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CRYSTAL STRUCTURE OF TRICYCLOHEXYLTIN CHLORIDE

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Summary

The structure of tricyclohexyltin chloride has been determined by X-ray analysis. The compound crystallizes in the space group $P2_{1/m}$ with a 10.386(6), b 17.195(9), c 5.713(3) Å, β 104.26(9)° and $Z = 2$. It consists of discrete tetrahedral (cyclo-C_6H_{11})$_3$SnCl units. The departure from the regular tetrahedral geometry is less than that in tricyclohexyltin acetate.

The quadrupole splitting value (Δ 3.49 mm s^{-1}), so large as to have been attributed to a penta-coordinated geometry, is shown to be consistent with the tetrahedral geometry when distortions are taken into account in the treatment of the point charge model.

Introduction

Considerable attention has been given to the Mössbauer study of the structure of organotin compounds containing bulky groups [1,2], but only rarely has the quadrupole splitting interpretation been fully correlated with X-ray diffraction data [3—6]. This lack is observed in particular for the cyclo-hexyltin halides (cyclo-C_6H_{11})$_3$SnX with X = F, Cl, Br and I. The Mössbauer quadrupole splitting values for the fluoride and chloride compounds, close to those of the trimethyltin analogues, have been interpreted in terms of polymeric structures involving five-coordinated tin atoms [1,2]. The quadrupole splitting values for the bromide and iodide compounds have been explained as due to a coordination geometry intermediate between four and five [2]. The only known struc-

TABLE 1

FRACTIONAL ATOMIC COORDINATES (× 10^4) AND THERMAL PARAMETERS (× 10^3)[a, b]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	362(1)	2500	2517(2)	75(1)	93(1)	71(1)	−12(5)	12(1)	−23(5)
Cl	347(7)	2500	−1706(9)	166(6)	203(8)	74(4)	−3(2)	38(4)	15(33)
C(1)	−1778(19)	2500	2338(39)	65(11)	149(21)	121(17)	0(156)	−10(11)	0(156)
C(2)	−2399(18)	3186(12)	1217(64)	76(12)	131(17)	598(52)	68(25)	42(21)	11(12)
C(3)	−3952(19)	3161(14)	1219(62)	86(13)	183(23)	505(49)	−71(28)	24(21)	21(14)
C(4)	−4571(24)	2500	−64(55)	91(17)	218(34)	168(25)	0(156)	−31(16)	0(156)
C(5)	1366(18)	3551(10)	3674(33)	119(13)	119(13)	161(15)	47(12)	48(12)	−16(11)
C(6)	972(26)	4155(16)	2346(69)	200(24)	133(23)	453(53)	38(29)	−107(27)	−64(20)
C(7)	1676(29)	4980(15)	3419(76)	174(23)	109(18)	649(66)	6(30)	−6(32)	−10(18)
C(8)	2985(24)	4933(16)	3500(52)	130(16)	206(25)	300(30)	100(22)	28(18)	−71(17)
C(9)	3369(26)	4328(19)	5092(71)	153(22)	204(32)	447(51)	47(33)	−87(26)	−49(22)
C(10)	2695(18)	3521(12)	3908(75)	91(12)	107(16)	752(69)	−71(28)	36(24)	−45(13)

[a] In parentheses the estimated standard deviation. [b] The thermal parameters U_{ij} (Å^2) are in the form $\exp[-2\pi^2(\Sigma_i\Sigma_j h_i h_j a_i^* a_j^* U_{ij})]$.

ture of tricyclohexyltins is that of the corresponding acetate, which has a distorted tetrahedral geometry [7] in spite of its large Mössbauer quadrupole splitting value.

Thus, in furtherance of our work in the field of X-ray and Mössbauer characterization of organotin compounds [8—11], we undertook the crystal structure analysis of the title compound. Our aim was to verify its molecular conformation in the light of the previous chemico-physical interpretations [1,2] mainly based on the Mössbauer quadrupole splitting value.

Experimental

Tricyclohexyltin chloride: Crystal and intensity data

Tricyclohexyltin chloride was prepared following the procedure previously described [12]. Suitable crystals for X-ray analysis were obtained from a chloroform/n-hexane solution, m.p. 128°C; Lit. [12] 129—130°C.

$C_{18}H_{33}SnCl$, m.w. 403.2, monoclinic, a 10.383(6), b 17.195(9), c 5.713(3) Å, β 104.26(9)°; U 988.5 Å^3, D_m 1.34 g cm^{-3}, Z 2, D_c 1.35 g cm^{-3}, $F(000)$ 416, λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 14.07 cm^{-1}. Space group $P2_{1/m}$ (confirmed by structural refinement).

The compound was found to decompose in the X-ray beam and two crystals were used for the collection of intensity data. The dimensions of the crystals were 0.5 × 0.5 × 0.2 mm. Accurate lattice and orientation parameters were obtained by least-squares treatment of 25 symmetry-related reflections.

Intensity data were measured by use of the ϑ — 2ϑ scan method with a Philips PW 1100 computer controlled four-circle diffractometer, with graphite monochromator. After half data collection the intensities dropped to 7% of the initial intensity and the crystal was changed. The intensities were corrected for Lorenz and polarization effects and were scaled using nearly 70 common reflections. No absorption corrections were made. The data were scaled to give 1420 independent F_{hkl} values for which I was greater of 2 σ (I).

Solution and refinement of the structure

The positions of the Sn and Cl atoms were determined from a three-dimensional Patterson synthesis. A difference electron density synthesis, based upon the Sn and Cl signs, revealed the positions of all the non-hydrogen atoms. Five cycles of isotropic refinement with unit weights reduced the R value to 0.107. Anisotropic temperature factors of the form

$$\exp - [2\,\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + ... + 2U_{12}hk\,a^*b^* + ...)]$$

were assigned to the tin and chlorine atoms and three more cycles of least squares lowered R to 0.089. Three further cycles with anisotropic temperature factors for all atoms reduced R to 0.070 assuming the space group to be $P2_{1/m}$. Refinement in space group $P2_1$ yielded appreciably higher values of R.

Hydrogen atoms were not included in the calculations. The weighting scheme used in the very last calculations was of the form $W^{-1} = a_i|F_0|^i$. The a_i parameters were calculated using the program PESO [13]. Scattering factors for the atoms were taken from Cromer and Waber [14], the scattering factor of the Sn atom was corrected for the real and imaginary parts of anomalous dis-

TABLE 2

BOND DISTANCES AND BOND ANGLES WITH ESTIMATED STANDARD DEVIATIONS

Atoms	Bond distance (Å)	Atoms	Bond angles (°)
Sn—Cl	2.407(5)	C(1)—Sn—Cl	101.9(0.5)
Sn—C(1)	2.162(20)	C(5)—Sn—Cl	101.4(0.5)
Sn—C(5)	2.065(22)	C(1)—Sn—C(5)	115.0(0.6)
C(1)—C(2)	1.447(24)	C(5)—Sn—C(5′)	119.0(0.5)
C(2)—C(3)	1.687(24)	Sn—C(1)—C(2)	110.4(1.3)
C(3)—C(4)	1.461(29)	C(1)—C(2)—C(3)	107.5(2.0)
C(5)—C(6)	1.343(29)	C(2)—C(3)—C(4)	107.6(2.6)
C(6)—C(7)	1.690(29)	C(3)—C(4)—C(3′)	114.0(2.0)
C(7)—C(8)	1.423(33)	C(2′)—C(1)—C(2)	114.0(2.0)
C(8)—C(9)	1.410(35)	Sn—C(5)—C(6)	116.9(1.6)
C(9)—C(10)	1.686(29)	Sn—C(5)—C(10)	115.3(1.6)
C(5)—C(10)	1.416(23)	C(5)—C(6)—C(7)	114.7(2.6)
		C(6)—C(7)—C(8)	106.3(2.6)
		C(7)—C(8)—C(9)	101.0(2.3)
		C(8)—C(9)—C(10)	107.6(3.2)
		C(9)—C(10)—C(5)	110.5(2.2)
		C(10)—C(5)—C(6)	105.1(1.8)

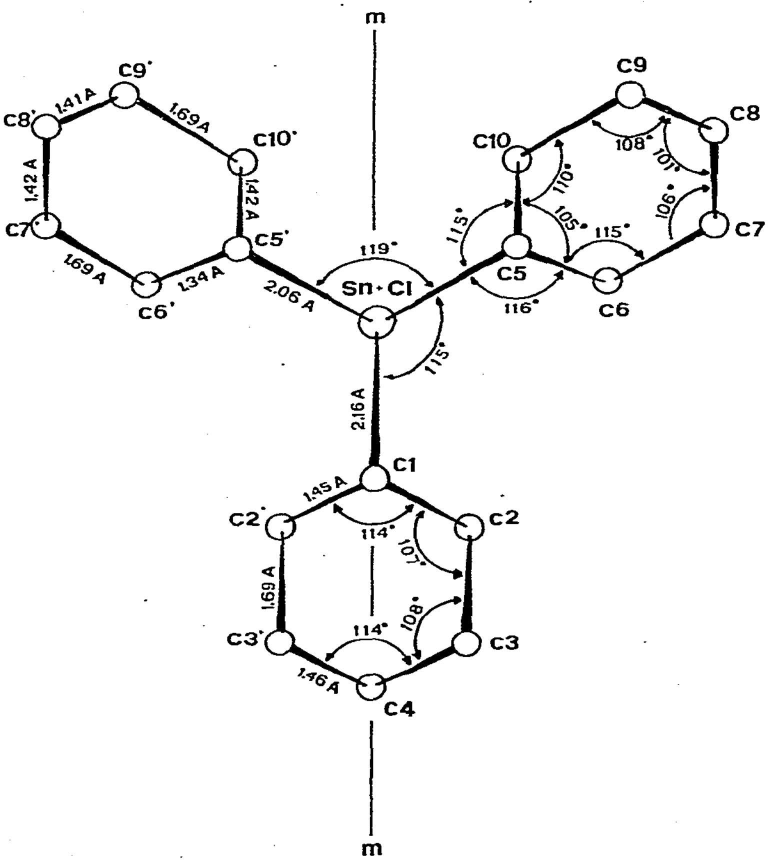

Fig. 1. Molecular model for (cyclo-C_6H_{11})$_3$SnCl as viewed along the Sn—Cl axis; some bond lengths and bond angles are reported.

persion using Cromer's values [15]. Final atomic coordinates and temperature factors are listed in Table 1, bond lengths and angles are reported in Table 2 and in Fig. 1.

All calculations were carried out on a CDC Cyber 76 computer, using a program of ref. 16. The lists of the observed and calculated structure factors are available from the authors on request.

Results and discussion

The internal geometrical parameters shown in Table 2 and Fig. 1 indicate a distorted tetrahedral coordination about the tin atom. The bond lengths Sn—C and Sn—Cl are very close to those reported for similar compounds [3]: the bond angles C—Sn—Cl and C—Sn—C can hardly be considered as derived from a distorted trigonal bipiramidal coordination; the intermolecular Sn ... Cl distance of 3.30 Å does not involve significant electronic interaction. It is interesting to observe that the coordination geometry about the tin atom is almost identical to that determined for $(CH_3)_3SnCl$ by electron diffraction in the gaseous phase [18], where the molecules are necessarily discrete.

The very high vibration amplitudes for some atoms of the cyclohexyl group are noteworthy. The ellipsoid thermal parameters of these atoms (cf. Table 1) could easily be explained in terms of large librations of the cyclohexyl groups

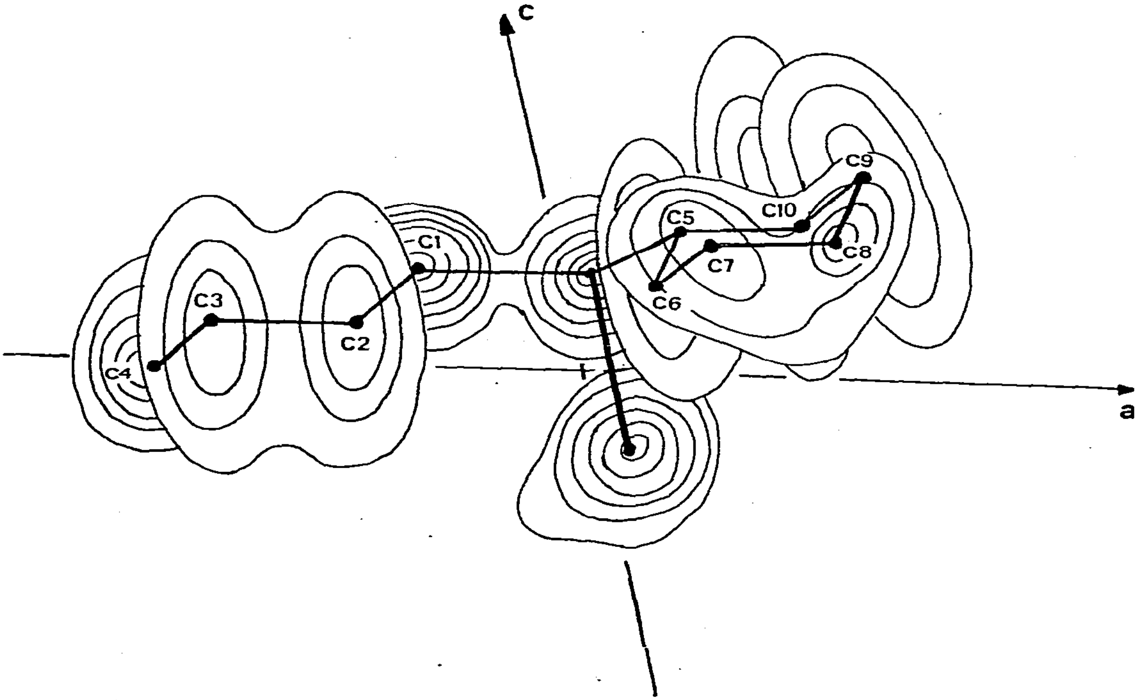

Fig. 2. (cyclo-C_6H_{11})$_3$SnCl: superimposed map of the electron density as viewed along the *b* axis; the contour interval is 0.7 e/Å^3 for all carbon atoms starting from 0.7 e/Å^3. The maximum corresponding to C(5) is not visible. The higher the anisotropic thermal parameters, the more is the electron density of the corresponding atom spread out in the expected direction.

about the corresponding Sn—C bonds, but we believe that they are most likely to be related to some sort of conformational disorder. Calculations in this sense were made but no significant improvement for the *R* factor was obtained.

Figure 2 shows the effect of the highly anisotropic thermal parameters on the Fourier map of the electron density. The high thermal parameters account also for the conformational distortions observed for the cyclohexyl groups.

Figure 3 shows a model of packing on [010]; only the intermolecular contact distances shorter than 4 Å are reported. Interactions occur mostly along the *c* direction, Sn ... Cl′ = 3.30 Å, Cl′ ... C(1) = 3.60 Å and Cl′ ... C(5) = 3.62 Å. Long intermolecular contact distances allow large libration of the cyclo-hexyl groups; the relatively weak cohesion among molecules accounts for the low melting point, 128°C.

The structure, which is characterized by a not very distorted tetrahedral coordination about the tin atom, is associated with a Mössbauer quadrupole splitting value of 3.49 mm s^{-1}. On the basis of this value it has been previously suggested that tricyclohexyltin chloride has a polymeric structure containing penta-coordinated tin atoms [1,2]. The splitting is even higher than that found for the tricyclohexyltin acetate (3.27 mm s^{-1}), although the distortions from the tetrahedral geometry in this case are larger than those found for the title compound. On the other hand calculation of the quadrupole splitting value for the compound assumed as tetrahedral by simple point-charge model gives Δ —2.74 mm s^{-1}. The following partial quadrupole splitting values (mm s^{-1}): Cl = 0.00, cyclohexyl ≃ alkyl = 1.37 [19] have been used. The disagreement

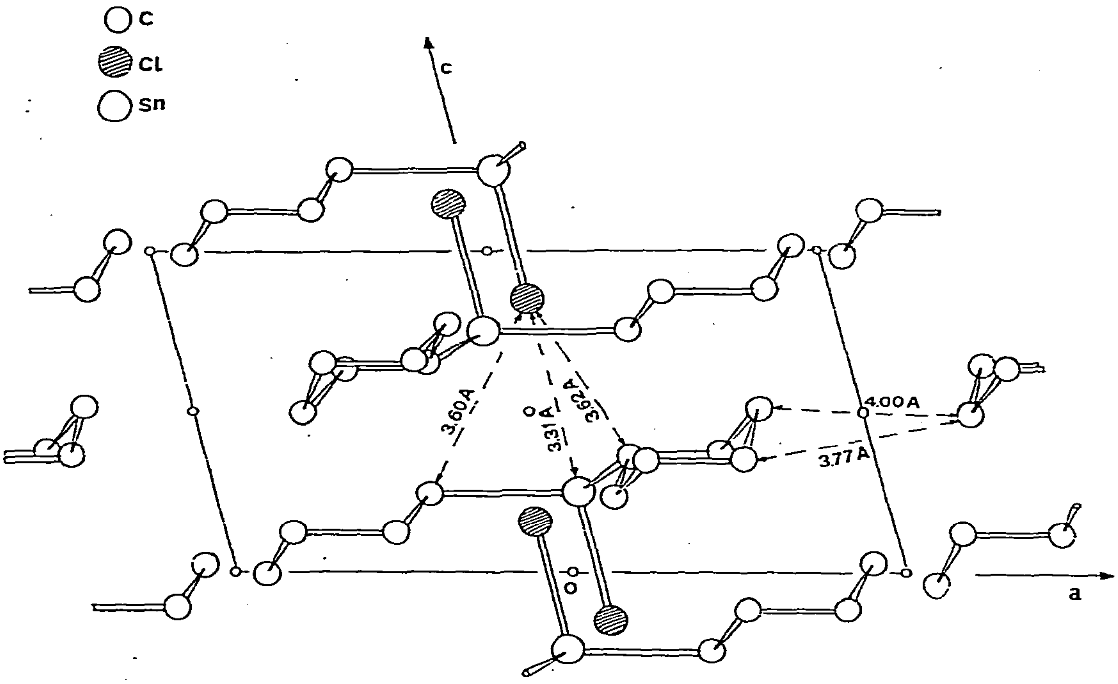

Fig. 3. Molecular packing of (cyclo-C_6H_{11})$_3$SnCl as viewed along the *b* axis. Intermolecular contact distances shorter than 4.00 Å are reported.

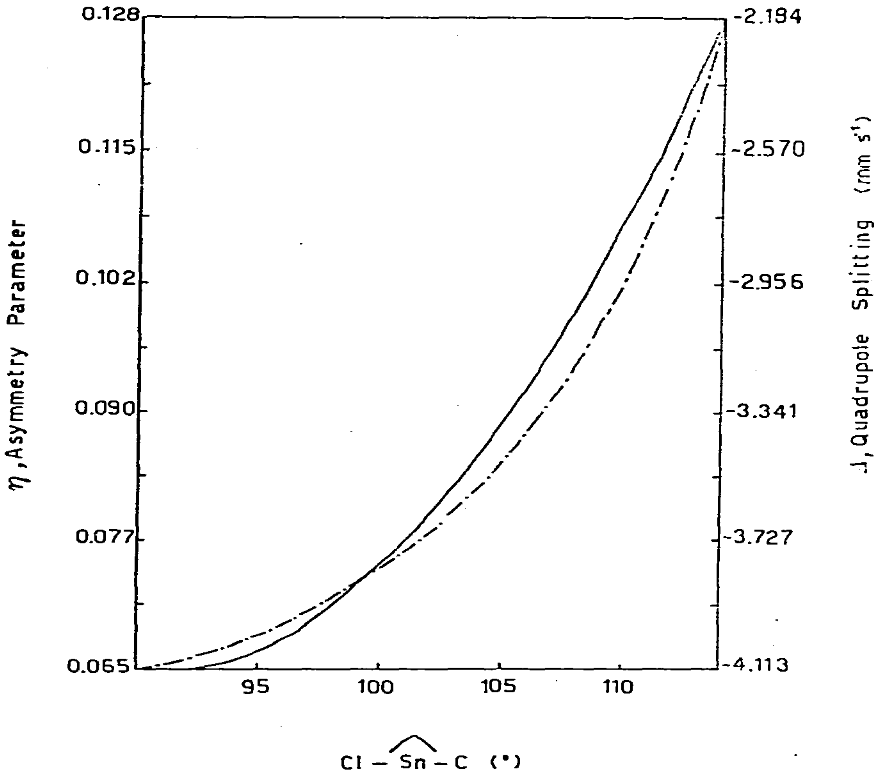

Fig. 4. Variation of the quadrupole splitting (Δ ———) and the asymmetry parameter (η · — · — ·) with the Cl—Sn—C bond angle.

between observed and calculated values is removed on a semi-quantitative basis by including distortions in the treatment [20] of the point charge model [21, 22].

We used the program Quadrupole, developed to handle variable geometry systems [23]. The results are reported in Fig. 4. Figure 4 shows the variation of the quadrupole splitting (Δ) and the asymmetry parameter (η) as functions of the Cl—Sn—C bond angle. The C—Sn—C bond angles were taken to be constant using the values found in the present crystal structure. The above reported partial quadrupole splitting parameters were used. The calculated Δ value for the observed Cl—Sn—C angle (~102°) is —3.64 mm s^{-1}, which is in good agreement with the experimental value 3.49 mm s^{-1}.

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References

1 R.H. Platt, J. Organometal. Chem., 24 (1970) C23.
2 A.G. Maddock and R.H. Platt, J. Chem. Soc. (A), (1971) 1191.

3 J.A. Zubieta and J.J. Zuckermann, in S.J. Lippard (Ed.), Progress in Inorganic Chemistry, Vol. 24, Wiley, New York, 1978, p. 251.

4 R.V. Parish, in S.J. Lippard (Ed.), Progress in Inorganic Chemistry, Vol. 15, Wiley, New York, 1972.

5 B.Y.K. Ho and J.J. Zuckermann, J. Organometal. Chem., 49 (1973) 1.

6 P.G. Harrison, in J.J. Zuckermann (Ed.), Organotin Compounds: New Chemistry and Applications, Advances in Chemistry Series 157, American Chemical Society, Washington, 1976, p. 258.

7 N.W. Alcock and R.E. Timms, J. Chem. Soc., (1968) 1876.

8 R. Graziani, G. Bombieri, E. Forsellini, P. Furlan, V. Peruzzo and G. Tagliavini, J. Organometal. Chem., 125 (1977) 43.

9 S. Calogero, R. Furlan, V. Peruzzo and G. Plazzogna, Inorg. Chim. Acta, 22 (1977) 55.

10 S. Calogero, P. Furlan, V. Peruzzo and G. Tagliavini, J. Organometal. Chem., 128 (1977) 177.

11 S. Calogero, D.A. Clemente, V. Peruzzo and G. Tagliavini, J. Chem. Soc. Dalton, in press.

12 E. Krause and R. Pohland, Ber., 57 (1924) 532.

13 G. Bandoli and D.A. Clemente, J. Chem. Soc. Perkin II, (1976) 413.

14 D.T. Cromer and J.T. Waber, Acta Cryst., 18 (1965) 104.

15 D.T. Cromer, Acta Cryst., 18 (1965) 17.

16 J.M. Stewart, F.A. Kundell and J.C. Baldwin, X-ray System of Programs, Technical Report TR 646, University of Maryland.

17 B. Beagley, K. McAloon and J.M. Freeman, Acta Cryst., B30 (1974) 444.

18 H.A. Skinner and L.E. Sutton, Trans. Faraday Soc., 40 (1944) 164.

19 G.M. Bancroft and K.D. Bitler, Inorg. Chim. Acta, 15 (1975) 57.

20 R.A. La Rossa and T.L. Brown, J. Amer. Chem. Soc., 96 (1974) 2072.

21 M.G. Clark, A.G. Maddock and R.H. Platt, J. Chem. Soc. Dalton, (1972) 281.

22 G.M. Bancroft, K.D. Butler and A.T. Rake, J. Organometal. Chem., 34 (1972) 137.

23 S. Calogero and C. D'Arrigo, Quantum Chemistry Program Exchange, Indiana University, Newsletter, (1978) 63.