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SYNTHESIS AND SPECTROSCOPIC STUDIES OF MONO- AND DI-ORGANOTIN(IV) DERIVATIVES OF PYRIDINECARBOXYLIC ACIDS

ALAN J. CROWE, ROBIN HILL, PETER J. SMITH

International Tin Research Institute, Greenford, Middlesex, UB6 7AQ (Great Britain)

JOHN S. BROOKS and RALPH FORMSTONE

Department of Applied Physics, Sheffield City Polytechnic, Pond Street, Sheffield, S1 1WB (Great Britain)

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Summary

A series of diorganotin bis(pyridinecarboxylates), $R_2Sn(O.CO.C_5H_4N\text{-}n)_2$ (R = Me, n = 2—4; R = Ph, n = 2 or 3), diorganochlorotin pyridinecarboxylates, $R_2ClSnO.CO.C_5H_4N\text{-}n$ (R = Me or Ph, n = 2; R = Me, n = 4) and monoorganodichlorotin pyridinecarboxylates, $RCl_2Sn(O.CO.C_5H_4N\text{-}2)$ (R = Bu or Ph), has been synthesised and their structures investigated by ^{119m}Sn Mössbauer and infrared spectroscopy.

The spectra indicate that, in the solid state, the three dimethyltin bis(pyridinecarboxylates), along with diphenyltin bis(3-pyridinecarboxylate) and dimethylchloro- and diphenylchloro-tin 2-pyridinecarboxylate, adopt a *trans*-octahedral R_2SnX_4 geometry. Dimethylchlorotin 4-pyridinecarboxylate, however, possesses a five-coordinate trigonal bipyramidal *cis*-R_2SnX_3 stereochemistry, whilst diphenyltin bis(2-pyridinecarboxylate) adopts an octahedral *cis*-R_2SnX_4 structure, with two bidentate *N*-chelating pyridinecarboxylate groups.

Introduction

In an earlier paper [1], we described the Mössbauer and infrared spectra of a series of tributyltin pyridinecarboxylates, $Bu_3SnO.CO.C_5H_4N\text{-}n$, and it was concluded that, in the solid state, these exist as polymers containing five-coordinate tin atoms in a trigonal bipyramidal R_3SnX_2 geometry, due to intermolecular bridging by the carboxyl group. In trimethyltin 2-pyridinecarboxylate monohydrate, $Me_3SnO.CO.C_5H_4N\text{-}2 \cdot H_2O$, however, pentacoordination of the tin is achieved by a donor water molecule occupying an axial position and the 2-pyridinecarboxylate ligand is unidentate [2]. No coordination of the pyridine nitrogen atom to tin was observed in these cases. In contrast, X-ray dif-

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fraction studies have indicated the occurrence of intermolecular and weak intramolecular N → Sn coordination in the compounds, $Ph_3SnSC_5H_4N$-4 [3] and $Bu_2Sn(SC_5H_3N$-2, NO_2-5$)_2$ [4], respectively. It was therefore of interest to extend our original study to the di- and mono-organotin(IV) derivatives of pyridinecarboxylic acids, in order to determine whether an increase in Lewis Acidity of the tin atom would favour chelation by the carboxylate group and/or the pyridine nitrogen.

The principal method of synthesis investigated for these compounds was a room temperature exchange reaction between the appropriate tributyltin pyridinecarboxylate [1] and the corresponding organotin chloride in methanol:

$$R_2SnCl_2 + Bu_3SnO.CO.C_5H_4N \rightarrow R_2ClSn(O.CO.C_5H_4N) + Bu_3SnCl$$

$$R_2SnCl_2 + 2\ Bu_3SnO.CO.C_5H_4N \rightarrow R_2Sn(O.CO.C_5H_4N)_2 + 2\ Bu_3SnCl$$

This method has been used previously [5] to prepare a number of dimethyl- and diphenyl-tin bis(carboxylates) and chloride carboxylates, although it was not always possible to isolate the pure product from solution.

Experimental

(a) Syntheses via exchange reactions

$RSnCl_2(O.CO.C_5H_4N$-2), R = Bu or Ph. Methanolic solutions of tributyltin 2-pyridinecarboxylate (1 mole) and butyltin trichloride (1 mole) or phenyltin trichloride (1 mole) were mixed with stirring and the products, which precipitated immediately, or on cooling, were recrystallised from the same solvent. Attempts to make higher substituted mono-organotin products by the exchange reaction, using 2 or 3 moles of tributyltin 2-pyridinecarboxylate per mole of organotin trichloride, were unsuccessful. Additionally, it was not possible to synthesise derivatives of monobutyl- or monophenyl-tin trichlorides with 3- or 4-pyridinecarboxylic acids by this route.

$R_2Sn(O.CO.C_5H_4N$-$n)_2$, $R = Me$, $n = 2$ or 3; $R = Ph$, $n = 2$ and R_2ClSn-$(O \cdot CO \cdot C_5H_4N$-$n)$, $R = Me$ or Ph, $n = 2$; $R = Me$, $n = 4$. On mixing methanol solutions of tributyltin 2-pyridinecarboxylate and dimethyl- or diphenyl-tin dichloride at room temperature, partial or complete exchange of the chloride was found to occur, depending on the mole ratios used. The products usually precipitated from solution within minutes and could be purified by recrystallisation from methanol. Dimethyltin dichloride and tributyltin 3-pyridinecarboxylate deposited dimethyltin bis(3-pyridinecarboxylate) from methanol, independent of the mole ratios used, whereas dimethyltin dichloride and tributyltin 4-pyridinecarboxylate (1 : 1 or 1 : 2 in methanol) returned dimethylchlorotin 4-pyridinecarboxylate.

(b) Syntheses of $Me_2Sn(O.CO.C_5H_4N$-4$)_2$ and $Ph_2Sn(O.CO.C_5H_4N$-3$)_2$

Diphenyltin bis(3-pyridinecarboxylate) was obtained as a white precipitate when methanolic solutions of sodium 3-pyridinecarboxylate (from sodium methoxide and 3-pyridinecarboxylic acid) and diphenyltin dichloride were mixed in a 2 : 1 or 1 : 1 mole ratio and the resulting solution cooled to 0°C.

Dimethyltin bis(4-pyridinecarboxylate) was prepared by refluxing a suspension of dimethyltin oxide (1 mole) and 4-pyridinecarboxylic acid (2 moles) in

TABLE 1

ANALYTICAL DATA FOR DI- AND MONO-ORGANOTIN PYRIDINECARBOXYLATES

	M.P. (°C)	Analysis: Found (calcd.)(%)			
		C	H	N	Cl
$BuCl_2Sn(O.CO.C_5H_4N\text{-}2)$	242—244(d)	32.72 (32.57)	3.66 (3.55)	4.14 (3.80)	19.34 (19.23)
$PhCl_2Sn(O.CO.C_5H_4N\text{-}2)$	156—157	37.21 (37.07)	3.11 (2.33)	3.50 (3.60)	17.65 (18.24)
$Ph_2ClSn(O.CO.C_5H_4N\text{-}2)$	221—223 [a]	49.86 (50.23)	3.48 (3.28)	3.31 (3.25)	7.78 (8.24)
$Ph_2Sn(O.CO.C_5H_4N\text{-}2)_2$	274—277 (280—282) [b]	55.30 (55.70)	3.54 (3.48)	5.31 (5.42)	— —
$Ph_2Sn(O.CO.C_5H_4N\text{-}3)_2$	263—266	55.31 (55.70)	3.55 (3.48)	5.41 (5.42)	— —
$Me_2ClSn(O.CO.C_5H_4N\text{-}2)$	172—175	31.01 (31.37)	3.39 (3.29)	4.71 (4.57)	12.60 (11.60)
$Me_2Sn(O.CO.C_5H_4N\text{-}2)_2$	258—261 (267—268) [c]	42.65 (42.75)	3.73 (3.56)	6.70 (7.12)	— —
$Me_2Sn(O.CO.C_5H_4N\text{-}3)_2$	282—284	42.76 (42.75)	3.70 (3.56)	7.05 (7.12)	— —
$Me_2ClSn(O.CO.C_5H_4N\text{-}4)$	251—253	31.59 (31.37)	3.37 (3.29)	4.77 (4.57)	11.30 (11.60)
$Me_2Sn(O.CO.C_5H_4N\text{-}4)_2$	248—251	42.70 (42.75)	3.68 (3.56)	7.34 (7.12)	— —

[a] M.p. not quoted in Ref. 7. [b] Ref. 8. [c] Ref. 6.

50% v/v methanol/toluene for 3 h. The resulting cloudy solution was filtered, the solvents were removed in vacuo and the residue recrystallised from methanol. A similar method has been used by McGrady and Tobias to prepare dimethyltin bis(2-pyridinecarboxylate) [6]. Attempts to synthesise the diphenyltin derivatives of 4-pyridinecarboxylic acid and dimethylchloro- or diphenylchloro-tin 3-pyridinecarboxylate by the above routes were unsuccessful. The melting points and elemental analyses for the new compounds are recorded in Table 1.

(c) Spectroscopic measurements

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration spectrometer, which has been described in detail in a previous paper [1]. A 15 mCi Ca $^{119m}SnO_3$ source was used at room temperature, and the samples were packed in perspex discs and cooled to 80 K using a continuous flow cryostat with Helium exchange gas.

The infrared spectra were obtained as Nujol mulls on a Grubb-Parsons Spectromaster Mark I instrument. Potassium bromide plates were used.

Results and discussion

The ^{119m}Sn Mössbauer parameters and the antisymmetric carbonyl stretching frequencies for the series of di- and mono-organotin pyridinecarboxylates are

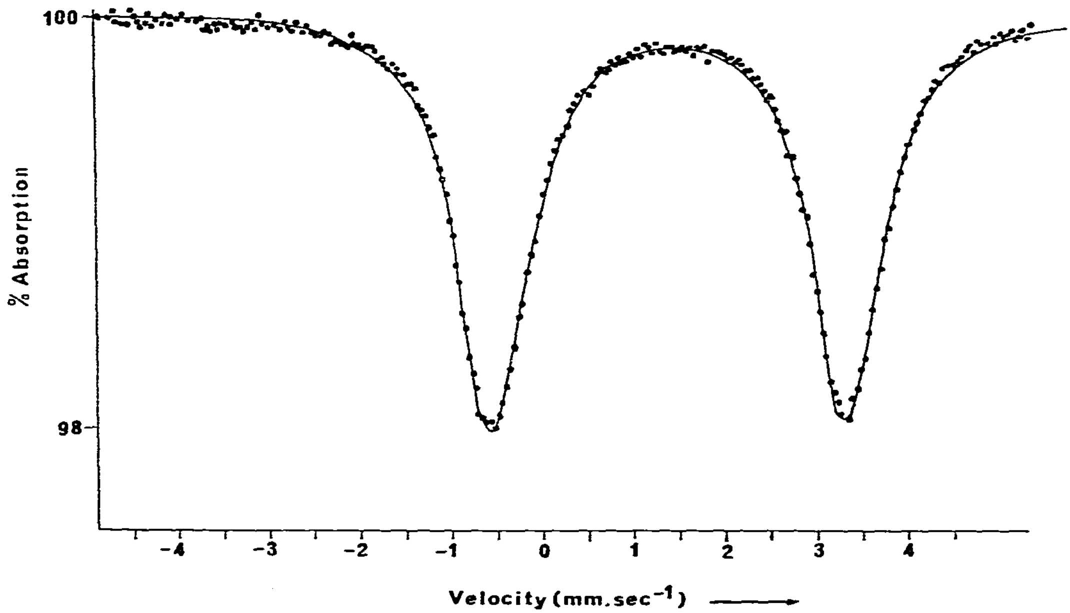


Fig. 1. Tin-119m Mössbauer spectrum of $Ph_2Sn(O.CO.C_5H_4N\text{-}3)_2$ at 80 K.

shown in Table 2. The Mössbauer spectra are well resolved quadrupole split lines, an example of which is shown in Figure 1. The solid line represents the best computer fit of Lorentzian functions by a least squares fitting programme.

(a) Diorganotin bis(pyridinecarboxylates)

The ΔE_Q values for the dimethyltin bis(pyridinecarboxylates) and diphenyltin bis(3-pyridinecarboxylate) are indicative of an octahedral *trans*-R_2SnX_4 geometry, with a linear R—Sn—R unit. The position of the antisymmetric car-

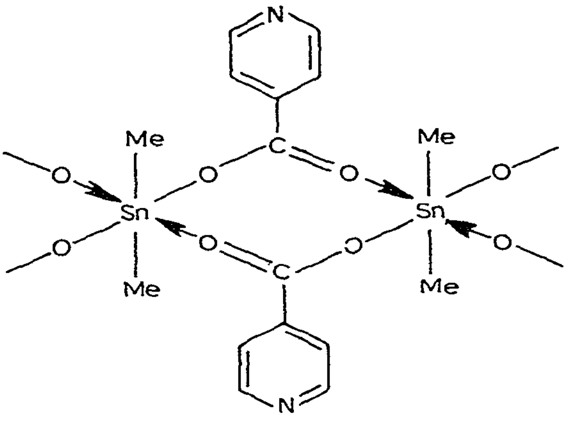
TABLE 2

^{119m}Sn MÖSSBAUER DATA AND ANTISYMMETRIC CARBONYL STRETCHING FREQUENCIES

Compound	δ (mm s^{-1}) [a]	ΔE_Q (mm s^{-1})	ν_{as}(CO) (cm^{-1})
$PhCl_2Sn(O.CO.C_5H_4N\text{-}2)$	0.77	1.81	1653, 1592, 1562
$BuCl_2Sn(O.CO.C_5H_4N\text{-}2)$	0.97	1.98	1618, 1587, 1562
$Ph_2ClSn(O.CO.C_5H_4N\text{-}2)$	1.27	3.76	1608, 1575, 1550
$Me_2ClSn(O.CO.C_5H_4N\text{-}2)$	1.39	4.05	1605, 1577, 1560
$Me_2ClSn(O.CO.C_5H_4N\text{-}4)$	1.32	3.30	1613
$Ph_2Sn(O.CO.C_5H_4N\text{-}3)_2$	1.29	3.86	1587
$Ph_2Sn(O.CO.C_5H_4N\text{-}2)_2$	0.83	1.92	1672
$Ph_2Sn(O.CO.C_5H_4N\text{-}2)_2$	0.80 [b]	1.94 [b]	1680 [b]
$Me_2Sn(O.CO.C_5H_4N\text{-}2)_2$	1.32	4.23	1667, 1618, 1580, 1562
$Me_2Sn(O.CO.C_5H_4N\text{-}2)_2$	1.28 [c]	4.43 [c]	—
$Me_2Sn(O.CO.C_5H_4N\text{-}3)_2$	1.43	4.22	1582
$Me_2Sn(O.CO.C_5H_4N\text{-}4)_2$	1.39	4.28	1582

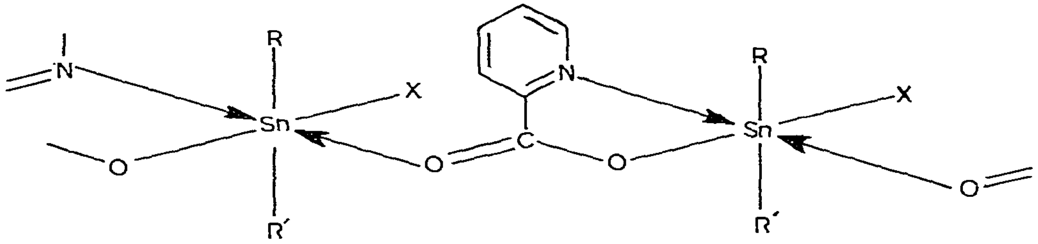
[a] Relative to $CaSnO_3$ (error in δ and ΔE_Q is ±0.02 mm s^{-1}). [b] Ref. 8. [c] Ref. 9.

bonyl stretching band for dimethyltin bis(3-pyridinecarboxylate) is very similar to that observed for other dimethyltin bis(carboxylates) [5,10] and suggests that, in the solid state, these compounds possess a polymeric structure [10], with bridging carboxylate groups (I).



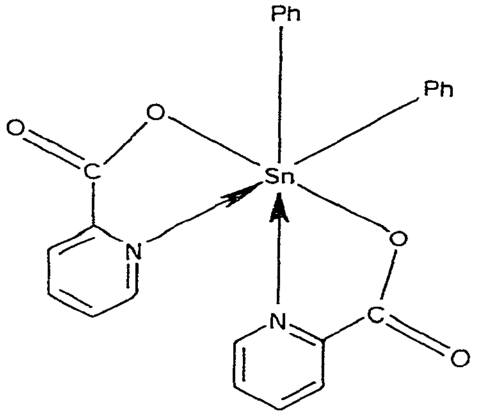
(I)

Dimethyltin bis(2-pyridinecarboxylate), however, shows three low frequency $\nu_{as}(CO)$ bands (as do the four organochlorotin derivatives of 2-pyridinecarboxylic acid, c.f. ref. 11.), as well as an uncoordinated carbonyl resonance at 1667 cm^{-1}. The visible spectrum of this compound indicates that, although coordination of the 2-pyridinecarboxylate ligand is primarily via oxygen, some interaction of the nitrogen atom also occurs [6]. Hence, the structure of dimethyltin bis(2-pyridinecarboxylate) is likely to involve both bridging and terminal carboxylate groups and coordination from the pyridine nitrogen atom to tin (II, R = R′ = Me; X = $O.CO.C_5H_4N$-2). Recent work by Howard and Nelson [12] has indicated that the diethyl-, di-n-octyl- and dicyclohexyl-tin derivatives of 2-pyridinecarboxylic acid adopt a similar structure in solid phase.



(II)

The Mössbauer parameters for diphenyltin bis(2-pyridinecarboxylate) are indicative of a *cis*-octahedral diphenyltin complex [8] and the presence of an uncoordinated $\nu_{as}(CO)$ band suggests that the 2-pyridinecarboxylate ligand is coordinated through nitrogen (III).

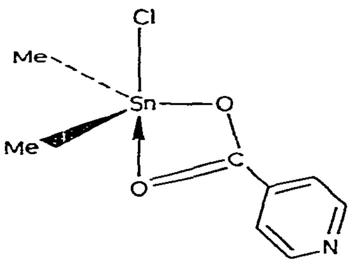


(III)

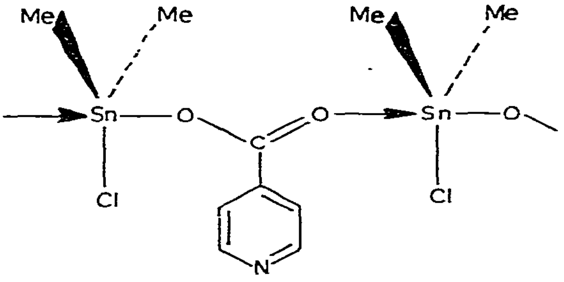
An interesting comparison may be drawn here with diphenyltin bis(3-pyridinecarboxylate), which has *trans*-phenyl groups (Table 2) and probably adopts a polymeric structure similar to I in the solid state.

(b) Diorganochlorotin pyridinecarboxylates

The Mössbauer parameters observed for dimethylchlorotin 4-pyridinecarboxylate (Table 2) closely resemble those found [13] for other diorganotin halide carboxylates and are in accordance with a pentacoordinate trigonal bipyramidal *cis*-R_2SnX_3 tin atom geometry, as in the monomeric structure (IVa), or in the polymeric associated structure (IVb). Interestingly, howeve, the values of ΔE_Q shown by dimethyl- and diphenyl-chlorotin 2-pyridinecarboxylate indicate an octahedral *trans*-R_2SnX_4 tin atom geometry and the similarity of the three coordinated carbonyl bands in these compounds to those in dimethyltin bis(2-pyridinecarboxylate) suggest a very similar structure (II, $R = R' =$ Me or Ph; $X =$ Cl). A single crystal X-ray study is currently under way on dimethylchlorotin 2-pyridinecarboxylate, in order to obtain further information on the structure.



(IVa)



(IVb)

(c) Mono-organodichlorotin pyridinecarboxylates

The two mono-organotin derivatives of 2-pyridinecarboxylic acid show a

TABLE 3

COORDINATION BEHAVIOUR OF THE 2-PYRIDINECARBOXYLATO LIGAND IN ITS ORGANOTIN DERIVATIVES

Complex [a]	Coordination behaviour of $O.CO.C_5H_4N$-2 ligand
$Bu_3SnO.CO.C_5H_4N$-2	bidentate (via O) [b]
$Me_3SnO.CO.C_5H_4N$-$2.H_2O$	unidentate [c]
$Me_2Sn(O.CO.C_5H_4N$-$2)_2$	1 unidentate and 1 tridentate
$Me_2ClSn(O.CO.C_5H_4N$-2)	tridentate
$Ph_2Sn(O.CO.C_5H_4N$-$2)_2$	2 bidentate (via O and N) [d]
$Ph_2ClSn(O.CO.C_5H_4N$-2)	tridentate
$BuCl_2Sn(O.CO.C_5H_4N$-2)	tridentate
$PhCl_2Sn(O.CO.C_5H_4N$-2)	tridentate

[a] Increasing Lewis acidity of the Sn atom down the series. [b] Ref. 1. [c] Ref. 2. [d] Ref. 8.

similar pattern of coordinated carbonyl bands to those in $Me_2Sn(O.CO.C_5H_4N$-$2)_2$ and $Me_2ClSn(O.CO.C_5H_4N$-2) and probably also possess a polymeric associated structure (II, R = Bu or Ph; R′ = X = Cl), containing six coordinate tin atoms.

(d) Conclusions

It is apparent from this work that the 2-pyridinecarboxylate group may function as a mono-, bi- or tri-dentate ligand towards organotin(IV) and, in Table 3, its coordination behaviour is summarised as a function of the Lewis Acidity of the tin atom. An increase in Lewis Acidity favours participation of the nitrogen atom in coordination to tin, whilst the 3- and 4-pyridinecarboxylate ligands appear to bind exclusively via oxygen.

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