Inorganica Chimica Acta, 12 (1975) 123–126

Infrared and Mössbauer Studies on Adducts $R_3SnOH \cdot R_3MX$ (M = Sn, Pb; X = Pseudohalide)

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Received July 5, 1974

The synthesis of the solid adducts $Me_3SnOH \cdot Me_3SnNCO$, $Me_3SnOH \cdot Me_3SnNCS$, $Me_3SnOH \cdot Me_3PbN_3$, $Ph_3SnOH \cdot Ph_3SnN_3$ *is reported. The compounds have been investigated by infrared and Mössbauer spectroscopy. Their structure probably consists of polymeric* $OH–R_3Sn–X–R_3Sn(Pb)$ *chains in which hydroxyl and pseudohalide (X) groups are bridging pentacoordinate tin atoms. In contrast to the triphenyl compound, the trimethyl derivatives show evidence of hydrogen bonding between adjacent chains.*

Introduction

The occurrence in the solid state of compounds $Me_3SnOH \cdot Me_3SnNCO$[1] and $Me_3SnOH \cdot Me_3SnN_3$[1,2] has been recently reported. Both compounds have been first obtained occasionally from hydrolised samples of the corresponding trimethyltin pseudohalide[1], and subsequently we demonstrated that the azide–hydroxide could be prepared from stoichiometric amounts of parent trimethyltin derivatives in a suitable solvent[2]. The essential structural features of the isocyanate–hydroxide have been elucidated by a X-ray study[1] which showed that in the crystal there are chains of Me_3Sn^{IV} units alternatively bridged by oxygen (from OH) and nitrogen (from NCO) atoms, interconnected by $NCO \cdots HO$ hydrogen bonds. Vibrational and Mössbauer spectroscopic investigations[2] pointed to an analogous structure for $Me_3SnOH \cdot Me_3SnN_3$.

No other derivatives of this type seem to have been reported in the literature; besides, the possible occurrence of a large class of compounds obtainable by simple 1:1 addition reaction of different triorganotin salts has not been investigated. Such a possibility, as well as that of obtaining adducts between triorganotin and triorganolead salts, has been preliminarily explored in our laboratory, and the present work reports a number of novel compounds of this class which have been characterised by infrared and Mössbauer spectroscopy.

Experimental

The reagent compounds Me_3SnOH and Ph_3SnOH were FLUKA purum commercial products, while Me_3SnNCS[3], Me_3SnNCO[4], Me_3PbN_3[5] and Ph_3SnN_3[6] were prepared according to literature methods and their purity checked from m.p. and IR spectra.

Following the preparative scheme reported for $Me_3SnOH \cdot Me_3SnN_3$[2], the possible syntheses of compounds $Me_3SnOH \cdot Me_3SnX$ (X = NCS, CN), $Me_3SnOH \cdot Me_3PbX$ (X = NCS, N_3) and $Ph_3SnOH \cdot Ph_3SnX$ (X = N_3, NCO, NCS) were investigated. This was effected by mixing equimolar amounts of the reagents (4–5 mmol) dissolved in hot solvents (25–50 ml of benzene, n-hexane, acetone, acetonitrile, ethanol, or solvent mixtures). The white crystalline adducts $Me_3SnOH \cdot Me_3SnNCS$, $Me_3SnOH \cdot Me_3SnNCO$, $Me_3SnOH \cdot Me_3PbN_3$ and $Ph_3SnOH \cdot Ph_3SnN_3$ precipitated (mostly on cooling), and were filtered off, recrystallized (or washed) using the solvent or solvent mixture employed in the preparation ($Me_3SnOH \cdot Me_3SnNCS$ and $Me_3SnOH \cdot Me_3SnNCO$: 1:1 n-hexane–benzene; $Me_3SnOH \cdot Me_3PbN_3$: 1:2 n-hexane–benzene; $Ph_3SnOH \cdot Ph_3SnN_3$: acetonitrile), and dried under vacuum. Analytical data of novel compounds are in Table I. Syntheses attempted in this way from other couples of R_3MX compounds did not give the desired adduct; on cooling and/or partially evaporating the reaction mixture a single salt or a non-stoichiometric solid were recovered.

The already known compound $Me_3SnOH \cdot Me_3SnNCO$[1] was investigated here in order to get the spectroscopic characteristics of a term of the series having a known molecular structure. On the other hand, we were unable to synthesize the compound described by Hall and Britton[1], m.p. 105 °C, either by sublimation of intimate equimolar mixtures of reactants[1] or by reaction in solution phase (see earlier). With thc latter method a compound was obtained which was gradually sublimating above ~65 °C and showed a sharp melting point at 81–82 °C. This compound, which contains

TABLE I. Analytical Data [found (calcd.)%].

Compound	M.p.(°C, unc.)	C	H	N	O	Sn
$Me_3SnOH \cdot Me_3SnNCS$[a]	109–111	20.66	4.58	3.36	3.90	59.47
		(20.88)	(4.76)	(3.48)	(3.87)	(58.95)
$Me_3SnOH \cdot Me_3PbN_3$	b	14.94	3.93	8.98	3.54	
		(15.17)	(4.18)	(8.84)	(3.37)	
$Ph_3SnOH \cdot Ph_3SnN_3$	120–122[c]	57.68	4.32	5.40	2.31	31.44
		(56.95)	(4.13)	(5.54)	(2.11)	(31.27)

[a] S: 8.11(7.96). [b] Phase transition at 120° C. [c] Phase transition at 85–90° C.

TABLE II. Relevant IR Bands (cm^{-1}) of Trimethyltin Mixed Salts[a].

$Me_3SnOH \cdot Me_3SnNCS$	$Me_3SnOH \cdot Me_3SnNCO$	$Me_3SnOH \cdot Me_3PbN_3$	Assignments
3400 m, br	3520 m, br	3480 m, br	ν(OH)
2095 vs 2065 s	2165 vs	2050 vs	ν_{as}(Pseudohalide)
		1335 m	$2\times\delta(N_3)$
	1290 mw	1290 m	ν_s(N_3 or NCO)
1025 m, br	1045 m, br	1060 m, br	δ(OH)
	670 m		?
	620 m	660 m	δ(N_3 or NCO)
580 sh			ν(SnO)?
555 s	550 s	550 ms	$\nu_{as}(SnC_3)$
545 ms			$\nu_{as}(SnC_3)$?
525 m	525 mw	520 w	$\nu_s(SnC_3)$
		495 ms	$\nu_{as}(PbC_3)$
490 ms, br	480 ms, br		ν(SnO)
		480 460 br 435	$\nu(SnO)+\nu_s(PbC_3)$
435 w 420 mw			δ(NCS)?

[a] s = strong; m = medium; w = weak; br = broad; sh = shoulder; v = very.

both OH and NCO groups (from the IR spectrum), was recovered unchanged on recrystallization. *Anal.* for $C_7H_{19}NO_2Sn$, found (calcd.)%: N, 3.40 (3.62); Sn, 61.16 (61.40). This suggests that a modified form of the desired adduct has been obtained.

The IR spectra of the compounds were investigated as Nujol mulls in the range 4000–250 cm^{-1} with a Perkin–Elmer model 457 spectrometer. The assignments of relevant absorptions of the trimethyl derivatives are reported in Table II. The IR bands of $Ph_3SnOH \cdot Ph_3SnN_3$ (except those in the regions covered by nujol bands) are as follows: 3620 vw; 3060 m; 3040 m; 2090 ms; 2050 s; 1480 m; 1425 ms; 1375 w; 1300 w; 1255 w; 1185 vw; 1150 w; 1075 m; 1020 mw; 995 m; 975 vw; 960 vw; 910 m; 890 m; 845 w; 725 sh; 720 vs; 690 vs; 655 mw; 445 m br; 370 m br; 300 m br; 270 sh.

Mössbauer spectra were determined using a Elscint (Haifa) transducer assembly operating at constant acceleration, triangular waveform, in conjunction with a Laben 400 (Milano) multichannel analyser operating in the multiscaler mode. The absorber was held at

TABLE III. Mössbauer Parameters (mm sec^{-1}) at Liquid N_2 Temperature.

Compound	δ[a]	ΔE[b]	Γ_+[c]	Γ_-[c]
$Me_3SnOH \cdot Me_3SnNCS$	1.28	3.16	1.30	1.22
$Me_3SnOH \cdot Me_3SnNCO$[d]	1.31	3.24	1.11	1.16
$Me_3SnOH \cdot Me_3PbN_3$	1.28	3.12	1.08	0.88
$Me_3SnOH \cdot Me_3SnN_3$[e]	1.29	3.25	1.01	0.98
$Ph_3SnOH \cdot Ph_3SnN_3$	1.21	2.90	1.16	1.06

[a] Isomer shift, relative to the centroid of a $BaSnO_3$–$BaSnO_3$ r.t. spectrum. [b] Nuclear quadrupole splitting. [c] Full width at half height of the resonant peaks. [d] The compound prepared in this work, m.p. 81–82° C. [e] Ref. 2.

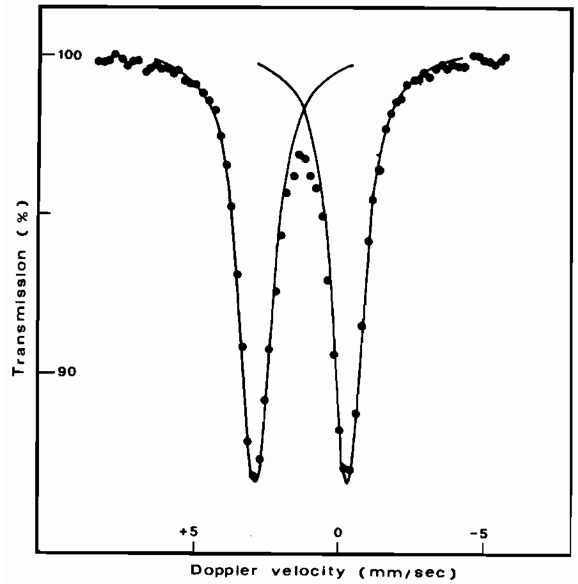

Figure 1. Mössbauer spectrum of $Me_3SnOH \cdot Me_3SnNCS$ at 78 °K. The Doppler velocity is reported with respect to the centre of a $BaSnO_3$ spectrum at room temperature. The full curves are the computer fitted Lorentzian lines.

liquid N_2 temperature, monitorized by a thermocouple. The source was $Ba^{119m}SnO_3$ at room temperature. Spectrometer calibration was obtained from replicated six line spectra of Fe foils, 99.9% purity. The zero of the Doppler velocity scale was determined from $BaSnO_3$–$BaSnO_3$ room temperature spectra. Data reduction was effected by computer treatment (IBM 360/44 at C.U.C., Palermo) using a suitable program. A typical spectrum is shown in Fig. 1. The Mössbauer parameters are summarized in Table III.

Discussion

A careful comparison of the infrared spectra of mixed hydroxide–pseudohalide trimethyltin(IV) derivatives so far prepared with those of the reacting salts allowed the assignments of relevant vibrational bands reported in Table II. With respect to the values 3620 cm^{-1} and 920 cm^{-1} observed for ν(OH) and δ(OH), respectively, in polymeric Me_3SnOH[7,8] (whose molecular structure[9] consists of —OH–Me_3Sn–OH–Me_3Sn— non interacting chains), the corresponding bands in the mixed salts are broadened and shifted to lower and higher frequencies respectively. This is consistent with the occurrence of hydrogen bonds in the compounds here investigated. For $Me_3SnOH \cdot Me_3SnNCS$, modes associated to ν(SnO) or ν(SnOSn) vibrations seem to contribute to the absorptions at 580 cm^{-1} and 490 cm^{-1} (Table II). A band occurs around 490 cm^{-1} in all mixed salts, and the proposed assignments (Table II) correspond to those for $(Me_3SnOH)_2 \cdot Me_3SnBr$, $Me_3SnOH \cdot Me_3SnBr \cdot H_2O$ and $(Me_3Sn)_3OBr$[10]. Infrared active $\nu_s(SnC_3)$ modes occur in all spectra showing that the trimethyltin(IV) moiety sistematically deviates from a planar configuration in our adducts. An analogous conclusion seems to be valid for the Me_3Pb^{IV} unit in the compounds $Me_3SnOH \cdot Me_3PbN_3$, for which a component vibration of the broad band centered at 460 cm^{-1} (mainly concerned with metal–oxygen modes) may be probably attributed to $\nu_s(PbC_3)$ (Table II). A double $\nu_{as}(SnC_3)$ mode seems to appear in the IR spectrum of the hydroxide–thiocyanate mixed salt (Table II). This could be explained by admitting, for instance, that the NCS group is asymmetrically linking two adjacent tin atoms analogously to findings for the NCO ligand in the hydroxide–isocyanate[1]. Moreover, the IR spectrum of this compound shows two weak bands at 435 cm^{-1} and 420 cm^{-1}, absent in the spectra of both Me_3SnOH[7,8] and Me_3SnNCS[11], which have been tentatively assigned to δ(NCS).

Further elucidations of structures can be extracted from Mössbauer data. It has been reported that the trimethyltin derivatives Me_3SnX (X = OH[9], N_3[12], NCO[13], NCS[14]) are polymeric compounds in the solid state, with hydroxyl or pseudohalide groups more or less strongly bridging Me_3Sn^{IV} moieties, the environment of the tin(IV) atom being trigonal bipyramidal (axial X). The values of the quadrupole splitting parameter, ΔE, of Table III suggest that a similar coordination around the tin atom is retained in the mixed salts. Moreover, on the basis of an additive model for the contribution of the different ligands to the total ΔE at the tin nucleus, for a trigonal bipyramidal arrangement of the type $X(SnMe_3)X'$ (apical X) the ΔE parameter can be expressed[15–18] as $\{2[X] + 2[X'] - 3[Me]\}$, where the bracketed terms represent the contributions of the different ligands. The fact that the ΔE values for the hydroxide–pseudohalide compounds are intermediate between those of Me_3SnOH[2] and the corresponding Me_3Snpseudohalide[2,13,19] suggests that both ligands (OH, pseudohalide) are linked to any tin(IV) atom. This hypothesis appears to be supported by analogous considerations about the isomer shift, δ, data, this parameter being related to the electron density at the tin nucleus. Again, it is observed that δ values of compounds in Table III are intermediate between those for Me_3SnOH and the pseudohalide. Besides, the line widths of the two quadrupole split components are narrow enough to exclude the presence of non-equivalent tin atoms.

It seems, therefore, that the previously reported structure of $Me_3SnOH \cdot Me_3SnNCO$[1] may be proposed also for $Me_3SnOH \cdot Me_3SnNCS$, $Me_3SnOH \cdot Me_3PbN_3$, as well as for the hydroxide–isocyanate obtained in this work, notwithstanding that the latter compound should differ in some respect from that of Hall and

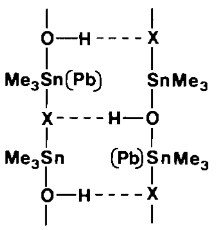

Figure 2. Proposed structure of trimethylmetal hydroxide–pseudohalide mixed salts. Pseudohalide groups, X (= N_3, NCO, NCS), presumably bridge two trimethylmetal moieties through bidentate N atom.

Britton[1]. This type of structure is shown in Figure 2. From the considerations reported above, as well as from the fact that the very similar Mössbauer parameters displayed by the mixed compounds in Table III suggest that the tin atom experiences, in all cases, a very similar chemical environment, we are inclined to assume the pseudohalide groups (X = N_3, NCO, NCS) coordinating through bidentate α-N atom.

In the case of the hydroxide–thiocyanate, the latter hypothesis may appear at variance with the previous assignments to δ(NCS) of infrared bands in the region 450–400 cm^{-1}, which is a typical range for S-bonded thiocyanate groups[20–22]. On the other hand, it is not clear whether this spectral behaviour should be ascribed to the hydrogen bond eventually explicated by the S atom.

As far as the compound $Ph_3SnOH \cdot Ph_3SnN_3$ is concerned, the IR spectrum (reported under Experimental) practically consists of the superposition of the spectra of the two triphenyltin parent salts[6,24]. Noticeably, bands at 2090 cm^{-1} and 2050 cm^{-1} ($\nu_{as}(N_3)$), 3620 cm^{-1} (ν(OH)), 910 cm^{-1} and 890 cm^{-1} (δ(OH)) strictly correspond to analogous bands occurring in the spectra of Ph_3SnN_3[6] and Ph_3SnOH[24], which suggests that N_3 and OH groups are involved in the same type of bonds in both the original and mixed salts. The molecular structures of Ph_3SnN_3 and Ph_3SnOH have not been reported, although polymeric solids are likely to exist; moreover, the frequency values associated with OH modes would suggest that no hydrogen bonding is present in Ph_3SnOH as well as in $Ph_3SnOH \cdot Ph_3SnN_3$.

From Mössbauer data, the presence of pentacoordinate tin atoms should be inferred in both Ph_3SnOH and Ph_3SnN_3 whose reported values[25] for δ and ΔE are, respectively, 1.18, 2.68 mm sec^{-1} (for the hydroxide) and 1.40, 3.19 mm sec^{-1} (for the azide). Thus, the observed values for triphenyltin hydroxide–azide Mössbauer parameters do not exclude the possible occurrence of $(OH)Ph_3Sn(N_3)Ph_3Sn$ polymeric chains also in this compound. This hypothesis is also supported by the average width of Mössbauer peaks which rules out the presence of non-equivalent tin atoms.

The absence of the hydrogen bond interaction seems then to constitute the main difference with respect to the structure of the analogous trimethyltin compound, and is very probably due to the larger interchain distance necessary to locate the larger triphenyltin moiety.

Acknowledgements

The financial support by CNR (Roma) is acknowledged.

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