

## Molecular adducts of some triphenyltin(IV) *O,O'*-alkylene dithiophosphates

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The interactions of triphenyltin(IV) *O,O'*-alkylenedithiophosphates, [(X<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnS(S)POGO], (G = -CH<sub>2</sub>C(H)-CH<sub>3</sub>, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>- and -C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>C-) with various N, O and S donor Lewis bases have yielded new stable molecular adducts. The results suggest the presence of five- and six-coordinated tin atom in case of unidentate and bidentate Lewis bases, respectively.

In continuation of our earlier work on the synthesis and reactivity of organometal *O,O'*-alkylenedithiophosphates (dtp)<sup>1,2</sup>, we now report the reactivity of triphenyltin(IV) *O,O'*-alkylenedithiophosphates with several Lewis bases, such as dimethylsulfoxide (DMSO), dimethyl-formamide (DMF), 2,6-lutidine-*N*-oxide (2,6-Lut-O), 1-methyl-2-pyrrolidinone (1-Me-2-pyrr), triphenylphosphine oxide (TPPO), dimethyl acetamide (DMA), antipyrine (ap), thiourea (Tu), triphenylphosphine sulfide (TPPS), tetramethylthiuramdisulfide, (Me<sub>4</sub>tds), 1,10-phenanthroline (*o*-phen) and 2,2'-bipyridyl (2,2'-bipy).

### Results and discussion

The analytical data (Table 1) correspond to 1 : 1 (metal dtp : base) stoichiometry. The adducts are crystalline solid, thermally stable at room temperature and unaffected by atmospheric oxygen and moisture. They are soluble in common organic solvents. The adducts are non-conducting in nitrobenzene (1.86–3.96 Ω<sup>-1</sup> cm<sup>-1</sup> mol<sup>-1</sup>), indicating the absence of ionic species in solution.

In the IR spectra of the molecular adducts, the bands due to the ν<sub>(P)-O-C</sub>, ν<sub>P-O-(C)</sub> and ν<sub>P=S</sub> identified at 1070 ± 2, 851 ± 1 and 700 ± 2 cm<sup>-1</sup>, respectively, in the parent triphenyltin *O,O'*-alkylenedithiophosphate<sup>2</sup>, have consistently been observed in almost the same regions. The absorption due to ν<sub>P-S</sub> shows a positive shift and appears at 560 ± 2 cm<sup>-1</sup> in the molecular adducts. Two weak intensity bands are observed at 410 (Sn-S)<sup>3</sup> and 265 ± 5 cm<sup>-1</sup> (Sn-Ph)<sup>4</sup>.

**N-Donors** : The ν<sub>C=N</sub> modes appearing at 1569 ± 9 cm<sup>-1</sup> in free *o*-phen and 2,2'-bipy<sup>5</sup> undergo positive shifts and are located at 1587 ± 5 cm<sup>-1</sup> in the corresponding adducts, suggesting the presence of coordinated bases.

**O-Donors** : A considerable shift of ν<sub>C=O</sub> stretching mode from 1649 ± 17 cm<sup>-1</sup> in various free bases<sup>5</sup> to a lower frequency 1623 ± 3 cm<sup>-1</sup> in case of the adducts, indicates coordination through the carbonyl oxygen. In the far-IR spectra, ν<sub>Sn←N</sub> is identified at 388 cm<sup>-1</sup> which is close to a reported value<sup>5</sup>. Absorptions of strong intensity for ν<sub>S=O</sub>, ν<sub>P=O</sub> and ν<sub>N=O</sub> at 1045, 1195 and 1245 cm<sup>-1</sup> respectively in the spectra of the free ligand<sup>5</sup> undergo negative shifts on complexation. The corresponding absorption in the spectra of the adducts appear at 982 ± 3, 1145 and 1209 ± 1 cm<sup>-1</sup>, suggesting coordination from oxygen atom of the bases. A band at 342 ± 6 cm<sup>-1</sup> is assigned to ν<sub>Sn←O</sub> mode of vibration.

**S-Donors** : In the spectra of the sulfur donor ligands, such as Me<sub>4</sub>tds and Tu, the ν<sub>C=S</sub> appearing at 988 and 1090 cm<sup>-1</sup>, respectively, undergo shift to lower wavenumbers on complexation and appear at 982 and 1082 cm<sup>-1</sup>, respectively, in the adducts. These observations indicate coordination through S atom of the linear thiuramdisulfide chain in case of Me<sub>4</sub>tds and Sn←S bonding<sup>5</sup> in the case of Tu. TPPS coordinates through its S-atom, is evident from the negative shift of ν<sub>P=S</sub> from 637 cm<sup>-1</sup> in the free base to 630 cm<sup>-1</sup> in adducts<sup>6</sup>.

In the <sup>1</sup>H NMR spectra of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnS(S)POC(CH<sub>3</sub>)<sub>2</sub>-(CH<sub>3</sub>)<sub>2</sub>CO].DMF and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnS(S)POCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>O].DMSO, the characteristic proton signals due to aryl group of Lewis acid are almost unaffected and appear at δ 8.43–7.34 (m), whereas the signals due to O-CH<sub>2</sub>, CH<sub>2</sub> and CH<sub>3</sub> shift to high field and appear at δ 4.04–4.01, 3.40–3.36 and 1.47, respectively, indicating considerable drift of electrons from Lewis base to the metal atom.

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Table I. Analytical data of  $[(C_6H_5)_3Sn(S)POGO].L^*$ 

L	M.p. °C	G = -CH <sub>2</sub> C(H)-CH <sub>3</sub>		G = -C(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> C-		M.p. °C	G = -CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> -		
		Sn%		Sn%			Sn%		
		Found	(Calcd.)	Found	(Calcd.)		Found	(Calcd.)	
DMSO	104	19.86	(19.87)	96	18.58	(18.57)	108	18.97	(18.99)
DMF	108	20.03	(20.04)	92	18.70	(18.72)	96	19.15	(19.14)
2,6-Lut-O	222	18.50	(18.49)	102	17.36	(17.35)	110	17.70	(17.71)
1-Me-2-pyrr	96	19.19	(19.20)	102	17.96	(17.98)	86	18.38	(18.37)
TPPO	102	14.90	(14.88)	97	14.16	(14.15)	78	14.36	(14.38)
DMA	104	19.60	(19.58)	120	18.32	(18.31)	100	18.71	(18.72)
ap	108	16.75	(16.77)	98	15.86	(15.84)	110	16.16	(16.15)
Tu	157	19.94	(19.93)	165	18.61	(18.63)	175	19.04	(19.05)
TPPS	140	14.58	(14.59)	122	13.90	(13.88)	134	14.12	(14.11)
Me <sub>4</sub> tds	120	15.66	(15.64)	108	14.80	(14.82)	112	15.10	(15.08)
<i>o</i> -Phen	112	16.98	(16.97)	108	16.03	(16.01)	98	16.31	(16.32)
2,2'-bipy	122	17.55	(17.57)	112	16.56	(16.55)	103	16.90	(16.88)

\* All compounds gave satisfactory S analysis.

The spectra of  $[(C_6H_5)_3Sn(S)POC(CH_3)_2-(CH_3)_2CO].-$  DMF and  $[(C_6H_5)_3Sn(S)POCH_2(CH_2)_3CH_2O].DMSO$  show a singlet at  $\delta$  2.54 and 2.32, respectively, which is attributed to methyl protons of Lewis base. The positions and integrations of the peaks are consistent with the proposed stoichiometry of the adducts.

On the basis of the foregoing discussion it is proposed that tin atom in the molecular adducts triphenyltin(IV) *O,O'*-alkylenedithiophosphate.L,  $[(C_6H_5)_3Sn(S)POGO].L$  (L = unidentate base), is five-coordinated while it is six-coordinated in  $[(C_6H_5)_3Sn(S)POGO].L$  (L = bidentate base).

### Experimental

$[(C_6H_5)_3Sn(S)POCH_2(CH_2)_3CH_2O]$ ,  $[(C_6H_5)_3Sn(S)-POCH_2C(H)O-CH_3]$  and  $[(C_6H_5)_3Sn(S)-$

$PO(CH_3)_2C.C(CH_3)_2O]$  were synthesized as reported earlier<sup>2</sup>. The Lewis bases were obtained from B.D.H., Eastman and Aldrich. The molar conductance was measured using a dip-type conductivity cell on a Decible DC 610 conductivity meter in anhydrous DMSO. IR spectra (KBr/CsI) were recorded on a Perkin-Elmer 883 and 1800 FTIR spectrophotometers and <sup>1</sup>H NMR spectra (DMSO-*d*<sub>6</sub>) on a Bruker WM-400 FT NMR spectrometer using TMS as internal standard.

The molecular adducts were prepared by the direct interaction of Lewis bases with triphenyltin *O,O'*-alkylenedithiophosphate in suitable solvent. In a representative ex-

periment, a solution of 1,10-phenanthroline (0.18 g, 0.001 mol) in acetone (15 ml) was added dropwise to a solution of triphenyltin tetramethylethylenedithiophosphate (0.562 g, 0.001 mol) in the same solvent (15 ml). The reaction mixture was refluxed on a water-bath for ~4 h. The excess solvent was then distilled off and the desired product was obtained by adding pet. ether (b.p. 60–80°). The precipitate was filtered, washed with pet. ether and diethyl ether and dried over P<sub>2</sub>O<sub>5</sub> *in vacuo*.

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