A Crystallographic Investigation of a Compound with a Composition corresponding to $Ph_2SnCl_2 \cdot \frac{3}{4}$ pyz (pyz = pyrazine)

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A compound previously postulated as the adduct $Ph_2SnCl_2 \cdot pyz$ (pyz = pyrazine) is shown crystallographically to have a composition corresponding to $Ph_2SnCl_2 \cdot \frac{3}{4}$ pyz and to have a structure composed of layers in which are packed zig-zag polymeric chains, $[Ph_2SnCl_2 \cdot pyz]_n$ with hexa-co-ordinated tin, alternating with layers which contain non-interacting molecules $(Ph_2SnCl_2)_2 \cdot pyz$ with penta-co-ordinated tin.

There are three obvious ways in which diphenyltin(IV) dichloride may combine with pyrazine through adduct formation, thus giving rise to formulations $Ph_2SnCl_2 \cdot 2\,pyz$, $(Ph_2SnCl_2)_2 \cdot pyz$, or $Ph_2SnCl_2 \cdot pyz$ (pyz = pyrazine). The last is reported to be obtained in pure form from the reaction of equimolar quantities of Ph_2SnCl_2 and pyrazine in benzene, followed by a recrystallization of the product from light petroleum.[1] This compound has a Mössbauer quadrupole splitting value (close to 3.0 mm s^{-1})[2,3] which is indicative of a C–Sn–C bond angle very much less than 180°. While the value is not inconsistent with trigonal bipyramidal geometry about tin, other evidence, base on recoil-free fraction data,[2] is rather suggestive of an associated lattice which would inevitably demand octahedral geometry (or approximately so)

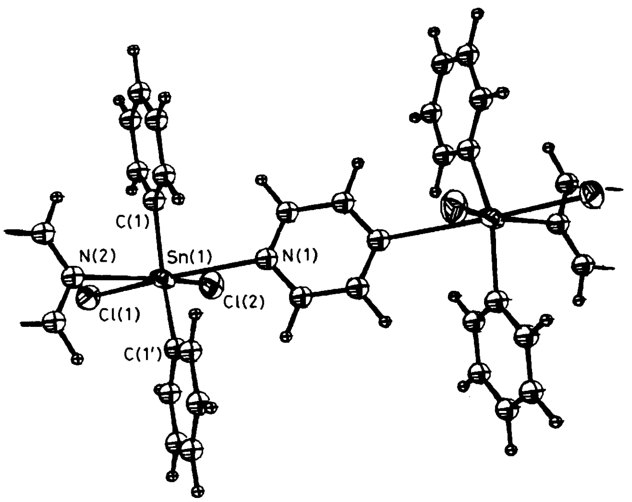

Figure 1. The structure of $Ph_2SnCl_2 \cdot pyz$. Selected dimensions: Sn(1)–N(1) 2.782(11), Sn(1)–N(2) 2.965(11), Sn(1)–Cl(1) 2.403(4), Sn(1)–Cl(2) 2.384(4), Sn(1)–C(1) 2.098(5) Å; C(1)–Sn(1)–C(1') 137.7(2), N(1)–Sn(1)–N(2) 117.9(3), N(1)–Sn(1)–Cl(1) 166.9(2), N(1)–Sn(1)–Cl(2) 75.9(2), N(1)–Sn(1)–C(1) 81.7(2), N(2)–Sn(1)–C(1) 77.0(2)°. Nitrogen, chlorine, and tin atoms are in a mirror plane and there is an inversion centre in each pyrazine.

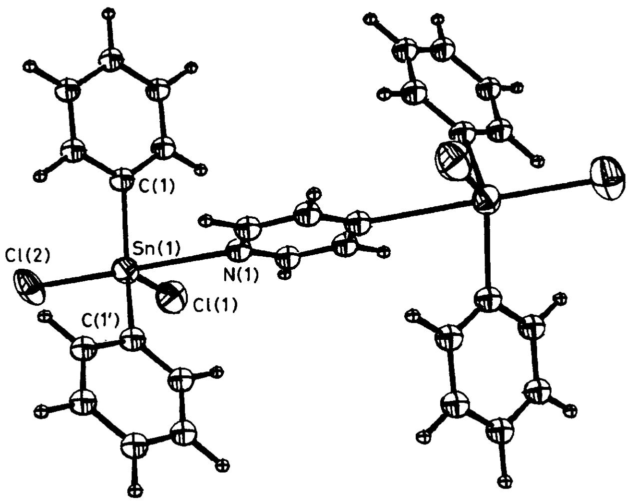

Figure 2. The structure of $(Ph_2SnCl_2)_2 \cdot pyz$. Selected dimensions: Sn(1)–N(1) 2.696(12), Sn(1)–Cl(1) 2.340(5), Sn(1)–Cl(2) 2.402(4), Sn(1)–C(1) 2.106(6) Å; N(1)–Sn(1)–Cl(2) 178.5(3), C(1)–Sn(1)–C(1') 133.1(2), C(1)–Sn(1)–Cl(1) 110.2(2)°. The molecule is centrosymmetric and all atoms, with the exception of those of the phenyl groups, lie in a mirror plane.

about tin. The latter structure has been proposed for the compound.[2,3] This communication reports a crystallographic study of the compound which has some novel and unexpected features.†

The most surprising feature of the structure is that within the lattice both $Ph_2SnCl_2 \cdot pyz$ and $(Ph_2SnCl_2)_2 \cdot pyz$ coexist and since an equal number of tin atoms is associated with each structural adduct entity the elemental analyses of the bulk material should correspond to a formulation $Ph_2SnCl_2 \cdot \frac{3}{4}$ pyz, which is what we find.‡ Curiously, our efforts to date to crystallise both the 1:1 and 2:1 adducts separately from petroleum solutions have been unsuccessful. For example, crystallizations in which Ph_2SnCl_2 and pyrazine were, in turn, in large excess in solution gave products with similar elemental analyses to the title compound and *X*-ray powder diffraction patterns of all samples were identical. The powder diffraction patterns can be indexed using the cell parameters obtained for the crystal used in the single-crystal study so this crystal is truly representative of the bulk material.

In broad descriptive terms the structure is composed of planes (mirror planes) in which infinite zig-zag polymeric chains $[Ph_2SnCl_2 \cdot pyz]_n$ are packed in parallel fashion with no intermolecular bonding existing between adjacent chains.

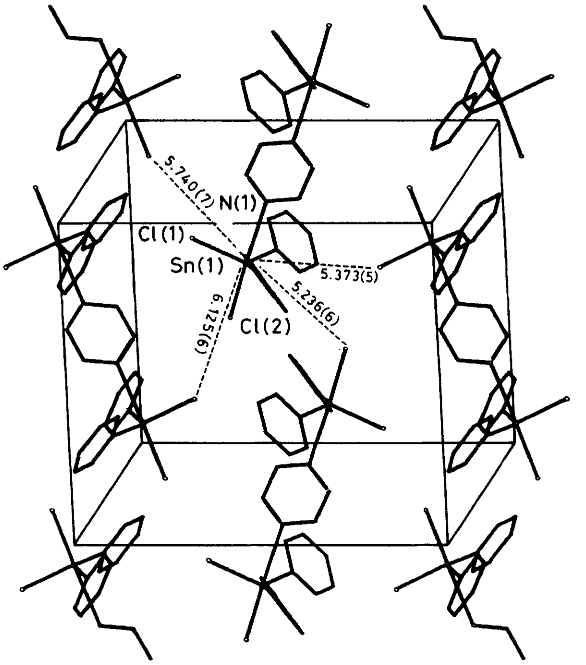

Figure 3. A packing view (along the *c* axis) of molecules of $(Ph_2SnCl_2)_2 \cdot pyz$ showing closest intermolecular tin–chlorine contacts (Å). Atom labelling corresponds to that in Figure 2.

These planes alternate with others (also mirror planes) which contain 2:1 adduct molecules $(Ph_2SnCl_2)_2 \cdot pyz$. There is no possibility of intermolecular bonding existing either between adjacent 2:1 adduct molecules or between 2:1 and 1:1 adducts in adjacent planes. In fact, this makes the inability to isolate the separate adducts more interesting.

The polymeric chains $[Ph_2SnCl_2 \cdot pyz]_n$ (see Figure 1) are generated by bridging pyrazine molecules. The nitrogen atoms of each pyrazine form identical donor bonds to neighbouring tin atoms (a centre of inversion exists at the centre of each pyrazine). However, there are two types of

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† *Crystal data:* orthorhombic, space group *Pbam*, $a = 14.935(2)$, $b = 13.409(3)$, $c = 15.959(3)$ Å; $U = 3196.00$ Å^3, $\mu(\text{Mo-}K_\alpha) = 17.72$ cm^{-1}, $\lambda = 0.71073$ Å, 8 tin atoms per unit cell comprising of 4 in special positions (Wyckoff notation *h*) associated with $(Ph_2SnCl_2)_2 \cdot pyz$ and 4 (Wyckoff notation *g*) associated with $[Ph_2SnCl_2 \cdot pyz]_n$, crystal dimensions $0.5 \times 0.3 \times 0.3$ mm^3, $R = 0.047$ and $R_w = 0.056$ for 1476 reflections with $I > 3\sigma(I)$ collected at room temperature on a Hilger & Watts Y290 diffractometer. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Found C, 44.49; H, 2.99; N, 5.45; Cl, 17.55%. $Ph_2SnCl_2 \cdot \frac{3}{4}$ pyz requires C, 44.60; H, 3.22; N, 5.20; Cl, 17.57%. $Ph_2SnCl_2 \cdot pyz$ requires C, 45.33; H, 3.31; N, 6.61; Cl, 16.74%.

bridging pyrazines which alternate along chains, thus providing each tin with Sn–N bonds of unequal length. Broadly speaking, the geometry at tin is octahedral with both chlorine and nitrogen atoms arranged *cis* and the carbon atoms providing very distorted *trans* geometry.

The tin atoms in each 2 : 1 adduct molecule (Figure 2) are in identical environments (in this case also there is a centre of inversion centred in each pyrazine) and, since there are no intermolecular contacts, tin atoms are penta-co-ordinated (see Figure 3). In fact, the geometry at tin conforms quite well to trigonal bipyramidal geometry with nitrogen and chlorine atoms occupying axial positions (the N–Sn–Cl bond angle is 178.6°).

The Sn–N bonds are extremely long and to our knowledge the longest such bonds so far reported. The longest Sn–N bonds previously reported for diorganotin(IV) complexes have been those for $Me_2Sn(CN)_2$ (Sn–N 2.68 Å, an intermolecular bond)[4] and for $Ph_2SnCl_2 \cdot SC_7H_5N$ (Sn–N 2.548 Å),[5] and in the case of the weaker Lewis acid Ph_3SnCl that for $Ph_3SnCl \cdot SC_5H_4N$ (Sn–N 2.62 Å).[6] Thus, the values for the Sn–N bond lengths in $[Ph_2SnCl_2 \cdot pyz]_n$ [2.965(11) and 2.782(11) Å] are considerably larger than the largest values previously encountered, while the Sn–N bond lengths in $(Ph_2SnCl_2)_2 \cdot pyz$ [2.696(12) Å] compare well with the intermolecular Sn–N bond length in $Me_2Sn(CN)_2$. As a result of the extremely weak donor–acceptor interactions the C–Sn–C bond angles {133.1° for $(Ph_2SnCl_2)_2 \cdot pyz$ and 137.7° for $[Ph_2SnCl_2 \cdot pyz]_n$} are very similar, and not markedly different from the average C–Sn–C bond angle of 125° found in Ph_2SnCl_2.[7] The inability to detect the presence of two tin sites in the structure of the title compound by Mössbauer spectroscopy[2,3] can be attributed to the very similar C–Sn–C bond angles in the 1 : 1 and 2 : 1 adduct species. The structure emphasises the fact that while Mössbauer quadrupole splitting data undoubtedly give a good assessment of the C–Sn–C bond angle in diorganotin(IV) complexes this is often not in itself a reliable criterion for assigning the tin co-ordination number, particularly when weak bonding interactions are present, either as a result of weakly donating atoms (as in the present structure) or as a result of weak intermolecular interactions. Finally, the ability to observe a Mössbauer spectrum for the title compound at room temperature[2] can now be attributed to the presence of the polymer chains $[Ph_2SnCl_2 \cdot pyz]_n$ within the lattice. Full details of this structure and of pyrazine adducts of other tin(IV) Lewis acids will be published elsewhere.

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