ (+65 to 167 ppm).[16,17] The chemical shifts for six and seven coordinate compounds occur at much lower frequencies then those observed for monoorganotin(IV) *O,O*-alkylene-dithiophosphates,[18] their chemical shifts in fact fit well with five coordinate tin compounds. As only one ^{31}P signal could be observed in ^{31}P NMR spectra, the ligands are regarded to be equivalent and hence it may be concluded that in these complexes all the ligands are equivalent weakly coordinated to tin leading to seven coordination environment, similar to corresponding dithiocarbamates.[19,20]

The observed ^{119}Sn chemical shift value (−204.7 ppm) for monoethyl-chlorotin(IV)bis(*O,O*-neopentyldithiophosphate) i.e.

$$EtSnCl[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$$

can be best interpreted in terms of weak chelation of ligand moieties in these derivatives leading to six coordination for tin. In the case of



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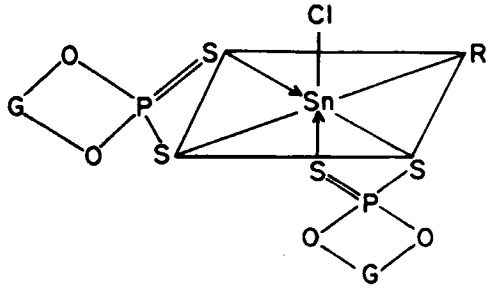

II

TABLE II

Reactions between monoorganotin(IV) trichlorides with ammonium *O,O*-alkylenedithiophosphates in 1 : 3 molar ratio

S. No.	$RSnCl_3$ R =	Reactants (g)	$NH_4S_2P(O)(O)G$ G =	Product (% yield)	Physical state (m.p. °C)	Analysis Found (calcd) %Sn	%S	Molecular weight Found (calcd)
1	C_6H_5	0.83	$CH_2C(CH_3)_2CH_2$ 2.65	$(C_6H_5)Sn[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_3$ (97)	Orange solid (105–107)	15.03 (15.12)	16.26 (16.31)	782 (784)
2	C_6H_5	1.04	$C(CH_3)C(CH_3)_2$ 2.38	$(C_6H_5)Sn[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_3$ (99)	Yellow solid (145, d)	14.40 (14.32)	23.32 (23.16)	— —
3	C_6H_5	0.88	$C(CH_3)_2CH_2CHCH_3$ 2.04	$(C_6H_5)Sn[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_3$ (89)	Yellow solid —	14.52 (14.32)	23.40 (23.16)	— —
4	n-C_4H_9	1.49	$CH_2(CH_3)_2CH_2$ 3.56	$(C_4H_9)Sn[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_3$ (91)	Yellow solid (92–94)	15.61 (15.68)	25.95 (25.37)	735 (756)
5	n-C_4H_9	1.04	$C(CH_3)_2C(CH_3)_2$ 2.72	$(C_4H_9)Sn[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_3$ (97)	White solid (192–193)	14.86 (14.85)	23.85 (24.04)	— —
6	n-C_4H_9	1.56	$C(CH_3)_2CH_2CHCH_3$ 2.37	$(C_2H_5)Sn[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_3$ (88)	Yellow sticky solid	14.87 (14.85)	23.85 (24.04)	— —
7	C_2H_5	0.88	$CH_2C(CH_3)_2CH_2$ 2.37	$(C_2H_5)Sn[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_3$ (86)	Yellow solid (121–123)	16.21 (16.05)	25.84 (25.97)	— —
8	C_2H_5	1.06	$C(CH_3)_2C(CH_3)_2$ 2.88	$(C_2H_5)Sn[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_3$ (90)	Sticky solid	15.21 (15.19)	24.15 (24.58)	— —
9	C_2H_5	0.89	$C(CH_3)_2CH_2CHCH_3$ 2.44	$(C_2H_5)Sn[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_3$ (85)	Yellow solid (80–85)	15.40 (15.19)	24.46 (24.58)	— —

TABLE III

Reactions between monoorganotin(IV) trichlorides with ammonium *O,O*-alkylenedithiophosphates in different stoichiometric ratios

S. No.	Reactants (g) $RSnCl_3$ R =	Reactants (g) $NH_4S_2P(O)_2G$ G =	Molar ratio	Product (% yield)	Physical state (m.p. °C)	Analysis Found (Calcd) %Sn	Analysis Found (Calcd) %S	Molecular weight Found (Calcd)
1	C_6H_5 1.95	$CH_2C(CH_3)_2CH_2$ 1.39	1 : 1	$C_6H_5SnCl_2[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$ (75)	Yellow solid (95)	26.00 (26.16)	13.59 (14.10)	— —
2	C_6H_5 1.08	$CH_2C(CH_3)_2CH_2$ 1.54	1 : 2	$C_6H_5SnCl[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$ (84)	Orange solid (100–105)	18.78 (18.98)	20.41 (20.47)	610 (625)
3	C_6H_5 1.99	$C(CH_3)_2C(CH_3)_2$ 1.51	1 : 1	$C_6H_5SnCl_2[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]$ (95)	Red solid (98–100)	— —	13.49 (13.38)	—
4	C_6H_5 1.24	$C(CH_3)_2C(CH_3)_2$ 1.92	1 : 2	$C_6H_5SnCl[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$ (88)	Orange solid (176, d)	18.78 (18.98)	20.41 (20.47)	— —
5	n-C_4H_9 1.41	$CH_2C(CH_3)_2CH_2$ 2.24	1 : 2	n-$C_4H_9SnCl[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$ (97)	Yellow solid (120–121)	19.84 (19.93)	21.54 (21.50)	—
6	n-C_4H_9 1.70	$(CH_3)_2C(CH_3)_2$ 2.85	1 : 2	n-$C_4H_9SnCl[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$ (92)	Yellow solid	18.90 (18.04)	20.67 (20.53)	590 (595)
7	n-C_4H_9 2.28	$C(CH_3)_2C(CH_3)_2$ 1.93	1 : 1	n-$C_4H_9SnCl[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$ (80)	Yellow oily liquid	26.44 (26.51)	14.00 (14.29)	440 (447)
8	C_2H_5 1.54	$CH_2C(CH_3)_2CH_2$ 2.62	1 : 2	$C_2H_5SnCl[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$ (91)	Yellow solid (102–105)	20.66 (20.52)	22.03 (22.11)	—
9	C_2H_5 1.23	$C(CH_3)_2CH_2$—$CHCH_3$ 2.21	1 : 2	$C_2H_5SnCl[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_2$ (96)	Viscous liquid	19.70 (19.57)	21.09 (21.11)	—
10	C_2H_5 1.77	$C(CH_3)_2CH_2CHCH_3$ 1.59	1 : 1	$C_2H_5SnCl[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]$ (96)		27.60 (27.62)	14.30 (14.89)	—

TABLE IV

Reactions of monobutyltin oxide with *O,O*-alkylenedithiophosphoric acids

S. No.	$BuSnO_{1.5}$	Reactants (g) $HS_2P\langle O \rangle G$		Product (% yield)	Physical state (m.p. °C)	Analysis Found (Calcd) %Sn	%S
1	2.23	$C(CH_3)_2C(CH_3)_2$	4.70	$(C_4H_9)Sn[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_3$ (78)	White solid (92–93)	14.48 (14.85)	23.57 (24.04)
2	1.20	$CH_2C(CH_3)_2CH_2$	1.83	$(C_4H_9)Sn[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_3$ (82)	Yellow solid (92–94)	15.39 (15.68)	24.94 (25.37)

dichloromonoorganotin(IV) derivatives the above conclusion about the chelation of the ligand is supported by a noticeable shifting of ν(P=S) to lower wave numbers in the infrared spectra in these derivatives, compared to its position in parent acid.

In view of the above, a trigonal bipyramidal (I) and octahedral (II) structures may be proposed for dichloro and monochloro derivatives respectively. The *cis* positions of Cl atoms in (I) and of Cl and R in (II) have been suggested in analogy with the corresponding dialkyldithiophosphate derivatives for the former and the observed crystal structure of $PhSnCl[S_2CNR_2]_2$[21] for the latter.

EXPERIMENTAL

O,O-alkylenedithiophosphoric acids were prepared by the method reported in literature.[10] Infrared spectra were recorded on a Perkin-Elmer 577 double grating spectrophotometer in the region 4000–400 cm^{-1}. Proton magnetic resonance spectra were recorded in $CDCl_3$ by a Perkin Elmer R12B spectrometer using TMS as internal reference. ^{31}P NMR and ^{119}Sn NMR spectra were recorded using H_3PO_4 and tetramethyltin as external references respectively.

Preparation of Complexes. (i) Reaction of monoorganotin(IV) chloride with ammonium *O,O*-alkylenedithiophosphates: To a suspension of ammonium *O,O*-alkylenedithiophosphate in benzene was added monoorganotin(IV) chloride in benzene with constant stirring at room temperature. The stirring was continued for 3–4 hours. From the clear filtrate obtained by removal of the precipitated ammonium chloride, the desired product i.e. monoorganotin(IV) *O,O*-alkylenedithiophosphates were obtained after removing the volatile solvent under reduced pressure.

Details regarding individual experiment have been tabulated in Table II and III.

(ii) Reaction of monoorganotin(IV) oxide with *O,O*-alkylenedithiophosphoric acid: To a suspension of monoorganotin(IV) oxide in benzene was added *O,O*-alkylenedithiophosphoric acid in benzene with constant stirring at room temperature. The whole reaction mixture was refluxed for 5–6 hrs and the water liberated was removed azeotropically.

The pertinent data about individual experiments have been tabulated in Table IV.

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