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On the Structure of Dicyclohexyltin Dichloride

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Several examples of polymorphism in organotin compounds have been cited, notably $Me_3SnS_2CNMe_2$ [1], $(Me_2SnS)_3$ [2], $Ph_3SnNO_3 \cdot pyO$ [3], $Me_2Sn(S_2CNEt_2)_2$ [4] and a series of organotin phosphonates and arsonates [5]. In those examples where different polymorphs have been studied crystallographically [1–4], the different forms have similar lattice and molecular structures. During the course of our studies of the structures of cyclohexyltin compounds, our groups have independently solved, by X-ray diffraction, the structure of dicyclohexyltin dichloride [6, 7]. The two structures, both of which are orthorhombic in nature, show quite different lattice structures. In view of the central role that lattice association plays in organotin chemistry, we have taken this opportunity to compare these structures, particularly in the light of variable-temperature Mössbauer spectroscopic experiments which can be used to probe lattice dynamics in tin compounds.

The intermolecular interactions between chlorine and tin in the two modifications are shown in Fig. 1. Form **I**, described by the Padua group as 'tetrahedral', has an intermolecular Sn–Cl distance of 3.54 Å. The Bath modification (**II**) forms chains of molecules, with intermolecular Sn–Cl at 3.33, 3.98 Å, and the coordination sphere about tin described as 'a severely distorted *trans*-R_2SnCl_4 octahedron'.

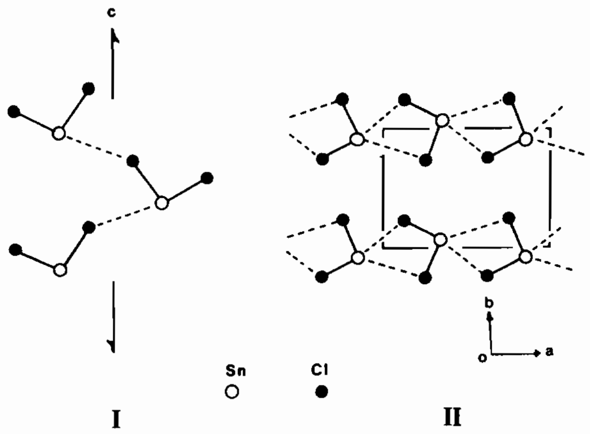

Fig. 1. The lattice structure of $(C_6H_{11})_2SnCl_2$ in modifications **I** and **II**. Only the Sn and Cl atoms are included for clarity. Intermolecular spacings are depicted by – – – lines.

Figure 2 shows the variable temperature Mössbauer spectroscopic data for the two polymorphs. We and others [8] have shown that the slope of these $d\ln A/dT$ plots reflects the tightness of binding of the Mössbauer atom (Sn) within the lattice, the steeper the slope the less rigid the binding. As anticipated, **I** shows a steeper slope than **II**, reflecting the 1-d ordering of molecules within the lattice of the latter (Table I). However, the difference in steepness of the slopes in Fig. 2 is less than might have been expected when comparing a molecular array (**I**) with an ordered polymer (**II**). In the light of these data, and from comparison of the bond angles about tin for the two polymorphs, it is opportune to compare the interpretations of the two crystal structures. Since the ∡ C–Sn–C is virtually identical in the two cases (131.0(9)°, 134.4(2)° for **I** and **II** respectively) despite differing intermolecular Sn–Cl contacts, it would seem that the enhanced coordination at tin in **II**, and particularly the interaction at 3.98 Å, has probably been over-emphasized, despite the suggestive lattice ordering. On the other hand, the Sn–Cl interaction at 3.54 Å in **I** which was discounted

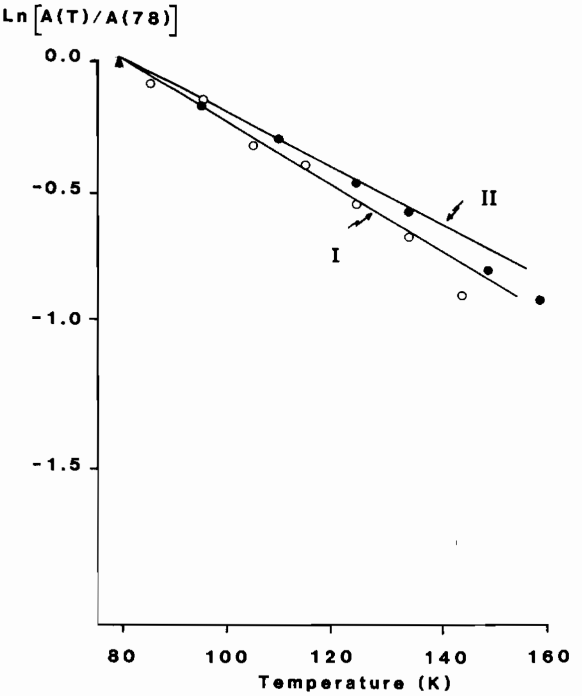

Fig. 2. Variable temperature Mössbauer spectroscopic data for **I** and **II**. Both plots show considerable deviation from non-linearity at $T > 135$ K, probably due to lattice anharmonicity. Numerical analysis of this data is given in Table I.

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TABLE I.

	Space group	Melting point (°C)	*IS* (mm s^{-1})	*QS* (mm s^{-1})	$-\mathrm{d}\ln A/\mathrm{d}T$ (K^{-1}) (T range; r; pts)	Reference
I	$P2_12_12_1$	83–84	1.66	3.36	1.19 (78–135; 0.996; 7)[a]	6
II	*Pbcm*	88–89	1.76	3.40	1.02 (78–135; 0.999; 5)[b]	7

[a] 1.22 (78–145; 0.997; 8). [b] 1.13 (78–160; 0.996; 7).

originally, might be making some small contribution to the overall lattice stabilization. Mössbauer Quadrupole Splitting (*QS*) values tentatively support this analysis. If the tenets of point charge model are accepted, the *QS* arises solely from the ∡ C–Sn–C and is given by [9]:

$$|QS| = 4\{R\}[1 - 3\sin^2\theta\cos^2\theta]^{1/2}$$

where ∡ C–Sn–C = 2θ and $\{R\}$ is the partial quadrupole splitting for R. $\{R\}$ is -1.37 mm s^{-1} for a tetrahedral geometry and -1.03 mm s^{-1} for octahedral or trigonal bipyramidal systems, in the latter case using the average value of $\{R_{ax}\}$ and $\{R_{eq}\}$ [9]. For **I**, the calculated ∡ C–Sn–C from a *QS* of 3.36 mm s^{-1} is 114° in a tetrahedral geometry and 138° when the coordination number is greater than 4. For **II**, the corresponding calculated angles are 115° and 139°. This model would then suggest that both forms of Cy_2SnCl_2 have a coordination number > 4. On the other hand Me_2SnCl_2, which has ∡ C–Sn–C = 123.5° and a lattice arrangement similar to **II** [10] has, on the basis of an analysis of this type [9], been designated tetrahedral.

From a structural point of view, however, it is possible to explain the variation in ∡ C–Sn–C for both **I** and **II** without invoking a coordination number > 4 simply in terms of the intramolecular steric requirements of the two bulky C_6H_{11} rings. Such interactions are absent in Me_2SnCl_2, hence the smaller ∡ C–Sn–C. In this light, the relative importance of the Mössbauer analysis depends largely on the confidence of the experimentalist in the assumptions of the point charge approach. What is clear, is that the interpretation of both crystallographic and spectral data for this type of structure is very much in the eye of the beholder.

Finally, we note that **II** which is prepared from $SnCl_4$ and Cy_4Sn has an identical melting point (88–89 °C) to that recorded for Cy_2SnCl_2 prepared by the action of HCl upon Cy_2SnO [11]. **I**, with melting point = 83–84 °C, was also obtained by this latter route, which implies that the formation of **I** *versus* **II** is controlled by the nature of the crystallization process. However, in the preparation of **II**, it was observed that the melting point of the bulk sample was 83–84 °C, and was assumed at the time to be due to an impure sample. It would now appear that this is the more common modification, while that reported by one of us (K.C.M.) and others [10] is the less common polymorph of the compound. We have so far failed in our attempts to interconvert the two structures.

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