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Fluxional Behavior in Dimeric Tetraorganodicarboxylato stannoxanes

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ABSTRACT

The mechanism of the fluxional process occurring in dimeric tetraorganodicarboxylato stannoxanes is presented on the basis of multinuclear NMR studies carried out in noncoordinating solvents. This fluxional process is a consequence of rapid migration of carboxylate groups from one tin atom to the other. It has been proposed that larger carboxylates will also execute this behavior. The effect of cis and trans positions on the fluxional process is discussed. The fluxional process is very fast and could not be stopped even at low temperatures, as measured on the NMR time scale.

INTRODUCTION

The structures adopted by the compounds of the stoichiometry $\{[(R_2SnL)_2O]_2\}$, commonly referred to as dimeric tetraorganodicarboxylato stannoxanes, have been the subject of many reports since their discovery in 1914 [1]. Such compounds were initially thought to be monomeric [1], but subsequent work has conclusively demonstrated not only their dimeric nature but also the presence of nonequivalent tin sites [2–4]. Of the information available through 1980, only a few reports have dealt with such carboxylate derivatives [4–7]. Since then, there has been a broad spectrum of studies dealing with their crystal structures and solution NMR spectroscopy [8–19].

The most economical and conventional method for the preparation of each such compound is the condensation of R_2SnO with a carboxylic acid at the reflux temperature of toluene, in a 1:1 molar ratio, a Dean and Stark apparatus being used for the azeotropic removal of water formed during the reaction.

Such compounds can also be prepared by the partial hydrolysis of diorganotin dicarboxylates. They can be produced accidentally during crystallization of diorganotin dicarboxylates from solvents containing traces of air or moisture [20]. We have observed furthermore that any attempt to synthesize a diorganotin dicarboxylate by reacting a diorganotin dihalide with the sodium or silver salt of an acid in a 1:2 molar ratio, in nondried solvents, under ordinary conditions, results in the formation of a dimeric stannoxane, and the desired compound appears only as a by-product. Crystal structures of such compounds show the presence of two distinct tin atoms, known as endo- and exocyclic tins [12,15,20–22].

Multinuclear NMR studies of such systems, in noncoordinating solvents, are quite interesting and suggest two different environments for the R groups linked with endo- and exocyclic tins but with only one environment for the carboxylate moieties [12,14,15,21–23]. It had been proposed that, in solution, a dynamic equilibrium may exist between various dimeric tetraorganodicarboxylato stannox-

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FIGURE 1 500 MHz ^1H NMR spectra of bis[(3-(2-furanyl)-2-propenoate)dimethyltin)oxide, in $CDCl_3$. Two types of proton signals describing two different environments for the methyl groups are seen; $^2J[^{119/117}Sn\text{-}^1H]$ are marked with • and ↓ for endo- and exocyclic methyl groups, respectively, and solvent with **S**. There is only one set of proton signals for the carboxylate groups.

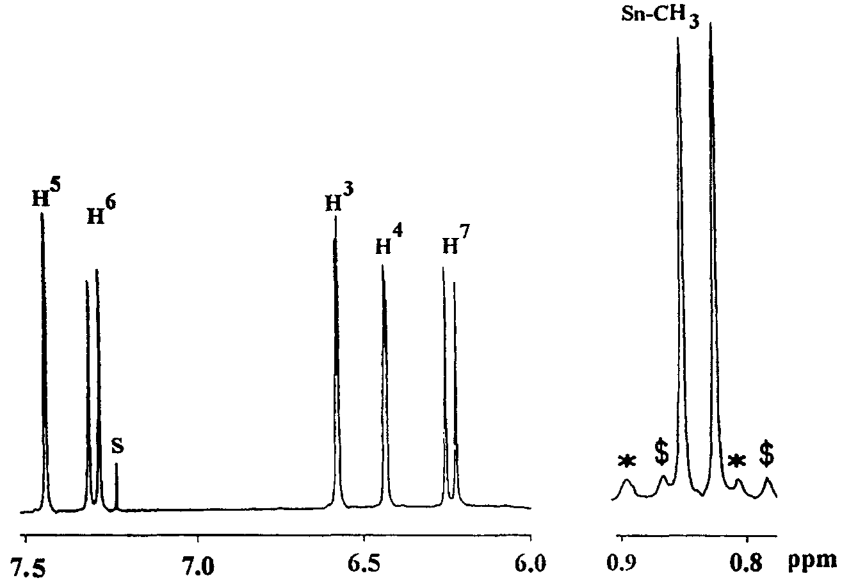
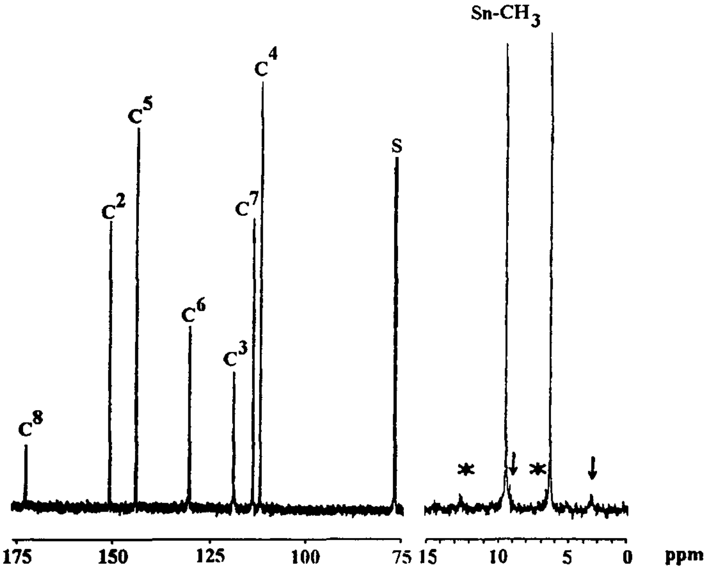


FIGURE 2 128.5 MHz ^{13}C NMR spectra of bis[(3-(2-furanyl)-2-propenoate)dimethyltin)oxide, in $CDCl_3$. Two types of carbon signals describing two different environments for methyl groups are seen; $^1J[^{119/117}Sn\text{-}^{13}C]$ are marked with • and ↓ for endo- and exocyclic methyl groups respectively, and solvent with **S**. There is only one set of carbon signals for the carboxylate groups.



anes leading to the equivalence of the carboxylate ligands [12].

RESULTS AND DISCUSSION

The results of multinuclear NMR studies performed for a representative compound, bis[(3-(2-furanyl)-2-propenoate)dimethyltin]oxide, are summarized here (the synthesis and characterization of this reference compound having been given elsewhere [19]). In the ^1H NMR spectra, two methyl resonances are observed (Figure 1) that show different $^2J[^{119}Sn\text{-}^1H]$ values. The ^{13}C spectra (Figure 2) display pairs of Me–Sn signals, with high-field resonances for exocyclic Me_2Sn carbon atoms and downfield resonances for endocyclic Me_2Sn carbon atoms. The ^{119}Sn NMR spectra (Figure 3) also show a similar dicotomy.

In our earlier report [19], we suggested that, in ^1H and ^{13}C NMR spectra, the carboxylate groups linked with endo- and excocyclic tin atoms should produce two sets of signals similar to the results observed for R groups. However, the NMR spectra reveal only one set of signals for the carboxylate groups, obviously due to a very similar environment. To date, there is no report of NMR data dealing with the nonequality of carboxylate ligands in such compounds. Thus, there may be a fast exchange in the coordination behavior of the carboxylate groups at-

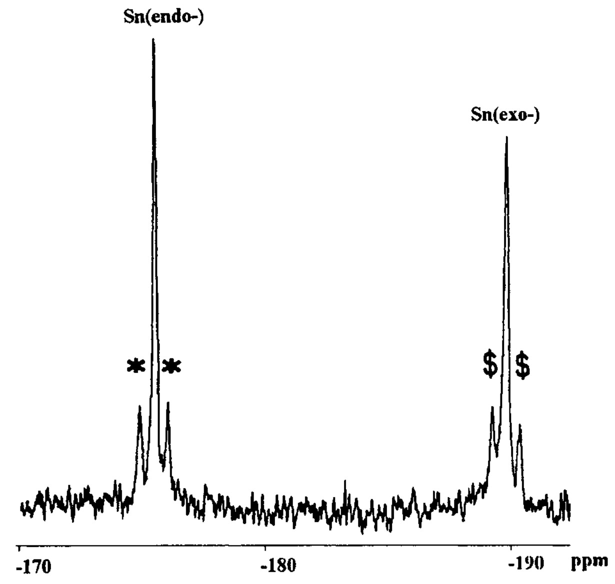


FIGURE 3 93.3 MHz ^{119}Sn NMR spectra of bis[(3-(2-furanyl)-2-propenoate)dimethyltin)oxide, in $CDCl_3$. Two signals due to two different environments for tin atoms are seen; endo- and exocyclic tin atoms are marked with * and $, respectively, and solvent with **S**.

tached to endo- and exocyclic tin atoms. This similar environment for the carboxylate groups is due to their fluxional behavior in the molecule. Here we report a possible mechanism to explain this fluxional process.

The important points that help us to understand the fluxional process depicted in structures 1–4 of Figure 4 may be summarized as follows:

1. If a fast exchange is possible between the carboxylates of tin atoms A and B, then there is equal possibility of such an exchange between A and D, B and C, or C and D.
2. In solution, bond angles between each tin atom and different groups cannot be fixed due to their rapid motion.
3. During this exchange process, the bond between tin atom A and O^a is broken (accompanied by a simultaneous bond formation between $O^{d'}$ and tin atom A), and a new bond between $O^{a'}$ and tin atom B is formed. Similarly, the bond between the tin atom C and $O^{b'}$ is formed, and the bond between tin atom B and O^b breaks; twisting around the Sn–O single bond taking place. The frequent twisting of the carboxylate group around the Sn–O single bond is possible, as there is no apparent steric hindrance (twisting of a ring around a single bond in the absence of steric hindrance is possible even in the solid state [20] hence the furanyl ring may also revolve around the single bond).
4. As a consequence of this twisting, O^a migrates toward tin atom C, O^b migrates toward tin atom D, and so on, as shown in structures 1–4 of Figure 4.
5. There is also a possibility that first a carboxylate group migrates from one exocyclic tin atom to one of the endocyclic tin atoms and from there to the second endocyclic tin atom and then to the second exocyclic tin atom and so on.

In this way, the carboxylate groups execute a fluxional behavior, and a very similar environment for them is created. This fluxional process is so fast that we are unable to stop it even at −95°C with respect to the NMR time scale, and multinuclear NMR spectra at low temperatures are similar to those seen at room temperature (Figures 1–3).

Factors Effecting the Fluxional Process

The ease of the fluxional process depends on R as well as on the carboxylate group. Carboxylate groups bonded to small chains instead of longer ones or cyclic systems, in combination with smaller R groups on the tin atom, may exhibit a high degree of this fluxional process. It should be noted that even the bulky nature of the carboxylate ligand will not hinder this process, as the twist of the COO part of the bulky ligand will cause it to move along the direction of the twist. In this way, the COO part will act as a rod bifurcated at one end that is revolving and moving in a circle. The bulky part may be visualized as a heavy piece of metal fixed at the other end with the help of bearings. Hence, the spinning of this rod will not result in spinning of the metal piece. However, the circular movement of this rod in a circle will also cause the metal piece to move. In the case of a bulky carboxylate, the COO part acts as a similar forked rod, and the bulky part of the ligand moves like a piece of metal without spinning. It is, therefore, suggested that the fluxional process is possible even in the presence of a bulky carboxylate.

The positions of the R groups around the tin atom may be influential. R groups residing at *trans*-positions may hinder this process as compared with those at *cis*-positions. Paradoxically, they do not hinder the process even in the former case, as crystallographic reports clearly show that the alkyl chains are not straight but rather in the zigzag form, and the C–Sn–C angle is always less than 180° [20–22]. The to and fro motion of the zigzag chain will not hinder the fluxional process. Furthermore, crys-

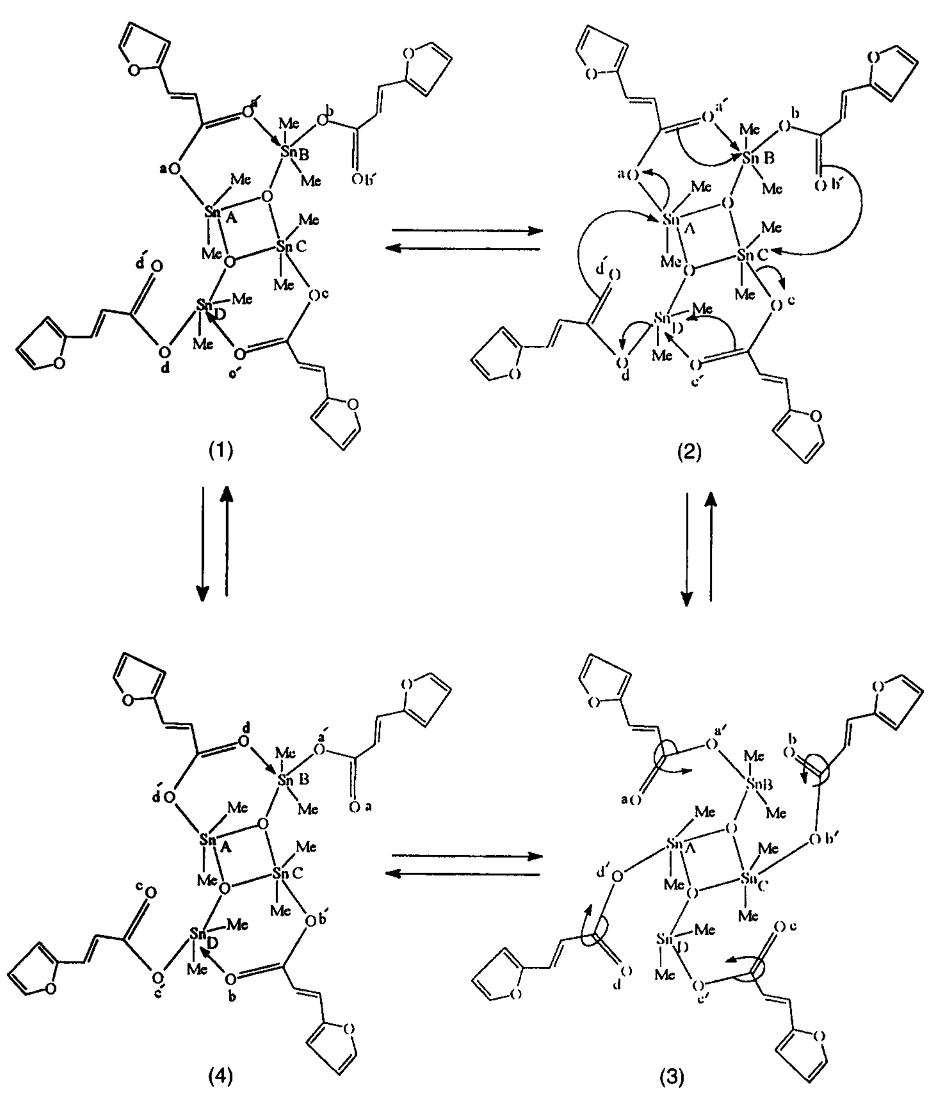


FIGURE 4 Schematic presentation of fluxional behavior of 3-(2-furanyl)-2-propenoate anion in [(3-(2-furanyl)-2-propenoate)dimethyltin)oxide, in $CDCl_3$.

tallographic data show that, due to steric reasons, bulky R groups (R = phenyl or cyclohexyl) always occupy the *cis*-position, which will favor this process.

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