

$(R_4N)_2AO_4[SnPh_3X]_m$  (R = Me, Et; A = Mo, Cr, S, C<sub>2</sub>;  
m = 2, 3; X = Cl, Br): SYNTHESIS AND SPECTROSCOPIC STUDIES

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### Abstract

A series of adducts of general formulae  $(R_4N)_2AO_4[SnPh_3X]_m$  has been synthesized and characterized by i.r., Mössbauer and NMR techniques; on the basis of the spectroscopic results, a discrete structure is proposed for all the compounds. The tin center presents a trigonal bipyramidal coordination geometry while the oxyanions behave as bi- or tridentate ligands.

### Introduction

Several studies on the interactions between triphenyltin(IV) halides and various Lewis bases have been reported; among them nitrogen or oxygen donors ligands have been intensively studied (1). In the case of the triphenyltin(IV) chloride 2-(aryloxy)pyridine complex, an extremely weak Sn-N connection has been found in solution (2), and a weak interaction in the case of  $Ph_3Sn[Cy_2P(O)C(S)N(H)Me]Cl$  in the solid state (3). In the scope of our research work on the coordination ability of various oxyanions towards triphenyltin(IV) halides adducts, we have recently reported the spectroscopic results obtained on  $Me_4NH_2PO_2[SnPh_3Cl]_2$  (4) and  $Et_4NNO_3[SnPh_3Cl]_3$  (5). As an extension of this work, we now describe the synthesis of new halo triphenyltin(IV) adducts with oxyanions such as molybdate, sulphate, chromate and oxalate with their characterization by means of i.r., Mössbauer and NMR techniques.

### Experimental

#### a) Preparation of the compounds

$Ph_3SnCl$ ,  $CrO_3$ ,  $MoO_3$ ,  $C_2O_4H_2 \cdot 2H_2O$ ,  $H_2SO_4$  (Aldrich) and  $Ph_3SnOH$  (Merck) were used without further purification.  $(R_4N)_2[A O_4] \cdot nH_2O$  (X = Mo, S, C<sub>2</sub>; n = 6, 4, 2 respectively in the case of molybdate, sulphate and oxalate) salts were collected as powders by slow solvent evaporation from solutions obtained by mixing  $R_4NOH$  (as aqueous solutions) with the corresponding acid in stoichiometric ratio.  $(Ph_3Sn)_2[CrO_4] \cdot H_2O$  was obtained as a yellow precipitate by reacting an ethanolic solution of triphenyltin(IV) hydroxyde with an aqueous solution of  $CrO_3$ .

$(Me_4N)_2C_2O_4[SnPh_3Cl]_2$  **1**,  $(Me_4N)_2MoO_4[SnPh_3Cl]_2$  **2**,  $(Et_4N)_2SO_4[SnPh_3Cl]_3$  **3**,  $(Me_4N)_2C_2O_4[SnPh_3Cl]_3$  **4** were obtained by allowing  $Ph_3SnCl$  dissolved in  $CH_3CN$  to react with ethanolic solutions of  $(R_4N)_2[A O_4] \cdot nH_2O$ , in 1:2 (**1**, **2**) and 1:3 (**3**, **4**) ratio.

The chromate adducts  $(Et_4N)_2CrO_4[SnPh_3Cl]_2$  **5** and  $(Et_4N)_2CrO_4[SnPh_3Br]_2$  **6** were obtained on mixing ethanolic solutions of  $Et_4NX$  (X = Cl, Br) with  $(Ph_3Sn)_2[Cr O_4] \cdot H_2O$  dissolved in  $CHCl_3$  (chromate) in 2:1 ratio.

**Table 1:** Elemental analyses of the title adducts.

Compounds	m.p		yield	Analytical data			Sn
	°C	%		C	H	N	
<b>1</b>	253	92	54.81(54.79)	5.36(5.25)	2.78(2.76)	7.05(6.94)	23.57(23.80)
<b>2</b>	>250	85	48.94(48.75)	5.00(4.98)	2.59(2.45)	6.58(6.32)	22.00(22.13)
<b>3</b>	245	83	55.57(55.62)	5.62(5.75)	1.85(1.79)	7.03(7.12)	23.53(23.42)
<b>4</b>	>250	82	55.13(54.74)	4.95(5.05)	2.00(2.11)	7.64(7.82)	25.56(25.22)
<b>5</b>	115	87	54.38(54.62)	6.10(5.99)	2.44(2.53)	6.18(6.31)	20.68(20.75)
<b>6</b>	129	80	50.49(50.10)	5.66(5.88)	2.26(2.38)	12.90(13.00)	19.20(19.42)



All the adducts were collected as powders by slow solvent evaporation; the chromato adducts are yellow while all the others are white. The adducts were recrystallized in methanol (sulphate and molybdate), acetonitrile (oxalates) or chloroform (chromates) and dried *in vacuo*.

The elemental analyses performed by the "Service Central d'Analyses" C.N.R.S. Vernaison - France, are reported in Table 1.

#### b°) Spectroscopic characterization.

The NMR spectra were recorded in methanol (sulphate and molybdate adducts), in chloroform (chromato adducts) and in acetonitrile (oxalato adducts) at the "Centre Régional des Mesures Physiques de l'Ouest", Université de Rennes, France, using a Bruker 300 spectrometer. The i.r spectra and Mössbauer spectra were obtained as reported in (6,7).

I.R data are given in  $cm^{-1}$ . I.r abbreviations: (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (md) medium doublet, (sd) strong doublet, (w) weak, (br,s) broad and strong. In all the i.r spectra appears a very strong band around  $275\text{ cm}^{-1}$  due to  $\nu_{as}SnC_3$ . In the i.r spectra of **2** and **4**, the broad and strong bands at  $190$  and  $189\text{ cm}^{-1}$  are due to  $(\nu_{SnCl} + \delta_{s}SnC_3)$ . Mössbauer parameters are given in mm/s: Q.S. = quadrupole splitting, I.S. = isomer shift,  $\Gamma$  is the line width.  $^1H$ ,  $^{13}C$  and  $^{119}Sn$  NMR chemical shifts are given in ppm and are referred to TMS and  $SnMe_4$ . NMR abbreviations: (s) singlet; (d) doublet, (t) triplet, (m) complex pattern ranging in the given  $\delta$  values. The coupling constants  $^nJ(^{119}Sn-^{13}C) = ^nJ$  are given in Hz.

**(Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>[SnPh<sub>3</sub>Cl]<sub>2</sub>**: i.r data: 1608(s)  $\nu_{as}CO_2$  1267 1251(sd)  $\nu_{s}CO_2$  657(w)  $\delta_{CO_2}$  235(s)  $\delta_{as}SnC_3$  213(s)  $\nu_{s}SnC_3$  200(s)  $\nu_{s}SnO$  194 sh  $\nu_{SnCl}$  190 s  $\delta_{s}SnC_3$ . Mössbauer data: IS = 1.30 QS = 2.98  $\Gamma$  = 0.79.  $^1H$  NMR data:  $\delta$ (phenyl protons): [7.8 - 7.4 (m) 30H]  $\delta$ (CH<sub>3</sub>) [3.01(s) 24H].  $^{13}C$  NMR data: C(i)146.0  $^1J$  = 752.9 C(o)137.7  $^2J$  = 47.6 C(m)128.9  $^3J$  = 67.0 C(p)129.4  $^4J$  = 11.7 COO 165.2  $\delta(^{119}Sn)$  = -252.

**(Me<sub>4</sub>N)<sub>2</sub>MoO<sub>4</sub>[SnPh<sub>3</sub>Cl]<sub>2</sub>**: i.r data: 932 m (873, 855) md 793 vs  $\nu_{AO_4}$  397 m325 vs  $\delta_{AO_4}$  224 s  $\delta_{as}SnC_3$  215 s  $\nu_{s}SnC_3$  202 sh  $\nu_{s}SnO$  190 br,s ( $\nu_{SnCl} + \delta_{s}SnC_3$ ). Mössbauer data: IS = 1.27 QS = 3.12  $\Gamma$  = 0.89.  $^1H$  NMR data:  $\delta$ (phenyl protons): [7.9 - 7.3 (m) 30H]  $\delta$ (CH<sub>3</sub>) [3.2(s) 24H].  $^{13}C$  NMR data: C(i)142.9 C(o)137.3  $^2J$  = 47.0 C(m)129.6  $^3J$  = 68.7 C(p)130.4  $\delta(^{119}Sn)$  = -179.

**(Et<sub>4</sub>N)<sub>2</sub>SO<sub>4</sub>[SnPh<sub>3</sub>Cl]<sub>3</sub>**: i.r data: 1220 vs 1115 vs 977 vs  $\nu_{AO_4}$  616 m 587 m 527 w  $\delta_{AO_4}$  225 sh  $\delta_{as}SnC_3$  218 s  $\nu_{s}SnC_3$  200 s  $\nu_{s}SnO$  192 s  $\nu_{SnCl}$  185 s  $\delta_{s}SnC_3$ . Mössbauer data: IS = 1.31 QS = 3.16  $\Gamma$  = 0.87.  $^1H$  NMR data:  $\delta$ (phenyl protons) [7.9 - 7.3 (m) 45H]  $\delta$ (CH<sub>2</sub>) [2.7(q), J = 7.2 Hz, 16H]  $\delta$ (CH<sub>3</sub>) [0.8(t), J = 7.19 Hz, 24H].  $^{13}C$  NMR data: C(i)142.7 C(o)136.8  $^2J$  = 47.3 C(m)128.3  $^3J$  = 65.7 C(p)129.2  $\delta(^{119}Sn)$  = -159.

**(Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>[SnPh<sub>3</sub>Cl]<sub>3</sub>**: i.r data: 1647 s 1612 m  $\nu_{as}CO_2$  1263 sh 1253 s  $\nu_{s}CO_2$  656 m  $\delta_{CO_2}$  231 m  $\delta_{as}SnC_3$  212 s  $\nu_{s}SnC_3$  200 s  $\nu_{s}SnO$  189 br,s ( $\nu_{SnCl} + \delta_{s}SnC_3$ ) Mössbauer data: IS = 1.33 QS = 2.98  $\Gamma$  = 0.84.  $^1H$  NMR data:  $\delta$ (phenyl protons) [7.7 - 7.4 (m) 45H]  $\delta$ (CH<sub>3</sub>) [3.01(s) 24H].  $^{13}C$  NMR data: C(i)145.7  $^1J$  = 745.4 C(o)137.5  $^2J$  = 47.7 C(m)129.6  $^3J$  = 67.2 C(p)129.8  $^4J$  = 13.8 COO 165.3  $\delta(^{119}Sn)$  = -206.

**(Et<sub>4</sub>N)<sub>2</sub>CrO<sub>4</sub>[SnPh<sub>3</sub>Cl]<sub>2</sub>**: i.r data: 933 s 902 s 840 sh 808 vs  $\nu_{AO_4}$  402 w 378 m 364 w 340 w  $\delta_{AO_4}$  227 s  $\delta_{as}SnC_3$  218 s  $\nu_{s}SnC_3$  203 s  $\nu_{s}SnO$  198 sh  $\nu_{SnCl}$  183 s  $\delta_{s}SnC_3$ . Mössbauer data: IS = 1.45 QS = 2.73  $\Gamma$  = 0.88.  $^1H$  NMR data:  $\delta$ (phenyl protons) [7.9 - 7.2 (m) 30H]  $\delta$ (CH<sub>2</sub>) [3.2(q) J = 6.9 Hz 16H]  $\delta$ (CH<sub>3</sub>) [1.2(t), J = 6.8 Hz, 24H].  $^{13}C$  NMR data: C(i)140.5  $^1J$  = 624 C(o)136.6  $^2J$  = 47.7 C(m)128.5  $^3J$  = 66.1 C(p)129.4  $\delta(^{119}Sn)$  = -83.

**(Et<sub>4</sub>N)<sub>2</sub>CrO<sub>4</sub>[SnPh<sub>3</sub>Br]<sub>2</sub>**: i.r data data: 933, s 900 s 842 sh 804 vs  $\nu_{AO_4}$  400 w 379 w 364 w 325 w  $\delta_{AO_4}$  225 s  $\delta_{as}SnC_3$  215 s  $\nu_{s}SnC_3$  203 s  $\nu_{s}SnO$  196 sh  $\nu_{SnCl}$  183 s  $\delta_{s}SnC_3$ . Mössbauer data: IS = 1.45 QS = 2.75  $\Gamma$  = 0.86.  $^1H$  NMR data:  $\delta$ (phenyl protons) [7.9 - 7.1 (m) 30H]  $\delta$ (CH<sub>2</sub>) [3.1(q) J = 6.5 Hz 16H]  $\delta$ (CH<sub>3</sub>) [1.01 (t), J = 6.5 Hz, 24H].  $^{13}C$  NMR data: C(i)140.6  $^1J$  = 644 C(o)136.5  $^2J$  = 48.0 C(m)128.6  $^3J$  = 66.2 C(p)129.7  $\delta(^{119}Sn)$  = -84.

## Discussion

### Infrared study:

The splitting of the vibration  $\nu_3$  of the oxyanions into three bands and the appearance of  $\nu_2$  as one band, in the case of **2**, **5** and **6**, indicate  $C_{2v}$  symmetry for the molybdate and the chromate. The sulphate (in **3**) has a  $C_{3v}$  symmetry, as  $\nu_3$  and  $\nu_4$  of the oxyanion split into two bands. The appearance of three or four stretching  $CO_2$  bands is indicative of  $C_{2v}$ ,  $C_s$  or  $C_1$  symmetry for the oxalate in **1** and **4**. In the i.r spectra of all the compounds the absence of the strong band localized at  $338\text{ cm}^{-1}$  and assigned to  $\nu_{s}SnCl$  by Tudela and Calleja in the i.r spectrum of  $SnPh_3Cl$  (8), is a clear indication of the presence of coordinated  $SnPh_3Cl$ . All the i.r spectra also present a band around  $210\text{-}215\text{ cm}^{-1}$ , localized in the same region on the i.r spectra of  $SnPh_3X$  ( $X = Cl, Br$ ) and



assigned by Wharf and al. (9) to  $vsSnC_3$ ; the presence of  $vsSnC_3$  is a clear indication of the presence of non planar  $SnC_3$  groups.

#### Mössbauer study:

The Mössbauer spectra of all the compounds which parameters are reported in Table 3, present a simple quadrupole split doublet with hyperfine parameters typical of pentacoordinated triorganotin(IV) derivatives; the low linewidth values support the present of a single and well defined tin site and the virtual identity of the  $SnPh_3Cl$  units in each compound. The QS values are in any case higher than the QS of triphenyltin chloride ( $2.55 \text{ mms}^{-1}$ ) (10): this increase of the quadrupole splitting can be related to an additional bond on the tin center as previously reported (11). The observed Mössbauer quadrupole splitting values  $ca 2.80 \text{ mms}^{-1}$  are close to the values of five coordinated  $SnPh_3Cl$  complexes (12). The suggested structures in the solid state are discrete and are reported in figures 1-4 (for steric reasons the oxalates are not planar).

#### NMR study:

The assignments of the resonances of the  $^1H$  NMR spectra reported above are based on known chemical shift range and expected couplings. The values observed for the  $^nJ(^{119}Sn-^{13}C)$  coupling constants allowed the easy assignment of the aromatic  $^{13}C$  resonances. The  $^{119}Sn$  NMR spectra of all the adducts exhibit a single resonance.

The chromato adducts (**5** and **6**) show lower chemical shifts ( $-83$  and  $-84$  ppm) and coupling constants ( $624$  and  $644$  Hz); these values of  $\delta(^{119}Sn)$  and coupling constants are indicative of the presence of coordinated  $Ph_3SnCl$ ; this is also evidenced by the values of  $\delta(^{13}C_{ipso})$  higher than  $140$  ppm (13) ( in  $CDCl_3$ , the  $^{119}Sn$  NMR spectra of  $SnPh_3Cl$  and  $SnPh_3Br$  exhibit a single resonance at  $-44.7$  ppm ( $^1J(^{119}Sn-^{13}C) = 614.3$  Hz) and  $-59.8$  ppm ( $^1J(^{119}Sn-^{13}C) = 595.0$  Hz) respectively (13)). The values of  $\delta(^{119}Sn)$  are consistent with weak interactions between the chromate and the tin center (in the triphenyltin(IV) chloride 2-(aryloxy)pyridine complexes (2), low  $\delta(^{119}Sn)$  values ( $-45.6$  and  $-47$  ppm) and  $^1J(^{119}Sn-^{13}C)$  ( $617$  and  $618$  Hz) have allowed to conclude to the presence of five coordinated tin atoms and extremely weak Sn-N connection in these complexes).

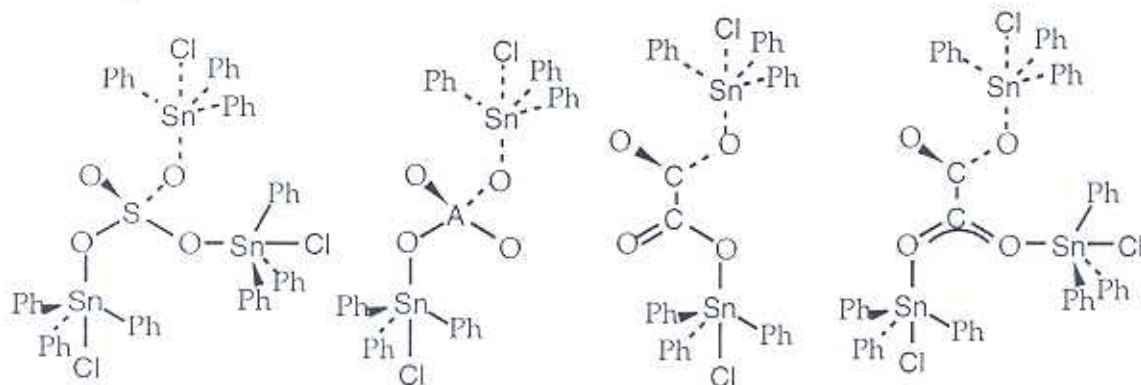
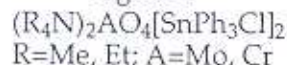


Figure 1

Figure 2

Figure 3

Figure 4



In the case of the oxalato adducts, the high values of  $\delta(^{119}Sn)$ : ( $-252$  ppm) (**1**) and ( $-206$  ppm) (**4**) and the coupling constants  $^1J(^{119}Sn-^{13}C)$   $752.9$  Hz and  $745.4$  Hz respectively are consistent with the presence of trans coordinated  $Ph_3Sn$  residues (in  $CD_3CN$ , the  $^{119}Sn$  NMR spectrum of  $SnPh_3Cl$  exhibits a resonance at  $-97$  ppm (14)).

The values of the chemical shift in the cases of the molybdate and sulphato adducts ( $-179$  and  $-159$  ppm) are also consistent with the presence of five coordinated tin atoms in these adducts (in MeOD, the  $^{119}Sn$  NMR spectrum of  $SnPh_3Cl$  exhibits a resonance at  $-175$  ppm (14)).

The variation of  $^{119}Sn$  NMR chemical shifts from  $-83$  to  $-252$  ppm, in this series of adducts, can be related to the differences of basicities of the oxyanions (the NMR spectra of  $Ph_3AsO.SnPh_3Cl$

( $CDCl_3$ ),  $Ph_3PO.SnPh_3Cl$  ( $CDCl_3$ ),  $SnPh_3Cl.dmsO$  (DMSO) and  $SnPh_3Cl.py$  (pyridine) exhibit a single resonance at -207, -75, -226.8 and -203.5 ppm respectively (13,14)).

### Conclusion

The suggested structures in the solid state as in solution, on the basis of the spectroscopic data are discrete, the oxyanions behaving as polydentate O-donors ligands, the tin centers having a bipyramidal trigonal environment with phenyl groups in equatorial positions.

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