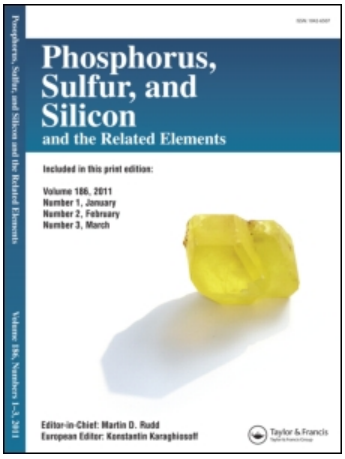

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Synthesis and Characterization of Dichlorotin(IV)trithiophosphates and Their Adducts with Nitrogen Donor Bases

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Dichlorotin(IV)trithiophosphates [(RO)P(S)S_2]$SnCl_2$ were prepared by the reaction of methanolic solution of $SnCl_4$ and dipotassium salt of trithiophosphates in a 1:1 molar ratio and their adducts [(RO)P(S)S_2]$SnCl_2.N_2C_{12}H_8$ and [(RO)P(S)S_2]$SnCl_2.N_2C_{10}H_8$ were prepared by the reaction of methanolic solution of [(RO)P(S)S_2]$SnCl_2$ and N-donor bases in a 1:1 molar ratio. These newly synthesised derivatives have been characterized by elemental analysis; molecular weight measurements; and IR, ^{13}C, ^{31}p and ^{119}Sn NMR spectral studies. Coordination number of four and six was suggested for dichlorotin (IV)trithiophosphates and their adducts with N-donor bases respectively.

Keywords Phosphorotrithioate; tin(IV)

INTRODUCTION

In the recent years, considerable interest has been evinced in the chemistry of metallic moieties bonded with sulfur ligands such as thiolates, dithiolates,[1] thio β-diketonates,[2] dithiocarbamates, and O,O′-alkylene dithiophosphates.[3–5] Some mono di- and tri-organo tin(IV) derivatives of diakyl dithiophosphates have been synthesised and characterized by ^{13}C, ^{31}P, and ^{119}Sn NMR and mossbauer spectral studies. The ^{119}Sn NMR chemical shifts and [$^1J(^{119}Sn—^{13}C)$] and [$^2J(^{119}Sn—^1H)$] of triorgano tin(IV) dialkyl dithiophosphates are consistent with tetrahedral geometry and four coordinated Sn, although a mossbauer study indicates five coordinated tin in solid state. These studies also reveal that in mono and diorgano tin(IV)dithiophosphates, a Sn atom is weakly coordinated to a ligand.[6–7] Organic trithiophosphates esters have been

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used as defoliants,[8] insecticides,[8–9] and nematodicidal[9] and inhibitors[10] of steel corrosion. Potassium trithiophosphates exist in two isomeric forms.

$$[(RO)P(S)S_2]K_2 \Leftrightarrow [(RS)P(O)S_2]K_2$$

The persual of literature revealed only two publications on the metallic ester of trithiophosphoric acids.[11–12] Trithiophosphates of the tin element have received no attention to the best of our knowledge. Hence, it was thought worthwhile to study the trithiophosphates of dichlorotin(IV) and their adducts with nitrogen-donor bases.

EXPERIMENTAL

Dipotassium salt of O-alkyl, O-cycloalkyl, and O-aryl trithiophosphates were prepared by reaction of the requisite anhydrous alcohol with P_2S_5 and triethylamine in a 1:3:3 molar ratio respectively, in anhydrous benzene. The reaction mixture was stirred for 30 min on a water bath. After stirring, salt was precipitated out. All chemicals were of A.R. grade and were used after the drying process. The derivatives described in the present article were synthesised by the following general routes.

Synthesis of $[(RO)P(S)S_2]SnCl_2$

A methanolic solution (15 mL) of tetrachlorotin(IV) and methanolic solution of dipotassium salt of trithiophosphates were mixed and refluxed for 10–12 h. The reaction was carried out in a 1:1 molar ratio. After refluxing, the solid KCl was precipitated out. Insolubles were filtered off and the product was obtained from the filtrate by removal of volatilesa under reduced pressure. The complexes numbers 1–10 were prepared by the same procedure. The analytical results are summarized in Table I.

Synthesis of $[(RO)P(S)S_2]SnCl_2.N_2C_{12}H_8$ and $[(RO)P(S)S_2]SnCl_2.N_2C_{10}H_8$

A methanolic solution (5 mL) of dichlorotin(IV)trithiophosphates and methanolic solution of 1,10-phenanthroline were mixed and stirred for 5–6 h. The reaction was carried out in a 1:1 molar ratio. After stirring, the methanol was removed under vacuum and yellow adducts were obtained. The adducts numbers 10–20 were prepared by this same procedure. The adducts with 2,2′-bipyridyl (21–30) were prepared by this same procedure. The analytical results are summarized in Tables II and III, respectively.

TABLE I Synthetic and Analytical Data for $[(RO)P(S)S_2]SnCl_2$

S. no.	Reactants (g)		Molar ratio	Product (g)	Yield (%)	Mol.Wt. found/ (calcd.)	Analysis (%) found/(calcd.)				
	$SnCl_4$	$[(RO)P(S)S_2]K_2$		$[(RO)P(S)S_2]SnCl_2$			C	H	S	Cl	Sn
1.	.75	$[(CH_3)P(S)S_2]K_2$	1:1	$[(CH_3)P(S)S_2]SnCl_2$	95	341.19	3.16	0.58	27.38	20.14	33.87
	0.68			.95		(347.78)	(3.45)	(0.86)	(27.66)	(20.38)	(34.12)
2.	.70	$[(C_2H_5)P(S)S_2]K_2$	1:1	$[(C_2H_5)P(S)S_2]SnCl_2$	90	354.78	6.38	1.11	26.23	19.29	32.58
	0.72			.87		(361.80)	(6.63)	(1.39)	(26.58)	(19.59)	(32.80)
3.	.66	$[n(C_3H_7)P(S)S_2]K_2$	1:1	$[n(C_3H_7)P(S)S_2]SnCl_2$	85	370.55	9.32	1.57	25.24	18.57	31.29
	0.76			.80		(375.83)	(9.58)	(1.87)	(25.59)	(18.86)	(31.58)
4.	.66	$[i(C_3H_7)P(S)S_2]K_2$	1:1	$[i(C_3H_7)P(S)S_2]SnCl_2$	90	369.50	9.30	1.59	25.20	18.56	31.28
	0.76			.85		(375.83)	(9.58)	(1.87)	(25.59)	(18.86)	(31.58)
5.	.65	$[n(C_4H_9)P(S)S_2]K_2$	1:1	$[n(C_4H_9)P(S)S_2]SnCl_2$	95	382.23	12.01	2.17	24.39	17.89	30.19
	0.80			.92		(389.86)	(12.32)	(2.32)	(24.67)	(18.18)	(30.44)
6.	.65	$[s(C_4H_9)P(S)S_2]K_2$	1:1	$[s(C_4H_9)P(S)S_2]SnCl_2$	90	383.48	12.01	2.18	24.36	17.88	30.19
	0.80			.87		(389.86)	(12.32)	(2.32)	(24.67)	(18.18)	(30.44)
7.	.65	$[i(C_4H_9)P(S)S_2]K_2$	1:1	$[i(C_4H_9)P(S)S_2]SnCl_2$	85	382.44	12.02	2.14	24.34	17.86	30.18
	0.80			.82		(389.86)	(12.32)	(2.32)	(24.67)	(18.18)	(30.44)
8.	.61	$[i(C_5H_{11})P(S)S_2]K_2$	1:1	$[i(C_5H_{11})P(S)S_2]SnCl_2$	90	398.21	14.56	2.46	23.50	17.26	29.10
	0.84			.85		(403.81)	(14.87)	(2.74)	(23.82)	(17.55)	(29.39)
9.	.57	$[(C_6H_{11})P(S)S_2]K_2$	1:1	$[(C_6H_{11})P(S)S_2]SnCl_2$	95	410.01	17.04	2.31	22.86	16.88	28.29
	0.87			.86		(415.90)	(17.32)	(2.66)	(23.13)	(16.04)	(28.53)
10.	.59	$[(C_6H_5)P(S)S_2]K_2$	1:1	$[(C_6H_5)P(S)S_2]SnCl_2$	90	402.27	17.28	1.10	23.18	17.10	28.64
	0.85			.83		(409.85)	(17.58)	(1.22)	(23.47)	(17.30)	(28.95)

TABLE II Synthetic and Analytical Data for $[(RO)P(S)S_2]SnCl_2.C_{12}H_8N_2$

S. no.	Reactants (g) $C_{12}H_8N_2$	Reactants (g) $[(RO)P(S)S_2]SnCl_2$	Molar ratio	Product (in g) $[(RO)P(S)S_2]SnCl_2.C_{12}H_8N_2$	Yield (%)	Mol.Wt. found/ (calcd.)	Analysis (%) found/(calcd.) C	H	N	S	Cl	Sn
1.	.52	$[(CH_3O)P(S)S_2]SnCl_2$ 1.00	1:1	$[(CH_3O)P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.50	99	521.11 (527.99)	29.30 (29.57)	1.82 (2.09)	5.10 (5.30)	18.18 (18.21)	13.38 (13.42)	22.40 (22.47)
2.	.52	$[(C_2H_5)P(S)S_2]SnCl_2$ 1.04	1:1	$[(C_2H_5)P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.53	98	536.79 (542.01)	29.84 (31.02)	2.24 (2.41)	4.90 (5.16)	17.68 (17.74)	12.98 (13.08)	21.79 (21.89)
3.	.52	$[n(C_3H_7)P(S)S_2]SnCl_2$ 1.08	1:1	$[n(C_3H_7)P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.55	97	549.47 (556.04)	32.19 (32.40)	2.49 (2.71)	4.87 (5.03)	17.20 (17.30)	12.64 (12.75)	21.28 (21.34)
4.	.52	$[i(C_3H_7)P(S)S_2]SnCl_2$ 1.08	1:1	$[i(C_3H_7)P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.58	99	550.57 (556.04)	32.18 (32.40)	2.48 (2.71)	4.89 (5.03)	17.21 (17.30)	12.64 (12.75)	21.29 (21.34)
5.	.52	$[n(C_4H_9)P(S)S_2]SnCl_2$ 1.12	1:1	$[n(C_4H_9)P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.61	98	563.15 (570.07)	33.48 (33.71)	2.87 (3.00)	4.68 (4.91)	16.79 (16.87)	12.31 (12.43)	20.78 (20.82)
6.	.52	$[s(C_4H_9)P(S)S_2]SnCl_2$ 1.12	1:1	$[s(C_4H_9)P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.62	99	56225 (570.07)	33.49 (33.71)	2.86 (3.00)	4.66 (4.91)	16.78 (16.87)	12.30 (12.43)	20.76 (20.82)
7.	.52	$[i(C_4H_9)P(S)S_2]SnCl_2$ 1.12	1:1	$[i(C_4H_9)P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.59	97	563.52 (570.07)	33.48 (33.71)	2.84 (3.00)	4.68 (4.91)	16.79 (16.87)	12.38 (12.43)	20.75 (20.82)
8.	.52	$[i(C_5H_{11})P(S)S_2]SnCl_2$ 1.16	1:1	$[i(C_5H_{11})P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.61	96	578.02 (584.02)	34.64 (34.96)	3.00 (3.27)	4.50 (4.79)	16.40 (16.47)	12.04 (12.14)	20.28 (20.32)
9.	.52	$[(C_6H_{11})P(S)S_2]SnCl_2$ 1.20	1:1	$[(C_6H_{11})P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.68	98	591.93 (596.10)	36.01 (36.26)	3.01 (3.21)	4.46 (4.69)	16.08 (16.13)	11.78 (11.89)	19.74 (19.89)
10.	.52	$[(C_6H_5)P(S)S_2]SnCl_2$ 1.18	1:1	$[(C_6H_5)P(S)S_2]SnCl_2.C_{12}H_8N_2$ 1.65	97	583.19 (590.06)	36.38 (36.63)	2.04 (2.22)	4.48 (4.74)	16.13 (16.30)	11.98 (12.01)	20.01 (20.11)

TABLE III Synthetic and Analytical Data for $[(RO)P(S)S_2]SnCl_2.C_{10}H_8N_2$

S. no.	Reactants (g)		Molar ratio	Product (in g)	Yield (%)	Mol.Wt. found/ (calcd.)	Analysis (%) found/(calcd.)					
	$C_{10}H_8N_2$	$[(RO)P(S)S_2]SnCl_2$		$[(RO)P(S)S_2]SnCl_2.C_{10}H_8N_2$			C	H	N	S	Cl	Sn
1.	.5	$[(CH_3O)P(S)S_2]SnCl_2$ 1.11	1:1	$[(CH_3O)P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.58	98	496.19 (503.97)	26.00 (26.21)	1.92 (2.19)	5.23 (5.55)	19.04 (19.08)	13.88 (16.06)	23.51 (23.55)
2.	.5	$[(C_2H_5)P(S)S_2]SnCl_2$ 1.15	1:1	$[(C_2H_5)P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.60	97	512.87 (517.99)	27.58 (27.82)	2.30 (2.52)	5.16 (5.40)	18.46 (18.57)	13.41 (13.68)	22.80 (22.91)
3.	.5	$[n(C_3H_7)P(S)S_2]SnCl_2$ 1.20	1:1	$[n(C_3H_7)P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.68	99	526.55 (532.02)	29.12 (29.17)	2.58 (2.84)	4.92 (5.26)	18.01 (18.08)	13.10 (13.32)	22.20 (22.30)
4.	.5	$[i(C_3H_7)P(S)S_2]SnCl_2$ 1.20	1:1	$[i(C_3H_7)P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.68	99	525.54 (532.02)	29.10 (29.34)	2.59 (2.84)	4.90 (5.26)	18.00 (18.08)	13.10 (13.32)	22.29 (22.30)
5.	.5	$[n(C_4H_9)P(S)S_2]SnCl_2$ 1.24	1:1	$[n(C_4H_9)P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.71	98	538.23 (546.05)	30.44 (30.79)	2.89 (3.13)	4.89 (5.13)	17.58 (17.61)	12.67 (12.98)	21.70 (21.73)
6.	.5	$[s(C_4H_9)P(S)S_2]SnCl_2$ 1.24	1:1	$[s(C_4H_9)P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.69	97	539.32 (546.05)	30.49 (3079)	2.86 (3.13)	4.88 (5.13)	17.58 (17.61)	12.68 (12.98)	21.65 (21.73)
7.	.5	$[i(C_4H_9)P(S)S_2]SnCl_2$ 1.24	1:1	$[i(C_4H_9)P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.67	96	539.40 (546.05)	30.42 (30.79)	2.88 (3.13)	4.86 (5.13)	17.59 (17.61)	12.60 (12.98)	21.69 (21.73)
8.	.5	$[i(C_5H_{11})P(S)S_2]SnCl_2$ 1.29	1:1	$[i(C_5H_{11})P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.73	97	552.21 (560.00	31.86 (32.17)	3.20 (3.41)	4.76 (5.00)	17.04 (17.17)	12.38 (12.66)	21.06 (21.19)
9.	.5	$[(C_6H_{11})P(S)S_2]SnCl_2$ 1.33	1:1	$[(C_6H_{11})P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.79	98	566.01 (572.09)	33.25 (33.59)	3.18 (3.34)	4.52 (4.89)	16.76 (16.81)	12.08 (12.39)	20.69 (20.74)
10.	.5	$[(C_6H_5)P(S)S_2]SnCl_2$ 1.31	1:1	$[(C_6H_5)P(S)S_2]SnCl_2.C_{10}H_8N_2$ 1.75	97	558.27 (566.04)	33.60 (33.95)	2.10 (2.31)	4.60 (4.94)	16.84 (16.99)	12.29 (12.52)	20.86 (20.96)

MEASUREMENTS

IR spectra were recorded in nujol mulls using Csl cells on a Perkin Elmer 577 spectrometer. In the range 4000–200 cm^{-1}, ^{13}C NMR, ^{31}P NMR, and ^{119}Sn NMR spectra of these derivatives have been recorded in $CDCl_3$ on a Bruker DRX-300 spectrometer using TMS, H_3PO_4, and tetramethyltin standards, respectively. Molecular weight were measured on a Knauer Vapour Pressure Osmometer in $CHCl_3$ at 45°C. Elemental analysis for Sn, Cl, and S were carried out by the standards procedure.[13] Carbon, hydrogen, and nitrogen were estimated by Coleman C.H.N. analyzers.

RESULT AND DISCUSSION

Dichlorotin(IV)trithiophosphates are yellow, solid, and sparingly soluble in common organic (benzene, dichloromethane, chloroform etc.) and coordinating (DMF, DMSO, THF, etc.) solvents. The complexes are unstable at room temperature and tend to decompose even under a closed environment. Decomposition is rather slow when these compounds are stored in a dry atmosphere at low temperature. Decomposition is marked by the color change from yellow to brown. The molecular weight measurements indicate a monomerio nature of these compounds in a dilute chloroform solution at 45°C.

IR Spectral Studies

In the IR spectrum the bands observed in the region 1034–1056 and 800–828 cm^{-1} have been assigned to ν[(P)—O—C] and ν[P—O—(C)], respectively. The ν[P=S] mode may be characterized by the presence of a band in the region 644–652 cm^{-1} which is quite similar to the ligand's P=S stretchining mode, indicating the bidentate nature of trithiophosphate ligand; this is also showing that there is no interaction of P=S to the metal. The band present in the region 629–646 cm^{-1} may be ascribed to ν[P—S] stretching mode. Appearance of a new band (in comparison to a free ligand) in the region 358–370 cm^{-1} indicates the formation of a ν[Sn—S] bond. The ν[Sn—Cl] bond band was found in the region 340–360 cm^{-1}. The IR spectral data are summarized in Table IV.

NMR Spectral Studies

The ^{13}C resonance for the carbon atom of the P—O—C group appears as a doublet due to coupling with ^{31}P nuclei. In the proton-decoupled ^{31}P NMR spectra, only one resonance for each compound in the range

TABLE IV IR Spectral Data (cm^{-1}) for $[(RO)P(S)S_2]SnCl_2$

S. no.	Compound	ν[(P)—O—C]	ν[P—O—(C)]	ν[P═S]	ν[P—S]	ν[Sn—S]	ν[Sn—C]	ν[Sn—Cl]
1.	$[MeO)P(S)S_2]SnCl_2$	1034(s)	800(s)	650(s)	629(m)	360(w)	622(m)	340(w)
2.	$[(EtO)P(S)S_2]SnCl_2$	1046(s)	810(s)	649(s)	632(m)	363(w)	626(m)	342(w)
3.	$[(Pr^nO)P(S)S_2]SnCl_2$	1045(s)	812(s)	651(s)	635(m)	361(w)	624(m)	344(w)
4.	$[(Pr^iO)\ P(S)S_2]SnCl_2$	1044(s)	808(s)	650(s)	630(m)	358(w)	634(m)	343(w)
5.	$[(Bu^nO)P(S)S_2]SnCl_2$	1052(s)	818(s)	645(s)	642(m)	366(w)	636(m)	345(w)
6.	$[(Bu^sO)P(S)S_2]SnCl_2$	1048(s)	814(s)	643(s)	637(m)	362(w)	630(m)	348(w)
7.	$[(Bu^iO)P(S)S_2]SnCl_2$	1050(s)	815(s)	644(s)	638(m)	364(w)	632(m)	349(w)
8.	$[(Am^iO)P(S)S_2]SnCl_2$	1056(s)	828(s)	652(s)	646(m)	370(w)	648(m)	346(w)
9.	$[(C.h.O)P(S)S_2]SnCl_2$	1055(s)	824(s)	647(s)	640(m)	369(w)	642(m)	358(w)
10.	$[(Ph.O)P(S)S_2]SnCl_2$	1051(s)	822(s)	646(s)	643(m)	367(w)	638(m)	360(w)

s = strong, m = medium, w = weak.

TABLE V ^{13}C NMR Spectral Data for $[(RO)P(S)S_2]SnCl_2$

S. no.	Compound	Chemical shift (δ, ppm) $S_2(S)P(OR)$ Carbons
1.	$[MeO)P(S)S_2]SnCl_2$	56.52,d,C; $^2J_{P-C}$ = 24CPS
2.	$[(EtO)P(S)S_2]SnCl_2$	68.41,d,C; $^2J_{P-C}$ = 27CPS 18.13,C_2
3.	$[(Pr^nO)P(S)S_2]SnCl_2$	72.90,d,C; $^2J_{P-C}$ = 30CPS 24.66,$C_2$15.48,C_3.
4.	$[(Pr^iO)$ $P(S)S_2]SnCl_2$	68.79,d,C; $^2J_{P-C}$ = 30CPS 24.83,C_2
5.	$[(Bu^nO)P(S)S_2]SnCl_2$	69.01,d,C; $^2J_{P-C}$ = 27CPS 35.29,C_2 22.17,C_3 18.91,C_4
6.	$[(Bu^sO)P(S)S_2]SnCl_2$	72.89,d,C_2; $^2J_{P-C}$ = 21CPS 36.61,C_3 15.12,C_4
7.	$[(Bu^iO)P(S)S_2]SnCl_2$	73.27,d,C; $^2J_{P-C}$ = 24CPS 30.12,C_2 22.04,C_3
8.	$[(Am^iO)P(S)S_2]SnCl_2$	63.78,d,C; $^2J_{P-C}$ = 33CPS 42.42,C_2 27.73,C_3 25.62,C_4
9.	$[(C.h.O)P(S)S_2]SnCl_2$	73.28,d,C; $^2J_{P-C}$ = 354CPS 33.85,$C_{2,6}$ 29.93,$C_{3,5}$ 29.01,C_4
10.	$[(Ph.O)P(S)S_2]SnCl_2$	161.5,d,C; $^2J_{P-C}$ = 450CPS 119.40,$C_{2,6}$ 134.50,$C_{3,5,}$ 125.7,C_4

95.16–97.14 ppm is obtained. In ^{119}Sn NMR spectra, the ^{119}Sn, NMR chemical shifts of all of the compounds have been observed in the range 251–268 ppm. These ^{119}Sn NMR chemical shifts suggest that in compound numbers 1–10, the tin(IV) is four coordinated. The NMR spectral data are summarized in Tables V and VI. The tentative structure of these derivatives are shown in Figure 1.

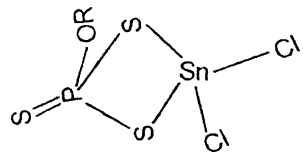

FIGURE 1 Structure of $[(RO)P(S)S_2]SnCl$.

TABLE VI ^{31}P and ^{119}Sn NMR Spectral Data for [(RO)P(S)S_2]$SnCl_2$

S. no.	Compound	Chemical shift (δ, ppm)	
		^{31}P NMR	^{119}Sn NMR
1.	[MeO)P(S)S_2]$SnCl_2$	95.16	252
2.	[(EtO)P(S)S_2]$SnCl_2$	96.02	254
3.	[(Pr^nO)P(S)S_2]$SnCl_2$	96.18	251
4.	[(Pr^iO) P(S)S_2]$SnCl_2$	96.28	253
5.	[(Bu^nO)P(S)S_2]$SnCl_2$	97.02	258
6.	[(Bu^sO)P(S)S_2]$SnCl_2$	96.48	255
7.	[(Bu^iO)P(S)S_2]$SnCl_2$	96.42	260
8.	[(Am^iO)P(S)S_2]$SnCl_2$	96.92	262
9.	[(C.h.O)P(S)S_2]$SnCl_2$	97.82	265
10.	[(Ph.O)P(S)S_2]$SnCl_2$	97.94	268

[(RO)P(S)S_2]$SnCl_2.N_2C_{12}H_8$

All the adducts are yellow solid and soluble in common organic (benzene, dichloromethane, chloroform, etc.) and coordinating (DMF, DMSO, THF, etc.) solvents. In comparison to the parent compound, the adducts are easily soluble in common organic solvents. The adducts are quite stable at room temperature. The molecular weight measurement indicates a monomeric nature of these adducts in a dilute chloroform solution at 45°C.

IR Spectral Studies

In the IR spectrum, the bands observed in the region 1042–1066 cm^{-1} and 820–846 cm^{-1} have been assigned to ν[(P)—O—C] and ν[P—O—(C)], respectively. The ν[P═S] mode may be characterized by the presence of a band in the region 662–650 cm^{-1}, which is quite similar to the ligand's P═S stretchining mode, indicating the bidentate nature of trithiophosphate ligand; this is also showing that their is no interaction of P═S to the metal. The band present in the region 632–648 cm^{-1} may be ascribed to a ν[P—S] strecthing mode. The appearance of a new band (in comparison to free ligand) in the region 368–388 cm^{-1} indicates the formation of a ν[Sn—S] bond. The IR values of ν[Sn—Cl] bond band found to be lowering in an increase of the coordination number of tin. In six coordiinated, Sn(IV) complexes, the ν[Sn—Cl] bond band was found in the regoin 275–286 cm^{-1}. The ν[Sn—N] bond band was found in the region 384–395.The ν[C═N] bond band was found in the region 1600–1623 cm^{-1}. The IR spectral data are summarized in Table VII.

TABLE VII IR Spectral Data (cm^{-1}) for $[(RO)P(S)S_2]SnCl_2.C_{12}H_8N_2$

S. no.	Compound	ν[(P)—O—C]	ν[P—O—(C)]	ν[P═S]	ν[P—S]	ν[Sn—S]	ν[Sn—Cl]	ν[Sn—N]	ν[C═N]
1.	$[MeO)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1050(s)	820(s)	658(s)	632(m)	368(w)	275(w)	384(w)	1600(s)
2.	$[(EtO)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1052(s)	824(s)	654(s)	636(m)	372(w)	278(w)	386(w)	1602(s)
3.	$[(Pr^nO)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1048(s)	827(s)	650(s)	639(m)	374(w)	276(w)	390(w)	1615(s)
4.	$[(Pr^iO)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1042(s)	825(s)	661(s)	637(m)	370(w)	279(w)	388(w)	1610(s)
5.	$[(Bu^nO)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1056(s)	834(s)	659(s)	645(m)	379(w)	277(w)	393(w)	1619(s)
6.	$[(Bu^sO)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1046(s)	828(s)	658(s)	638(m)	375(w)	274(w)	389(w)	1614(s)
7.	$[(Bu^iO)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1051(s)	830(s)	662(s)	641(m)	376(w)	279(w)	391(w)	1618(s)
8.	$[(Am^iO)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1066(s)	846(s)	661(s)	648(m)	388(w)	282(w)	393(w)	1623(s)
9.	$[(C.h.O)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1062(s)	842(s)	656(s)	646(m)	385(w)	284(w)	395(w)	1620(s)
10.	$[(Ph.O)P(S)S_2]SnCl_2.C_{12}H_8N_2$	1058(s)	841(s)	655(s)	640(m)	380(w)	286(w)	387(w)	1617(s)

s = strong, m = medium, w = weak.

TABLE VIII ^{13}C NMR Spectral Data for [(RO)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$

S. no.	Compound	Chemical shift (δ, ppm)	
		$S_2(S)P(OR)$ Carbons	$C_{12}H_8N_2$ Carbons
1.	[MeO)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	53.59,d,C; $^2J_{P-C}$ = 26cps	132.24, C_2, 129.48 C_3 124.82, C_4, 130.18, C_5 154.24 C_6
2.	[(EtO)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	54.58,d,C; $^2J_{P-C}$ = 26cps 16.49, C_2	132.45,C_2, 129.56,C_3 124.94,C_4, 129.56,C_5 152.42, C_6
3.	[(Pr^{n}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	71.89,d,C; $^2J_{P-C}$ = 90cps 25.68, C_2 12.46, C_3	134.44,C_2, 124.52, C_3, 121.12 C_4, 127.29, C_5 149.82, C_6
4.	[(Pr^{i}O) P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	70.98,d,C; $^2J_{P-C}$ = 63cps 24.70, C_2 13.49, C_3	131.62, C_2, 129.84, C_3 124.85 C_4, 130.45 C_5 157.62 C_6
5.	[(Bu^{n}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	72.28,d,C; $^2J_{P-C}$ = 16cps 33.16, C_2 12.15, C_3 16.26, C_4	130.92,C_2, 130.10, C_3, 126.18, C_4, 129.80, C_5 152.86 C_6,
6.	[(Bu^{s}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	71.82,d,C; $^2J_{P-C}$ = 18cps 32.24, C_2 14.09, C_3 15.62, C_4	130.65,C_2, 129.28, C_3 124.84, C_4, 132.88, C_5 154.28, C_6
7.	[(Bu^{i}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	72.28,d,C; $^2J_{P-C}$ = 16cps 31.54, C_2 13.21, C_3	134.60,C_2, 129.81, C_3 125.63, C_3, 130.45, C_5 152.28, C_6,
8.	[(Am^{i}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	66.99,d,C; $^2J_{P-C}$ = 24cps 42.54, C_2 26.18, C_3 24.89, C_4	135.82, C_2, 126.23, C_3 123.84, C_4, 129.26, C_5 149.9 C_6
9.	[(C.h.O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	76.91,d,C; $^2J_{P-C}$ = 342cps 32.80, $C_{2,6}$ 25.42, $C_{3,5}$ 26.92, C_4	136.84, C_2, 127.42, C_3, 126.28, C_4, 130.20, C_5 152.48, C_6,
10.	[(Ph.O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	159.60,d,C; $^2J_{P-C}$= 438cps 116.41,$C_{2,6}$ 127.72, $C_{3,5}$ 118.84,, C_4	137.62, C_2, 127.52, C_3, 124.46, C_4, 129.40, C_5 150.90 C_6

TABLE IX ^{31}P and ^{119}Sn NMR Spectral Data for [(RO)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$

S. no.	Compound	Chemical shift (δ, ppm)	
		^{31}P NMR	^{119}Sn NMR
1.	[MeO)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	97.81	272
2.	[(EtO)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	97.84	271
3.	[(Pr^{n}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	97.86	274
4.	[(Pr^{i}O) P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	97.85	273
5.	[(Bu^{n}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	97.94	278
6.	[(Bu^{s}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	97.98	276
7.	[(Bu^{i}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	98.10	277
8.	[(Am^{i}O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	99.28	280
9.	[(C.h.O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	99.29	282
10.	[(Ph.O)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$	99.49	285

NMR Spectral Studies

The ^{13}C NMR Spectra, of the adducts is quite similar to the parental compounds—only a slight difference has been found. The ^{13}C resonance for the carbon atom of the P—O—C group appears as a doublet due to coupling with ^{31}P nuclei. In the proton-decoupled ^{31}P NMR spectra, only one resonance for each compound in the range 97.81–99.49 ppm is obtained. In ^{119}Sn NMR spectra, the ^{119}Sn NMR chemical shifts of all the adducts have been observed in the range 277–285 ppm. Their ^{119}Sn NMR chemical shifts and IR spectral data suggest that in these adducts the tin(IV) is six coordinated. The NMR spectral data are summarized in Tables VIII and IX. The tentative structure of these adducts is shown in Figure 2.

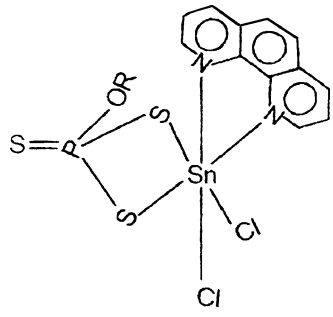

FIGURE 2 Structure of [(RO)P(S)S$_2$]SnCl$_2$.C$_{12}$H$_8$N$_2$.

TABLE X IR Spectral Data (cm^{-1}) for $[(RO)P(S)S_2]SnCl_2.C_{10}H_8N_2$

S. no.	Compound	ν[(P)—O—C]	ν[P—O—(C)]	ν[P═S]	ν[P—S]	ν[Sn—S]	ν[Sn—Cl]	ν[Sn—N]	ν[C═N]
1.	$[(MeO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1048(s)	824(s)	659(s)	636(s)	372(w)	282(w)	388(w)	1610(s)
2.	$[(EtO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1050(s)	826(s)	652(s)	639(s)	374(w)	281(w)	390(w)	1612(s)
3.	$[(Pr^nO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1052(s)	829(s)	656(s)	641(s)	378(w)	284(w)	393(w)	1618(s)
4.	$[(Pr^iO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1046(s)	823(s)	655(s)	840(s)	375(w)	283(w)	391(w)	1613(s)
5.	$[(Bu^nO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1059(s)	837(s)	657(s)	652(s)	382(w)	285(w)	394(w)	1630(s)
6.	$[(Bu^sO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1056(s)	833(s)	659(s)	648(s)	379(w)	288(w)	389(w)	1625(s)
7.	$[(Bu^iO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1058(s)	835(s)	661(s)	651(s)	381(w)	286(w)	392(w)	1628(s)
8.	$[(Am^iO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1068(s)	856(s)	660(s)	655(s)	384(w)	290(w)	396(w)	1638(s)
9.	$[(C.h.O)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1064(s)	854(s)	6654(s)	654(s)	383(w)	295(w)	395(w)	1635(s)
10.	$[(Ph.O)P(S)S_2]SnCl_2.C_{10}H_8N_2$	1057(s)	848(s)	653(s)	649(s)	376(w)	298(w)	387(w)	1632(s)

s = strong, m = medium, w = weak.

TABLE XI ^{13}C NMR Spectral Data for $[(RO)P(S)S_2]SnCl_2.C_{10}H_8N_2$

S. no.	Compound	Chemical shift (δ, ppm)	
		$S_2(S)P(OR)$ Carbons	$C_{10}H_8N_2$ Carbons
1.	$[MeO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	54.59,d,C; $^2J_{P-C} = 26$cps	146.58,C_2, 122.24, C_3 119.89, C_4, 136.52, C_5 151.86, C_6,
2.	$[(EtO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	54.68,d,C; $^2J_{P-C} = 26$cps 16.50, C_2	146.89, C_2, 122.88, C_3 120.42, C_4, 126.29, C_5 152.68, C_6
3.	$[(Pr^nO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	71.98,d,C; $^2J_{P-C} = 90$cps 25.86, C_2 12.64, C_3	147.96, C_2, 123.98, C_3 120.62, C_4, 134.68, C_5 153.42, C_6
4.	$[(Pr^iO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	70.96,d,C; $^2J_{P-C} = 63$cps 24.72, C_2 13.48, C_3	148.52, C_2, 123.62, C_3 120.28, C_4, 137.43, C_5 153.84, C_6
5.	$[(Bu^nO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	72.29,d,C; $^2J_{P-C} = 16$cps 33.61, C_2 12.51, C_3 16.62, C_4	147.48, C_2, 123.96, C_3 121.48, C_4, 137.64, C_5 153.54, C_6
6.	$[(Bu^sO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	71.28,d,C; $^2J_{P-C} = 18$cps 32.42, C_2 14.19, C_3 15.26, C_4	148.68, C_2, 124.48, C_3 121.62, C_4, 137.80, C_5 154.64, C_6
7.	$[(Bu^iO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	72.85,d,C; $^2J_{P-C} = 16$cps 31.45, C_2 13.28, C_3	148.28, C_2, 123.24, C_3 122.48, C_4, 137.24, C_5 154.55, C_6
8.	$[(Am^iO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	66.67,d,C; $^2J_{P-C} = 24$cps 42.58, C_2 26.81, C_3 24.90, C_4	149.29, C_2, 125.46, C_3 121.58, C_4, 138.44, C_5 154.14, C_6
9.	$[(C.h.O)P(S)S_2]SnCl_2.C_{10}H_8N_2$	76.94,d,C; $^2J_{P-C} = 342$cps 32.84, $C_{2,6}$ 25.49, $C_{3,5}$ 26.95, C_4	150.80, C_2, 127.22, C_3 124.18, C_4, 139.40, C_5 157.18, C_6
10.	$[(Ph.O)P(S)S_2]SnCl_2.C_{10}H_8N_2$	159.80,d,C; $^2J_{P-C} = 438$cps 116.49, $C_{2,6}$ 127.78, $C_{3,5}$ 118.85, C_4	149.98, C_2, 124.94, C_3 122.78, C_4, 137.68, C_5 155.60, C_6

$[(RO)P(S)S_2]SnCl_2.N_2C_{10}H_8$

The IR spectra of the adducts (21–30) have been recorded in the 4000–200 cm^{-1} region. The bands observed in the region 1048–1068 and 823–856 cm^{-1} have been assigned to ν[(P)—O—C] and ν[P—O—(C)], respectively. The mode ν[P=S] may be characterized by the presence of a band in the 660–652 cm^{-1} region, indicating the bidentate nature of trithiophosphate ligand. The band present in the 636–655 region may be ascribed to a ν[P—S] strecthing mode. The appearance of a new band (in comparison to a free ligand) in the 372–384 cm^{-1} region indicates the formation of a ν[Sn—S] bond. The IR values of a ν[Sn—Cl] bond band found to be lowering in an increase of the coordination number of tin. In six coordiinated Sn(IV) complexes, the ν[Sn—Cl] bond band was found in the 281–298 cm^{-1} region. The ν[Sn—N] bond band was found in the 388–396 cm^{-1} region. The ν[C=N] bond band was found in the 1610–1638 cm^{-1} region. The IR spectral data are summarized in Table X.

NMR Spectral Studies

The ^{13}C NMR Spectra of the adducts is quite similar to the parental compounds; only a slight difference has been found. The ^{13}C resonance for the carbon atom of the P—O—C group appears as a doublet due to coupling with ^{31}P nuclei. In the proton-decoupled ^{31}P NMR spectra, only one resonance for each compound in the range 96.81–98.49 ppm is obtained. In ^{119}Sn NMR spectra, the ^{119}Sn NMR chemical shifts of all the adducts has been observed in the range 270–284 ppm. Their

TABLE XII ^{31}P and ^{119}Sn NMR Spectral Data for $[(RO)P(S)S_2]SnCl_2.C_{10}H_8N_2$

S. no.	Compound	Chemical shift (δ, ppm)	
		^{31}P NMR	^{119}Sn NMR
1.	$[MeO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	96.81	270
2.	$[(EtO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	96.84	269
3.	$[(Pr^nO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	96.86	272
4.	$[(Pr^iO)\ P(S)S_2]SnCl_2.C_{10}H_8N_2$	96.85	271
5.	$[(Bu^nO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	96.94	275
6.	$[(Bu^sO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	96.98	274
7.	$[(Bu^iO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	97.10	276
8.	$[(Am^iO)P(S)S_2]SnCl_2.C_{10}H_8N_2$	98.28	279
9.	$[(C.h.O)P(S)S_2]SnCl_2.C_{10}H_8N_2$	98.29	281
10.	$[(Ph.O)P(S)S_2]SnCl_2.C_{10}H_8N_2$	98.49	284

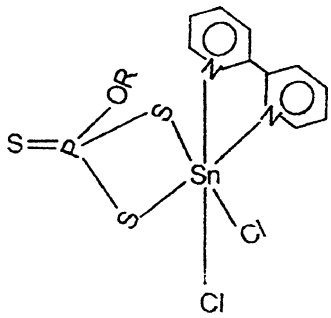

FIGURE 3 Structure of $[(RO)P(S)S_2]SnCl_2.C_{10}H_5N_2$.

^{119}Sn NMR chemical shifts and IR spectral data suggest that in these adducts the tin(IV) is six coordinated. All of the NMR spectral data are summarized in Tables XI and XII. The tentative structure of these adducts is shown in Figure 3.

REFERENCES

[1] R. Verma, V. D. Gupta, and R. C. Mehrotra, *Nat. Acad. Sci. Lett.*, **2,** 130 (1979).
[2] S. K. Saini, V. D. Gupta, and R. C. Mehrotra, *Inorg. Nucl. Chem. Lett.*, **14,** 109 (1978).
[3] S. K. Pandey, G. Srivastava, and R. C. Mehrotra, *Ind. J. Chem.*, **29A,** 339 (1990).
[4] R. Ratnan, G. Srivastava, and R. C. Mehrotra, *Inorg. Chem. Rev.*, **161,** 253 (1989).
[5] R. C. Mehrotra, G. Srivastava, and H. P. S. Chouhan, *Coord. Chem. Rev.*, **55,** 207 (1984).
[6] H. C. Clark, V. K. Jain, R. C. Mehrotra, B. P. Singh, G. Srivastava, T. Birchal, et al. *J. Organomet. Chem.*, **279,** 385 (1985).
[7] B. P. Singh, G. Srivastava, and R. C. Mehrotra, *Synth. React. Inorg. Met -Org. Chem.*, **13,** 963 (1983).
[8] V. I. Derybin Tr. Vses, Nanch. *Issl. Inst. Khlo.*, **28,** 86 (1974).
[9] S. Kishino, A. Shitamatsu, and K. Shiokava, Japan 7600, 179 (C1 A01Nl; C071) (1976).
[10] N. M. Kcxhenvikova and V. S. Mikhailov, *Khim. Sredstva Zashch Rast.*, **5,** 23 (1975).
[11] F. Goro and N. Koichl, *Mokuzai Kenya*, **32,** 15 (1964). *Chem. Asser.*, **65,** 6221 (1916).
[12] K. Kirschbaum, L. Scennighausen, E. Gesing, B. Krebs, G. Z. Henke, and B. Naturforch, *Chem. Sci.*, **45,** 245 (1990).
[13] A. I. Vogel, *Textbook of Quantitative Analysis*, London: ELBS and Longman Group Ltd. (1978).