

MOSSBAUER SPECTRAL STUDIES OF TRI-DI- AND CHLORODI-ORGANOTIN CARBOXYLATES

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^{119m}Sn Mossbauer data are reported for some organotin derivatives of type R₃SnL, R₂SnCIL, R₂SnL₂ and [(R₂SnL)₂O]₂ where R = CH₃, C₂H₅, n-C₄H₉, C₆H₅, C₆H₁₁, C₆H₅CH₂ and L = trans-3-(2-furanyl)-2-propenoic (FA) and trans-3-(3-methylphenyl)-2-propenoic (CA) acids. The stereochemistry of these derivatives and C-Sn-C bond angles for R₂SnL₂ and [(R₂SnL)₂O]₂ are calculated.

Key words: Mossbauer spectral, Chlorodi-Organotin.

Introduction

^{119m}Sn Mossbauer spectroscopy is a powerful tool for investigating the stereochemistry and bonding in organotin compounds (Omae 1989; Davies and Smith 1982). The most important Mossbauer parameters are the isomer shift (δ mm s⁻¹) and the quadrupole splitting (ΔE_q mm s⁻¹). The isomer shift values are dependent upon the s-electron density at the tin nucleus, and for all the tin compounds, fall in the range of ± 5 mm s⁻¹ with a positive δ corresponding to an increased nuclear s-electron density at the tin atom. On the other hand the quadrupole splitting reflects the p-electron imbalance on the tin atom, which seems to be related to the basicity of the ligand.

Recently this technique is used in organotin-biological systems to study the bonding and structural environments of tin atoms, mainly through the rationalization of the nuclear quadrupole splitting parameter by point-charge model approaches (Musmeci *et al* 1992). These studies have been further extended to determine the dynamics of tin nuclei in organotin (IV)-DNA condensates at variable-temperature Mossbauer spectroscopy (Barbieri *et al* 1992).

In present work, the stereochemistry of organotin carboxylates of the type R₃SnL, R₂SnCIL, R₂SnL₂ and [(R₂SnL)₂O]₂ where R = alkyl or aryl and L = R'COO⁻ have been investigated on the basis of Mossbauer spectra. The C-Sn-C bond angles for R₂SnL₂ and [(R₂SnL)₂O]₂ have been calculated by literature method and the results were compared with reported data of analogous compounds (Sham and Baneroft 1975).

Experimental

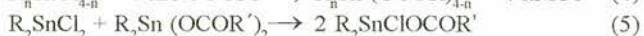
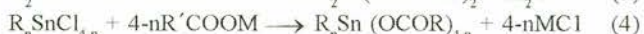
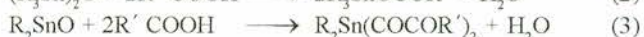
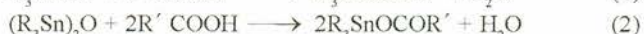
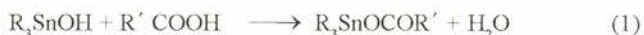
Mossbauer spectra were recorded with a constant acceleration, microprocessor controlled spectrometer (Cryophysics Ltd., Oxford, U.K.), with barium stannate source. The samples

were packed in Perspex disks and cooled to 80 K in a liquid nitrogen cryostat (Ali *et al* 1994).

Synthesis. Organotin carboxylates, R_nSn(OCOR')_{4-n} were prepared either by treating the corresponding organotin oxide or hydroxide with the carboxylic acid or from the reaction of the corresponding organotin chloride with the metal carboxylate (Davies 1995). The first group of reactions were carried out by refluxing in toluene. The water formed was removed by Dean and Stark apparatus. The reaction of organotin halides with metal carboxylates (M = Na, K or Ag) were carried out in solvent such as carbontetrachloride (CCl₄) or dichloromethane (CH₂Cl₂) (Ali *et al* 1993, Badshah *et al* 1994 and Danish *et al* 1995-1997). The chlorodiorganotin derivatives were prepared by redistribution method (Ali *et al* 1997).

Results and Discussion

Organotin carboxylates are commonly prepared by the following reactions (Equations 1-5).



The compounds have been characterized by different spectroscopic techniques such as multinuclear NMR, mass and IR and the results are reported elsewhere (Ali *et al* 1993; Badshah *et al* 1994 and Danish *et al* 1995-1997). In present work the Mossbauer data are reported and discussed according to various solid phase. For some compounds, C-Sn-C bond angles are calculated from Mossbauer data using literature method (Sham *et al* 1975).

Triorganotin Carboxylates (R₃SnL). ^{119m}Sn Mossbauer spectra show well defined doublets as shown for one repre-

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Table 1
Mossbauer data for investigated compounds

Compounds	Mossbauer Parameters					
	IS (mmS ⁻¹)	QS (mmS ⁻¹)	Γ_1 (mmS ⁻¹)	Γ_2 (mmS ⁻¹)	ρ (QS/IS)	<C-Sn-C (degree)
Me ₃ Sn FA	1.20	3.48	0.88	0.89	2.90	-
Et ₃ SnFA	1.24	3.54	0.90	1.06	2.85	-
Bu ₃ SnFA	1.38	3.50	0.92	0.91	2.54	-
Ph ₃ SnFA	1.26	3.39	1.01	1.00	2.69	-
Cy ₃ SnFA	1.46	2.80	0.96	0.98	1.92	-
Me ₃ SnCA	1.27	3.55	0.92	0.89	2.80	-
Bu ₃ SnCA	1.28	3.50	0.91	0.97	2.73	-
Ph ₃ SnCA	1.24	3.41	1.01	1.08	2.75	-
Cy ₃ SnCA	1.41	2.36	0.96	0.87	1.67	-
Et ₂ SnClFA	1.45	3.54	0.85	0.95	2.44	-
Bu ₂ SnClFA	1.52	3.72	0.82	0.83	2.45	-
Et ₂ SnClCA	1.55	3.73	0.83	0.83	2.41	-
Me ₂ Sn(FA) ₂	1.16	3.35	0.88	1.00	2.89	138
Et ₂ Sn(FA) ₂	1.49	3.89	0.82	0.85	2.61	158
Bu ₂ Sn(FA) ₂	1.16	3.21	0.87	0.98	2.77	134
Me ₂ Sn(CA) ₂	1.18	3.41	1.01	1.08	2.66	140
Bu ₂ Sn(CA) ₂	1.28	3.35	0.90	0.97	2.62	138
{[(Me) ₂ SnFA] ₂ O} ₂	1.29	3.36	0.99	0.98	2.60	138
{[(Bu) ₂ SnFA] ₂ O} ₂	1.28	3.35	0.89	0.97	2.62	138
{[(Me) ₂ SnCA] ₂ O} ₂	1.13/1.31	3.14/3.65	0.83/0.83	0.91/0.91	2.78/2.79	132/148

FA = Trans-3-(2-furanyl)-2-propenoic Acid; CA = Trans-3-(3-methylphenyl)-2-propenoic Acid; Me = CH₃, Et = C₂H₅, Bu = C₄H₉, Ph = C₆H₅, Cy = C₆H₁₁

sentative in Figure 1. Various reports show that quadrupole splitting parameters fall in the range 2.30-2.55 mm s⁻¹ for monomeric triorganotin carboxylates having trigonal bipyramidal geometry and a chelating bidentate carboxylate group, while those having five coordinate structure formed by bridging carboxylate groups give quadrupole splitting parameters in the range 3.59-3.70 mm s⁻¹ (Sharma *et al* 1988, Smith *et al* 1986, Lo *et al* 1991 and Ng *et al* 1991). In present investigation, only Cy₃SnCA shows the monomeric trigonal bipyramidal structure while all other R₃SnL show the bridging nature of carboxylate groups. This is further supported by crystal structure of Ph₃SnFA (Danish *et al* 1995).

Chlorodiorganotin Carboxylates [R₂Sn(Cl) L]. The representative Mossbauer spectrum of one compound is given in Figure 2. Mossbauer parameters observed for these compounds closely resemble those found (Sham *et al* 1975, Lochart *et al* 1986) for other diorganotin-halo-carboxylates and are in accordance with a penta-coordinate trigonal bipyramidal cis-O₂SnR₂X geometry.

Diorganotin Dicarboxylates [R₂SnL₂]. In diorganotin dicarboxylates, due to high electronegativity of oxygen atoms, there is distortion from perfect octahedral geometry which gives QS values similar to those for trigonal bipyramidal environment (Ng *et al* 1991) Based on QS values, the C-Sn-C angles have been calculated using Shams model (Sham *et al* 1975). These angles are comparable to that equivalent angle (140°) in dimethyltin diacetate (Lochart *et al* 1986). It has been reported earlier (Nadvornik *et al* 1984) that diorganotin dicarboxylates exhibiting ρ value (QS/IS) greater than 2.1 possess a trans octahedral geometry around the tin atom. Hence, a ρ value in the range 2.62-2.89 mm s⁻¹ strongly recommends octahedral geometry (Sham *et al* 1975, Sandhu *et al* 1990, Willem *et al* 1993)

Tetraorganodiarboxylato stannoxanes. (dimeric) {R₂SnL₂O}₂. Mossbauer spectroscopy usually does not distinguish the two different environments of tin atoms in the same molecule, (Willem *et al* 1993, Gielen *et al* 1993). This is not unexpected since Mossbauer spectroscopy has a small isomer shift range and is, therefore, less sensitive to small

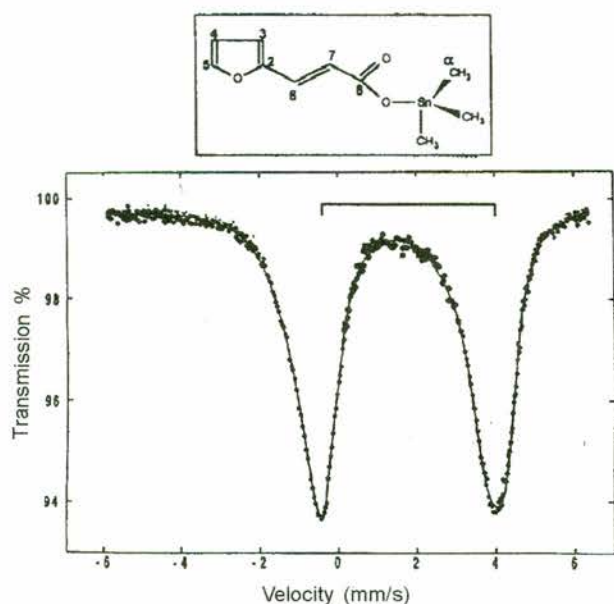


Fig 1. Mössbauer spectra of Trimethyltin (trans-3-(2-furanyl)-2-propenoate) at 80K. IS=1.20 mm s⁻¹, QS=3.48 mm s⁻¹, Γ_1 =0.88 mm s⁻¹, and Γ_2 =0.89 mm s⁻¹

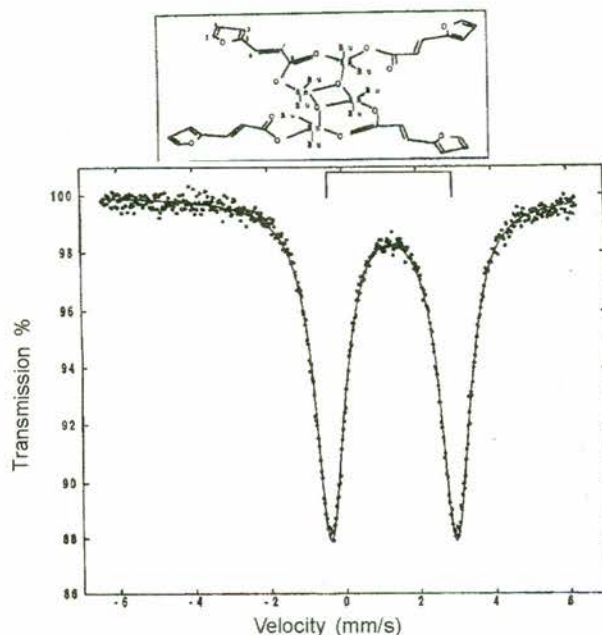


Fig 3. Mössbauer spectra of Tetrabutyltinbis(3-(2-furanyl)-2-propenoate), din-n-butyltin oxide, at 80 K shows only one doublet even two tin atoms have different environments in the same molecule. IS=1.28 mm s⁻¹, QS=3.35 mm s⁻¹, Γ_1 =0.89 mm s⁻¹, and Γ_2 =0.97 mm s⁻¹.

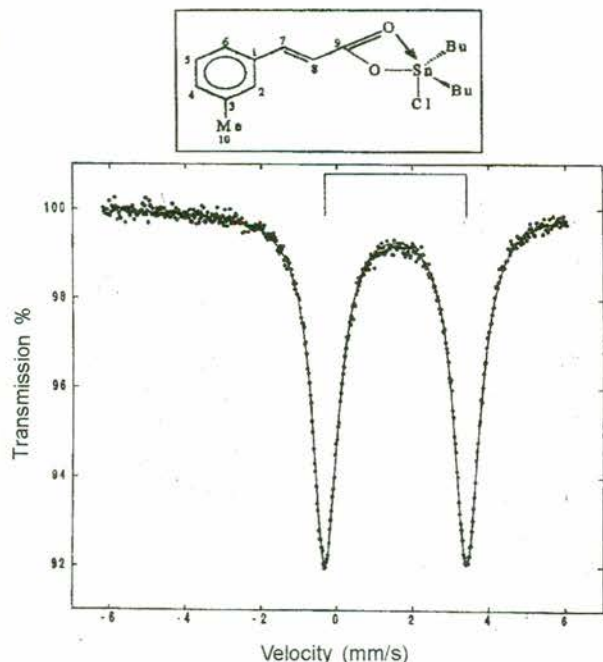


Fig 2. Mössbauer spectra of Chlorodibutyltin(trans(trans-3-(3-methylphenyl)-2-propenoate) at 80K. IS=1.55 mm s⁻¹, QS=3.37 mm s⁻¹, Γ_1 =0.83 mm s⁻¹, and Γ_2 =0.83 mm s⁻¹.

variation in tin environments; consequently only one doublet is observed (Figure 3). However, we luckily resolved two tin sites for bis (trans-3-(3-methylphenyl)-2-propenoate) di-n-methyltin]oxide (Figure 4) with QS values 3.14 and 3.65 mm s⁻¹

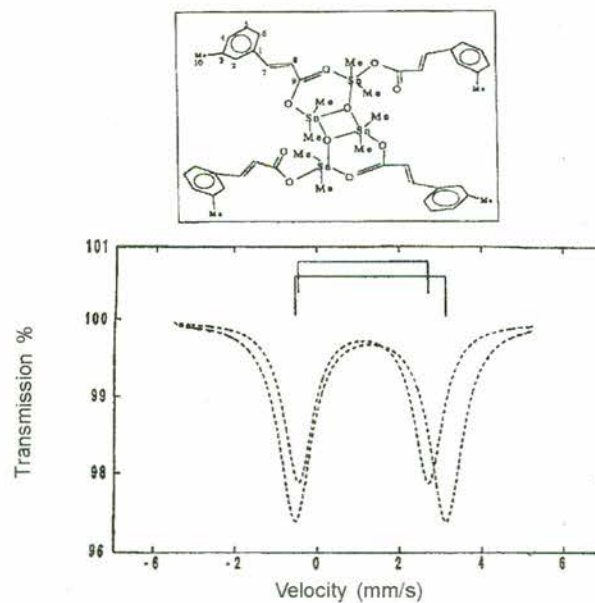


Fig 4. Mössbauer spectra of bis [(trans-3-(3-methylphenyl)-2-propenoate) dimethyltin] oxide, at 80K shows two doublet for two tin atoms having different environments. IS=1.13/1.31 mm s⁻¹, QS=3.14/3.65 mm s⁻¹, Γ_1 =0.83/0.83 mm s⁻¹ and Γ_2 =0.91/0.91 mm s⁻¹.

Conclusions

Following conclusions have been drawn from our previous observations based on multinuclear NMR (¹H, ¹³C, ¹¹⁹Sn), mass and X-ray crystal analysis (Ali et al 1993, Badshah et al 1994, and Danish et al 1995-1997.) and present Mössbauer studies.

- i) Triorganotin carboxylates from penta coordinate compounds in solid state whereas tetra coordinate in non-coordinating solvents.
- ii) Diorganotin dicarboxylates show hexa coordination in solid state while penta or tetra coordination in non-coordinating solvents.
- iii) Tetraorganodicyanostannoxanes (dimeric form) have two different environments for tin atoms, i.e., endo and exo tin atoms.
- iv) The investigated organotin carboxylates have high potential for biological activity.

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