SYNTHESIS, INFRARED, RAMAN, NMR AND MÖSSBAUER STUDIES OF SOME MONONUCLEAR INORGANIC MONO AND DIBASIC ACID TRIPHENYLTIN IV DERIVATIVES

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Abstract

Title mononuclear derivatives of general formulae Ph_3SnA ($\text{A}=\text{O}_2\text{PH}_2$, O_2PPh_2 , O_2AsMe_2 , $\text{O}_3\text{SC}_6\text{H}_5$, $\text{O}_3\text{SC}_6\text{H}_4\text{Me-4}$, $\text{O}_3\text{SC}_6\text{H}_3\text{Me}_2$ -2,5) and $[\text{R}_4\text{N}][\text{Ph}_3\text{Sn}(\text{O}_4\text{A}')]^+$ ($\text{R}=\text{Me}$, Et and $\text{A}'=\text{Cr}$, C_2) have been synthesized and characterized by elemental analyses, i.r., Raman, Mössbauer and NMR spectroscopies. The spectroscopic results suggest polymeric structures with bridging oxanions for all the derivatives with distorted (or not) trigonal bipyramidal geometries around the tin centers.

Introduction

The triphenyltin(IV) derivatives are known for their potential biological activity (1-8). Carboxylate derivatives have been extensively studied (9), while little attention has been devoted to pure inorganic oxyacids (10,13). I.r. studies for $\text{Ph}_3\text{SnO}_2\text{MR}_2$ ($\text{M}=\text{As}$, P ; $\text{R}=\text{Me}$, Ph) have yet been reported (14,15). An infinite chain structure has been reported for $\text{Ph}_3\text{SnO}_3\text{SC}_6\text{H}_5$ and $\text{Ph}_3\text{SnO}_3\text{SC}_6\text{H}_4\text{Me-4}$ (16), using Mössbauer spectroscopy. In the scope of our research work on the coordination ability of the oxanions (17, 19) and our interest to synthesize new triphenyl tin(IV) derivatives for biological tests, we now describe the synthesis of some mononuclear mono and dibasic triphenyltin(IV) derivatives of inorganic, organophosphorous, organoarsenic, arylsulfonic, oxalic and chromic acids, and their characterization by i.r., Raman, Mössbauer and NMR spectroscopies.

Experimental

Ph_3SnOH and the acids $\text{H}_3\text{PO}_2\text{H}$, $\text{Ph}_3\text{PO}_2\text{H}$, $\text{Me}_2\text{AsO}_2\text{H}$, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, 4- $\text{MeC}_6\text{H}_3\text{SO}_3\text{H}$, 2,5- $\text{Me}_2\text{C}_6\text{H}_3\text{SO}_3\text{H}$ and $\text{C}_2\text{O}_4\text{H}_2 \cdot 2\text{H}_2\text{O}$ are Aldrich Chemicals, and used without further purification. The chromate acidic salts $[\text{R}_4\text{N}][\text{HO}_4\text{Cr}]$ ($\text{R}=\text{Me}$, Et) were obtained by mixing water solutions of R_4NOH with CrO_3 in a 1:1 ratio (R_4NOH and CrO_3 are Merck chemicals). $(\text{Me}_4\text{N})_2\text{O}_4\text{C}_2 \cdot 2\text{H}_2\text{O}$ were prepared by neutralization of oxalic acid by an aqueous solution of Me_4NOH . The salts were obtained in very good yield (> 90%).

All the NMR spectra were recorded in methanol at the "Centre National des Mesures Physiques de l'Ouest" Rennes-France, using a Bruker 300 spectrometer, the elemental analyses performed by the "Service Central d'analyses" C.N.R.S. Vernaison France, the i.r. and Mössbauer spectra collected as described in (19-20) with CaSnO_3 (Amersham) as source. On Table 1 are reported the elemental data, the yields and the melting points of all the studied compounds. Raman spectra of polycrystalline samples sealed in glass tubes were examined on a T 800 CODERG triple monochromator using 5154 angstroms line of spectrophysics Ar^+ laser.

Preparation of the compounds

Ph_3SnA ($\text{A}=\text{O}_2\text{PH}_2$, O_2PPh_2 , O_2AsMe_2 , $\text{O}_3\text{SC}_6\text{H}_5$, $\text{O}_3\text{SC}_6\text{H}_4\text{Me-4}$, $\text{O}_3\text{SC}_6\text{H}_3\text{Me}_2$ -2,5).

The organotin derivatives, $\text{Ph}_3\text{SnO}_2\text{PH}_2$ **A**, $\text{Ph}_3\text{SnO}_2\text{PPh}_2$ **B**, $\text{Ph}_3\text{SnO}_2\text{AsMe}_2$ **C**, $\text{Ph}_3\text{SnO}_3\text{SC}_6\text{H}_5$ **D**, $\text{Ph}_3\text{SnO}_3\text{SC}_6\text{H}_4\text{Me-4}$ **E** and $\text{Ph}_3\text{SnO}_3\text{SC}_6\text{H}_3\text{Me}_2$ -2,5 **F** were prepared by

reacting stoichiometric amounts of the corresponding acid or acidic salt with triphenyltin hydroxyde in absolute ethanol. The arylsulfonate derivatives were obtained by slow solvent evaporation and recrystallized in MeOH, while all the other compounds, $\text{Ph}_3\text{SnO}_2\text{MR}_2$ ($\text{M}=\text{P}, \text{As}; \text{R}=\text{H}, \text{Ph}, \text{Me}$) were collected as white insoluble precipitates stirred for several hours, filtered, washed with hot ethanol and dried *in vacuo*.

[Me₄N][Ph₃Sn(O₄Cr)] G, [Et₄N][Ph₃Sn(O₄Cr)] H, [Me₄N][Ph₃Sn(O₄C₂)] I

A mixture of stoichiometric amounts of Ph_3SnOH and $[\text{R}_4\text{N}][\text{HO}_4\text{Cr}]$ ($\text{R}=\text{Me}, \text{Et}$) (in the case of **G** and **H**) in absolute ethanol stirred during more than two hours gives yellow precipitates, filtered, washed with hot ethanol and recrystallized in methanol. In the case of **I** $\text{Ph}_3\text{SnO}_3\text{SC}_6\text{H}_5$ and $(\text{Me}_4\text{N})_2\text{O}_4\text{C}_2\cdot 2\text{H}_2\text{O}$ were mixed and the white precipitate obtained was recrystallized in methanol. The derivatives **G**, **H** and **I** are obtained according to the reactions

Table 1: Analytical data, yields and melting points.

Compounds (%Found)	m.p		yield		Analytical data		%Calculated (
	°C	%	C	H	N	Sn	
A	225	93	52.04 (52.22)	4.09 (4.05)		28.60 (28.69)	
B	>300	96	63.49 (63.32)	4.40 (4.35)		20.93 (20.82)	
C	183	90	49.83 (49.52)	4.31 (4.44)		24.27 (24.06)	
D	253/255	86	56.78 (56.99)	3.94 (3.86)		23.41 (23.26)	
E	214/216	82	57.61 (57.41)	4.22 (4.31)		22.79 (22.04)	
F	239	83	58.24 (58.28)	4.66 (4.40)		22.15 (22.31)	
G	255 ^d	87	48.92 (49.17)	5.00 (4.90)	2.59 (2.47)	21.97 (21.88)	
H	245 ^d	85	52.32 (52.68)	5.87 (5.71)	2.34 (2.38)	19.90 (19.67)	
I	268/270	64	56.25 (56.76)	2.27 (2.16)	2.73 (2.67)	23.18 (23.04)	

The melting points for compounds **B**, **C**, **D** and **E** are in good agreement with those reported in ref 14, 15 and 16, ^d decomposition.

Spectroscopic characterization.

I.R. and Raman data are given in cm^{-1} ; Raman data are reported in brackets. Abbreviations : br.vs = broad and very strong, vs = very strong, s = strong, sh = shoulder, m=medium, w = weak. Mössbauer parameters are given in mm/s : Q.S. = quadrupole splitting, I.S. = isomer shift, Γ_1 and Γ_2 are the linewidth. ^1H and ^{13}C NMR chemical shifts are given in ppm and are referred to TMS, C_1 - C_6 are the carbons of the aromatic rings of the arylsulfonates ligands, C_7 and C_α are the carbons of the methyl linked to the aromatic rings of the arylsulfonates. $\delta(^{119}\text{Sn})$ NMR is also given in ppm and referred to SnMe_4 . Abbreviations : s = singulet, m = complex pattern ranging in the given δ values. The calculated values of the $\delta(^{13}\text{C})$ of the arylsulfonate ligands are given in parentheses at the right of the experimental values. The coupling constants $^n\text{J}(^{119}\text{Sn}-^{13}\text{C}) = ^n\text{J}$ are given in Hz.

Ph₃SnO₂PH₂ : i.r data : 2361(m) νPH_2 , 1146(vs) 1061(s) νPO_2 , 806(vs) δPH_2 , 496(m) δPO_2 , 225(m) δasSnC_3 , 200(sh) νSnO , 187(s) δsSnC_3 , [229(w) δasSnC_3 , 209(vs) νSnC_3 , 200(w) νSnO]; Mössbauer data : Q.S. = 3.54, I.S. = 1.27, Γ_1 = 0.85 and Γ_2 = 0.92.

Ph₃SnO₂PPh₂ : i.r data : 1144(sh) 1122(vs) νPO_2 , 750(m) νPC , 556(vs) 539(m) δPO_2 , 390(m) ρPO_2 , 333(sh) 317(s) (δ - ρ)PC, 226(m) δasSnC_3 , 199(m) νSnO , 190(m) δsSnC_3 , [228(w) δasSnC_3 , 213(vs) νSnC_3 , 200(m) νSnO]; Mössbauer data : Q.S. = 3.49, I.S. = 1.26, Γ_1 = 0.89 and Γ_2 = 0.98.

Ph₃SnO₂AsMe₂ : i.r data: 875(vs) 836(vs) νAsO_2 , 635(s) 601(m) νAsC_2 , 462(m) δAsC_2 , 402(s) 316(s) δAsO_2 , 230(m) δasSnC_3 , 211(trace) νSnC_3 , 191(sh) νSnO , 178(vs) δsSnC_3 , [230(w) δasSnC_3 , 211(vs) νSnC_3 , 191(w) νSnO]; Mössbauer data : Q.S. = 2.85, I.S. = 1.12, Γ_1 = 0.88 and Γ_2 = 0.90.

Ph₃SnO₃SC₆H₅ : i.r data: 1277(vs) 1120(s) 1086(s) 1060(s) νSO_3 , 754(vs) νCS , 614(s) 560(s) δSO_3 , 321(m) ρSO_3 , 222(s) δasSnC_3 , 193(m) νSnO , 172 (s) δsSnC_3 , [221(sh) δasSnC_3 , 214(s) νSnC_3 , 193(m) νSnO]; Mössbauer data : Q.S. = 4.03, I.S. = 1.38, Γ_1 = 0.88 and Γ_2 = 0.92; ^1H NMR data : δ (phenyl proton) [7.87 - 7.41 (m) (20 H)]; ^{13}C NMR data: C(i) 138.53⁻¹J = 777.7 C(o) 137.32 2J = 46.6 C(m) 130.54 3J=70.4 C(p) 131.82 C₁ 146.07 (143.5) C₂ 126.95 (126.3) C₃ 129.29 (129.8) C₄ 131.88 (132.3) $\delta(^{119}\text{Sn})$ = -198.

Ph₃SnO₃SC₆H₄Me-4: i.r data: 1249 (s) 1149 (s) 1111 (s) 998 (sh) vsSO₃ 815 (m) vCS 650 (sh) 561 (s) δSO₃ 398 (m) 311 (m) ρSO₃ 228(s) δasSnC₃ 200 (s) vSnO 178 (m) δsSnC₃. Mössbauer data : Q.S. = 3.85, I.S. = 1.33, Γ₁ = 0.81 and Γ₂ = 0.89; ¹H NMR data : δ(phenyl proton) [7.99 - 7.15 (m) (19 H)] δ(CH₃) 2.34 (s) (3 H), ¹³C NMR data : C(i) 138.59 ¹J=781.8 C(o) 137.32 ²J=46.6 C(m) 130.51 ³J = 70.5 C(p) 131.80 C₄ 141.78 (140.5) C₂ 126.88 (126.2) C₃ 129.86 (130.5) C₄ 143.15 (141.5), C₇ 21.34 δ(¹¹⁹Sn) = -194.

Ph₃SnO₃SC₆H₃Me₂-2,5: i.r data: 1258 (s) 1144 (m) 1103 (s) 998 (m) vsSO₃ 821 (m) vCS 621 (s) 570 (m) δSO₃ 351 (m) 340 (w) ρSO₃ 221(s) δasSnC₃ 202 (s) vSnO 182(m) δsSnC₃. [220(w) δasSnC₃ 210(vs) vsSnC₃ 190(m) vSnO]; Mössbauer data : Q.S. = 3.99, I.S. = 1.38, Γ₁ = 0.94 and Γ₂ = 0.94; ¹H NMR data : δ(phenyl proton) [7.86 - 7.10 (m) (18 H)] δ(CH₃) [ortho: 2.54 (s) (3 H), meta: 2.27 (s) (3H)]; ¹³C NMR data : C(i)139.91 ¹J=767.2 C(o)137.45 ²J = 46.6 C(m)130.40 ³J = 70.4 C(p)131.73, C₄143.464 (141.1) C₂132.53 (132.5) C₃ 132.172 (130.4) C₄ 134.440 (132.9) C₆ 136.039 (136) C₆ 128.834 (126.9) C₇ 21.10 C₈ 20.24 δ(¹¹⁹Sn) = -196.

[Me₄N][Ph₃Sn(O₄Cr)] i.r data : 930(vs) 905(vs) 837(m) 810(vs) (v₁+v₂) 400(m) 376(m) 366(m) 326(m) (v₄+v₂) 238(m) δasSnC₃ 213(s) vsSnC₃ 187(br,s) (δsSnC₃+vSnO). [235(w) δasSnC₃ 213(vs) vsSnC₃ 194(m) vSnO]; Mössbauer data : Q.S. = 2.80, I.S. = 1.16, Γ₁ = 0.98 and Γ₂ = 0.93; ¹H NMR data : δ(phenyl proton) [7.81 - 7.44 (m) (15 H)] δ(CH₃) [3.21(s) (12 H)]; ¹³C NMR data: C(i)140.85 ¹J = 748.8 C(o)137.61 ²J = 42.4 C(m)129.74 ³J = 63.9 C(p)130.55 ⁴J = 13.8 δ(¹¹⁹Sn) = -164.6.

[Et₄N][Ph₃Sn(O₄Cr)] i.r data: 925(vs) 905(vs) 840(m) 820(vs) (v₃+v₄) 393(m) 372(m)357(w) 320(w) (v₄+v₂) 237(m) δasSnC₃ 213(s) vsSnC₃ 200(m) vSnO 176(m) δsSnC₃. [234(w) δasSnC₃ 213(vs) vsSnC₃ 198(w) vSnO]; Mössbauer data : Q.S. = 2.81, I.S. = 1.18, Γ₁ = 0.87 and Γ₂ = 0.87; ¹H NMR data : δ(phenyl proton) [7.81 - 7.43 (m) (15 H)] δ(CH₂) : [3.31 (m) (8 H)]; δ(CH₃) [1.32(m) (12 H)]; ¹³C NMR data : C(i)140.85 ¹J = 748.1 C(o)137.61 ²J = 42.4 C(m)129.74 ³J = 65.5 C(p)130.54 ⁴J=13.6; δ(¹¹⁹Sn) = -164.4.

[Me₄N][Ph₃Sn(O₄C₂)] i.r data : 1608(br. vs) vasCOO- 1267(s) 1251(s) vsCOO- 810(s) 746(sh) δCOO- 443(s) ρCOO- 359 (s) wCOO- 245 (vs) δasSnC₃ 215 (m) vsSnC₃ 200(m) vSnO 177(m) δsSnC₃. [248(w) δasSnC₃ 212(s) vsSnC₃ 198(w) vSnO 172(m) δsSnC₃]; Mössbauer data: Q.S. = 3.02, I.S. = 1.19, Γ₁ = 0.86 and Γ₂ = 0.77; ¹H NMR data : δ(phenyl proton) [7.73 - 7.37 (m) (15 H)] δ(CH₃) [3.15 (s) (12 H)]; ¹³C NMR data : C(i)144.98 ¹J = 738.9 C(o)137.82 ²J = 46.7 C(m)129.20 ³J = 64.9 C(p)129.91, COO 165 δ(¹¹⁹Sn) = -225.26.

Results and discussion

According to the classification of Tiekink (21) for triorganotin carboxylates, it is reasonable to assume that the compounds of empirical formulae [R₃Sn(O₂MR'R'')] (R'=alkyl, phenyl; R''=alkyl, phenyl, O) may approach one of the three ideal structures shown in scheme 1.

Scheme 1 : The three ideal structures for [R₃Sn(O₂MR'R'')]

Infrared and Raman spectroscopies:

All the i.r. spectra exhibit a very strong band around 275 cm⁻¹ due to vasSnC₃. In the i.r. spectra of the chromate derivatives, the splitting of the bands corresponding to the stretching vibrations of the chromate into four bands at 930, 905, 837 and 810 cm⁻¹ (**G**), at 925, 905, 840 and 820 cm⁻¹ (**H**) is consistent with C_{2v} symmetry for the chromate. The appearance of a strong band and a very strong line due to vsSnC₃ on the i.r. and Raman spectra of the chromato derivatives is also consistent with the presence of pyramidal SnC₃ groups. On the Raman spectra of all these derivatives (**A-I**) a strong line appears around 210-215 cm⁻¹, localized in the same region on the Raman spectra of SnPh₃X (X=Cl, Br) reported by Wharf and al. (22) and assigned to vsSnC₃. On the i.r. spectra of **A**, **B**, **C**, **D**, **E**, and **F** the absence of the band due to vsSnC₃, or its appearance as a trace, are a clear indication of the presence of planar (or almost planar) SnC₃ groups. The i.r. spectrum of the oxalato derivative exhibits a strong band at 215 cm⁻¹ due to vsSnC₃ (in its Raman spectrum vsSnC₃ appears as a very strong line at 212 cm⁻¹); this is consistent with the presence of non planar SnC₂ groups. The splitting of the bands due to the stretching vibrations of the oxalate anion into three bands at

1608 cm^{-1} (ν_{asCOO^-}) and 1267, 1251 cm^{-1} (ν_{sCOO^-}) on the i.r spectrum indicates an oxalate of C_{2v} or C_s or C_1 symmetry (the broadness of the band at 1608 cm^{-1} is surely due to a splitting of ν_{asCOO^-} resulting of the lowering of the symmetry of the oxalate anion).

Mössbauer spectroscopy :

The Mössbauer spectra of all the compounds present a simple quadrupole split doublet typical of triorganotin(IV) derivatives with linewidth values that support the presence of a single well defined tin site. They can be easily divided into three groups : the first one including compounds **C**, **G**, **H** and **I** with the lowest values of both the isomer shift and the quadrupole splitting (the average values are 1.13 and 2.87 mms^{-1} respectively), the second one (**A** and **B**), with intermediate Mössbauer parameters (the average values are 1.26 and 3.51 mms^{-1} respectively), the third one (**D**, **E** and **F**) with the highest values for the hyperfine parameters (the average value are 1.38 and 4.00 mms^{-1} respectively).

As Mössbauer spectra show Q.S. values higher than 3.00 mms^{-1} for **A**, **B**, **D**, **E** and **F**, the structure of A-type may consequently be discarded (23). Molloy and al. (24) have reported variable temperature Mössbauer spectroscopic measurements for triphenyltin diphenylphosphinate and conclude to a polymeric structure containing planar Ph_3Sn residues bridged by diphenylphosphinate anions. Such a detailed study is not available for our compounds but they present significant absorption at room temperature. Therefore, from the i.r, Raman and Mössbauer data, a structure of the C-type is proposed for **A**, **B**, **D**, **E** and **F**. The Q.S. value of $\text{Ph}_3\text{SnO}_2\text{AsMe}_2$ (2.85 mms^{-1}) appears lower than the Q.S. of its previous homologous. The f -factor is also reduced but, as ν_{SnC_3} appears only as a trace on the i.r. spectrum, the presence of almost planar SnC_3 groups urges us to suggest a polymeric structure for this derivative (Ph_3SnOH exhibits a Q.S. of 2.83 mms^{-1} (25) and was found to be polymeric (26), with planar SnC_3 groups).

The appearance of ν_{SnC_3} as a strong band at 213 cm^{-1} on the i.r spectra of the chromato derivatives, and its appearance as a strong line at 213 cm^{-1} on their Raman spectra are a clear indication of the presence of non planar SnC_3 groups. Their Q.S. values (2.80 and 2.81 mms^{-1}) higher than 2.40 mms^{-1} exclude tetrahedral environment according to (23).

The Q.S. value of the oxalato derivative 3.02 mms^{-1} , its low f -factor and the presence of non planar SnC_3 groups are in favor of a structure of the C-type with asymmetric trans coordinated Ph_3Sn residues (27), the oxalate acting as a bridging ligand. The Q.S. value of the oxalate derivative is similar to those reported for $\text{Ph}_3\text{Sn}(\text{O}_2\text{CC}_6\text{H}_4\text{OH}-2)$ (28), $\text{Ph}_3\text{Sn}(\text{O}_2\text{CC}_6\text{H}_4\text{COC}_6\text{H}_5-2)$ (29) and $\text{Ph}_3\text{Sn}(\text{O}_2\text{CCH}_2\text{SC}_6\text{H}_4\text{N}-4)$ (30) (2.97, 3.07 and 2.91 mms^{-1} respectively) containing asymmetric transcoordinated Ph_3Sn residues.

The polymeric structure suggested is also supported by the value of the Q.S./I.S. ratio higher than 2.3 for all the compounds. The difference in the Q.S. values are probably due to deviations from the ideal geometry and to the different electronegativities of the anionic ligands. This fact can also justify the variety of values shown by the isomer shift and is supported by preliminary calculations on the electron density at the tin center. These calculations, based on the equalization of the electronegativities of the couple of atoms forming each bond, give increasing electron density values in full agreement with the isomer shift trend.

NMR spectroscopy :

The ^1H NMR data are reported above, in the case of the arylsulfonate derivatives, the resonances for the aromatic protons appear in the same region than the phenyl ones. A complex multiplet pattern ranging between 7 and 8 ppm is observed for all the aromatic protons. The basic assignment of the arylsulfonic ligands ^{13}C resonances were all obtained from the incremental rules for substituted benzene derivatives, using literature tables (31). Calculated values are given in parentheses at the right of experimental values. In general the differences between calculated and experimental chemical shifts is less than 2.5 ppm, in the case of the carbons 1 of the benzenesulfonic ring and around 2 ppm, in the case of the carbon 4 of the toluene-4-sulfonic derivative. Those kinds of discrepancies are lower than those reported by Meriem and al. (32) in the case of some diorganotin bis(ortho-aminobenzoates) derivatives. For the other carbons, a very good agreement between calculated and experimental values is obtained. The deviation in the case of the carbons 1 may be attributed to the fact that the calculations were executed using incremental values of the $-\text{SO}_3\text{H}$ group, those of $-\text{SO}_3\text{SnPh}_3$ groups being unavailable to our knowledge. The assignments of the aromatic ^{13}C resonances were performed from calculations using aromatic increments (31) and previous assignments (33). The values of $\delta(^{119}\text{Sn})$ of the arylsulfonate derivatives, (compounds **D**, **E** and **F**) -198, -194 and -196 ppm respectively are indicative of a five coordinated tin atom (33), the values of $^1J(^{119}\text{Sn}-^{13}\text{C})$ higher than 750 Hz falls in the normal range for trans bipyramidal trigonal environment around tin. The $\delta(^{119}\text{Sn})$

values (-164.6 and -164.4 ppm) for **G** and **H** lower than those expected for tetrahedral triphenyltin ($\delta(^{119}\text{Sn}) > -120$ ppm (33)) and the values of $^1J(^{119}\text{Sn}-^{13}\text{C})$ around 748 Hz are also consistent with trans bipyramidal trigonal tin environment and urge us to conclude to the presence in solution of trans O_2SnC_3 groups as in the solid state. The $\delta(^{119}\text{Sn})$ value (-225.26 ppm) for the oxalate derivative is an unambiguous indicator of the presence of trans-coordinated Ph_3Sn residues as reported in (33), the oxalate derivative behaving as bridging ligand. The high value of $^1J(^{119}\text{Sn}-^{13}\text{C})$, 738.9 Hz for the oxalate derivative is also indicative of a trans bipyramidal trigonal tin environment.

Conclusion

All the derivatives studied in this work have a polymeric structure in the solid state with symmetric or asymmetric trans-coordinated Ph_3Sn residues. The chromato, arylsulfonato and oxalato derivatives remain polymeric in methanol. We also note the non existence in this series, in the solid state, of a tetrahedral monocoordinated or a cis-coordinated tin IV derivative as reported for some carboxylates (9.f, 28, 34, and 35). In the chromato derivatives, the cation seems to have no influence on the way the Ph_3Sn residue is coordinated. In the compound $[(\text{C}-\text{C}_6\text{H}_{11})_2\text{NH}_2][\text{Ph}_3\text{Sn}(\text{O}_4\text{C}_2)]$ the Ph_3Sn residue is reported to be cis coordinated (34) and trans coordinated in $[\text{Me}_4\text{N}][\text{Ph}_3\text{Sn}(\text{O}_4\text{C}_2)]$ allowing to claim an important cation influence on the way the Ph_3Sn residue is coordinated in the anion $[\text{Ph}_3\text{Sn}(\text{O}_4\text{C}_2)]^-$.

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