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THE PREPARATION AND TIN-119*m* MÖSSBAUER SPECTRA OF TRI-n-BUTYLSTANNYL ESTERS OF HETEROCYCLIC AND SUBSTITUTED AROMATIC CARBOXYLIC ACIDS

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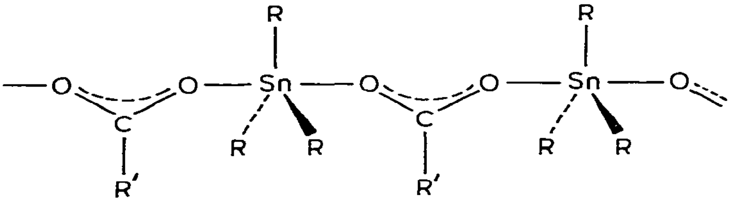
Summary

The ^{119m}Sn Mössbauer and infrared data are reported for fifteen tributyltin carboxylates. Although the Mössbauer data at 80 K shows them all to be pentacoordinate polymers, the infrared data indicates that, at room temperature, some of the compounds exist as tetracoordinate monomeric species.

Introduction

There has been considerable interest in the structure of trialkyl- and triaryltin carboxylates [1—7] which are reported [1—4] to form polymers of the type I involving bridging O—C—O groups and planar R_3Sn moieties in which the Sn is in a 5-coordinate trigonal bipyramidal geometry. It has been shown that, if R is bulky [5,8,9] or if R branches [2] at the α-carbon (e.g. triphenyltin 2-ethylhexoate), then the compounds exist as tetracoordinate monomeric esters.



(I)

A variety of techniques have been used to study the structure of such compounds. The crystal structures have been determined for tribenzyl- [4] and trimethyl-tin acetates [10], trimethyltin formate [11] and trifluoroacetate [10], all of which are polymeric with five-coordinate tin atoms, and for tricyclohexyltin acetate [5], in which the tin is four-coordinate. X-ray studies have also shown that trimethyltin glycinate [12] and pyridine-2-carboxylate monohydrate [13] contain pentacoordinate trigonal bipyramidal tin atoms. In the former, intermolecular bridging occurs via the NH_2 groups [12], whereas, in the latter, the pyridine-2-carboxylate anion functions as a monodentate ligand and the fifth coordination site is occupied by the water molecule [13].

Infrared data $\nu(C{=}O)$ has been used to infer coordination through the carbonyl oxygen or the presence of free carbonyl groups. In the trimethyltin carboxylates the absence of $\nu_{sym}(SnC_3)$ has been used as an indication of a planar SnC_3 configuration and hence five-coordination. The ^{119m}Sn Mössbauer spectra provide additional information concerning the electron density and site symmetry at the tin nucleus. Herber et al. [14] have suggested that the coordination number can be obtained from ρ, the ratio of the quadrupole splitting (ΔEq) to the isomer shift (δ), and that, for a value of ρ greater than 2.1, five-coordination can be assumed.

A series of tributyltin aryl and heteroaryl carboxylates have been investigated, and their structures deduced from both Mössbauer and infrared data.

Experimental

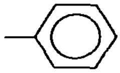
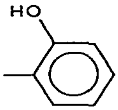
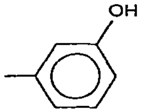
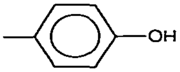
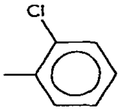
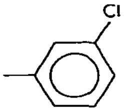
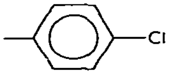
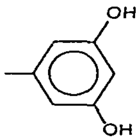
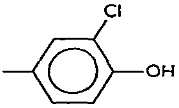
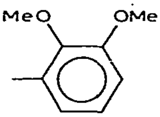
All the compounds were prepared by heating a mixture of bis(tri-n-butyltin) oxide (1 mol) and the appropriate carboxylic acid (2 mol) in toluene and removing the water azeotropically using a Dean and Stark apparatus. After all the water had been removed from the reaction mixture, the solvent was removed on a rotary evaporator and the residue either distilled in vacuo or recrystallised from petroleum ether (60—80). The physical data for all the compounds, together with the literature values, where known, are shown in Table 1.

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration spectrometer, the symmetrical triangular velocity drive waveform being derived from the multichannel analyser driven in the time mode by an external crystal controlled oscillator; 512 channels were used thorughout. A 15 mCi $Ca^{119}SnO_3$ source was used at room temperature, and the samples were packed in perspex discs and cooled to 80 K using a continueous flow cryostat with Helium exchange gas. The spectrometer was calibrated using the magnetic splitting of an enriched ^{57}Fe absorber foil. The data were folded to determine the zero velocity position, and the folded data fitted with Lorentzian functions by a least squares fitting program [20]. The non-linearity of the spectrometer was determined, by a free fit of the Fe data, to be less than ±0.06%. The quoted experimental error of ±0.02 mm sec^{-1} in the measured values of isomer shift and quadrupole splitting takes into account errors associated with non-linearities, calibration, zero velocity determination and computer fitting.

The infrared spectra were obtained as either liquids, Nujol mulls or KBr discs on a Unicam SP200 spectrophotometer.

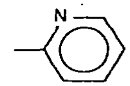
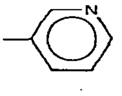
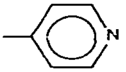
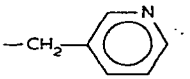
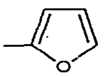
TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR TRIBUTYLTIN CARBOXYLATES

R in $Bu_3SnOCOR$	M.p. (°C)	B.p. (°C/mmHg)	Analysis (Found (calcd.) (%))			
			C	H	N	Cl
		128—130/0.07 (166—168/1)[a]	55.40 (55.47)	7.98 (7.79)	—	—
		159/0.15[b]	53.69 (53.40)	7.70 (7.49)	—	—
		oil[c]	53.66 (53.40)	7.89 (7.49)	—	—
	65—67 (71—73)[d]		53.66 (53.40)	7.55 (7.49)	—	—
	54—57		51.70 (51.18)	7.01 (6.96)		8.17 (7.97)
		152—154/0.15	51.02 (51.18)	6.95 (6.96)	—	8.26 (7.97)
		144—148/0.2	51.01 (51.18)	7.04 (6.96)	—	7.54 (7.97)
	75		51.14 (51.47)	7.49 (7.23)	—	—
	67—70		49.56 (49.40)	6.74 (6.72)	—	7.51 (7.69)
	49—50		53.90 (53.50)	7.68 (7.64)	—	—

continued

TABLE 1 (continued)

R in $Bu_3SnOCOR$	M.p. (°C)	B.p. (°C/mmHg)	Analysis (Found (calcd.) (%))			
			C	H	N	Cl
	118—120		52.46 (52.43)	7.52 (7.52)	3.46 (3.39)	—
	68—70 (70) [e]		52.35 (52.43)	7.45 (7.52)	3.25 (3.39)	—
	134—136 (136—137) [f]		52.57 (52.43)	7.54 (7.52)	3.56 (3.39)	—
		152—154/0.15	53.71 (53.52)	7.99 (7.75)	3.15 (3.29)	—
	86 (86—87) [e]		50.62 (50.87)	7.67 (7.48)	—	—

[a] Ref. 15. [b] Ref. 16 reports d_{20} 1.210 g cm^{-3}. [c] Decomposes on distillation in vacuo. [d] Ref. 17. [e] Ref. 18. [f] Ref. 19.

Results and discussion

Table 2 shows the ^{119m}Sn Mössbauer data for the series of tributyltin carboxylates. The spectra are well resolved quadrupole split lines, an example of which is shown in Fig. 1.

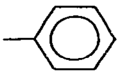
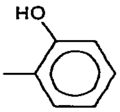
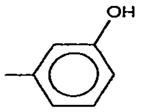
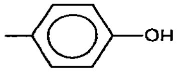
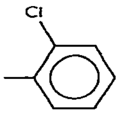
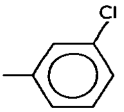
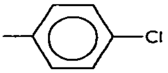
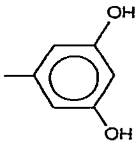
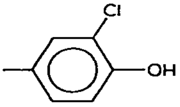
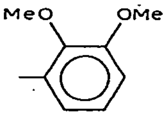
The isomer shift values are consistent with other trialkyl- [3] or triaryl-tin carboxylates [2] in that they are all within a small range, in this case 1.45 ± 0.05 mm sec^{-1}. This shows there to be very little change in the total *s*-electron density at the tin nucleus, which suggests that there is no significant change in the electron withdrawal from the tin with changes in electronegativity of the aryl rings.

All the values of ρ are larger than 2.10, with one exception, and, therefore, at 80 K, these samples can be interpreted from the Mössbauer data as having the pentacoordinate structure (I). The only apparent exception to this is the tributyltin 3,5-dihydroxybenzoate which has a value of $\rho = 2.04$. Other organotin carboxylates that have been shown to be tetracoordinate have $\Delta < 2.4$ mm sec^{-1}. It is felt that, in this case the reduced value may indicate a more symmetric O--Sn—O unit in II.

All the series showed a very slight asymmetry in the relative depths of the lines; this has previously been noted by Debye et al. [1] in a similar series of

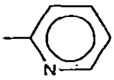
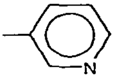
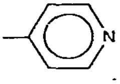
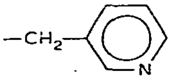
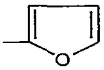
TABLE 2

MÖSSBAUER DATA FOR 
$Bu_3SnO\overset{O}{\overset{\|}{C}}R$

R	Isomer shift[a] $\delta \pm 0.02$ (mm s^{-1})	Quadrupole splitting $\Delta \pm 0.02$ (mm s^{-1})	$\rho \pm 0.05$
	1.47	3.59	2.44
	1.48	3.66	2.27
	1.45	3.22	2.22
	1.44	3.19	2.22
	1.49	3.72	2.50
	1.47	3.52	2.39
	1.47	3.65	2.48
	1.43	2.92	2.04
	1.45	3.23	2.22
	1.47	3.72	2.53

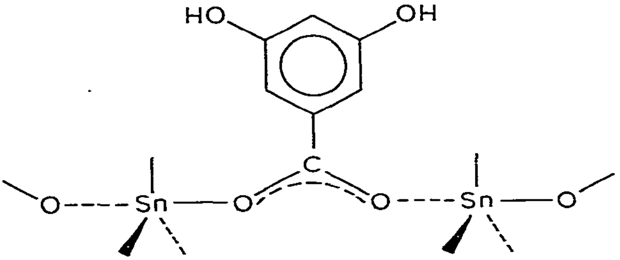
continued

TABLE 2 (continued)

R	Isomer shift[a] $\delta \pm 0.02$ mm sec^{-1}	quadrupole splitting $\Delta \pm 0.02$ mm sec^{-1}	$\rho \pm 0.05$
	1.45	3.75	2.59
	1.40	3.28	2.34
	1.41	3.30	2.34
	1.42	3.34	2.35
	1.48	3.78	2.55

[a] Isomer shift relative to $CaSnO_3$.

trialkyltin acetates. It is interesting to note that the Mössbauer spectra of tributyltin pyridine-4-carboxylate gave a very large asymmetry with the line intensities having a ratio of 1/1.5. We interpret this as being due to the partial alignment of the polycrystalline sample within the absorber holder. A duplicate spectrum, recorded, on rotating the sample through 45° reduced the intensity ratio to 1 : 1.06.



(II)

The infra-red data is shown in Table 3.

If a triorganotin carboxylate is pentacoordinate it has been shown [2] that the IR data for the solid state COO absorptions are far removed from the usual

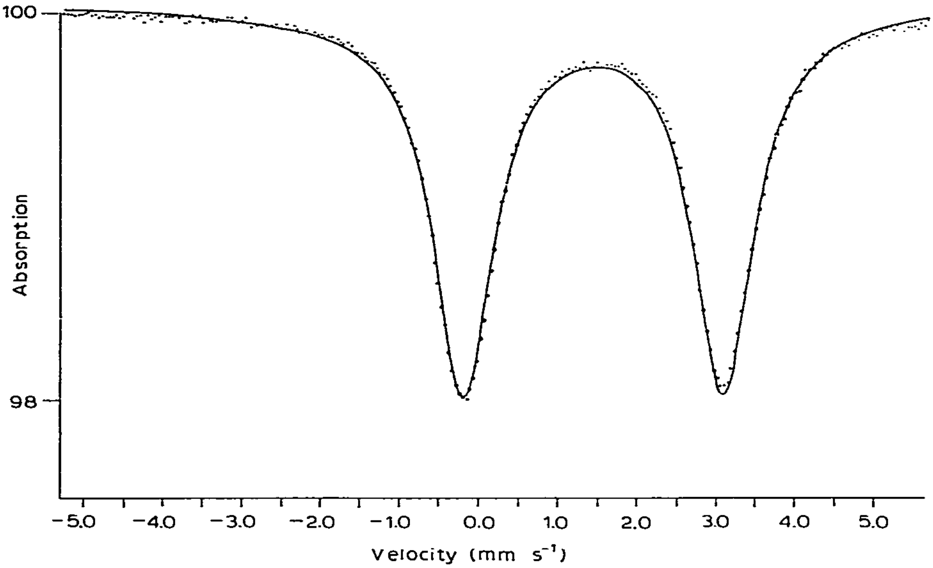


Fig. 1. ^{119m}Sn Mössbauer spectrum of tributyltin 3-pyridylcarboxylate.

organic ester absorptions (1740 and 1240 cm^{-1}) and occur at approximately 1560 and 1370 cm^{-1}. If, however, the compounds are diluted in CCl_4 then these bands should shift towards the normal ester frequencies resulting from monomeric tetrahedral tin atoms. Following this interpretation of the shift, the ν(C=O) absorption indicates that five of the samples, which are solid at room temperature, show pentacoordination. The ν(C—O) frequency was not used because it was very broad and difficult to assign. These are the tributyltin 2-chlorobenzoate, 3-chloro-4-hydroxybenzoate, 2,3-dimethoxybenzoate, pyridine-2-carboxylate and furan-2-carboxylate.

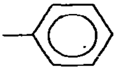
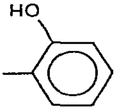
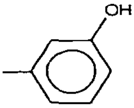
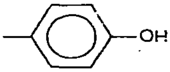
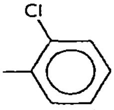
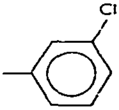
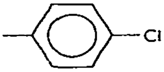
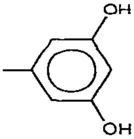
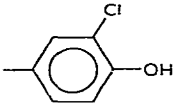
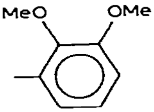
The six tributyltin carboxylates which are liquid at room temperature all show carbonyl absorption frequencies consistent with monomeric tetracoordinate tin species, while the Mössbauer results indicate a pentacoordinate structure at 80 K. An infrared spectrum of tributyltin benzoate was recorded at 140 K and showed a shift in the carbonyl frequencies from 1653 → 1578 cm^{-1} corresponding to an increase in coordination number from four to five. We conclude for the samples which are liquid at room temperature that a tetrahedral monomeric structure exists, while on solidification the pentacoordinate polymeric structure I is stabilised. This change in structure from the liquid to solid state has also been observed [21] for tributyltin methoxide and phenoxide.

Four tributyltin carboxylates are solid at room temperature and do not show the expected shift in the carbonyl absorptions when diluted in CCl_4. Two of these, tributyltin 4-hydroxybenzoate and 3,5-dihydroxybenzoate show ν(C=O) at 1610 and 1590 cm^{-1} respectively. Comparing these with the remainder of the series it might be expected that these are pentacoordinate and that, on dilution with CCl_4, they remain as associated polymers.

The other two compounds, tributyltin pyridine-3-carboxylate and pyridine-4-carboxylate show carbonyl absorption frequencies at 1650 cm^{-1}, which would

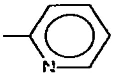
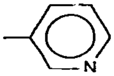
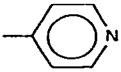
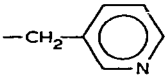
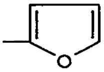
TABLE 3

ν(C=O) FREQUENCIES FOR $Bu_3SnO\overset{\overset{O}{\|}}{C}R$ (cm^{-1})

R	Liquid film	In CCl$_4$ compensated cells
	1653	1647
	1640/1602	1638/1605
	1635/1590	1638/1607
	1575/1618[a]	1613
	1570[b]	1660
	1558/1645	1600/1650
	1592/1641	1608/1650
	1590[a]	1583
	1647/1615[a]	1610/1647
	1570[a]	1650

continued

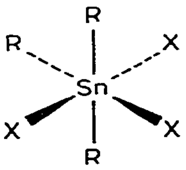
TABLE 3 (continued)

R	Liquid film	In CCl$_4$ compensated cells
	1538/1550/1577/ 1603	1600[c]/1642
	1601/1643[a]	1601/1650
	1653[a]	1658
	1592/1639	1600/1660
	1546/1572[b]	1598*/1665

[a] KBr disc. [b] Nujol mull. [c] Medium.

indicate that any pentacoordination does not occur through the carbonyl oxygen but instead involves the nitrogen of the pyridine ring, as in the triphenyltin derivative of 4-thiopyridone [22].

The tributyltin pyridine-2-carboxylate shows several intense infrared bands in the region 1538—1603 cm^{-1}. The analogous trimethyltin derivative shows [23] similar absorptions and also multiple tin—carbon stretching modes. The latter compound has been suggested to have the *mer*-6-coordinate structure III because of the apparent absence of a planar SnC$_3$ unit, ruling out the normal *trans*-5-coordinate structure I. Furthermore, the magnitude of the Mössbauer quadrupole splitting eliminates both *cis*-five- and *fac*-six-coordinate structures for this compound. On the basis of our spectroscopic data, a similar structural assignment can be made for the tributyltin pyridine-2-carboxylate.



(III)

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