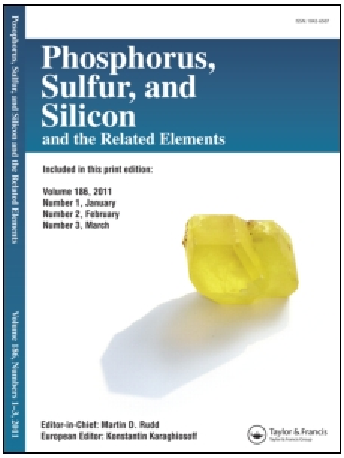

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterizations of Tin(IV)trithiophosphates and Their Adducts With Nitrogen Donor Bases

U. N. Tripathi[a]; D. K. Sharma[b]; Nisha Jain[b]; M. Soni[c]
[a] Department of chemistry, Deen Dayal Upadhyay University, Gorakhpur, (Uttar Pradesh), India [b] Department of Chemistry, Government Arts and Science College, Ratlam, (MP), India [c] Mandsaur Institute of Pharmacy, Mandsaur, (MP), India

To cite this Article Tripathi, U. N. , Sharma, D. K. , Jain, Nisha and Soni, M.(2007) 'Synthesis and Characterizations of Tin(IV)trithiophosphates and Their Adducts With Nitrogen Donor Bases', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 5, 1033 — 1044

To link to this Article: DOI: 10.1080/10426500601091063

URL: http://dx.doi.org/10.1080/10426500601091063

Phosphorus, Sulfur, and Silicon, 182:1033–1044, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500601091063

Synthesis and Characterizations of Tin(IV)trithiophosphates and Their Adducts With Nitrogen Donor Bases

U. N. Tripathi
Department of chemistry, Deen Dayal Upadhyay University, Gorakhpur (Uttar Pradesh), India

D. K. Sharma
Nisha Jain
Department of Chemistry, Government Arts and Science College, Ratlam (MP), India

M. Soni
Mandsaur Institute of Pharmacy, Mandsaur (MP), India

Bis-(trithiophosphato)tin(IV) $[(RO)P(S)S_2]_2Sn$ *(where* $R = n\text{-}C_3H_7, i\text{-}C_3H_7, i\text{-}C_5H_{11}, \text{-}C_6H_{11}, \text{-}C_6H_5$*) were prepared by a reaction of methanolic solution of* $SnCl_4$ *and dipotassium salt of trithiophosphates in a 1:2 molar ratio, and their adducts* $[(RO)P(S)S_2]_2Sn.N_2C_{12}H_8$ *and* $[(RO)P(S)S_2]_2Sn.N_2C_{10}H_8$ *were prepared by a reaction of methanolic solution of* $[(RO)P(S)S_2]_2Sn$ *and N-donor bases in a 1:1 molar ratio. These newly synthesized derivatives have been characterized by elemental analysis; molecular weight measurement; and IR,* ^{13}C, ^{31}P, *and* ^{119}Sn *NMR spectral studies. A coordination number of four and six is suggested for trithiophosphates of tin(IV) and their adducts with N-donor bases, respectively.*

Keywords 1,10-phenanthroline; 2,2′-bipyridyl; phosphorotrithioate; Tin(IV)

INTRODUCTION

In recent years considerable interest has been produced in the chemistry of metallic moieties bonded with sulfur ligands such as thiolates, dithiolates,[1] thio-β-diketonates,[2] dithiocarbamates, and O,O′-alkylene

Received September 11, 2006; accepted October 6, 2006.

We are thankful to the CDRI, Lucknow (India), NCL, Pune (India), RSIC, Banglore (India), and USIC, Delhi University (India), for elemental and spectral analysis of the synthesized compounds.

Address correspondence to U. N. Tripathi, Department of Chemistry, DDU University, Gorakhpur (UP), India. E-mail: un_tripathi@yahoo. com

dithiophosphates[3–5] Some mono-; di-, and tri-organo tin (IV) derivatives of dialkyl dithiophosphates have been synthesized and characterized by ^{13}C, ^{31}P, and ^{119}Sn NMR and mossbauer spectral studies. The ^{119}Sn NMR chemical shift and [^{1} J(^{119}Sn-^{13}C)] and [^{2} J(^{119}Sn-^{1}H)] of triorgano tin(IV) dialkyl dithiophosphates are consistent with tetrahedral geometry and four-coordinated Sn, although a mossbauer study indicates five-coordinated tin in a solid state. These studies also reveal that in mono-, and di-organo tin(IV) dithiophosphates, the Sn atom is weakly coordinated to ligand.[6,7] Organic trithiophosphates esters have been used as defoliants,[8] insecticides[8,9] and nematodicidal[9] and inhibitors[10] of steel corrosion. Potassium trithiophosphates exist in two isomeric forms.

$$[(RO)P(S)S_2]\,K_2 \longleftrightarrow [(RS)P(O)S_2]\,K_2 \qquad (1)$$

The persual of literature revealed only a few publications on the metallic ester of trithiophosphoric acid[11,12] and trithiophosphates of tin(IV) moieties.[13] Hence it was thought worthwhile to study the trithiophosphato of tin (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 half an hour 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 compound and adducts described in this article were synthesized by the following general routes.

Synthesis of $[(RO)P(S)S_2]_2Sn$

A methanolic solution (15 mL) of tetrachorotin(IV) and a methanolic solution of dipotassium salt of trithiophosphates were mixed and refluxed for 10–12 h. The reaction was carried out in a 1:2 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 volatiles under reduced pressure. Complex numbers 1–5 were prepared by the same procedure. The analytical results are summarized in Table I.

Synthesis of $[(RO)P(S)S_2]_2Sn.\ N_2C_{12}H_8$ and $[(RO)P(S)S_2]_2$ $Sn.N_2C_{10}H_8$

A methanolic solution (5 mL) of bis-(trithiophosphato)tin(IV) and a methanolic solution of 1,10-phenanthroline were mixed and stirred for

TABLE I Synthetic and Analytical Data for $[(RO)P(S)S_2]_2Sn$

						Analysis % Found/(Calcd.)				
S. No.	Reactants (in g,mmoles)	Molar ratio	Product (in g)	Yield (%)	State	C	H	S	Sn	$SnCl_4$
	$[(RO)P(S)S_2]K_2$		$[(RO)P(S)S_2]_2Sn$							
1.	$[n(C_3H_7O)P(S)S_2]K_2$ 1.51,5.70	1:2	$[n(C_3H_7O)P(S)S_2]_2Sn$ 0.57	92	Yellow Solid	14.48 (14.66)	2.62 (2.87)	38.14 (39.15)	23.92 (24.15)	0.33,2.85
2.	$[i(C_3H_7O)P(S)S_2]K_2$ 1.51,5.70	1:2	$[i(C_3H_7O)P(S)S_2]_2Sn$ 1.58	93	“”	14.40 (14.66)	2.60 (2.87)	38.90 (39.15)	23.90 (24.15)	0.33,2.85
3.	$[i(C_5H_{11}O)P(S)S_2]K_2$ 1.51,5.1	1:2	$[i(C_5H_{11}O)P(S)S_2]_2Sn$ 0.56	90	“”	21.67 (21.94)	3.88 (4.05)	34.90 (35.15)	21.40 (21.68)	0.30,2.55
4.	$[(C_6H_{11}O)P(S)S_2]K_2$ 1.51,4.90	1:2	$[(C_6H_{11}O)P(S)S_2]_2Sn$ 0.58	92	“”	25.08 (25.22)	3.60 (3.88)	33.50 (33.66)	20.50 (20.76)	0.29,2.45
5.	$[(C_6H_5O)P(S)S_2]K_2$ 1.51,5.0	1:2	$[s(C_6H_5O)P(S)S_2]_2Sn$ 0.56	90	“”	25.40 (25.76)	1.50 (1.81)	34.10 (34.39)	20.99 (21.21)	0.29,2.50

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. Adducts numbers 6–10 were prepared by this same procedure. The adducts with 2,2′-bipyridyl (11–15) were prepared by this same procedure. The analytical results are summarized in Table II.

MEASUREMENTS

IR spectra were recorded in nujol mulls using CsI 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 was measured for Sn and S and were carried out by standard procedure.[14] Carbon, hydrogen, and nitrogen were estimated by coleman C.H.N. analyzers.

RESULT AND DISCUSSION

$[(RO)P(S)S_2]_2Sn$

Bis-(trithiophosphato)tin(IV) are a yellow solid and sparingly soluble in common organic (benzene, dichoromethane, chloroform, etc.) and coordinating (DMF, DMSO, THF, etc.) solvents. The complexes are unstable at r.t. and tend to decompose, even under a closed environment. Decomposition is rather slow when these compounds are stored in a dry atmosphere at a low temperature. Decomposition is marked by the color change from yellow to brown. Molecular weight measurements could not be done due to the polymeric nature of the compounds.

IR Spectra

In the IR spectrum the bands observed in the region 1043–1068 and 850–868 cm^{-1} have been assigned to ν[(P)-O-C] and [P-O-(C)], respectively. The ν[P=S] mode may be characterized by the presence of band in the region 642–660 cm^{-1} indicating the bidentate nature of trithiophosphate ligand. The band present in the region 593–609 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 360–375 cm^{-1} indicates the formation of a [Sn—S] bond. The IR spectral data of ligands and deirvatives are summarized in Table III.

NMR Spectra

The ^{13}C resonance for the carbon atom of the P-O-C group appears as doublet due to coupling with ^{31}P nuclei. In the proton decoupled

TABLE II Synthetic and Analytical Data for $[(RO)P(S)S_2]Sn{\cdot}C_{12}H_8N_2$ and $[(RO)P(S)S_2]Sn{\cdot}C_{10}H_8N_2$

						Analysis (%) Found/(Calcd.)					
S. No.	Reactants (in g, mmoles)	Molar ratio	Product (in g)	Yield (%)	Mol. Wt. Found/(Calcd.)	C	H	N	S	Sn	And $C_{10}H_8N_2$
	$C_{12}H_8N_2[(RO)P(S)S_2]_2Sn$		$[(RO)P(S)S_2]_2Sn{\cdot}C_{12}H_8N_2$								
1.	$[n(C_3H_7O)P(S)S_2]_2Sn$	1:1	$[n(C_3H_7O)P(S)S_2]_2Sn{\cdot}C_{12}H_8N_2$	99	640.42	31.90	3.12	4.00	28.33	17.51	2.72
	1,5.55		3.68			(647.32)	(32.19)	(3.30)	(4.17)	(28.65)	(17.67)
2.	$[i((C_3H_7O)P(S)S_2]_2Sn$	1:1	$[i((C_3H_7O)P(S)S_2]_2Sn{\cdot}C_{12}H_8N_2$	99	639.24	31.88	3.24	4.00	28.35	17.50	3.03
	1,5.55		3.68			(647.32)	(32.19)	(3.30)	(4.17)	(28.65)	(17.67)
3.	$[i(C_5H_{11}O)P(S)S_2]_2Sn$	1:1	$[i(C_5H_{11}O)P(S)S_2]_2Sn{\cdot}C_{12}H_8N$	98	695.70	36.10	4.00	3.60	26.20	16.29	2.54
	1,5.55		3.94			(703.28)	(36.32)	(4.15)	(3.85)	(26.44)	(16.31)
4.	$[(C_6H_{11}O)P(S)S_2]_2Sn$	1:1	$[(C_6H_{11}O)P(S)S_2]_2Sn{\cdot}C_{12}H_8N_2$	99	719.34	38.16	3.86	3.52	25.23	15.68	3.17
	1,5.55		4.12			(727.45)	(38.35)	(4.02)	(3.72)	(25.59)	(15.79)
5.	$[(C_6H_5O)P(S)S_2]_2Sn$	1:1	$[(C_6H_5O)P(S)S_2]_2Sn{\cdot}C_{12}H_8N_2$	99	708.86	38.60	2.20	3.50	25.84	15.90	3.10
	1,5.55		4.05			(715.35)	(38.97)	(2.45)	(3.78)	(26.00)	(16.04)
6.	$[n(C_3H_7O)P(S)S_2]_2Sn$	1:1	$[n(C_3H_7O)P(S)S_2]_2Sn{\cdot}C_{10}H_8N$	97	662.34	29.40	3.18	4.12	29.50	18.27	3.14
	1,6.40		3.97			(671.53)	(29.67)	(3.42)	(4.32)	(29.71)	(18.33)
7.	$[i(C_3H_7O)P(S)S_2]_2Sn$	1:1	$[i(C_3H_7O)P(S)S_2]_2Sn{\cdot}C_{10}H_8N_2$	98	661.43	29.41	3.19	4.10	29.50	18.28	3.14
0	1,6.40		4.01			(671.53)	(29.67)	(3.42)	(4.32)	(29.71)	(18.33)
8.	$[i(C_5H_{11}O)P(S)S_2]_2Sn$	1:1	$[i(C_5H_{11}O)P(S)S_2]_2Sn{\cdot}C_{10}H_8N$	98	720.66	32.60	3.88	3.61	26.10	16.18	3.67
	1,6.40		4.57			(727.49)	(32.88)	(4.13)	(3.83)	(26.33)	(16.24)
9.	$[(C_6H_{11}O)P(S)S_2]_2Sn$	1:1	$[(C_6H_{11}O)P(S)S_2]_2Sn{\cdot}C_{10}H_8N_2$	97	742.26	36.10	2.84	3.59	22.10	16.10	3.65
	1,6.40		4.51			(751.64)	(36.31)	(3.04)	(3.85)	(22.31)	(16.31)
10.	$[(C_6H_5O)P(S)S_2]_2Sn$	1:1	$[(C_6H_5O)P(S)S_2]_2Sn{\cdot}C_{10}H_8N_2$	97	729.78	36.62	2.28	3.70	26.50	16.33	3.58
	1,6.40		4.44			(739.56)	(36.92)	(2.53)	(3.91)	(26.88)	(16.58)

TABLE III IR Spectral Data (cm^{-1}) for[(RO)P(S)S_2]K_2 and [(RO)P(S)S_2]$_2$Sn

S. No.	Compound	ν[(P)-O-C]	ν[P-O-(C)]	ν[P=S]	ν[P–S]	ν[Sn–S]
1.	[(Pr^{n}O) P(S)S_2]$_2$Sn	$1012_{(s)}$	$816_{(s)}$	$643_{(m)}$	$437_{(m)}$	–
2.	[(Pr^{i}O) P(S)S_2]$_2$Sn	$1009_{(s)}$	$810_{(s)}$	$640_{(m)}$	$441_{(m)}$	–
3.	[(Am^{i}O) P(S)S_2]$_2$Sn	$1012_{(s)}$	$812_{(s)}$	$648_{(m)}$	$439_{(m)}$	–
4.	[(C. h. O) P(S)S_2]$_2$Sn	$1013_{(s)}$	$841_{(s)}$	$644_{(m)}$	$445_{(m)}$	–
5.	[(PhO) P(S)S_2]$_2$Sn	$1011_{(s)}$	$800_{(s)}$	$640_{(m)}$	$443_{(m)}$	–
6.	[(Pr^{n}O) P(S)S_2]$_2$Sn	$1046_{(s)}$	$855_{(s)}$	$650_{(m)}$	$598_{(m)}$	$366_{(w)}$
7.	[(Pr^{i}O) P(S)S_2]$_2$Sn	$1043_{(s)}$	$850_{(s)}$	$642_{(m)}$	$593_{(m)}$	$360_{(w)}$
8.	[(Am^{i}O) P(S)S_2]$_2$Sn	$1068_{(s)}$	$868_{(s)}$	$660_{(m)}$	$609_{(m)}$	$375_{(w)}$
9.	[(C. h. O) P(S)S_2]$_2$Sn	$1066_{(s)}$	$865_{(s)}$	$655_{(m)}$	$605_{(m)}$	$373_{(w)}$
10.	[(PhO) P(S)S_2]$_2$Sn	$1062_{(s)}$	$853_{(s)}$	$651_{(m)}$	$601_{(m)}$	$370_{(w)}$

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

^{31}P NMR spectra, only one resonance for each compound in the range 96.28–97.49 ppm is obtained. In ^{119}Sn NMR spectra the ^{119}Sn NMR chemical shifts of all the compounds have been observed in the range 250–272 ppm. These ^{119}Sn NMR chemical shifts suggest that in compound numbers 1–5 the tin(IV) is four coordinated.[14] The NMR spectral data are summarized in Tables IV and V. In solid state studies such as IR the polymeric nature was obtained, but in solution, which is quite difficult to form (under drastic conditions), the polymeric nature may be reduced to a monomeric nature, hence the coordination number decreases to four. The tentative structure is shown in Figure 1.

[(RO)P(S)S_2]$_2$Sn.$N_2C_{12}H_8$ ($C_{12}H_8N_2$ = 1,10-phenanthroline)

All the adducts are a 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 r.t. The molecular weight measurment indicates a

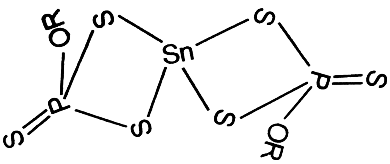

FIGURE 1 Structure of [(RO)P(S)S_2]$_2$Sn.

TABLE IV ^{13}C NMR Spectral data (δ, ppm) for $[(RO)P(S)S_2]_2Sn$

S. No.	Compound	$S_2(S)P(OR)$ Carbons	Chemical shift (δ, ppm)
1.	$[(Pr^nO)P(S)S_2]_2Sn$	72.92, d, C; $^2J_{P-}$	C = 30 cps
	24.65, C_2	15.49, C_3	
2.	$[(Pr^iO)P(S)S_2]_2Sn$	68.78, d, C; $^2J_{P-}$	C = 30 cps
	24.84, C_2		
3.	$[(Am^iO)P(S)S_2]_2Sn$	63.80, d, C; $^2J_{P-}$	C = 33 cps
	42.48, C_2		
	27.75, C_3		
	25.68, C_4		
4.	$[(C.\ h.\ O)P(S)S_2]_2Sn$	73.72, d, C; $^2J_{P-}$	C = 354 cps
	33.88, $C_{2,6}$		
	29.98, $C_{3,5}$		
	29.08, C_4		
5.	$[(PhO)P(S)S_2]_2Sn$	161.52, d, C; $^2J_{P-}$	C = 450 cps
	119.48, $C_{2,6}$		
	134.52, $C_{3,5}$		
	125.78, C_4		

monomeric nature of these adducts in diluted chloroform solution at 45°C.

IR Spectra

In the IR spectrum the bands observed in the region 1042–1065 cm^{-1} and 842–856 cm^{-1} have been assigned to ν[(P)-O-C] and [P-O-(C)], respectively. The ν [P=S] mode may be characterized by the presence of a band in the region 639–652 cm^{-1}, which is quite similar to the ligand's P=S stretching mode, indicating the bidentate nature of trithiophosphate ligand, this also shows that there is no interaction of P=S to the metal. The band present in the region 592–596 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 359–372 cm^{-1}, indicates

TABLE V ^{31}P and ^{119}Sn NMR Spectral Data (δ, ppm) for $[(RO)P(S)S_2]_2Sn$

S. no.	^{119}Sn NMR	Compound	^{31}P NMR
1.	250	$[(Pr^nO)P(S)S_2]_2Sn$	96.28
2.	252	$[(Pr^iO)P(S)S_2]_2Sn$	96.38
3.	268	$[(Am^iO)P(S)S_2]_2Sn$	96.29
4.	269	$[(C.\ hO)P(S)S_2]_2Sn$	97.28
5.	272	$[(PhO)P(S)S_2]_2Sn$	97.49

TABLE VI IR Spectral Data (cm-1) for $[(RO)P(S)S_2]_2Sn.C_{12}H_8N_2$ and $[(RO)P(S)S_2]_2Sn.C_{10}H_8N_2$

S. no.	Compound	ν[(P)-O-C]	ν[P-O-(C)]	ν[P=S]	ν[P=S]	ν[Sn-S]	ν[Sn—N]	ν[C—N]
1.	$[(Pr^nO)P(S)S_2]_2Sn.C_{12}H_8N_2$	$1048_{(s)}$	$842_{(s)}$	$639_{(m)}$	$592_{(m)}$	$361_{(w)}$	$385_{(w)}$	$1592_{(s)}$
2.	$[(Pr^iO)P(S)S_2]_2Sn.C_{12}H_8N_2$	$1042_{(s)}$	$845_{(s)}$	$640_{(m)}$	$596_{(m)}$	$359_{(w)}$	$383_{(w)}$	$1591_{(s)}$
3.	$[(Am^iO)P(S)S_2]_2Sn.C_{12}H_8N_2$	$1065_{(s)}$	$856_{(s)}$	$650_{(m)}$	$593_{(m)}$	$372_{(w)}$	$397_{(w)}$	$1605_{(s)}$
4.	$[(C.\ h.\ O)P(S)S_2]_2Sn.C_{12}H_8N_2$	$1063_{(s)}$	$852_{(s)}$	$652_{(m)}$	$592_{(m)}$	$369_{(w)}$	$391_{(w)}$	$1601_{(s)}$
5.	$[(PhO)P(S)S_2]_2Sn.C_{12}H_8N_2$	$1059_{(s)}$	$847_{(s)}$	$645_{(m)}$	$588_{(m)}$	$366_{(w)}$	$384_{(w)}$	$1588_{(s)}$
6.	$[(Pr^nO)P(S)S_2]_2Sn.C_{10}H_8N_2$	$1049_{(s)}$	$844_{(s)}$	$638_{(m)}$	$594_{(m)}$	$365_{(w)}$	$388_{(w)}$	$1598_{(s)}$
7.	$[(Pr^iO)P(S)S_2]_2Sn.C_{10}H_8N_2$	$1041_{(s)}$	$843_{(s)}$	$640_{(m)}$	$592_{(m)}$	$360_{(w)}$	$384_{(w)}$	$1595_{(s)}$
8.	$[(Am^iO)P(S)S_2]_2Sn.C_{10}H_8N_2$	$1067_{(s)}$	$858_{(s)}$	$648_{(m)}$	$599_{(m)}$	$370_{(w)}$	$394_{(w)}$	$1615_{(s)}$
9.	$[(C.\ h.\ O)P(S)S_2]_2Sn.C_{10}H_8N_2$	$1064_{(s)}$	$853_{(s)}$	$645_{(m)}$	$597_{(m)}$	$368_{(w)}$	$393_{(w)}$	$1609_{(s)}$
10.	$[(PhO)P(S)S_2]_2Sn.C_{10}H_8N_2$	$1057_{(s)}$	$849_{(s)}$	$642_{(m)}$	$590_{(m)}$	$364_{(w)}$	$392_{(w)}$	$1606_{(s)}$

^{s}Strong
^{m}Medium
^{w}Week

TABLE VII ^{13}C NMR Spectral Data (δ, ppm) for $[(RO)P(S)S_2]_2Sn.C_{12}H_8N_2$ and $[(RO)P(S)S_2]_2Sn.C_{10}H_8N_2$

S. No.	Compound	$S_2(S)P(OR)$ carbons	$C_{12}H_8N_2$ carbons
1.	$[(Pr^no)P(S)S_2]_2Sn.C_{12}H_8N_2$	69.89, d, C; $^2J_{P-C} = 90$ cps 23.68, C_2 10.46, C_3	131.44,C_2; 121.52,C_3; 126.12, C_4; 125.29, C_5; 150.82, C_6.
2.	$[(Pr^io)P(S)S_2]_2Sn.C_{12}H_8N_2$	69.98, d, C; $^2J_{P-C} = 63$ cps 22.70, C_2	129.62, C_2; 127.84, C_3; 122.85, C_4; 128.45, C_5; 152.62, C_6.
3.	$[(Am^io)P(S)S_2]_2Sn.C_{12}H_8N_2$	63.99, d, C; $^2J_{P-C} = 24$ cps 39.54, C_2 23.18, C_3; 21. 89, C_4	134.82, C_2; 125.23, C_3; 123.84, C_4; 128.26, C_5; 152.90, C_6.
4.	$[(C. h.^io)P(S)S_2]_2Sn.C_{12}H_8N_2$	73.91, d, C; $^2J_{P-C} = 342$ cps 31.80, $C_{2,6}$ 24.42, $C_{3,5}$; 25.92, C_4	136.94, C_2; 127.24, C_3; 126.82, C_4; 130.02, C_5; 152.18, C_6.
5.	$[(Pho)P(S)S_2]_2Sn.C_{12}H_8N_2$	156.60, d, C; $^2J_{P-C} = 438$ cps 112.41, $C_{2,6}$ 125.72, $C_{3,5}$116.84, C_4	137. 26, C_2; 127.25, C_3; 124.64, C_4; 129.04, C_5; 150. 09, C_6
6.	$[(Pr^no)P(S)S_2]_2Sn.C_{10}H_8N_2$	69.88, d, C; $^2J_{P-C} = 90$ cps 23.62, C_2 10.41, C_3	131.48, C_2; 121.58, C_3; 126.18, C_4; 125.30, C_5; 150.84, C_6.
7.	$[(Pr^io)P(S)S_2]_2Sn.C_{10}H_8N_2$	69.92,d, C; $^2J_{P-C} = 63$ cps 22.71, C_2	129.68, C_2; 127.88, C_3; 122.86, C_4; 128.48, C_5; 152.65, C_6.
8.	$[(Am^io)P(S)S_2]_2Sn.C_{10}H_8N_2$	63.89, d, C; $^2J_{P-C} = 24$ cps 39.52,C_2 23.19, $C_{3;}$ 21. 84, C_4	134.92, C_2; 125.33, C_3; 123.94, C_4;128.36, C_5; 152.98, C_6
9.	$[(C. h. o)P(S)S_2]_2Sn.C_{10}H_8N_2$	73.90,d, C; $^2J_{P-C} = 342$ cps 31.81,$C_{2,6}$ 24.45, $C_{3,5;}$25.90, C_4	136.96, C_2; 127.28, C_3; 126.92, C_4; 130.12, C_5; 152.28, C_6.
10.	$[(Pho)P(S)S_2]_2Sn.C_{10}H_8N_2$	156.68,d,C;$^2J_{P-C} = 438$ cps 112.42,$C_{2,6}$ 125.74, $C_{3,5}$; 116.86, C_4	137. 36, C_2; 127.35, C_3; 124.74, C_4; 129.14, C_5; 150. 19, C_6

the formation of ν[Sn—S] bond.[16,17] The band present in the region 383–397 cm^{-1} may be ascribed to ν[Sn—N] stretching mode.[16,18] The ν[C=N] bond band was found in the region 1591–1605 cm^{-1}. The IR spectral data are summarized in Table VI.

NMR Spectra

The ^{13}C NMR spectra of the adducts is quite similar to the parental compounds; only slight differences have 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 adduct in the range 95.85–98.29 ppm was obtained. In ^{119}Sn NMR spectra the ^{119}Sn NMR chemical shifts of all the adducts have been observed in the range at 269–281 ppm. These

TABLE VIII ^{31}P and ^{119}Sn NMR Spectral Data (δ,ppm) for $[(RO)P(S)S_2]_2Sn.C_{12}H_8N_2$ and $[(RO)P(S)S_2]_2Sn.C_{10}H_8N_2$

S. no.	Compound	^{31}P NMR	^{119}Sn NMR
1.	$[(Pr^nO)P(S)S_2]_2Sn.C_{12}H_8N_2$	95.86	270
2.	$[(Pr^iO)P(S)S_2]_2Sn.C_{12}H_8N_2$	95.85	269
3.	$[(Am^iO)P(S)S_2]_2Sn.C_{12}H_8N_2$	98.28	278
4.	$[(C.\ h.\ O)P(S)S_2]_2Sn.C_{12}H_8N_2$	98.29	279
5.	$[(PhO)P(S)S_2]_2Sn.C_{12}H_8N_2$	97.49	281
6.	$[(Pr^nO)P(S)S_2]_2Sn.C_{10}H_8N_2$	95.68	269
7.	$[(Pr^iO)P(S)S_2]_2Sn.C_{10}H_8N_2$	95.58	270
8.	$[(Am^iO)P(S)S_2]_2Sn.C_{10}H_8N_2$	98.82	277
9.	$[(C.\ h.\ O)P(S)S_2]_2Sn.C_{10}H_8N_2$	98.92	278
10.	$[(PhO)P(S)S_2]_2Sn.C_{10}H_8N_2$	98.94	282

$n\text{-}C_3H_7 = \overset{3}{C}H_3\text{-}\overset{2}{C}H_2\text{-}\overset{1}{C}H_2\text{-};iso\text{-}C_3H_7 = (\overset{2}{C}H_3)_2\text{-}\overset{1}{C}H\text{-};iso\text{-}C_5H_{11} = (\overset{4}{C}H_3)_2\text{-}\overset{3}{C}H\text{-}\overset{2}{C}H_2\text{-}\overset{1}{C}H_2\text{-}.$

^{119}Sn NMR chemical shifts and IR spectral data suggest that in these adducts the tin (IV) is six coordinated.[17] The NMR spectral data are summarized in Tables VII and VIII. The tentative structure of these adducts is shown in Figure II.

$[(RO)P(S)\ S_2]_2Sn.N_2C_{10}H_8(C_{10}H_8N_2 = 2,2'\text{-bipyridyl})$

IR Spectra

In the IR spectrum the bands observed in the region 1041–1067 cm^{-1} and 843–858 cm^{-1} have been assigned to ν[(P)-O-C] and [P-O-(C)], respectively. The ν[P=S] mode may be characterized by the presence of a band in the region 638–648 cm^{-1} indicating the bidentate nature of trithiophosphate ligand. The band present in the region 592–599 cm^{-1} may be ascribed to ν[P—S] stretching mode. The appearance of a new

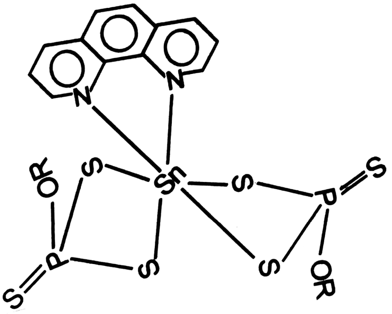

FIGURE 2 Structure of $[(RO)P(S)S_2]_2Sn.C_{12}H_8N_2$.

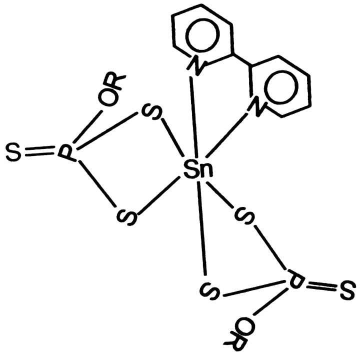

FIGURE 3 Structure of $[(RO)P(S)S_2]_2Sn.C_{10}H_8N_2$.

band (in comparison to a free ligand) in the region 360–370 cm^{-1} indicates the formation of ν[Sn—S] bond.[16,17] The band present in the region 383–397 cm^{-1} may be ascribed to ν[Sn—N] stretching mode.[16,18] The ν[C=N] bond band was found in the region 1595–1615 cm^{-1}. The IR spectral data are summarized in Table VI.

NMR Spectra

The ^{13}C NMR spectra of the adducts is quite similar to the parental compounds; only slight differences have 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 adduct in the range 95.58–98.94 ppm is obtained. In ^{119}Sn NMR chemical shifts, NMR chemical shifts of all the adducts have been observed in the range 269–282 ppm. These ^{119}Sn NMR chemical shifts and IR spectral data suggest that in these adducts the tin(IV) is six coordinated.[17] The NMR spectral data are summarized in Tables VII and VIII. The tentative structure of these adducts is shown in Figure 3.

CONCLUSION

On the basis of IR, NMR, elemental analysis, and molecular weight measurements, the various coordination numbers of tin and varying modes of bonding of the ligand have been established.

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. Ratnani, G. Srivastava, and R. C. Mehrotra, *Inorg. Acta,* **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, and T. Birchall, *J. Organomet. chem.*, **279,** 385 (1985).
[7] B. P. Singh, G. Srivastava, and R. C. Mehrotra, *Synth. React. In Met-Org. Chem.*, **19,** 963–976 (1983).
[8] V. I. Derybin and T. Vses, *Nanch. Issi. Inst. Khlo.*, **28,** 86, 93 (1974).
[9] S. Kishino, A. Shitamatsu, and K. Shiokava, Japan 7600,*179,*($C1A01N; C07F$) (1976).
[10] N. M. Koxhenvikova and V. S. Mikhaolav, *Khim. Sredstva. Zashch. Rast.*, **5,** 43–45 (1975).
[11] F. Goro and N. Koichi, *Kenya Mokuzai,* **32**, 15 (1964); *Chem Abstr.* **65,** 6221n (1916),
[12] K. Kirschbaum, U. Boennighausen, E. Gesing, B. Krebs, G. Hendel, and Z. Naturforsch. *Chem. Sc.*, **45,** 245 (1990)
[13] U. N. Tripathi and D. K. Sharma, *Main Group Metal Chem.*, **27,** 135—144 (2004).
[14] A. I. Vogel, *Textbook of Quantitative Analysis*, ELBS and Longman Group Ltd, London (1978).
[15] T. N. Srivastava, M. A. Siddiqi, and S. K. Srivastava, *Indian J. Chem. Sec. A.*, **26,** 267(1987).
[16] I. R. Beattie, *Quart Revs.*, **17382** (1963).
[17] H. D. Yin, C. H. Wang, Y. Wang, R. F. Zhang, and C. L. Ma, *WujiaxueXuebao*, **18,** 201–204 (2002); *Chem. Abstr.,* **136,** 340762p (2002).
[18] I. Wharf, R.Wojtowski, and M. Onyszchuk, *J. Indian Chem. Soc.*, **62,** 800–804 (1985).