

CRYSTAL AND MOLECULAR STRUCTURE OF BIS(CHLORODIPHENYLSTANNYL)METHANE

J. MEUNIER-PIRET, M. VAN MEERSSCHE

Laboratoire de Chimie physique et de Cristallographie, Université de Louvain, Bâtiment Lavoisier, Place L. Pasteur, 1, B-1348 Louvain-la-Neuve (Belgium)

K. JURKSCHAT * and M. GIELEN

Vrije Universiteit Brussel, T.W.-A.O.S.C., Pleinlaan 2, B-1050 Brussel (Belgium)

(Received December 5th, 1984)

Summary

Bis(chlorodiphenylstannyl)methane $[(C_6H_5)_2ClSn]_2CH_2$ crystallizes in the orthorhombic space group *Pbca*. The unit cell, with dimensions *a* 23.992(24), *b* 20.602(16) and *c* 10.158(8) Å, *V* 5021(8) Å³, contains eight molecules. The structure was refined to a final *R*-value of 0.082 for 1990 independent reflections. Both tin atoms are pentacoordinated, with intra- and inter-molecular chlorine bridges. The Sn–Cl distances are 2.375, 2.441, 3.368 (intramolecular bridge) and 3.235 Å (intermolecular bridge). The structure consists of polymeric chains (parallel to *c* axis), with the molecules held together by Sn...Cl bonds (3.235 Å).

Introduction

Bis(organostannyl)methanes have been shown to have useful properties as building blocks for tin-containing heterocycles [1–5]. Some of them behave as bidentate Lewis acids [6–8]. For instance, the crystal structure of the complex $[(C_6H_5)_2-XSn]_2CH_2 \cdot HMPA$ (with X = Cl and Br) [8] shows a distorted trigonal bipyramidal geometry for both tin atoms but the two tin environments are not equivalent because HMPA is not a bridging ligand. Furthermore, the biological (antitumor) activity of these compounds is of considerable interest [9]. In a recent paper we inferred a trigonal bipyramidal environment around the tin atoms of the title compound from Mössbauer measurements [10]. In order to prove this and to provide data for systematic studies of bis(organostannyl)methanes we have determined the crystal and molecular structure of bis(chlorodiphenylstannyl)methane (1).

* Present address: Sektion Chemie der Martin-Luther-Universität, Halle-Wittenberg, 4020 Halle/S., Weinbergweg 16 (D.D.R.)

Experimental

The preparation of compound **1** has been described elsewhere [11]. Single crystals were obtained from ether/hexane. Observed systematic extinctions on Weissenberg photographs indicated space group *Pbca*. The unit-cell parameters were obtained by least-squares refinement from the setting angles of 15 reflections: *a* 23.992(24), *b* 20.602(16), *c* 10.158(8) Å, *Z* = 8, *D*_{calc} 1.67 g cm⁻³, *F*(000) 2448 electrons.

Intensities of reflections were collected in the ω -scan mode (width 1.3°) with a Syntex P2₁ diffractometer, using monochromatic Mo-*K*_α radiation (λ 0.71069 Å) to $2\theta_{\max}$ 47°. 3717 independent intensities were measured, of which only 1190 were considered as observed using the criterion $I > 2.5\sigma(I)$. The structure was solved from Patterson map (Sn positions) and Fourier synthesis (Cl and C positions), the two H atoms of methane were obtained from a difference density map. The full-matrix least-squares refinement of the positional and thermal anisotropic parameters of five atoms (Sn(1), Sn(2), Cl(1), Cl(2) and C(1)) was carried out using the

TABLE 1
ATOMIC COORDINATES ($\times 10^4$, 10^3 for H-atoms)

	<i>x</i>	<i>y</i>	<i>z</i>
Sn(1)	821(1)	2381(1)	2222(2)
Sn(2)	1872(1)	1158(1)	1853(2)
Cl(1)	879(3)	1890(3)	39(6)
Cl(2)	2561(3)	719(4)	3275(8)
C(1)	1507(9)	1896(11)	3102(24)
H(1)	183(6)	225(7)	330(14)
H(2)	137	167	399
C(2)	-2(9)	2082(11)	2760(24)
C(3)	-299	2454	3667
C(4)	-829	2257	4070
C(5)	-1061	1688	3566
C(6)	-763	1316	2659
C(7)	-234	1513	2256
C(8)	997(10)	3364(12)	1704(24)
C(9)	600	3740	1053
C(10)	716	4387	749
C(11)	1229	4656	1096
C(12)	1626	4280	1747
C(13)	1510	3633	2051
C(14)	2367(10)	1486(11)	272(25)
C(15)	2474	2149	149
C(16)	2828	2372	-843
C(17)	3073	1933	-1713
C(18)	2965	1270	-1590
C(19)	2612	1047	-598
C(20)	1348(19)	350(22)	1425(49)
C(21)	1314	55	191
C(22)	959	-472	-2
C(23)	636	-704	1039
C(24)	669	-409	2273
C(25)	1025	118	2466

Symmetry code: Sn(11), *x*, 1/2 - *y*, *z* - 1/2; Cl(11), *x*, 1/2 - *y*, *z* + 1/2.

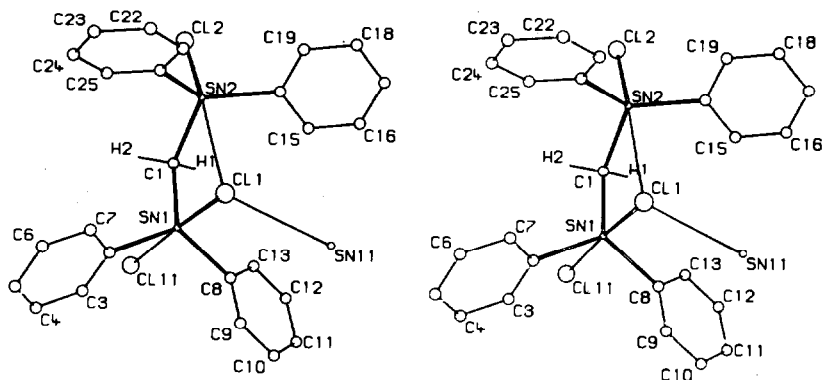


Fig. 1. Molecular structure of $(\text{Ph}_2\text{ClSn})_2\text{CH}_2$.

SHELX 76-program. The four phenyl rings and the two H atoms located were refined as rigid groups, with isotropic thermal parameters. The weighting scheme applied was $[\sigma^2(F) + 0.0016 F^2]^{-1}$. The atomic scattering factors used were those included in the SHELX 76-program. The final R index is 0.082 for the set of observed reflections; R_w is 0.089. Apart from some peaks around the tin atoms the final difference map was featureless. The final atomic coordinates are listed in Table 1, using the numbering indicated in Fig. 1. Table of observed and calculated structure factors may be obtained from the author (J. M.-P.).

Discussion

Table 2 lists a selection of bond lengths and angles. The Sn–Cl distances of the chlorine atoms directly bonded to tin (2.44 and 2.38 Å) are different, but fall in the range of lengths found in other pentacoordinated tin compounds [6,12,13]. Those

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Sn(1)–Cl(1)	2.441(6)	Sn(2)–Cl(2)	2.375(7)
Sn(1)–C(1)	2.123(20)	Sn(2)–C(1)	2.165(24)
Sn(1)–C(2)	2.139(20)	Sn(2)–C(14)	2.107(26)
Sn(1)–C(8)	2.134(22)	Sn(2)–C(20)	2.132(45)
Sn(1) ⋯ Cl(11)	3.235(6)	Sn(2) ⋯ Cl(1)	3.368(7)
Cl(1)–Sn(1)–C(1)	98.3(7)	Cl(2)–Sn(2)–C(1)	101.1(6)
Cl(1)–Sn(1)–C(2)	99.5(7)	Cl(2)–Sn(2)–C(14)	101.2(7)
Cl(1)–Sn(1)–C(8)	99.1(8)	Cl(2)–Sn(2)–C(20)	103.7(10)
C(1)–Sn(1)–C(2)	118.2(9)	C(1)–Sn(2)–C(14)	116.7(11)
C(2)–Sn(1)–C(8)	121.2(11)	C(14)–Sn(2)–C(20)	115.3(14)
C(1)–Sn(1)–C(8)	113.4(10)	C(1)–Sn(2)–C(20)	115.4(14)
Cl(1)–Sn(1) ⋯ Cl(11)	173.5(4)	Cl(2)–Sn(2) ⋯ Cl(1)	174.8(4)
Sn(1)–C(1)–Sn(2)	113.4(10)		
Sn(1)–Cl(1) ⋯ Sn(2)	74.2(9)		
Sn(1)–Cl(1) ⋯ Sn(11)	127.5(9)		
Sn(11) ⋯ Cl(1) ⋯ Sn(2)	136.2(9)		

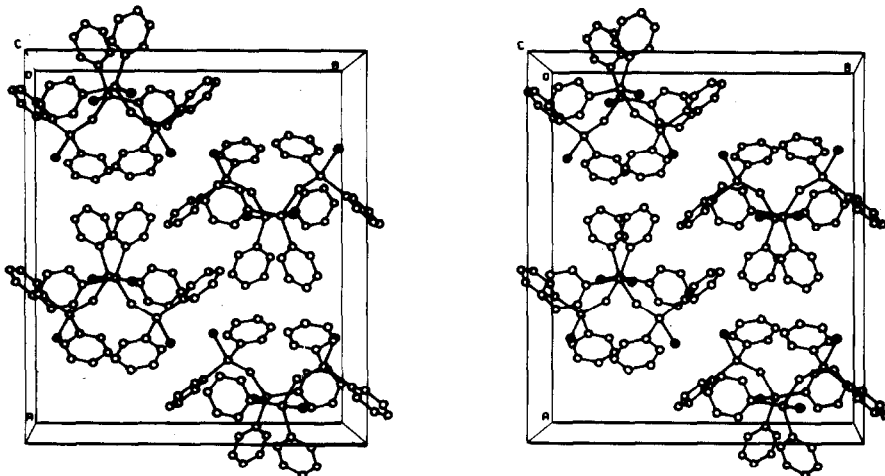


Fig. 2. Stereoview of the unit cell showing four columns of polymeric chain parallel to c (with two molecules in each chain).

bonds are more unequal in the HMPA complex described in ref. 8. The tin-carbon distances to the methylene bridge and to the phenyl groups are similar to those in other compounds [8,13,14]. Both tin atoms are pentacoordinated, but the two tin environments are not equivalent because of the different nature of the two chlorine atoms. Whereas Cl(2) is only bonded to Sn(2), Cl(1) interacts with three tin centres, via two intramolecular and one intermolecular bonds. Figure 2 shows the crystal

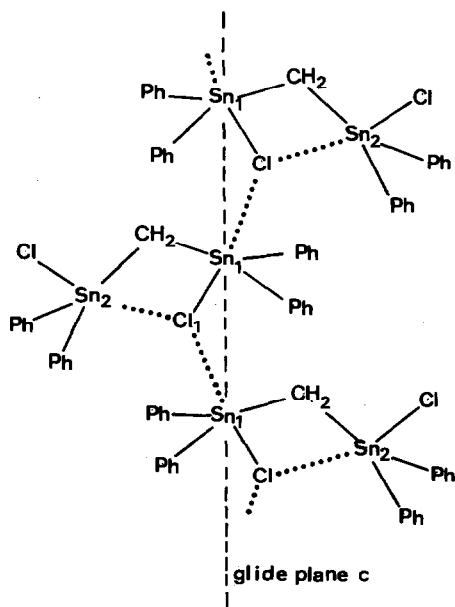


Fig. 3. Schematic representation of the polymeric chain with three molecules symmetric along the glide plane c .

packing in the unit cell. The structure consists of polymeric chains parallel to the *c* axis wherein the molecules are related together by the *c* glide plane and the chlorine atoms, Cl(1) bridge non-planar triorganotin fragments (Sn(1)). Figure 3 represents schematically a section of one column. A similar structure with a zig-zag $\cdots \text{Cl-Sn} \cdots \text{Cl-Sn} \cdots \text{Cl-Sn} \cdots$ chain has been reported for Me_3SnCl [12]. The angles Cl(1)–Sn(1) \cdots Cl(11) and Cl(2)–Sn(2) \cdots Cl(1) of 173.5 and 174.8° are near the ideal value of 180° expected for a trigonal bipyramidal coordination. On the other hand the sums of the equatorial carbon–tin–carbon bond angles around Sn(1) and Sn(2), 353 and 347°, respectively (instead of 360°) indicate a significant deformation of this coordination. This deformation is greater than in the HMPA complex [8]. Thus the environment of Sn(2) in particular can also be described in terms of a monocapped tetrahedron. The intermolecular Sn(1)–Cl(1) \cdots Sn(11) angle of 127.5° is considerably smaller than that, viz 150.3°, reported for Me_3SnCl [12]. Obviously this effect is caused by the proximity of the second Lewis-acid center Sn(2) leading to a third tin–chlorine interaction (Cl(1) \cdots Sn(2)). The intramolecular Sn(1)–Cl(1) \cdots Sn(2) angle of 74.2° is smaller than the corresponding angle of 78.4° in the HMPA complex [8]; though the distances between the two tins of the molecule are similar in the two structures (3.58 Å here, 3.57 in ref. 8). The Cl(1) \cdots Sn(2) interaction is considerably weaker (3.37 Å) in comparison to the corresponding length (3.02 Å) in the HMPA complex. However the intermolecular Cl(1) \cdots Sn(11) (3.24 Å) is stronger; the similar contact in Me_3SnCl [12] is 3.27 Å. During the complexation this intermolecular interaction is broken, one oxygen takes the place of this intermolecular bridge, the complex is monomeric.

Acknowledgement

The authors thank Zakia Kerouache for her assistance in this work.

References

- 1 K. Jurkschat and M. Gielen, *J. Organomet. Chem.*, 236 (1982) 69.
- 2 J. Meunier-Piret, M. Van Meerssche, M. Gielen and K. Jurkschat, *J. Organomet. Chem.*, 252 (1983) 289.
- 3 H. Preut, P. Bleckmann, T. Mitchell and B. Fabisch, *Acta Cryst.*, C40 (1984) 370.
- 4 K. Jurkschat and A. Tzschach, in preparation.
- 5 R. Willem, M. Gielen, J. Meunier-Piret, M. Van Meerssche, K. Jurkschat and A. Tzschach, *J. Organomet. Chem.*, 277 (1984) 335.
- 6 T.J. Karol, J.P. Hutchinson, J.R. Hyde, H.G. Kuivila and J. Zubieta, *Organometallics*, 2 (1983) 106.
- 7 K. Jurkschat and M. Gielen, *Bull. Soc. Chim. Belg.*, 91 (1982) 803.
- 8 M. Gielen, K. Jurkschat, J. Meunier-Piret and M. Van Meerssche, *Bull. Soc. Chim. Belg.*, 93 (1984) 379.
- 9 M. Gielen, K. Jurkschat and G. Atassi, *Bull. Soc. Chim. Belg.*, 93 (1984) 153.
- 10 M. Gielen, K. Jurkschat, B. Mahieu and D. Apers, *J. Organomet. Chem.*, in press.
- 11 M. Gielen and K. Jurkschat, *J. Organomet. Chem.*, 273 (1984) 303.
- 12 J.L. Lefferts, K.C. Molloy, M.B. Hossain, D. van der Helm and J.J. Zuckerman, *J. Organomet. Chem.*, 240 (1982) 349.
- 13 M. Dräger and H. Guttman, *J. Organomet. Chem.*, 212 (1981) 171.
- 14 P.G. Harrison and T.J. King, *J. Chem. Soc. Dalton*, (1974) 2298; G.M. Bancroft, B.W. Davies, N.C. Payne and T.K. Sham, *J. Chem. Soc. Dalton*, (1975) 973.