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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XXI *. COMPLEX FORMATION BETWEEN DIPHENYLTIN DICHLORIDE AND BENZTHIAZOLE AND 2-AMINOBENZTHIAZOLE

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Summary

Diphenyltin dichloride forms 1/1 adducts with both benzthiazole and 2-aminobenzthiazole, for which tin-119m Mössbauer quadrupole splitting data suggest trigonal bipyramidal and distorted octahedral geometries, respectively. X-ray diffraction studies of the adduct with benzthiazole confirm the five-coordinated structure, and crystals are orthorhombic, space group $P2_12_12_1$ with *a* 11.521(4), *b* 12.349(8) and *c* 13.500(5) Å. The structure was determined from diffractometer data using Patterson and Fourier techniques, and crystals consist of discrete non-interacting $Ph_2SnCl_2 \cdot$ (benzthiazole) molecules. The two phenyl groups occupy two equatorial positions of the trigonal bipyramidal arrangement about the tin (mean Sn—C 2.112(8) Å), the third equatorial site being occupied by a chlorine atom at a Sn—Cl distance of 2.336(1) Å. The second chlorine atom and the nitrogen atom of the benzthiazole ligand occupy the two axial positions (Sn—Cl 2.446(1) Å; Sn—N 2.548(2) Å].

Introduction

The ability of diorganotin(IV) dihalides to form complexes of higher coordination number with Lewis bases has been known for a long time. Generally, coordination saturation at tin in such complexes is reached at six, and many complexes of the type $R_2SnX_2 \cdot 2$ L (L = unidentate ligand) and $R_2SnX_2 \cdot$ L⌒L (L⌒L = bidentate ligand) have been characterised for a wide range of oxygen and nitrogen donor ligands [2].

In the six-coordinate complexes, *trans*-R_2 geometry at the tin is universally adopted [2,3], whilst the two chlorine atoms may be mutually *cis* [4] or *trans*

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* For part XX see ref. 1.

[5] depending on the nature of the ligands L or L⌒L. The formation of $R_2SnX_2 \cdot 2L$ complexes must, a priori, proceed via a five-coordinate $R_2SnX_2 \cdot L$ species, yet, although both 1/1 and 1/2 complexes of diorganotin dihalides with unidentate oxygen donor ligands have been characterised spectroscopically [6], no 1/1 complexes with a nitrogenous donor have yet been identified. This omission is made more surprising since both five- and six-coordinated complex anions $R_2SnCl_3^-$ and $R_2SnCl_4^{2-}$ are well established [7]. In an attempt to characterise 1/1 complexes of nitrogen donor ligands, we have studied the complexation of diphenyltin dichloride with two bulky ligands, benzthiazole (BT) and 2-aminobenzthiazole (Habt).

Experimental

Synthesis of the complexes

(a) Reaction of Ph_2SnCl_2 with BT in acetone

1/1 reaction. Equimolecular quantities of diphenyltin dichloride and benzthiazole, dissolved in the minimum of dry acetone, were stirred together at room temperature for 24 h. Concentration of the solution yielded a brown oil, from which crystallised a white solid on the addition of a small quantity of pentane. Recrystallisation from dry benzene afforded colourless crystals of the 1/1 adduct, $Ph_2SnCl_2 \cdot BT$ (m.p. 228—230°C with decomposition). Found: C, 47.53; H, 3.38; N, 2.77; Cl, 14.16. $C_{19}H_{15}Cl_2NSSn$ calcd.: C, 47.67; H, 3.16; N, 2.92; Cl, 14.80%.

1/2 Reaction. Diphenyltin dichloride (0.01 mol) and BT (0.02 mol) were treated as above. After recrystallisation from benzene, the product was identified as the 1/1 by spectroscopic comparison with an authentic sample (*IS* 1.31 mm s^{-1}, *QS* 2.98 min s^{-1}).

(b) Reaction of Ph_2SnCl_2 with Habt in benzene

To a solution of Habt (1.50 g, 0.01 mol) in warm dry freshly-distilled benzene (25 ml), was added a solution of diphenyltin dichloride (3.44 g, 0.01 mol) in the minimum amount of dry benzene, over a period of one minute. After a few minutes a white precipitate began to form, and the solution was filtered after 0.5 h. The 1/1 adduct, $Ph_2SnCl_2 \cdot Habt$, was washed with dry benzene and dried in vacuo (m.p. ca. 135°C with decomposition). Found: C, 46.46; H, 4.04; N, 6.76; Cl, 14.68. $C_{19}H_{16}Cl_2N_2SSn$ calcd.: C, 46.20; H, 3.27; N, 6.67; Cl, 14.35%.

Recrystallisation of $Ph_2SnCl_2 \cdot Habt$ from dry absolute ethanol yielded a colourless crystalline material, identified as $H_2abt^+ Cl^-$ (Found: C, 44.94; H, 3.83; N, 14.56. $C_7H_7ClSN_2$ calcd.: C, 45.29; H, 3.81; N, 15.08%.

(c) Reaction of Ph_2SnCl_2 with Habt in acetone

Equimolar, dry acetone solutions of diphenyltin dichloride and Habt were mixed under an inert (argon) atmosphere, and, after stirring for 0.5 h, a white precipitate formed. After 3 h the product was filtered off, washed and dried, and identified as 1,1,3,3-tetraphenyl-1,3-dichlorodistannoxane. Found: C, 44.94; H, 3.06; N, 0.00; Cl, 10.95. $C_{24}H_{20}Cl_2OSn_2$ calcd.: C, 45.56; H, 3.19; N, 0.00; Cl, 11.21%. M.p. 190—195°C (lit. [8] 190—195°C). *IS* 1.26 mm s^{-1}, *QS* 3.03 mm s^{-1}.

Crystal structure determination of $Ph_2SnCl_2 \cdot BT$

Crystal preparation and data. Crystals suitable for intensity measurements were obtained by recrystallisation from hot benzene. The colourless, rectangular crystals were stable to both moist air and X-rays, and a crystal of approximate dimensions 0.3 × 0.3 × 0.4 mm was mounted in a Lindemann capillary and used to obtain initial cell parameters and the subsequent intensity data.

$C_{19}H_{15}Cl_2NSSn$, M 478.93, orthorhombic with a 11.521(4), b 12.349(8), c 13.500(5) Å, U 1920.54 Å^3, $Z = 4$, $F(000)$ 944, $\mu(\text{Mo-}K_\alpha) = 10.18$ cm^{-1}. Space group $P2_12_12_1$ by systematic absences $h00$ for $h = 2n + 1$, $0k0$ = for $k = 2n + 1$, $00l$ for $l = 2n + 1$.

Cell measurements and data collection. The space group and initial cell parameters were obtained from oscillation and zero- and first-layer Weissenberg photographs, obtained using a Leeds Weissenberg camera. The cell parameters were further refined by least squares methods using ca. 2459 reflections. Relative intensities upto θ 27.5° were collected using Mo-K_α radiation (λ 0.71069 Å) on a Hilger and Watts Y290 four-circle diffractometer. The reflections were counted for 20 s and the two associated background counts for 10 s. The reflections were brought to the same relative intensity by a reference reflection every 100 reflections; the diffractometer being referenced every 200 reflections. The background counts were low and were included in the usual manner. All reflections with a corrected count of less than three times the estimated standard deviation of the total counts were considered as non-observed and were not used further, reducing the total number of reflections from 2459 to 2343. The intensities were corrected for Lorentz and polarisation effects but no absorption correction was applied since the value of μ was low.

Structure determination and refinement. A three-dimensional Patterson synthesis was used to obtain the positional parameters of the tin atom, which were used to phase the initial structure factor calculation. An initial difference Fourier synthesis yielded only the position of one chlorine atom with any certainty. The number of reflections used in subsequent refinements was limited by the expression $0.2 \leqslant F_o/F_c \leqslant 4.0$. Following one cycle of full-matrix isotopic refinement of the tin and chlorine positional parameters, a difference Fourier yielded the positions of the sulphur, nitrogen and second chlorine atoms. Known positional parameters were refined by one cycle of full-matrix isotropic least-squares, before a third Fourier synthesis yielded the positions of the 13 carbon atoms. Two further cycles of full-matrix isotropic least-squares for all positional parameters except those of the tin atom, which was allowed to vary anisotropically, were required before a Fourier synthesis enabled the positions of five of the six outstanding carbon atoms to be located. After two cycles of full-matrix least-squares refinement, the resulting positional parameters were used to calculate the position of the remaining carbon atom. The condition limiting the number of reflections used was now removed, and three cycles of mixed least-squares refinement and four cycles of full-matrix anisotropic (all atoms) least-squares refinement produced convergence at an R-value of 0.038. At this point, the weighting scheme $\sqrt{w} = 1$ ($F_0 \leqslant P$) and $\sqrt{w} = P/F_0$ ($F_0 > P$) where $P = 45.0$, was introduced, and two final cycles of full-matrix anisotropic least-squares refinement produced a final R-value of 0.032.

Final fractional atomic coordinates and anisotropic thermal parameters are

TABLE 1

FINAL FRACTIONAL ATOMIC COORDINATION FOR $Ph_2SnCl_2 \cdot BT$ (estimated standard deviation in parentheses)

Atom	*x/a*	*y/b*	*z/c*
Sn(1)	0.11693(3)	0.91752(3)	0.00638(2)
Cl(1)	0.1360(2)	1.1037(1)	0.0320(1)
Cl(2)	0.3231(1)	0.8953(1)	−0.0315(1)
N(1)	−0.0982(2)	0.9510(2)	0.0375(1)
S(1)	−0.3015(4)	0.9150(4)	0.0981(4)
C(1)	0.0552(7)	0.8735(5)	−0.1349(6)
C(2)	0.1022(8)	0.9240(6)	−0.2185(6)
C(3)	0.0587(6)	0.8990(7)	−0.3116(5)
C(4)	−0.0278(6)	0.8196(6)	−0.3222(4)
C(5)	−0.0708(5)	0.7700(5)	−0.2388(4)
C(6)	−0.0316(5)	0.7967(6)	−0.1460(5)
C(7)	0.1150(5)	0.8376(5)	0.1449(5)
C(8)	0.0988(4)	0.7246(4)	0.1501(4)
C(9)	0.1027(5)	0.6744(5)	0.2411(4)
C(10)	0.1252(6)	0.7332(5)	0.3276(5)
C(11)	0.1406(6)	0.8442(6)	0.3223(5)
C(12)	0.1335(6)	0.8949(6)	0.2301(4)
C(13)	−0.3739(5)	1.0611(4)	−0.0511(4)
C(14)	−0.2886(5)	1.0037(4)	0.0004(4)
C(15)	−0.1712(6)	1.0159(6)	−0.0215(5)
C(16)	−0.1357(6)	1.0880(7)	−0.0955(5)
C(17)	−0.2205(6)	1.1449(6)	−0.1459(6)
C(18)	−0.3384(5)	1.1325(5)	−0.1233(5)
C(19)	−0.1567(8)	0.8950(7)	0.1007(5)

TABLE 2

FINAL ANISOTROPIC TEMPERATURE PARAMETERS FOR $Ph_2SnCl_2 \cdot BT$ (estimated standard deviation in parentheses)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	4.56(2)	4.54(2)	5.01(2)	0.31(2)	0.51(2)	0.10(1)
Cl(1)	6.26(8)	4.46(6)	8.22(9)	−0.28(6)	0.49(3)	−0.28(6)
Cl(2)	3.99(6)	6.85(9)	8.7(1)	1.22(8)	−0.34(7)	0.30(6)
S(1)	5.0(2)	9.7(3)	8.2(2)	2.2(2)	1.4(2)	0.3(2)
N(1)	4.7(8)	5.6(1)	5.4(1)	0.2(1)	0.0(8)	0.0(1)
C(1)	3.7(4)	4.4(3)	4.9(4)	0.3(3)	0.0(4)	0.1(3)
C(2)	6.1(6)	6.2(4)	5.8(5)	0.6(4)	0.4(5)	−0.4(4)
C(3)	9.0(4)	9.8(5)	5.0(4)	0.3(3)	0.6(3)	0.7(4)
C(4)	6.3(3)	7.8(5)	6.4(3)	−1.4(3)	−1.4(2)	0.8(3)
C(5)	5.1(3)	6.1(3)	8.5(3)	−1.0(3)	−1.0(2)	−0.4(3)
C(6)	4.5(3)	5.3(4)	6.6(4)	0.2(3)	−0.2(3)	−0.7(3)
C(7)	4.1(3)	5.0(3)	4.9(3)	0.4(3)	−0.6(3)	0.3(2)
C(8)	7.9(2)	5.3(2)	7.4(3)	0.4(2)	−0.4(2)	−0.5(2)
C(9)	9.4(3)	5.9(3)	8.6(3)	2.0(3)	0.3(2)	0.4(3)
C(10)	6.4(4)	9.2(3)	6.2(4)	2.4(3)	0.7(3)	0.5(3)
C(11)	4.6(3)	8.7(4)	5.1(4)	0.3(3)	0.1(3)	0.4(3)
C(12)	4.1(3)	6.4(4)	5.6(3)	−0.3(3)	−0.4(3)	−0.3(3)
C(13)	4.3(3)	7.5(3)	7.3(2)	−0.9(2)	−0.5(2)	0.6(2)
C(14)	4.6(2)	5.9(2)	5.7(3)	−0.5(2)	0.7(2)	−0.1(2)
C(15)	3.8(4)	4.7(4)	4.9(3)	−0.8(3)	−0.1(3)	0.6(4)
C(16)	5.1(4)	5.3(4)	6.4(4)	0.5(3)	−0.3(3)	0.1(4)
C(17)	6.0(3)	5.6(3)	6.6(5)	−0.2(4)	−1.2(3)	0.7(3)
C(18)	5.4(3)	6.3(3)	6.9(3)	−1.4(3)	−0.8(3)	1.1(3)
C(19)	5.2(5)	6.9(5)	5.6(3)	0.2(3)	0.5(3)	−0.3(5)

U_{ij} are of the form: $10^2 \exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2hlU_{13}a^*c^* + 2klU_{23}b^*c^*)]$.

TABLE 3

INTERMOLECULAR BOND DISTANCES (Å) AND ANGLES (°) IN $Ph_2SnCl_2 \cdot BT$ (estimated standard deviation in parentheses)

(a) Bond distances

Sn—Cl(1)	2.336(1)	C(13)—C(14)	1.397(7)
Sn—Cl(2)	2.446(1)	C(14)—C(15)	1.393(9)
Sn—C(1)	2.108(8)	C(15)—C(16)	1.400(10)
Sn—C(7)	2.115(6)	C(16)—C(17)	1.382(10)
Sn—N(1)	2.548(2)	C(17)—C(18)	1.401(9)
		C(18)—C(13)	1.376(9)
C(1)—C(2)	1.402(12)		
C(2)—C(3)	1.384(10)	S(1)—C(14)	1.725(7)
C(3)—C(4)	1.405(10)	S(1)—C(19)	1.723(10)
C(4)—C(5)	1.374(9)		
C(5)—C(6)	1.373(9)	N(1)—C(15)	1.408(7)
C(6)—C(1)	1.386(10)	N(1)—C(19)	1.289(5)
C(7)—C(8)	1.410(0)		
C(8)—C(9)	1.377(8)		
C(9)—C(10)	1.399(9)		
C(10)—C(11)	1.384(10)		
C(11)—C(12)	1.396(10)		
C(12)—C(7)	1.367(9)		

(b) Bond angles

Cl(1)—Sn(1)—Cl(2)	92.8(8)	Sn(1)—N(1)—C(15)	125.4(4)
Cl(1)—Sn(1)—C(1)	114.8(4)	Sn(1)—N(1)—C(19)	122.0(6)
Cl(1)—Sn(1)—C(7)	189.2(3)	C(15)—N(1)—C(19)	111.5(6)
Cl(1)—Sn(1)—N(1)	84.6(6)	N(1)—C(19)—S(1)	115.3(0)
Cl(2)—Sn(1)—C(1)	96.3(0)	C(19)—S(1)—C(14)	89.8(4)
Cl(2)—Sn(1)—C(7)	98.2(0)	S(1)—C(14)—C(15)	109.7(7)
Cl(2)—Sn(1)—N(1)	176.1(7)	S(1)—C(14)—C(13)	128.7(1)
C(1)—Sn(1)—C(7)	132.5(7)	C(15)—C(14)—C(13)	121.4(9)
C(1)—Sn(1)—N(1)	81.1(2)	C(14)—C(13)—C(18)	117.9(7)
N(1)—Sn(1)—C(7)	85.4(0)	C(13)—C(18)—C(17)	120.8(0)
		C(18)—C(17)—C(16)	121.5(1)
Sn(1)—C(1)—C(2)	119.0(5)	C(17)—C(16)—C(15)	117.9(6)
Sn(1)—C(1)—C(6)	121.1(6)	C(16)—C(15)—C(14)	120.2(5)
C(2)—C(1)—C(6)	119.7(9)	C(16)—C(15)—N(1)	126.2(9)
C(1)—C(2)—C(3)	119.4(4)	N(1)—C(15)—C(14)	113.4(6)
C(2)—C(3)—C(4)	120.3(3)		
C(3)—C(4)—C(5)	118.9(0)		
C(4)—C(5)—C(6)	121.4(8)		
C(5)—C(6)—C(1)	119.9(9)		
Sn(1)—C(7)—C(8)	120.5(0)		
Sn(1)—C(7)—C(12)	120.0(3)		
C(8)—C(7)—C(12)	119.4(3)		
C(7)—C(8)—C(9)	119.0(7)		
C(8)—C(9)—C(10)	121.1(0)		
C(9)—C(10)—C(11)	119.6(9)		
C(10)—C(11)—C(12)	118.0(7)		
C(11)—C(12)—C(7)	121.7(7)		

given in Tables 1 and 2, respectively. Intramolecular bond distances and angles are given in Table 3, and least-squares planes data in Table 4. Atomic numbering is shown in Fig. 1, and the projection onto the *ab* plane in Fig. 2.

Scattering factors used were those for neutral atoms [9], and refinement carried out using the CRYSTALS suite of programmes.

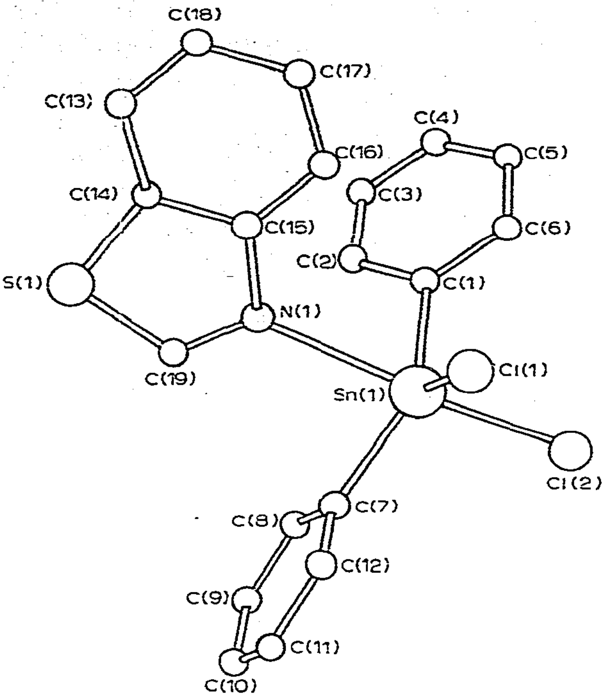


Fig. 1. The structure of $Ph_2SnCl_2 \cdot BT$ showing atomic numbering.

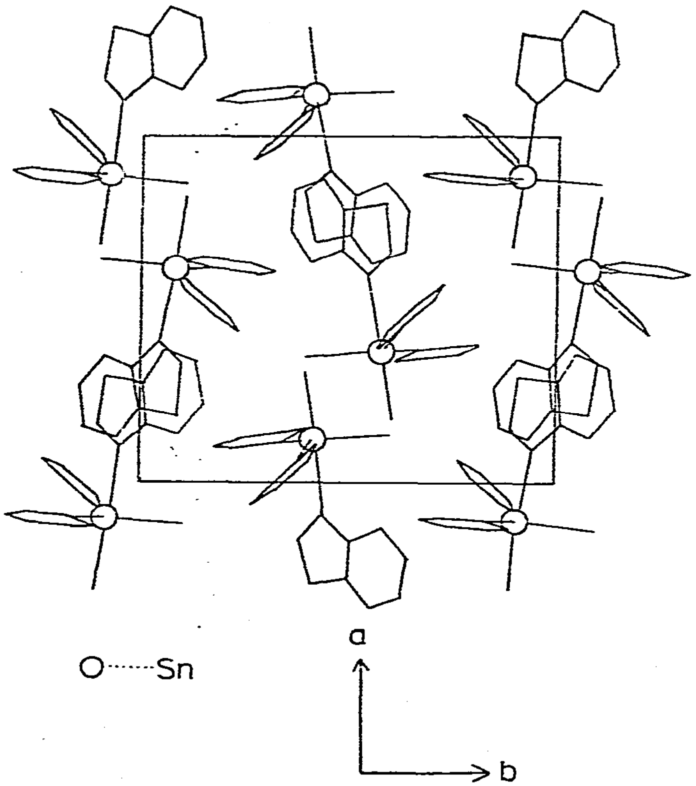


Fig. 2. Projection of the unit cell of $Ph_2SnCl_2 \cdot BT$ onto the *ab* plane.

TABLE 4

MEAN PLANES OF Ph_2SnCl_2 · BT AND DEVIATIONS FROM THE PLANES (Å)

The mean plane containing three (or more) atoms, can be represented by the equation

$px + qy + rz = s$

where p, q, r and s are real numbers.

Equation of plane 1, containing Sn(1), Cl(1), C(1) and C(7) is given by:

$11.1579x - 1.9268y - 2.6238z = -0.649$

Deviations (Å) of atoms in that plane:

Sn 0.169, Cl(1) −0.044, C(1) −0.064, C(7) −0.061

Plane 2, containing Sn(1), Cl(1), Cl(2) and N(1):

$-1.8507x + 2.2194y - 13.1018z = 1.779$

Sn −0.043, Cl(1) −0.001, Cl(2) 0.022, N 0.022

Plane 3, containing the benzthiazole ligand:

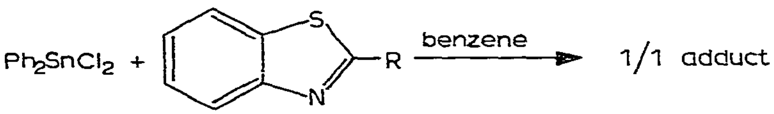
$1.0667x + 9.8879y + 9.0545z = 8.878$

S 0.000, C(19) 0.020, N 0.000, C(13) −0.096, C(14) −0.060, C(15) −0.023, C(16) 0.000, C(17) −0.029, C(18) −0.063.

Angle between planes 1 and 2: 89.72°
Angle between planes 1 and 3: 98.94°
Angle between planes 2 and 3: 122.25°

Discussion

1/1 Adducts of diphenyltin dichloride and the bases, benzthiazole (BT) 2-aminobenzthiazole (Habt), are formed on mixing equimolecular dry benzene solutions of the respective reagents, viz.:



Attempts to prepare 1/2 adducts by using a 1/2 molar ratio of reactants produced only the 1/1 adduct. The reaction of diphenyltin dichloride and Habt is, however, complex, the nature of the product obtained being solvent-dependent. Thus, whilst Ph_2SnCl_2 and BT yield a 1/1 adduct in either dry benzene or dry acetone, Ph_2SnCl_2 and Habt form the 1/1 adduct in dry benzene only, and 1,1,3,3-tetraphenyl-1,3-dichlorodistannoxane is the product when the reaction is carried out in dry acetone. Under the anhydrous conditions used, this product cannot result from adventitious hydrolysis, and its formation requires participation of the solvent in the reaction. Since no distannoxane formation was observed for the reaction of Ph_2SnCl_2 with BT in acetone, the primary amine group of the Habt would seem to be important for the formation of this alternative product.

Crystals of Ph_2SnCl_2 · BT consist of non-interacting monomers (Fig. 2), with each molecule possessing a distorted *cis*-R_2SnX_3 trigonal-bipyramidal geometry at tin (Fig. 1). Two equatorial sites are occupied by the two phenyl groups at a mean Sn—C distance of 2.112(8) Å, a value which compares with the Sn—C_{eq}

bond distances in $Ph_3SnON(Ph)COPh$ [10], $Ph_3SnSC_5H_4N$ [11] and Ph_3SnNCS [12] (Table 5). The third equatorial position is occupied by one chlorine at a distance of 2.336(1) Å. The second chlorine atom occupies an axial site at a not-unexpectedly longer distance of 2.446(1) Å. The planar (Table 4) benzthiazole ligand is coordinated to the tin via the nitrogen atom (Sn—N 2.548 Å). Other dimensions within the BT ligand are normal. The tin—nitrogen bond distance is exceptionally long, only that in $Ph_3SnSC_5H_4N$ [11] being longer, and is ~0.3 Å longer than the coordinate Sn—N bond distance in $Me_3SnCl \cdot py$ [13], a distance which is similar to the covalent Sn—N bond distances in Ph_3SnNCS [12] and $(NO_3)Sn(abt)$ [14]. The long Sn—N distance in $Ph_2SnCl_2 \cdot BT$ cannot be ascribed to weak Lewis acidity of the tin atom, which is most probably the case in $Ph_3SnSC_5H_4N$ [11], or the weak donor ability of the nitrogen atom since the donor strengths of benzthiazole and pyridine must be similar, and the Sn—N bond distance in the pyridine complex of the more weakly Lewis acidic Me_3SnCl is short. It would seem, therefore, that the long bond distance in $Ph_2SnCl_2 \cdot BT$ is most probably due to the bulkiness of the benzthiazole ligand together with the two phenyl groups. The inability a further molecule of benzthiazole to coordinate to tin to form a 1/2 six-coordinate adduct is probably a consequence of the combination of large steric requirement and weak donor capacity of the benzthiazole ligand.

The $Sn—N—Cl_{ax}$ linkage is almost linear (176.2°), and the SnC_2Cl_{eq} skeleton essentially planar (Table 4), but the C—Sn—C angle is opened out to 132.6°. This may be interpreted as a preferential redistribution of the available tin 5 *s* character towards the bonds to electropositive carbon at the expense of the bonds to the more electronegative ligands, in accordance with the predictions of isovalent hybridisation [15].

Tin-119*m* Mössbauer parameters for the two complexes, $Ph_2SnCl_2 \cdot BT$ and $Ph_2SnCl_2 \cdot Habt$, together with ^1H NMR data for the former are listed in Table 6. The value of the quadrupole splitting in $Ph_2SnCl_2 \cdot BT$ (2.92 mm s^{-1}) is quite consistent with the observed trigonal bipyramidal geometry, and reasonable agreement is obtained when the *QS* is estimated using the point charge

TABLE 5

COMPARISON OF TIN—LIGAND BOND LENGTHS (Å) IN $Ph_2SnCl_2 \cdot BT$ WITH THOSE IN RELATED COMPOUNDS[a]

Molecule	Sn—C(Ph)	$Sn—Cl_{eq}$	$Sn—Cl_{ax}$	Sn—N	References
$Ph_2SnCl_2 \cdot BT$	2.112(8)[c]	2.336(1)	2.446(1)	2.548(1)	This work
$Ph_3SnON(Ph)CO \cdot Ph$	$2.136(8)_{eq}$[c] $2.176(9)_{ax}$				10
$(NO_3)Sn^{II}$ (abt)	2.50[f]			2.23	14
$Ph_3SnSC_5H_4N$	2.16(2)[c]			2.62(2)[b]	11
Ph_3NCS	2.09(3)[c]			2.22(5)	12
$Me_3SnCl \cdot py$			2.42	2.26	13
$Me_2SnCl_2 \cdot SAlH$		2.35(6)	2.40(6)		18
$Me_2SnCl_3^-$		2.35(3)	2.54(3)		19
$Me_3SnCl \cdot Ph_3P{=}CHCOMe$			2.57		20

[a] All trigonal bipyramidal geometry except $(NO_3)Sn^{II}$ (abt). [b] Intermolecular Sn···N distance. [c] Mean value. [d] With $Me_2SnCl(terpyridyl)^+$ as the cation. [e] Distorted tetrahedral geometry at tin. [f] Intermolecular Sn···C(Ph) distance.

TABLE 6

SPECTROSCOPIC DATA FOR $Ph_2SnCl_2 \cdot BT$, $Ph_2SnCl_2 \cdot Habt$ AND RELATED COMPOUNDS

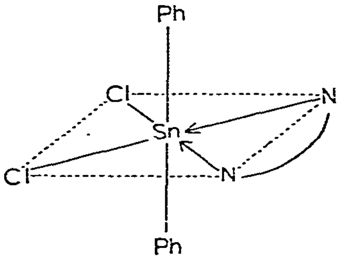
Compound	*TS*	*QS*	Γ_1	Γ_2	^1H chemical shift (τ, ppm)	Reference
$Ph_2SnCl_2 \cdot BT$	1.36	2.92	0.92	0.89	1.11s (1, S—C(H)=N) 1.90—2.90m (14, aromatic)	This work
$Ph_2SnCl_2 \cdot Habt$	1.46	3.73	0.90	0.88		This work
BT					1.13s (1, S—C($\underline{H}$)=N) 1.85—2.94m (4, aromatic)	
$Ph_3SnCl \cdot pip^{e,b}$	1.25	2.95				20
$Ph_3SnCl \cdot isoquin^{a,b}$	1.35	2.92				20
$Ph_2SnCl_2 \cdot bipy^{a,c}$	1.26	3.51				16

[a] pip = pipiridine, isoquin = isoquinoline, bipy = 2,2′ bipyridyl. [b] Those compounds have trigonal bipyramidal, R_3SnX_2 structures, with equatorial R groups and mutually *trans*-X groups. [c] Octahedral with *trans*-Ph and *cis*-Cl.

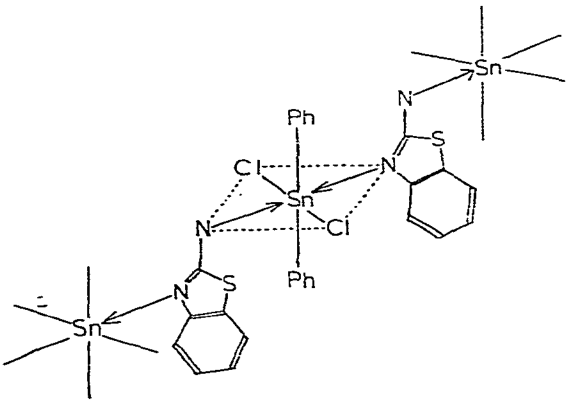
approximation and the partial quadrupole splitting values for individual ligands recently derived by Bancroft [16]. Thus, for a trigonal bipyramidal R_2SnL_2L' species with *cis*-R_{eq} and axial L′ ligands, the value of the *QS* is given by the expression

$$-\sqrt{7}(R)^{tbe} + [4(L')^{tbe} + 4(L)^{tba} + (L)^{tba}]/\sqrt{7}$$

where the superscripts tbe and tba refer to trigonal bipyramidal equatorial and



(I)



(II)

Fig. 3. Possible structures of $Ph_2SnCl_2 \cdot Habt$.

axial, respectively. Using the values $(\mathrm{Ph})^{\mathrm{tbe}} = 0.98$ mm s^{-1}, $(\mathrm{Cl})^{\mathrm{tba}} = 0$, $(\mathrm{Cl})^{\mathrm{tbe}} = +0.20$ mm s^{-1}, and assuming that $(\mathrm{BT})^{\mathrm{tba}} = (\mathrm{py})^{\mathrm{tba}} = -0.035$ mm s^{-1}, a value of 2.62 mm s^{-1} can be deduced for the quadrupole splitting. The discrepancy between calculated and observed may be ascribed to deviations from ideal geometry, particularly in the equatorial plane, and also to the use of partial quadrupole splitting of pyridine in place of that of benzthiazole. However, agreement is within the tolerance of the model (±0.4 mm s^{-1}).

The observed quadrupole splitting for $\mathrm{Ph_2SnCl_2 \cdot Habt}$ is substantially larger than that of $\mathrm{Ph_2SnCl_2 \cdot BT}$, and its value (3.73 mm s^{-1}) suggests a *trans*-$\mathrm{R_2SnCl_2 \cdot L{-}L}$ six-coordinate rather than a trigonal bipyramidal five-coordinate geometry. This is supported by the increase in the isomer shift on complexation with Habt rather than BT, which indicates an increase in the linearity of the C—Sn—C. The stereochemistry of the remaining groups depends on the nature of the lattice formed. For a monomeric species, the bidentate nature of the Habt ligand imposes a *cis*-Cl, *cis*-N—N orientation (I) (Fig. 3). For a polymeric lattice, i.e. $\mathrm{Ph_2SnCl_2}$ units linked by bridging Habt ligands, both *cis, cis* and *trans, trans* (II) (Fig. 3) geometries are possible, although the former structure is unlikely due to the bulk of the ligand. Similar bridging occurs in trialkyltin imidazole derivatives [17]. The very low solubility of the complex might seem to indicate a bridged structure, although solution does occur in ethanol accompanied by decomposition to give $\mathrm{H_2abt^+\,Cl^-}$ and presumably the distannoxane. However, the low melting point (135°C) and the absence of a Mössbauer resonance at ambient temperatures makes a bridged structure unlikely.

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