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CRYSTAL AND MOLECULAR STRUCTURES OF DICYCLOHEXYLTIN DICHLORIDE AND DIBROMIDE

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Summary

The crystal structures of $(C_6H_{11})_2SnCl_2$ (**A**) and $(C_6H_{11})_2SnBr_2$ (**B**) have been determined. The compounds are isomorphous, and the molecules have nearly the same geometry. In both cases the coordination can be regarded as tetrahedral on the basis of the geometrical parameters. The data are critically analysed with that published for analogous compounds.

Introduction

Attribution of the coordination number to tin in organometallic compounds is a much discussed problem, not only in the case of rather complicated molecular structures but even for very simple compounds such as R_2SnX_2 (X = halogen).

When the coordination and its geometry is assigned, for lack of X-ray structural data, on the basis of spectroscopic data, (e.g. Mössbauer or IR), or other physicochemical evidence, there is always some degree of uncertainty, and consequently diverging opinions can arise. More surprising is that opinions are sometimes still in conflict even when detailed and accurate crystal structural data are available.

Complexes having almost identical geometries about the tin atom have been described in terms of completely different coordinations [1–5], and some authors assert that the geometrical parameters are not in themselves to be regarded as compelling evidence [5]. A geometry very distorted from regular tetrahedral, trigonal bipyramidal etc., coordination can lead to different structural interpretations, and in such cases accurate information on the relative positions of the nearest atoms of

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adjacent molecules can be very helpful [6]. However, when the geometry is only slightly distorted or the distorsion is clearly explained in terms of intramolecular steric requirements it is no longer justified to reject the geometrical arguments in favour of other, weaker, evidence. So far, attribution of a coordination number to tin has been based on the greater or smaller weight given to the X-ray structural data relative to less certain spectroscopic data or to more sophisticated interpretations of the crystal structures. The case of $(C_2H_5)_2SnI_2$ [2] is typical: in spite of Sn...I distances of 4.28 Å, these have been used to assign an octahedral coordination to tin probably by analogy with $(C_2H_5)_2SnCl_2$ and $(C_2H_5)_2SnBr_2$ [2] for which the six-coordination was suggested by Δ-Mössbauer high values [7]. Similarly $(C_6H_5)_2SnCl_2$, stated to be tetrahedral [3], was later assumed to be partially hexa-coordinated in order to achieve a better agreement with the Δ-value [4].

Bis(biphenylyl-2)tin dichloride [5], with a completely identical geometry about tin, has been conclusively shown to be tetrahedral (in spite of the Δ-value of 2.70 mm s^{-1}, similar to that for $(C_6H_5)_2SnCl_2$, 2.90 mm s^{-1} [8]) because all the intermolecular Sn...Cl distances are larger than 6 Å.

We describe here the crystal structures of $(C_6H_{11})_2SnX_2$ with X = Cl, Br, and attempt an impartial interpretation of them.

Experimental

Dicyclohexyltin dichloride and dibromide: crystal and intensity data

Dicyclohexyltin dichloride (**A**) and dibromide (**B**) were prepared by published procedures [9]. Suitable crystals for X-ray analysis were obtained from petrol ether (40–60°C) and ethyl alcohol (96%) for **A** and **B** respectively; m.p., (**A**) 83–84°C (lit. [9], m.p. 88–89°C) *; m.p. (**B**) 59–59.5°C (lit. [9] 58°C).

(**A**): $C_{12}H_{22}SnCl_2$, MW, 355.9, orthorhombic, a 20.085(11), b 12.535(6), c 6.023(3) Å, U 1516.4 Å^3, D_c 1.55 g cm^{-3} $Z = 4$, $F(000)$ 712, λ(Mo-K_α) 0.7107, μ(Mo-K_α) 19.7 cm^{-1}, space group $P2_12_12_1$, T 25°C.

(**B**): $C_{12}H_{22}SnBr_2$, m.w. 444.8, orthorhombic, a 20.028(12), b 12.719(6), c 6.270(3) Å, U 1597.2 Å^3, D_c 1.85 g cm^{-1} $Z = 4$, $F(000)$ 856, λ(Mo-K_α) 0.7107, μ(Mo-K_α) 68.1 cm^{-1}, space group $P2_12_12_1$, T 25°C.

Both compounds are stable in the X-ray beam. The dimensions of the crystals were 0.3 × 0.3 × 0.5 mm for **A** and 0.3 × 0.2 × 0.7 mm for **B**. Accurate lattice and orientation parameters were obtained by least-squares treatment of 25 symmetry-related reflections. Intensity data were measured by the ϑ-2ϑ scan method with a Philips PW 1100 computer controlled four-circle diffractometer, with graphite monochromator. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

The data were scaled to give 964 independent F_{hkl} values for **A** and 1159 for **B** with $I > 2\sigma(I)$.

Solution and refinement of the structures

The positions of tin and of the halogen atoms were determined from three-dimensional Patterson syntheses. The carbon atoms were located from subsequent Fourier maps. The hydrogen atoms were also located from the final difference Fourier

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* The m.p. 88–89°C [9] probably refers to a polymorphic modification.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH THE ESTIMATED STANDARD DEVIATIONS

Dicyclohexyltin dichloride (**A**)				Dicyclohexyltin dibromide (**B**)			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn	6762(1)	3537(1)	38(3)	Sn	6733(1)	3424(1)	239(2)
Cl(1)	7179(3)	4364(5)	3337(12)	Br(1)	7169(1)	4322(2)	3533(3)
Cl(2)	6092(4)	2214(6)	1852(16)	Br(2)	6034(1)	2059(2)	2013(5)
C(1)	6060(14)	4631(22)	−1440(54)	C(1)	6070(8)	4493(14)	−1321(31)
C(2)	5515(17)	4016(27)	−2621(65)	C(2)	5500(11)	3891(18)	−2408(41)
C(3)	5010(21)	4826(33)	−3596(76)	C(3)	5016(15)	4676(24)	−3475(52)
C(4)	4746(19)	5618(31)	−1852(72)	C(4)	4793(15)	5575(23)	−2047(51)
C(5)	5352(21)	6213(33)	−923(70)	C(5)	5383(14)	6126(24)	−1000(52)
C(6)	5847(14)	5467(23)	324(63)	C(6)	5850(10)	5378(17)	206(41)
C(7)	7596(13)	2694(22)	−1378(48)	C(7)	7558(10)	2683(18)	−1297(37)
C(8)	8114(15)	2502(24)	392(74)	C(8)	8201(17)	2514(26)	93(55)
C(9)	8687(19)	1881(31)	−786(68)	C(9)	8774(17)	1873(27)	−874(60)
C(10)	8543(17)	856(29)	−2030(69)	C(10)	8554(18)	912(25)	−2166(63)
C(11)	7973(22)	1154(33)	−3537(74)	C(11)	7962(18)	1116(30)	−3646(58)
C(12)	7355(9)	1739(16)	−2713(34)	C(12)	7396(13)	1687(21)	−2514(45)

synthesis, and were included in the calculations but not refined. Anisotropic thermal parameters were used only for tin and halogen atoms. Blocked-cascade least-squares refinements were used; they converged to the conventional *R* index of 0.046 for **A** and of 0.043 for **B**.

The weighting scheme used in the final calculations was of the form $W^{-1} = a_i |F_0|^i$. The a_i parameters were calculated using the program PESO [10]. Scattering factors for the atoms were taken from Cromer and Waber [11]; the scattering factors for tin and bromine were corrected for the real and the imaginary parts of anomalous dispersion using Cromer's values [12]. All computations were carried out on a CDC Cyber 76 computer using the programs of ref. 13. The positional parameters of the non-hydrogen atoms are listed in Table 1, the labelling scheme being shown in Fig. 1 *.

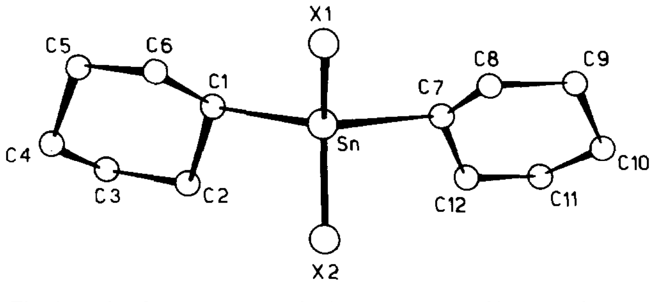

Fig. 1. Molecular structure of $(C_6H_{11})_2SnX_2$ (X = Cl or Br) viewed down the *c* axis.

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* Data listed refer to the left-hand enantiomer for both **A** and **B**, the *R* residuals for the right-hand enantiomer were only slightly and probably not significantly higher (0.010 for **A** and 0.017 for **B**).

Thermal factors, hydrogen atom coordinates with their thermal parameters, and lists of the structure factors are available from the authors upon request.

Description of the structures and comments

The relevant geometrical parameters for **A** and **B** are shown in Table 2. The two structures are isomorphous, and the molecules have nearly the same geometry. Figure 2 shows the molecules stacked along the 2_1 axis parallel to *c*. The geometry of **A** is, within the standard deviations, identical to that of $(C_2H_5)_2SnCl_2$ [2],

TABLE 2

GEOMETRICAL PARAMETERS FOR $(C_6H_{11})_2SnX_2$ (X = Cl, Br) WITH ESTIMATED STANDARD DEVIATIONS

	X = Cl	X = Br
Bond lengths (Å)		
Sn–X(1)	2.393(4)	2.516(2)
Sn–X(2)	2.400(5)	2.492(3)
Sn–C(1)	2.159(7)	2.136(9)
Sn–C(7)	2.156(7)	2.132(8)
C(1)–C(2)	1.52(2)	1.53(2)
C(2)–C(3)	1.55(2)	1.54(2)
C(3)–C(4)	1.54(2)	1.52(3)
C(4)–C(5)	1.53(3)	1.52(3)
C(5)–C(6)	1.56(3)	1.53(2)
C(6)–C(1)	1.55(2)	1.54(2)
C(7)–C(8)	1.51(3)	1.57(3)
C(8)–C(9)	1.56(2)	1.53(2)
C(9)–C(10)	1.52(2)	1.52(2)
C(10)–C(11)	1.51(2)	1.53(3)
C(11)–C(12)	1.53(2)	1.52(3)
C(12)–C(7)	1.52(2)	1.52(2)
Bond angles (°)		
X(1)–Sn–X(2)	96.8(2)	98.3(1)
X(1)–Sn–C(1)	107.2(7)	107.6(6)
X(1)–Sn–C(7)	105.6(7)	107.5(6)
X(2)–Sn–C(1)	105.1(6)	107.3(5)
X(2)–Sn–C(7)	106.1(6)	109.2(6)
C(1)–Sn–C(7)	131.0(9)	123.8(8)
C(1)–C(2)–C(3)	108.5(12)	109.7(11)
C(2)–C(3)–C(4)	112.9(10)	114.6(12)
C(3)–C(4)–C(5)	106.8(13)	111.9(10)
C(4)–C(5)–C(6)	113.0(10)	113.6(13)
C(5)–C(6)–C(1)	104.5(14)	108.7(12)
C(6)–C(1)–C(2)	117.7(11)	115.3(11)
C(7)–C(8)–C(9)	105.5(12)	117.9(10)
C(8)–C(9)–C(10)	120.5(14)	117.7(14)
C(9)–C(10)–C(11)	103.4(16)	111.1(14)
C(10)–C(11)–C(12)	122.8(11)	114.9(12)
C(11)–C(12)–C(7)	106.9(12)	115.0(14)
C(12)–C(7)–C(8)	117.9(12)	112.0(11)

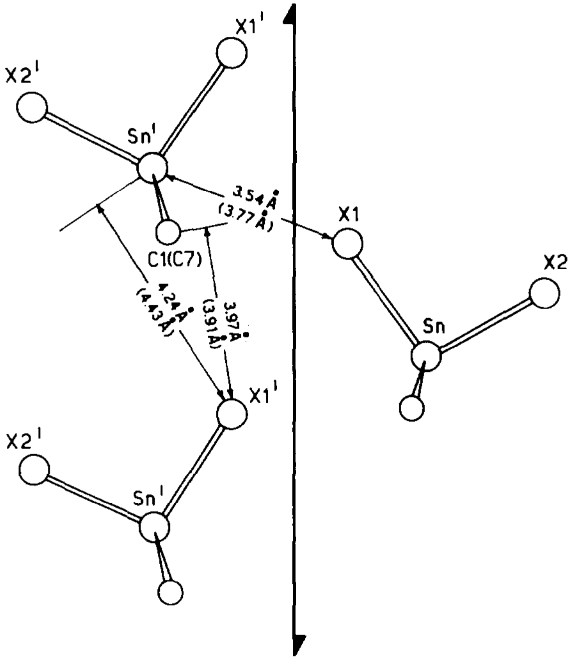

Fig. 2. Molecules of $(C_6H_{11})_2SnX_2$ (X = Cl or Br) piled along the 2_1 axis parallel to *c*. For simplicity the cyclohexyl rings are omitted except for C(1) and C(7) (overlapped in this view). The figures in parentheses refer to the bromine derivative.

$(C_6H_5)_2SnCl_2$ [4], and bis(biphenylyl-2) tin dichloride [5], and corresponds to a distorted tetrahedral coordination. The molecule has a pseudosymmetry mirror plane through Cl(1), Sn and Cl(2) nearly coincident with the crystallographic plane [420]. Moreover the plane through C(1), Sn and C(7) almost exactly bisects the angle Cl(1)-Sn-Cl(2).

The large angle C(1)-Sn-C(7) (134°) is due to the need to relieve intramolecular interactions between the two cyclohexyl groups and intermolecular interactions between C(1), C(7) and Cl(2)' of the adjacent molecule translated along *c* (see Fig. 2). The same considerations apply to the bromo derivative.

Molecules piled along 2_1 (parallel to *c*) show contact distances of 3.54 and 3.77 Å, respectively for Sn... Cl(1) and Sn... Br(1). However, such distances seem not to require five-coordination. From consideration of the geometry about the tin atom we would expect in the case of pentacoordination that: (a) the plane through C(1), Sn and C(7) would no longer bisect the angle Cl(1)-Sn-Cl(2); (b) the bond angles Cl(2)-Sn-C (Br(2)-Sn-C) would be much more closed towards 90°; (c) the bond angles Cl(1)-Sn-C (Br(1)-Sn-C) would be opened towards 120°.

Moreover, the Δ-value of 3.47 mm s^{-1} for **A** is only slightly different from those of R_2SnCl_2 for $R = CH_3$ (3.55 mm s^{-1}) [1] and $R = C_2H_5$ (3.81 mm s^{-1}) [2]. If the assignment of octahedral coordination to the latter species is correct, the coordination in our structures must be assumed five, and it would be necessary to reach the absurd conclusion that the Mössbauer response is completely independent of the coordination at tin. On the other hand, if the coordination attributed to Me_2SnCl_2 and Et_2SnCl_2 is uncorrect, then it would be that the Δ-values should be almost the same since the molecular structures are also the same, that is tetrahedral, as shown by almost identical geometries. It is our opinion that to identical, or almost identical, geometrical parameters must correspond identical coördination. Using the arguments we used in the case of the structures of R_2SnX_2, we should conclude that Me_2SnCl_2 and Et_2SnCl_2 also involve tetrahedral coordination. Certainly, our arguments are at least as valid as those we criticise, and it is evident that much care must be taken in detailed interpretation of crystal data.

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