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Some triphenyltin(IV) complexes containing potentially bidentate, biologically active anionic groups *

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Abstract

Triphenyltin(IV) derivatives have been synthesized which contain anions from various biologically active acids. The coordination about the tin atom was investigated by infrared, ^{119}Sn NMR and Mössbauer spectroscopic methods. The triphenyltin cation with S-bonding groups generally acquires a four-coordinated structure. On the other hand, combination with O-bonding groups can produce several structural possibilities: four-coordinate, five-coordinate *cis*- and *trans*-trigonal bipyramidal and bridging carboxylate examples being obtained. Some of the higher coordination number species appear to dissociate in solution.

Introduction

The biocidal properties of organotin compounds have been widely explored and exploited [1]. In general, the *in vitro* fungicidal and antibacterial properties of organotins have indicated the general order of activity:

$$RSnX_3 < R_2SnX_2 < R_4Sn \ll R_3SnX$$

together with the conclusion that the anionic X group exerts little influence on activity [2]. However, based on some preliminary experiments, we felt it was possible that the combination of two biologically active entities in the same molecule could enhance the toxicity and suppress the development of tolerant strains, while providing a system which was still able to degrade in the environment to relatively non-toxic residues. This led us to investigate the linking of the triphenyltin(IV) center with various dithiocarbamate groups [3] along with orga-

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Table 1

Compounds from which anionic groups were derived, indicating abbreviations used in the text and Tables

AET	aminoethanethiol	PAA	phenoxyacetic acid
ASA	acetylsalicylic acid	PEA	p-ethoxyacetic acid
ATP	4-aminothiophenol	PNO	2-mercaptopyridine-N-oxide
BHZ	N-benzoyl-N^1-isopropylidenehydrazine	PTA	phthalic acid
CPA	2,4-dichlorophenoxyacetic acid	PTH	phthiacol
DBM	dibenzoylmethane	SAL	salicylaldehyde
DTZ	diphenylthiocarbazone	SUA	N-benzylpropanamide-3-carboxylic acid
END	endonorbornene-*cis* 5,6-dicarboxylic acid	TGA	thioglycolic acid
MBT	2-mercaptobenzothiazole	TPC	thiophene carboxylic acid
MET	2-mercaptoethanol	VAN	vanillin
NPE	2-nitropropane		

notin derivatives of some other groups having biological significance [4,5]. A virtually identical theme was later taken up by Zuckerman's group in relation to triphenyltin dithiophosphate derivatives [6].

In support of this strategy, a report by Pieters [7] and a more recent one by Blunden *et al.* [8] have shown that the X group does indeed exert some effect on the biological properties of organotins within a particular series. Specifically for triphenyltin(IV) derivatives, Pieters noted that:

oxalate < hydroxide < acetate

Blunden *et al.* noted the variation in activity with change in the coordination number about the tin atom. Our own investigations on mono- and dithiocarbamate derivatives of triphenyltin(IV) also revealed changes in activity as the alkyl substituents on the anion nitrogen atom were varied [9].

An aim of this work, then, was to synthesize triphenyltin(IV) derivatives of a range of biologically-active groups, but further, to employ some groups which offer the choice of unidentate or bidentate bonding modes to the tin atom. The uni-negative anionic groups, all of which were potentially chelating, were derived from the compounds listed in Table 1, which also shows the abbreviations employed. In addition, the coordination about the tin center was investigated using common spectroscopic probes. The results of these investigations are reported here.

Experimental

Syntheses

The compounds were prepared *via* commonly used procedures, namely (a) nucleophilic displacement of chloride from triphenyltin chloride by the sodium (or thallium) salt of the appropriate group; (b) by employing an organic base (usually triethylamine) to assist dehydrohalogenation; and (c) water displacement using triphenyltin oxide or hydroxide and the free ligand.

Essentially, any one of these synthetic routes was found to be suitable for the synthesis of the compounds with the best choice ultimately depending on the solubility of the reactants and products and nature of the ligand. For ligands that

were 'acidic' in nature due to tautomerism, *i.e.* for the BHZ and the phenolic derivatives, the most convenient method of synthesis was method (c) in which it was necessary azeotropically to remove the water formed in order to increase the yield and hence the purity of the product. The use of thallous ethoxide rather than sodium ethoxide in method (a) was advantageous since the removal of the finely divided sodium chloride that formed often proved difficult. Carboxylic acid and thiol derivatives were most easily prepared (in high yield and purity) by method (c) without the necessity of removing the water azeotropically.

All the starting materials were purchased from the Aldrich Chemical Co., and used without further purification. Microanalyses ^{1}H and ^{13}C NMR spectra were employed routinely to establish the presence of the expected coordinating groups and the stoichiometry of the products (Tables 2 and 3). While some of the microanalytical data were slightly unsatisfactory, the melting points were generally sharp and purity was supported by excellent proton integration data. Over the time required to obtain the microanalyses however, a number of the compounds, especially those with Sn–S bonds, were observed to discolor slightly.

Measurements

Infrared spectra were recorded as KBr pressed disks, and also as solutions in $CHCl_3$ where possible, using a Perkin-Elmer Model 1430 ratio recording spectrophotometer.

^{119}Sn NMR spectra were recorded ($CDCl_3$ solution, where possible; Me_4Sn reference) using a JEOL JNM-FX200 instrument equipped with a multinuclear tuneable probe operating at 74.38 MHz in pulse mode with Fourier transform and with complete proton decoupling.

Mössbauer spectra were obtained on samples cooled to 78 K on a microprocessor-controlled, constant acceleration spectrometer, with a 5 mCi $Ca^{119}SnO_3$ source at room temperature.

Results and discussion

Triphenyltin compounds are rich with structural possibilities: four-coordinate tetrahedral, monomeric *cis*, *trans* and *mer* five-coordinate and five-coordinate bridged polymers are all feasible [1,10]. In the absence of unequivocal structural data from X-ray crystal studies, it is usual to infer structures from available spectroscopic data. Thus ^{1}H, ^{13}C and ^{119}Sn NMR, infrared and ^{119}Sn Mössbauer spectroscopy may be employed with varying degrees of success to ascertain the geometries of triphenyltins in solution and in the solid phase [1].

Infrared spectra generally permit rapid characterizations to be made, since the "group frequency" concept applies for organotins in much the same way as for organic compounds [11]. Characteristic peaks are usually readily identified and significant features ascertained [12].

Coupling constants $^{1}J(^{13}C-^{119}Sn)$ of the triphenyltin entity are directly related to the *s*-character of the hybrid orbitals employed by the tin and thus are dependent on the coordination number and the geometry in the coordination sphere of the metal [13]. In view of the relatively large number of pulses generally required for its accurate measurement in Ph_3Sn compounds, this parameter was

Table 2

Analytical [a] and ^{1}H NMR characterization of the triphenyltin compounds (values in parentheses are calculated for Ph_3SnX)

Compound	Prep. method [b]	%C	%H	%Other	MP	δ, ^{1}H NMR [c]	Form [d]
AET	C	57.7 (56.3)	5.01 (4.9)	3.7 (3.3) [e] 7.5 (7.5) [f]	111–112	7.75–7.52 (m), 15H, $-C_6H_5$ 2.72 (s), 4H, $-CH_2$ 1.31 (s), 2H, $-NH_2$	wh. cryst.
ASA	C	59.8 (59.0)	4.2 (4.1)		113–114	8.22–7.14 (m), 19H, arom. 2.12 (s), 3H, $-CH_3$	wh. cryst.
ATP	B	62.5 (60.7)	4.6 (4.4)	3.3 (2.9) [e] 6.8 (6.7) [f]	115–116	7.5 (m), 15H, $-C_6H_5$ 7.06 (d), 2H, arom. 6.33 (d), 2H, arom. 3.49 (s), 2H, $-NH_2$	wh. cryst.
BHZ	C	65.1 (64.0)	4.8 (4.9)	5.5 (5.4) [e]	160–161	7.73–7.19 (m), 20H, arom. 2.30 (s), 3H, $-CH_3$ 1.44 (s), 3H, $-CH_3$	wh. cryst.
CPA	C	52.7 (51.5)	3.5 (3.3)		177–178	7.72–6.61 (m), 18H, arom. [g] 4.50 (s), 2H, $-CH_2$ [g]	wh. powd.
DBM	A	69.3 (69.0)	4.4 (4.5)		145–146	8.08–7.25 (m), 25H, arom. 6.78 (s), 1H, –CH	yw. cryst.
DTZ	C	62.1 (61.5)	3.9 (4.0)	10.9 (9.2) [e]	143–145	9.71 (s), 1H, –NH 7.71–7.24 (m) 25H, arom.	br. cryst.
END	C	60.8 (60.9)	4.6 (4.7)		138–139	7.81–7.44 (m), 15H, $-C_6H_5$ [g] 5.83 (s), 2H, =CH [g] 3.11 (s), 2H, –CH [g] 2.92 (s), 2H, –CH [g] 2.12 (s), 1H –COOH [g] 1.20 (s), 2H, $-CH_2$	wh. powd.
MBT	C	59.1 (58.1)	3.9 (3.7)	13.4 (12.4) [f]	89– 91	7.82–7.00 (m), arom.	wh. cryst.

MET	B	56.6 (56.2)	4.7 (4.6)	7.6 (7.5) [f]	89– 90	7.78–7.52 (m), 15H, $-C_6H_5$ 3.58 (t), 2H, $-SCH_2$ 2.79 (t), 2H, $-OCH_2$ 2.26 (s), 1H, –OH	wh. cryst.
NPE	A	57.7 (57.5)	4.9 (4.7)	3.3 (3.2) [e]	130–131	7.73–7.47 (m), 15H, $-C_6H_5$ 2.01 (s), 6H, $-CH_3$	wh. cryst.
PAA	C	62.5 (62.3)	4.3 (4.4)		156–158	7.72–6.61 (m), 20H, arom. [g] 4.38 (s), 2H, $-CH_2$ [g]	wh. powd.
PEA	C	64.3 (62.9)	4.5 (4.6)		135–136	8.22 (d), 2H, arom. 7.90–7.38 (m), 15H, $-C_6H_5$ 6.93 (d), 2H, arom. 3.79 (q), 2H, $-CH_2$ 1.32 (t), 3H, $-CH_3$	wh. cryst
PNO	A	58.3 (57.9)	4.1 (3.9)		111–113	7.62–7.31 (m), arom.	wh. cryst.
PTA	C	60.6 (60.5)	4.1 (4.3)		128–129	7.91–7.44 (m), 19H, arom. [g] 1.52 (s), 1H, $-CO_2H$ [g]	wh. powd.
PTH	C	63.6 (62.5)	4.5 (4.6)		212–214	8.18–7.28 (m), 19H, arom. 2.24 (s), 3H, $-CH_3$	or. cryst.
SAL	A	64.1 (63.7)	4.4 (4.2)		164–165	10.24 (s), 1H, –CHO 7.74–7.30 (m), 19H, arom.	lm. cryst.
SUA	C	64.4 (63.3)	5.1 (4.9)	2.4 (2.7) [e]	118–119	7.66–7.17 (m), 25H, arom. 2.68 (m), 4H, $-CH_2$	wh. powd.
TGA	C	52.8 (54.4)	3.8 (4.0)	7.3 (7.2) [f]	146–147	7.60–7.30 (m), 15H, $-C_6H_5$ [g] 3.31 (s), 2H, $-CH_2$ [g] 2.13 (s), 1H, –SH [g]	wh. powd.
TPC	C	59.4 (57.9)	3.5 (3.7)		111–112	7.87–7.30 (m), arom.	wh. cryst.
VAN	A	62.2 (62.3)	4.6 (4.4)		132–133	10.82 (s), 1H, –CHO 7.50–6.78 (m), 18H, arom. 3.32 (s), 3H, $-CH_3$	yw. cryst.

[a] Microanalyses were performed by AMDEL Laboratories, Melbourne. [b] See text. [c] Solvent $CDCl_3$, unless specified. [d] br. = brown; lm. = lime green; or. = orange; yw. = yellow; wh. = white; cryst. = crystalline; powd. = powder. [e] Nitrogen microanalysis. [f] Sulfur microanalysis. [g] DMSO solvent.

not recorded in this work. The ^{13}C- and ^{1}H-NMR spectra were generally employed only in order to confirm the stoichiometry of the compounds (Tables 2 and 3).

An important parameter is the ^{119}Sn chemical shift, $\delta(Sn)$. This is dependent on the total electron density at the central tin atom. An increase in the coordination number is accompanied by an appreciable upfield shift [14]. It appears that ^{119}Sn chemical shift ranges of approximately -40 to -120, -180 to -230 and -230 to -260 ppm are typical of closely related compounds which are tetrahedral, *cis*-tbp and *trans*-tbp, respectively [1,13,15]. Further, $\delta(Sn)$ values are generally independent of concentration, except for those compounds which exhibit intermolecular association in the solid. In those cases, the shift moves to lower frequencies with increasing concentration [16].

While ^{119}Sn NMR data are useful for examining structural forms in solution, Mössbauer spectroscopy probes the geometry around the tin atom in the solid state. The quadrupole splitting parameter, ΔE_Q, reflects any imbalance in the Sn $5p$ electrons which, in turn, are affected by the spatial arrangements of the ligating organic groups [17]. Typical ranges for ΔE_Q again have been associated with particular geometries: 1.0–1.9 mm s^{-1} (tetrahedral); 1.7–2.3 mm s^{-1} (*cis*-tbp); 3.0–3.9 mm s^{-1} (*trans*-tbp), while the so-far uncertain *mer*-tbp arrangement is expected to produce a ΔE_Q value in the range 3.5–4.1 mm s^{-1} [18].

There has also been a tendency to infer the coordination number for organotin(IV) compounds from the ratio (ρ) of the quadrupole splitting to the isomer shift. In general, if $\rho < 1.7$, the compound is considered to be four coordinate, while $\rho > 1.7$ reflects higher coordination numbers [10,18].

The derivatives containing potentially bidentate anions were examined using the above generalizations. Some features worthy of comment are evident in the abbreviated infrared data presented in Table 4. For example, in the case of the AET, MET and ATP derivatives, it is clear that the Ph_3Sn group bonds preferentially to sulfur when the choice is presented. In this respect, these derivatives parallel the behaviour of the monothiocarbamates (MTC) which are also S-bonded to the triphenyltin moiety [19]. Frequencies of the pendant OH (MET) and NH_2 (AET and ATP) groups are clearly observed in the respective spectra. The four-coordinate natures of AET and MET extend to the solid state as evidenced by their Mössbauer data (Table 5), which are quite unambiguous.

The $\delta(Sn)$ values for the compounds listed in Table 6 largely fall into the expected ranges stated above, with the values for the AET, MET and ATP derivatives again reflecting the four coordination suggested by the infrared spectra. Unequivocally falling in this group also are the ASA, DTZ, MBT and TPC compounds. The DBM derivative (included as a five-coordinate *cis*-tbp standard) [20] displayed an unexceptional shift. Several compounds were insufficiently soluble in $CDCl_3$ and were presumably associated. These dissolved in DMSO but yielded $\delta(Sn)$ values which were ambiguous because of the coordinating nature of the solvent.

The BHZ complex is particularly interesting. Its $\delta(Sn)$ value (-192 ppm) is typical of five-coordinate *cis* geometry. The N–H bands of the hydrazine ligand at 3280 and 3215 cm^{-1} are absent. This suggests their loss *via* enolization since the carbonyl frequency at 1660 cm^{-1} also disappears and a second C=N band appears at 1679 cm^{-1}. Further, a strong $\nu(CNO)$ absorption at 1530 cm^{-1} [21] is also found. The N–N frequency of the ligand (791 cm^{-1}) shifts to 829 cm^{-1}, suggesting

Table 3

^{13}C NMR spectral data for the triphenyltin compounds

Compound [a]	$\delta(^{13}C)$ [d] (ppm)				^2J(Sn–C) (Hz)	^3J(Sn–C) (Hz)	Ligand shifts (ppm)
	$\delta(C)_1$	$\delta(C)_2$	$\delta(C)_3$	$\delta(C)_4$			
AET	138.9	136.4	128.7	129.4	42.7	56.4	44.9, 31.0
ASA	138.1	136.8	128.8	130.1	48.3	63.0	169.6, 150.8, 133.5, 132.9, 125.8, 123.4 20.8
ATP	137.7	136.6	128.6	129.5	27.8	55.6	145.0, 135.9, 118.5, 115.4
BHZ	145.5	135.7	128.3	129.6	45.3	[c]	166.4, 134.2, 130.4, 127.8, 127.4, 24.3, 20.5
CPA [b]	142.6	136.1	128.2	128.9	45.3	87.7	170.4, 152.6, 127.3, 123.9, 121.9, 114.5, 66.5
DBM	144.9	136.9	128.1	128.9	50.3	[c]	186.8, 138.6, 131.7, 128.4, 127.5, 95.0
DTZ	138.2	136.0	128.7	129.5	45.1	[c]	150.7, 147.7, 142.3, 129.8, 129.4, 128.4, 122.9, 122.7, 114.8
END [b]	142.7	136.4	128.0	128.6	45.4	71.2	176.3, 175.4, 134.3, 48.6, 47.8, 46.2
MBT	138.8	136.5	128.6	129.5	45.1	61.0	173.1, 152.0, 137.6, 125.6, 123.7, 120.7, 119.2
MET	137.4	136.5	128.8	129.7	42.7	57.3	64.1, 30.3
NPE	141.9	136.6	129.2	128.4	48.2	74.5	120.4, 18.6
PEA	138.6	136.8	128.8	129.9	48.3	63.1	162.6, 132.6, 122.5, 113.8, 63.5, 14.6
PNO	137.6	136.6	128.1	128.6	43.8	[c]	153.5, 136.4, 128.3, 127.6, 119.5
PTA [b]	143.0	136.4	128.2	128.8	45.3	[c]	169.8, 134.2, 130.0, 128.5
PTH	141.2	136.8	128.6	129.7	47.1	73.0	185.0, 184.3, 156.9, 134.9, 133.4, 132.0, 126.3, 122.9, 9.5
SAL	135.9	136.3	128.3	129.2	45.4	59.6	192.1, 161.2, 133.5, 130.1, 129.2, 119.6, 117.4
SUA	137.8	136.7	128.9	130.2	45.0	[c]	179.5, 170.4, 138.1, 128.7, 128.3, 119.7, 33.2, 30.1
TPC	137.9	136.8	128.9	130.2	48.3	63.0	166.6, 133.9, 132.3, 127.6
VAN	139.8	136.4	128.9	129.5	47.2	63.1	191.0, 155.5, 149.5, 126.3, 119.5, 117.4, 115.5, 54.5

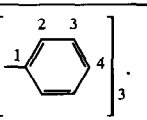
[a] $CDCl_3$ solvent unless specified. [b] DMSO solvent. [c] Assignment uncertain. [d] X–Sn 

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Table 4

Infrared absorbances in solution and in the solid state

Compound	ν(solid) (cm^{-1})					ν(solution) (cm^{-1})	
	ν(Sn–Ph)	ν(Sn–C)	ν(Sn–O/S)	ν_{as}(COO)	other	ν_{as}(COO)	other
AET	450 s	275 m	340 m, b (S)		3380 m [c]		3395 m [c]
		255 s			3260 m [d]		3260 m [d]
ASA	435 s	265 s	351 m	1640 s	1760 m [b]	1640 s	1760 s
		239 m					
ATP	445 s	290 w	355 m (S)		3455 m [c]		3465 [c]
		265 s			3360 m [d]		3375 m [d]
BHZ	438 s	265 m	355 w, b		1679, 1640 [a]		
		245 s			1530 [g], 829 [h]		
CPA	440 s	265 s	350 m	1570 s, b	1440 s [j]	1670 s, b	
DTZ	450 s	270 w	331 m (S)		3285 m [f]		3290 m [f]
		245 s					
END	450 s	280 s	350 m	1670 s, b	2900 s, b	1672 s, b	
		250 s					
MBT	450 s	270 m	350 m (S)				
		240 s					
MET	440 s	obsc.	330 m, b (S)		3470 b [e]		3440 b [e]
NPE	441 s	265 m	345 w, b		1650 m [a]		
		239 s					
PAA	448 s	270 s	345 m	1570 s			
PEA	438 s	290 w	340 m	1630 s		1634 s	
		250 s					
PNO	442 s	273 m	370 m (S)				
		235 s					
PTA	448 s	290 s	360 m, b	1650 s, b			
		265 s					
PTH	440 s	obsc.	obsc.		1635 s [k]	1670 s [k]	
SAL	448 s	obsc.	375 m, b		1622 s [k]		
SUA	448 s	268 s	360 m, b	1590 s, b	3260 [f], 3265 [f]		3345 m, b [f]
					1645 s [i]		1655 s [i]
TGA	440 s	285 m	380 m	1580 s		1582 s	
		255 s					
TPC	449 s	265 w	340 w, b	1620 s		1620 s	
		245 s					
VAN	448 s	obsc.	370 m, b		1630 s, b [k]	1665 s [k]	

w = weak, m = medium; s = strong; b = broad; obsc. = obscured. [a] ν(C=N). [b] ν(CO) of ester group. [c] ν_{as}(NH). [d] ν_s(NH). [e] ν(OH). [f] ν(NH). [g] ν(CNO). [h] ν(N–N). [i] ν(CO) of amide group. [j] ν_s(COO). [k] ν(CO).

coordination of the metal through a nitrogen atom. The methyl protons of the ligand are found at 2.08 and 2.13 ppm. In the complex, however, while one shifts downfield (2.28 ppm) the other appears upfield, at 1.43 ppm. All these data are consistent with a structure such as that in Fig. 1.

While the spectral data indicated that in general the Ph_3Sn moiety had a preference to bond to sulfur donors, the data for oxygen donors were particularly interesting. The following discussion examines a number of these derivatives in turn.

For the PTH compound, the disappearance of the O–H vibration in the free phthiocol, between 3150 and 3300 cm^{-1} and the appearance of a Sn–O mode at 485 cm^{-1} confirms bonding to the Ph_3Sn group through the phenolic oxygen. The

Table 5

Mössbauer data (for samples at 78 K)

Compound	isomer shift [a], δ (mm s^{-1})	quadrupole splitting, ΔE_Q (mm s^{-1})
AET	1.17	1.19
DBM	1.07	2.25
END	1.297	3.39
MET	1.26	1.37
NPE	1.128	2.10
PNO	1.17	1.67
PTH	1.18	2.22
VAN	1.264	3.00
DTC [b]	1.26–1.43	1.71–1.87 (Ref. 6)
MTC [b]	1.25–1.39	1.51–1.86

[a] Isomer shifts are measured with respect to $CaSnO_3$. [b] DTC = dithiocarbamate derivatives; MTC = monothiocarbamate derivatives.

strong band at 1670 cm^{-1} in the spectrum of phthiacol, which is characteristic of the carbonyl group, is shifted to 1635 cm^{-1} in the complex. Similar observations with other organometallics have attributed this to coordination through the carbonyl oxygen to the metal, since a reduction in the carbonyl electron density would lower its frequency of vibration [22]. An increase in coordination number of the tin

Table 6

^{119}Sn NMR spectral data [a]

Compound	$\delta(^{119}Sn)$ [c] (ppm)	
	A	B
AET	−66.2	−66.3
ASA	−106.8	−106.2
ATP	−70.5	−70.8
BHZ	−191.8	−192.5
CPA [b]	−265.2	−265.1
DBM	−224.2	−224.2
DTZ	−95.3	−95.5
END [b]	−238.9	−239.4
MBT	−84.5	−84.1
MET	−52.5	−51.1
NPE	−205.3	−205.3
PAA [b]	−265.4	−265.4
PEA	−113.9	−114.7
PNO	−162.5	−162.6
PTA [b]	−239.8	−240.4
PTH	−129.1	−129.2
SAL	−112.0	−112.1
SUA	−106.8	−107.4
TGA [b]	−202.2	−202.2
TPC	−106.7	−106.9
VAN	−104.1	−103.8

[a] In $CDCl_3$, unless otherwise indicated. [b] In DMSO solvent. [c] A: concentration *ca.* 70 mg cm^{-3}; B: saturated solution.

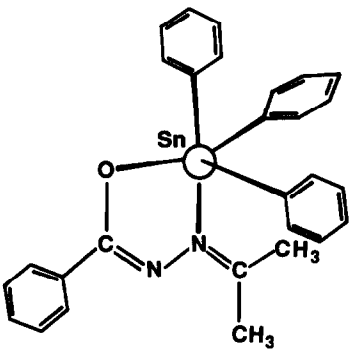

Fig. 1. Suggested structure for N-benzoyl-N^1-isopropylidene-hydrazino triphenylstannane(IV), BHZ complex.

atom is also suggested by the Mössbauer ΔE_Q value. The Mössbauer spectrum for the compound (Fig. 2) is thus indicative of a *cis*-trigonal bipyramidal geometry around the tin centre. In solution however, the carbonyl band is shifted to a higher wavenumber, implying therefore, that the strength of chelation is weak in solution and a change in coordination has occurred. This is supported by the δ(Sn) value of -129 ppm, indicative of four coordination (Table 6).

The carboxylic protons of endo-norbornene-*cis*-5,6 dicarboxylic acid are found at 11.35 ppm in the NMR spectrum. In the triphenyltin complex (END), resonances characteristic of carboxylic protons do not appear in the region expected; however, a new peak at 2.12 ppm is observed, with intensity equivalent to one proton. Since a very broad band, centering at *ca.* 2900 cm^{-1}, in the infrared spectrum of the complex remains, indicative of the presence of a hydroxyl group, the NMR peak at 2.12 ppm is therefore, assigned to the proton of the second (hence unreacted) carboxylic acid moiety. The upfield shift is then most likely a result of coordination to the tin atom through an oxygen of the carboxylic acid

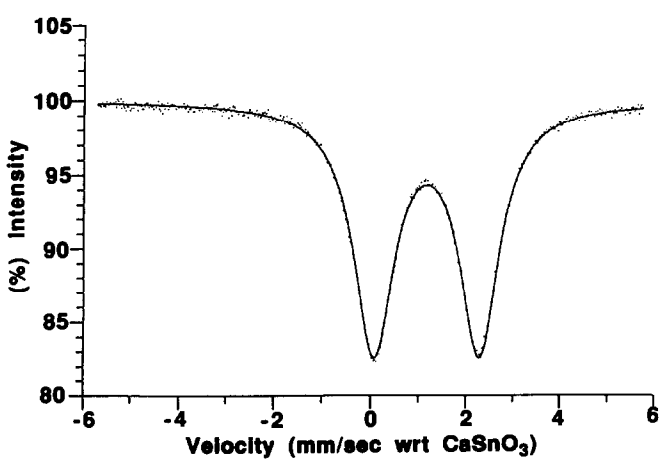

Fig. 2. Mössbauer spectrum of the PTH complex.

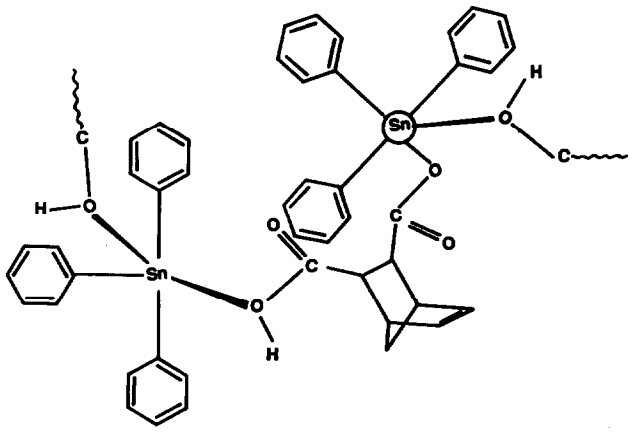

Fig. 3. Suggested polymeric structure for the END complex.

group. As the broad asymmetric COO stretching frequency is centered at *ca.* 1700 cm^{-1} in both the ligand and the complex, it would appear that it is the oxygen of the hydroxy moiety that participates in the coordination to the tin. Higher coordination is also suggested by the ^{119}Sn chemical shift, at -239 ppm, and by the ρ value of 3.00.

Difficulty arises however in determining the geometry around the tin center. Although the value of the quadrupole splitting parameter lies in the range typical of *trans*-isomers, it is also very near to the range suggested for *mer*-isomers. The δ(Sn) value (-239 ppm) is also indicative of *trans* type geometry: however, as no chemical shifts for authentic *mer*-compounds have been reported, and hence their range of absorbances are unknown, this possibility cannot be completely ruled out. Thus, while a *mer* geometry is possible on steric grounds, the insolubility of the complex suggests that a more likely structure is one in which the ligand is bridging and forms a polymer (Fig. 3). Here, the tin center retains the *trans*-tbp geometry. The PTA derivative, also having neighbouring carboxylic acid groups would appear to be similar.

The appearance of a ν(C=N) vibration at 1650 cm^{-1}, dimethyl absorbances at 1170 and 1120 cm^{-1} and a Sn–O stretching mode at 345 cm^{-1} confirm the formation of the propane-2-nitronato derivative, NPE. With a ^{119}Sn chemical shift of -205 ppm it is apparent that this ligand behaves in a bidentate manner and, together with the Mössbauer quadrupole splitting (2.10 mm s^{-1}), the evidence is consistent with *cis*-trigonal bipyramidal geometry around the tin center. These observations are consistent with those of other workers [23].

The phenolic proton, which gives a resonance at 10.85 ppm in the ^1H NMR spectrum of 1-hydroxy-2 methoxy benzaldehyde, disappears in the spectrum of the VAN complex, thus indicating its deprotonation and participation in the metal–oxygen bond formation. This is further supported by the appearance of a Sn–O infrared vibration at 372 cm^{-1}. The carbonyl band, observed at 1668 cm^{-1} in the infrared spectrum of the free ligand is shifted to 1630 cm^{-1} in the complex, showing its coordination to the metal center. This observation implies that the compound is five-coordinate in the solid state. The Mössbauer data strongly suggest that equatorial phenyl groups are present and that *trans* oxygen ligands

make up the coordination sphere. This geometry is easily accommodated because the phenolic oxygen and the aldehyde group are mutually *para* on the ligand aromatic ring. The –CHO to Sn interaction can be easily broken leading to a four coordinated structure in solution (Table 4). This is supported by the move of the carbonyl frequency to higher wavenumber in solution.

The $\Delta\nu$ value ($\Delta\nu = \nu_{as}(COO) - \nu_{s}(COO)$) which is useful in drawing structural inferences in the case of metal carboxylates is also used to determine the nature of bonding of the carboxylate group to organotin compounds [24]. For the 2,4-dichlorophenoxy acetic acid complex, CPA, the carboxylate group behaves in a bidentate manner, since $\Delta\nu$ is comparable to that in the sodium salt of the ligand. The observation of only one Sn–C vibration, at 270 cm^{-1}, also implies a planar SnC_3 skeleton [11]. These observations are consistent with a trigonal bipyramidal geometry around a five-coordinate tin atom, with the carboxylate moiety acting as a bridging bidentate. In solution (DMSO), the shift in the carboxyl group frequency to 1670 cm^{-1} indicates that the polymeric structure is disrupted and monomeric four coordinate units form. While solid/solution behavior of this type may be considered as characteristic of polymeric triphenyltin compounds [25], the ^{119}Sn chemical shift (−265 ppm), typical of five-coordinate compounds, suggests otherwise. The large upfield shift, however, is expected since DMSO is known to coordinate with four coordinate triphenyltin complexes in solution [26]. Similar structural implications can be drawn for the PAA derivative.

Finally, the spectroscopic data for the PNO derivative are somewhat ambiguous. A $\delta(Sn)$ value of −162.5 ppm falls between the generally accepted ranges for four- and five-coordination, while the Mössbauer ΔE_Q value (1.67 mm s^{-1}) lies in the middle of the range observed for the monothiocarbamates, which are four-coordinate compounds. In the absence of further data, we currently favor a four-coordinate description, but studies on such systems are continuing.

Conclusion

The triphenyltin moiety generally assumes a four-coordinate structure when combined with sulfur ligands. With oxygen donors, however, clear examples of four-coordinate (*e.g.* ASA, PEA, SAL), five-coordinate *cis*-tbp (*e.g.* PTH, NPE) or *trans*-tbp (*e.g.* END, VAN) and bridging carboxylate species (*e.g.* CPA) are obtained.

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