An *X*-Ray Crystallographic Investigation of the Structures of Pyrazine Adducts of Diphenyltin Dichloride and Dimethyltin Dichloride†

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Reaction of $SnPh_2Cl_2$ with pyrazine (pyz) leads exclusively to the formation of an adduct having the bulk composition $SnPh_2Cl_2$·0.75pyz. It has a structure composed of layers in which zig-zag polymeric chains, $(SnPh_2Cl_2\cdot pyz)_n$, with six-co-ordinate tin, alternate with layers containing non-interacting molecules of $(SnPh_2Cl_2)_2$·pyz, with five-co-ordinate tin. The Sn–N bond lengths are abnormally long; each tin atom in the polymeric chains has Sn–N bond lengths of 2.961(10) and 2.783(10) Å, and the Sn–N bond length in $(SnPh_2Cl_2)_2$·pyz is 2.683(11) Å. Mössbauer spectroscopy does not identify the presence of the two tin sites in the solid whereas ^{119}Sn n.m.r. does. *X*-Ray crystallographic details are: space group *Pbam* (orthorhombic), a = 14.935(2), b = 13.409(3), c = 14.959(3) Å, Z = 8(Sn), R = 0.047 (R' = 0.056) for 1 478 observed reflections with $I > 3\sigma(I)$. Reaction of $SnMe_2Cl_2$ with pyrazine leads exclusively to formation of the adduct $(SnMe_2Cl_2)_2$·pyz; the distannoxane $(SnMe_2Cl)_2O$ is also formed if solutions are not protected from the atmosphere. The adduct has a chain polymeric structure with six-co-ordinate tin atoms alternatively linked by chloride ions and pyrazine molecules. The Sn–N bond length [2.746(6) Å] is abnormally long. The polymeric chains pack into well defined planes, with chains in alternate planes propagating in orthogonal directions. Crystallographic details are: space group $P2_1/n$ (monoclinic), a = 6.855(1), b = 10.344(2), c = 12.014(3) Å, β = 92.590(7)°, Z = 2, R = 0.03 (R' = 0.033) for 727 observed reflections with $I > 3\sigma(I)$.

The current interest in pyrazine complexes stems both from the electronic structure and bifunctional nature of the pyrazine molecule, as a result of which it provides a mechanism for magnetic superexchange,[1] and facilitates electron transfer as, for example, in the well known Creutz-Taube anion.[2] However, the structural chemistry of pyrazine complexes is also of considerable interest. Crystallographic data have revealed several structural roles for pyrazine, examples of which are as follows. It acts as a monofunctional ligand in PCl_5·pyz[3] (pyz = pyrazine), $[Fe(CO)_4]$·pyz,[4] and in the cations $[Ru(NH_3)_5\cdot pyz]^{n+}$ (n = 2 or 3).[5] As a bifunctional ligand it may link only two Lewis-acid moieties, as in the cations $[(NH_3)_5Ru\cdot pyz\cdot Ru(NH_3)_5]^{n+}$ (n = 4—6),[6] and the osmium(III) analogue (n = 6),[7] in $(C_5H_5)_3Yb\cdot pyz\cdot Yb(C_5H_5)_3$,[8] and in $[(hfac)_2Cu\cdot pyz\cdot Cu(hfac)_2]$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate).[9] It may generate infinite chain structures as, for example, in $Cu(hfac)_2$·pyz,[9] $M_2(O_2CMe)_4$·pyz (M = Cu or Cr),[10,11] and $Cu(NO_3)_2$·pyz.[12] More extensive pyrazine bridging in orthogonal directions in $Cu(O_3SMe)_2$·2pyz,[13] $Cu(ClO_4)_2$·2pyz,[14] and in $CoCl_2$·2pyz[15] results in layer-type structures. Not surprisingly, crystallographic investigations of pyrazine adducts of transition metals greatly exceed those of main group elements. Several preparative and spectroscopic investigations of tin(IV)–pyrazine adducts have been reported,[16—21] but, until our recent preliminary report of the crystal structure of a pyrazine adduct of diphenyltin(IV) dichloride,[22] there were no crystallographic data available for these adducts. This paper describes in detail the novel structural features of the adduct '$SnPh_2Cl_2$·0.75pyz' and compares its structure with that of $(SnMe_2Cl_2)_2$·pyz.

The reaction of diphenyltin(IV) dichloride with pyrazine to give what was postulated to be the 1:1 adduct $SnPh_2Cl_2$·pyz was first reported by Poller and Tooley.[16] The ratio of the room-temperature ^{119}Sn Mössbauer effect to that at 77 K for the adduct was found to be 0.035, from which it was concluded that it was polymeric (as a result of pyrazine bridging) thus giving tin a co-ordination number of six.[17] Furthermore, on the basis of the assignment of a symmetric and an asymmetric mode of vibration to the $SnCl_2$ moiety it was concluded that chlorine atoms were *cis* co-ordinated to tin.[18] An x.p.s. study of a series of tin–pyrazine adducts, including the diphenyltin dichloride adduct, has more recently been reported, but no further conclusions regarding the structure of the latter adduct were made.[21]

Results and Discussion

Crystals of the diphenyltin–pyrazine adduct for the present study were grown in light petroleum (b.p. 40—60 °C) as described in the literature.[16] Attempts were also made to prepare $(SnPh_2Cl_2)_2$·pyz and $SnPh_2Cl_2$·2pyz by varying the acid to base ratio (see Experimental section), but all of the crystalline products gave identical *X*-ray powder diffraction patterns, i.r. and Mössbauer spectra, and similar analytical data. However, an interesting observation regarding the colour of the crystals was made as a result of these preparative attempts. When the mole ratios of acid to base were fairly similar the crystals were colourless, but when either acid or base was present in large excess they always had a pale, but nonetheless clearly discernible, green or blue colour; the cause of the colour

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

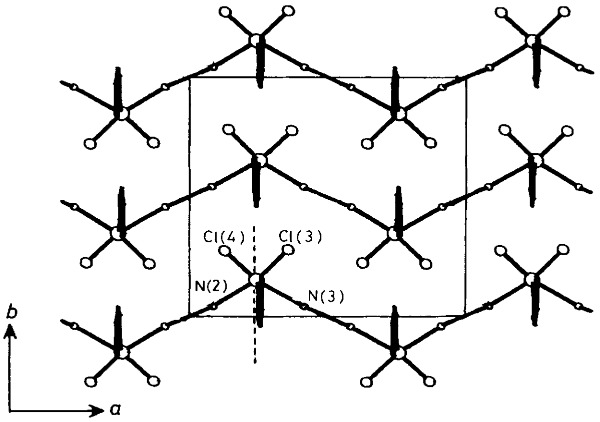

Figure 1. The packing arrangement of polymeric chains $(SnPh_2Cl_2\cdot pyz)_n$ in the structure of $SnPh_2Cl_2\cdot 0.75$ pyz. The dotted line indicates the virtual mirror plane (see text)

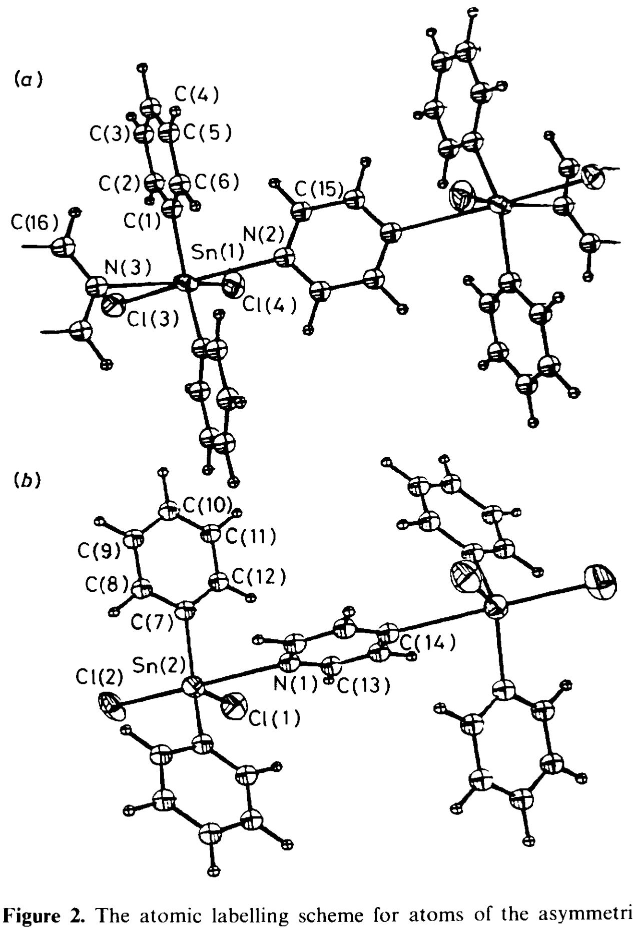

Figure 2. The atomic labelling scheme for atoms of the asymmetric unit of $SnPh_2Cl_2\cdot 0.75$pyz comprising (*a*) polymeric $(SnPh_2Cl_2\cdot pyz)_n$ and (*b*) adduct $(SnPh_2Cl_2)_2\cdot$pyz

is presently unknown. A well formed colourless crystal was selected for the crystallographic study.

One of the remarkable revelations of the crystallographic study relates to the chemical composition of the crystals. They belong to the orthorhombic space group *Pbam*, which has eight symmetry-related positions in the unit cell. It was found that, of the eight tin atoms in the unit cell, one set of four are on special positions on a mirror plane, while the second set are on special positions on the neighbouring mirror plane. Refinement of the structure revealed that tin atoms on one plane belong to polymeric chains $(SnPh_2Cl_2\cdot pyz)_n$ ($n = \infty$), whereas the others belong to discrete molecules $(SnPh_2Cl_2)_2\cdot$pyz. Thus, in broad descriptive terms the crystal structure can be described as being composed of planes containing polymeric chains of $SnPh_2Cl_2\cdot$pyz which are interleaved by planes containing molecules of $(SnPh_2Cl_2)_2\cdot$pyz. The planes are separated by almost 8 Å, and there are therefore no intermolecular bonding contacts between planes. Thus, the crystal composition is most accurately represented as $SnPh_2Cl_2\cdot$pyz–$(SnPh_2Cl_2)_2\cdot$pyz, and the average composition is $SnPh_2Cl_2\cdot 0.75$pyz. This composition could not realistically have been deduced from analytical data (see Experimental section).

Table 1. Selected bond lengths (Å) and angles (°) for the six-co-ordinate tin site in $(SnPh_2Cl_2\cdot pyz)_n$

Sn(1)–Cl(3)	2.404(4)	Sn(1)–Cl(4)	2.379(4)
Sn(1)–C(1)	2.100(5)	Sn(1)–N(2)	2.783(10)
Sn(1)–N(3)	2.961(10)	N(2)–C(15)	1.312(11)
N(3)–C(16)	1.303(11)		
Cl(3)–Sn(1)–Cl(4)	90.9(1)	Cl(3)–Sn(1)–C(1)	102.6(2)
Cl(3)–Sn(1)–N(2)	166.7(2)	Cl(3)–Sn(1)–N(3)	75.3(2)
Cl(4)–Sn(1)–C(1)	106.5(2)	Cl(4)–Sn(1)–N(2)	75.8(2)
Cl(4)–Sn(1)–N(3)	166.2(2)	C(1)–Sn(1)–N(2)	81.6(2)
C(1)–Sn(1)–N(3)	77.1(2)	C(1)–Sn(1)–C(1′)	137.7(3)
N2–Sn(1)–N(3)	117.9(3)	Sn(1)–N(2)–C(15)	122.9(5)
Sn(1)–N(3)–C(16)	122.2(6)		

The polymeric chains, $(SnPh_2Cl_2\cdot pyz)_n$ propagate in a zig-zag fashion parallel to the *a* axis as shown in Figure 1. The closest inter-chain Sn–Cl contact is approximately 5.8 Å, so there are no cross-linking bonding contacts. Chlorine, nitrogen, and tin atoms all lie in the mirror plane, and bridging pyrazine groups, which sit about inversion centres, are perpendicular to this plane. Two types of pyrazine alternate along the chains, providing tin with unequal bond lengths. Tin achieves six-co-ordination, and its co-ordination geometry can be described as very distorted octahedral (see Figure 2 and Table 1). The co-ordination geometry does however possess symmetry since the nitrogen, chlorine, and tin atoms lie in the mirror plane. Furthermore, since the N–Sn–Cl acute bond angles are almost equal (75.8 and 75.3°), and the phenyl groups fall quite symmetrically between the nitrogen atoms, there is a virtual mirror plane bisecting the Cl(3)–Sn–Cl(4) bond angle and perpendicular to the real mirror plane (see Figure 1); the phenyl groups are slightly displaced from this plane towards N(3) and Cl(3). The C–Sn–C bond angle is 137.7°, and this represents the most serious deviation from regular octahedral geometry. The nitrogen atoms are *cis*-co-ordinated [the N(2)–Sn–N(3) bond angle is 117.9°], and this contrasts with the chain polymeric structure of $SnMe_2Br_2\cdot$pyz in which nitrogen atoms adopt perfect *trans* geometry about tin.[23] The Sn–C and Sn–Cl bond lengths are quite normal, but the Sn–N bonds are abnormally long (see Table 1). These latter bond lengths are more appropriately considered, in conjunction with other Sn–N bond lengths, later in the discussion.

The packing arrangement of the molecules of $(SnPh_2Cl_2)_2\cdot$pyz is shown in Figure 3. The most significant feature of the packing is that the closest intermolecular Sn–Cl contacts, all being greater than 5.2 Å (see Figure 3), greatly exceed the sum of the tin and chlorine van der Waals radii, and hence tin is truly five-co-ordinate. This adduct, along with adducts of diphenyltin(IV) dichloride with benzothiazole[24] and 2,6-dimethylpyridine *N*-oxide[25] represent the only examples to date of adducts of

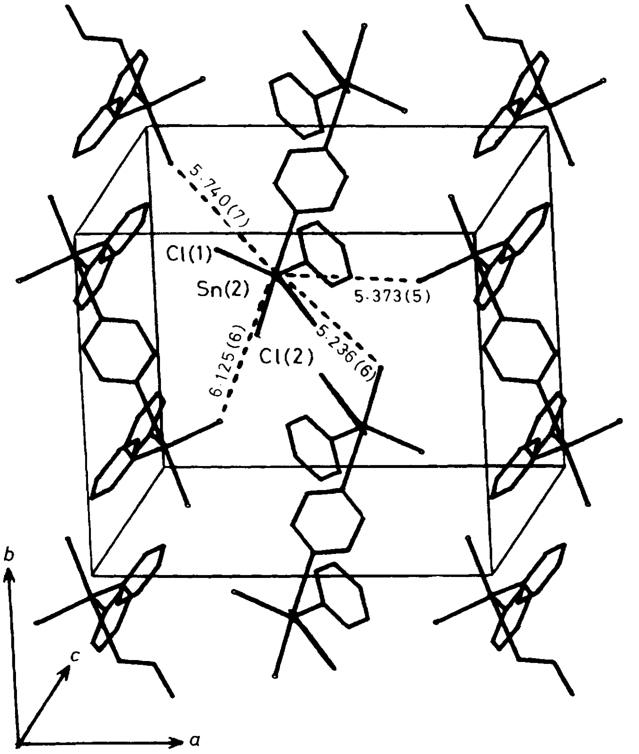

Figure 3. The packing arrangement of $(SnPh_2Cl_2)_2$·pyz molecular units, indicating closest intermolecular Sn–Cl contacts, in the structure of $SnPh_2Cl_2$·0.75pyz

Table 2. A comparison of bond lengths (Å) and bond angles (°) for the six- and five-co-ordinate tin sites in $(SnMe_2Cl_2)_2$·pyz and $(SnPh_2Cl_2)_2$·pyz respectively

$(SnMe_2Cl_2)_2$·pyz		$(SnPh_2Cl_2)_2$·pyz	
Sn–Cl(1)	2.366(2)	Sn(2)–Cl(1)	2.340(4)
Sn–Cl(2)	2.424(2)	Sn(2)–Cl(2)	2.404(2)
Sn–N	2.746(6)	Sn(2)–N(1)	2.683(11)
Sn–C(3)	2.095(8)	Sn(2)–C(7)	2.109(5)
Sn–C(4)	2.102(8)	Sn(2)–C(7′)	2.109(5)
N–C(1)	1.322(10)	N(1)–C(13)	1.313(18)
C(1)–C(2)	1.384(11)	C(13)–C(14)	1.395(23)
N–Sn–Cl(2)	173.2(1)	N(1)–Sn(2)–Cl(2)	178.5(3)
N–Sn–C(3)	83.6(3)	N(1)–Sn(2)–C(7)	80.7(2)
N–Sn–C(4)	79.6(3)	N(1)–Sn(2)–C(7′)	80.7(2)
N–Sn–Cl(1)	80.9(1)	N(1)–Sn(2)–Cl(1)	83.6(3)
Cl(1)–Sn–C(3)	108.3(3)	Cl(1)–Sn(2)–C(7)	110.3(2)
Cl(1)–Sn–C(4)	108.3(2)	Cl(1)–Sn(2)–C(7′)	110.3(2)
Cl(2)–Sn–C(3)	101.0(3)	Cl(2)–Sn(2)–C(7)	98.7(2)
Cl(2)–Sn–C(4)	100.1(2)	Cl(2)–Sn(2)–C(7′)	98.7(2)
Cl(1)–Sn–Cl(2)	92.8(1)	Cl(1)–Sn(2)–Cl(2)	97.8(2)
C(3)–Sn–C(4)	136.5(4)	C(7)–Sn(2)–C(7′)	133.1(2)
Sn–N–C(1)	120.9(4)	Sn(2)–N(1)–C(13)	115.9(9)
N–C(1)–C(2)	122.9(6)	N(1)–C(13)–C(14)	122.0(10)

diorganotin(IV) dichlorides having five-co-ordinate tin. In the case of $(SnPh_2Cl_2)_2$·pyz, tin and chlorine atoms, and the pyrazine molecule, lie in a mirror plane. Pyrazine also sits about an inversion centre. Structural features of the co-ordination geometry about tin are shown in Figure 2 and Table 2. The geometry conforms quite well to trigonal bipyramidal with the carbon atoms and Cl(1) lying in the equatorial plane. In fact, the tin atom is 0.32 Å removed from the least-squares plane defined by the carbon atoms and Cl(1) towards the axial chlorine atom. The C–Sn–C bond angle is opened from the true trigonal-bipyramidal value to 133.1° with the result that the Cl(1)–Sn–C bond angles, which are equal by symmetry requirements, are reduced to 110.3°. The axial N–Sn–Cl(2) bond angle is 178.5°. The geometry, in gross features, compares very closely with that in the benzothiazole adduct of diphenyltin dichloride.[24] In the latter adduct the C–Sn–C bond angle is 132.5°, and the sum of the three equatorial plane bond angles is 356.5°, which compares with 353.7° in the pyrazine adduct. The tin atom in the benzothiazole adduct is again removed from the plane defined by the equatorial carbon and chlorine atoms towards the axial chlorine. The Sn–C bond lengths are normal in the pyrazine adduct, and the axial Sn–Cl bond is slightly longer than the equatorial Sn–Cl bond, as has been observed in the structures of the other five-co-ordinated tin adducts.[24,25] The Sn–N bond length is shorter than either of the Sn–N bond lengths in the polymer, but is still abnormally long. The structure of $(SnPh_2Cl_2)_2$·pyz makes an interesting comparison with that of its dimethyltin analogue $(SnMe_2Cl_2)_2$·pyz.*

A number of pyrazine adducts of organotin halides are known to be unstable, but the reason for their instability has not been reported.[16] In the present study it was observed that crystals of pyrazine adducts of dimethyltin dichloride, and of n-butyltin trichloride, which were grown from benzene (the preparative solvent of the previous study [16]), rapidly crumble to powders when removed from the solvent. This appears to be due to loss of benzene of crystallization. More stable crystals of an adduct having the composition $(SnMe_2Cl_2)_2$·pyz, and which proved suitable for a structure determination, were obtained from petroleum spirit. This is the adduct which crystallizes from solution irrespective of the ratio of pyrazine to dimethyltin dichloride in solution. However, it was further established crystallographically that crystals of the distannoxane $(SnMe_2Cl)_2O$ also grow from such solutions if they are not protected from the atmosphere, and distannoxane formation may be responsible for the fine white powder deposit which forms on the surface of crystals of $(SnMe_2Cl_2)_2$·pyz when they are exposed to the atmosphere.

The packing arrangement of molecules of $(SnMe_2Cl_2)_2$·pyz in the unit cell is shown in Figure 4, and the local molecular geometry is shown in Figure 5. The most significant feature of the packing arrangement, which has not been adequately described in the previous crystallographic report,[23] is the existence of close intermolecular Sn–Cl contacts of 3.48 Å which give rise to polymeric chains, within which tin atoms are linked alternatively by double chloride and pyrazine bridges. Chains of this type pack so as to generate a layer-type structure with chains propagating in perpendicular directions in neighbouring layers. Similar chloride bridging occurs in the structures of 1:1 adducts of diphenylcyclopropenone and 2,6-dimethylpyridine *N*-oxide with dimethyltin dichloride, where the intermolecular Sn–Cl bond lengths are 3.5607 and 3.399 Å respectively.[26–28] Weak intermolecular Sn–Cl bonds (3.54 Å) also occur in the structure of dimethyltin dichloride to give an associated chain structure.[29] The general opinion is that, in associated structures of this type, tin is best considered as being six- rather than five-co-ordinate (as implicated in the previous crystallographic study of the pyrazine adduct).[23] Nonetheless, it is interesting that, despite the intermolecular contacts, the immediate geometry about tin in $(SnMe_2Cl_2)_2$·pyz does not differ significantly from the trigonal-bipyramidal geometry of its diphenyltin analogue. For example, the marginally longer

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* While preparing this paper the crystal structure of $(SnMe_2Cl_2)_2$·pyz was independently reported (see ref. 23).

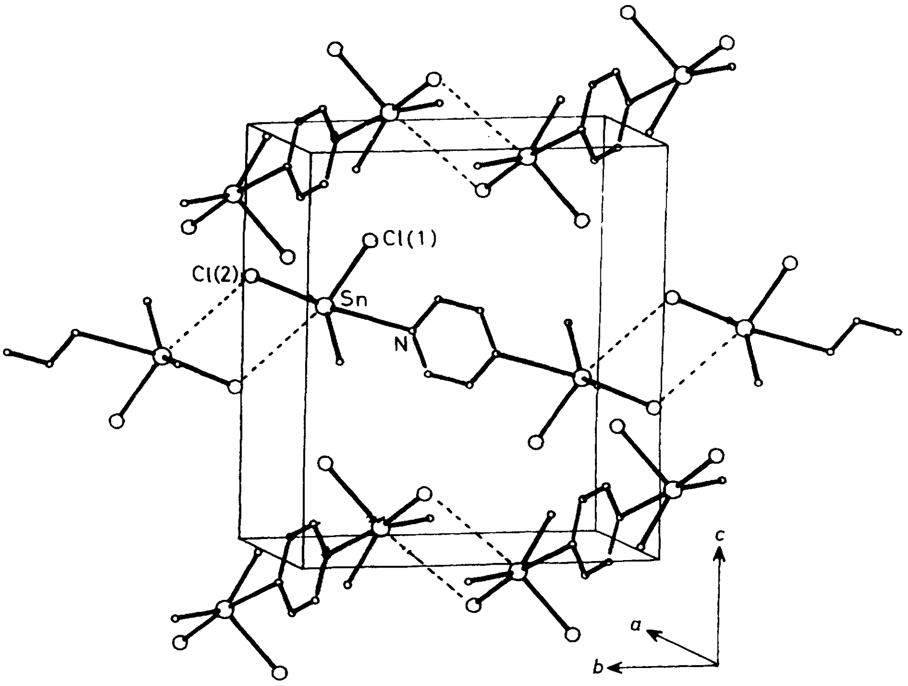

Figure 4. The packing arrangement of molecules in the structure of $(SnMe_2Cl_2)_2 \cdot pyz$. The dotted lines indicate short Sn–Cl(2) intermolecular contacts of 3.48 Å

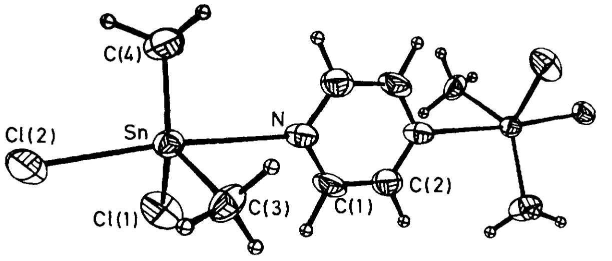

Figure 5. The atomic labelling scheme for the asymmetric unit of $(SnMe_2Cl_2)_2 \cdot pyz$

Sn–Cl bond lengths in the dimethyltin adduct are consistent with the expected lower *s* character of these bonds compared to those in the diphenyltin adduct, while the longer Sn–N bond length in the dimethyltin adduct is consistent with the expected weaker donor interaction in this case. The greatest angular deviation (5.3°) is seen in the N–Sn–Cl(axial) bond angles, and the greatest angular deviation in the equatorial plane is in the C–Sn–C bond angles, the angle being 3.4° greater in the dimethyltin adduct. Furthermore, in each adduct the tin atom is displaced from the least-squares plane defined by the equatorial chloride and carbon atoms, in the direction of the axial chloride, by an almost identical distance (0.32 Å).

The Sn–N bond lengths of the present structures are of particular interest since they are among the longest hitherto reported. The longest bonds have been observed in the 1:1 adduct of diethyltin dichloride with 2-(5′-methyl-1′,2′,4′-oxadiazol-3′-yl)-1,10-phenanthroline, bond lengths being 3.013, 2.951, and 2.860 Å.[30] An examination of this structure suggests that the abnormal bonds result from tin optimizing its overlap with the sp^2 orbitals of the nitrogen donor atoms, and to this extent bond lengths are a consequence of the stereochemistry of the donor ligand. Likewise, the recently reported Sn–N bond length of 2.841 Å for [3-(2-pyridyl)-2-thienyl-*C*,*N*]tri(*p*-tolyl)tin(IV) is attributed to steric factors.[31] Alternate pyrazine molecules in the polymeric chains of $(SnPh_2Cl_2 \cdot pyz)_n$ provide Sn–N bond lengths of 2.961 and 2.783 Å, while the Sn–N bond lengths in $(SnPh_2Cl_2)_2 \cdot pyz$ are 2.683 Å. The Sn–N bond lengths of 2.746 Å in $(SnMe_2Cl_2)_2 \cdot pyz$, being longer than those in the diphenyltin analogue, are consistent with the greater Lewis-acid strength of the latter. However, in overall terms of Lewis-acid strength the bond lengths are totally anomalous since the Sn–N bond lengths in $SnMe_2Br_2 \cdot pyz$ are 2.40 Å,[23] and furthermore, tin-119 solution n.m.r. line-shift studies (which will shortly be reported) clearly confirm the expected order of Lewis acid–pyrazine interaction, *i.e.* $SnPh_2Cl_2 > SnBu_2Cl_2 > SnBu_2Br_2$. There are no obvious steric factors which would account for the anomalous bond lengths in the pyrazine adducts. For example, in the case of the diphenyltin dichloride–pyrazine adduct, Figures 1 and 3 do not reveal any special steric demands resulting from the packing of molecules within the mirror

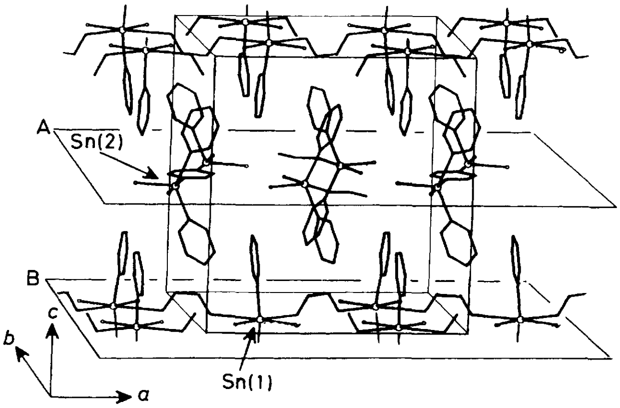

Figure 6. A view of the packing arrangement of phenyl groups within the unit cell of $SnPh_2Cl_2 \cdot 0.75pyz$. A and B identify neighbouring crystallographic mirror planes containing $(SnPh_2Cl_2)_2 \cdot pyz$ and $(SnPh_2Cl_2 \cdot pyz)_n$ respectively

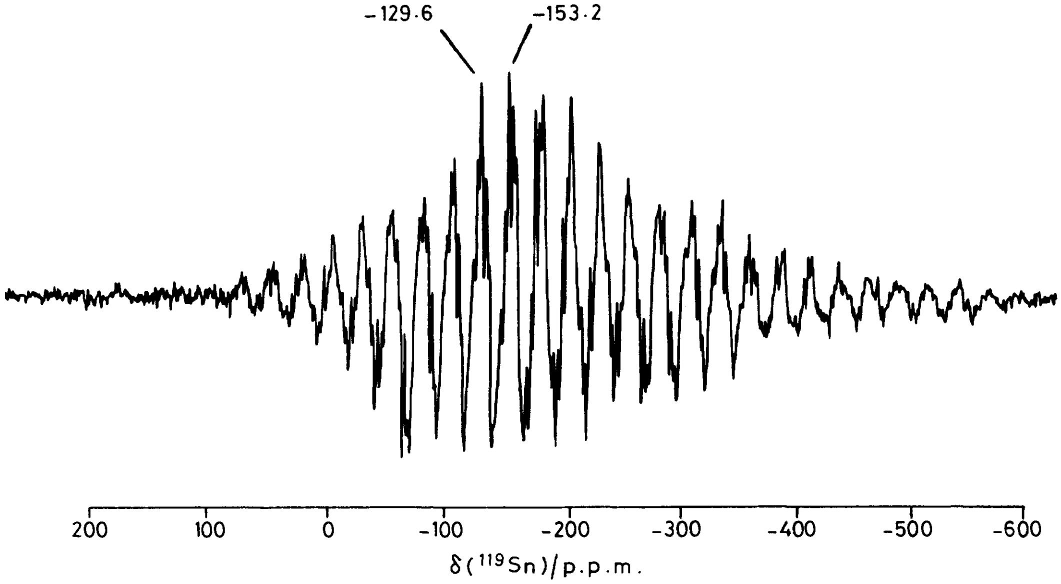

Figure 7. The solid-state ^{119}Sn n.m.r. spectrum of $SnPh_2Cl_2{\cdot}0.75pyz$

planes, and Figure 6, which shows the packing arrangement of phenyl groups between the mirror planes in the unit cell, does not reveal any convincing evidence for the necessity of creating long Sn–N bonds to alleviate steric crowding of phenyl groups.

There is, however, one curious structural feature in the pyrazine adduct structures which may be significant. The available structural data show that when Lewis-acid centres (M) are linked by pyrazine groups the M–N–N–M system is either linear or close to being linear, and in the case of $SnMe_2Br_2{\cdot}pyz$ (which contains normal Sn–N bonds) it is perfectly linear.[23] However, within the diphenyltin dichloride–pyrazine structure significant deviations from linearity occur. The non-linearity occurs as a result of two types of distortion. First, in the case of molecules of $(SnPh_2Cl_2)_2{\cdot}pyz$, tin atoms sit within the pyrazine plane (a crystallographic mirror plane), and the non-linearity of the Sn–N–N–Sn system results from an in-plane twisting of the pyrazine group about its centre of inversion (a crystallographic centre of inversion) to give very unequal Sn–N–C(pyrazine) bond angles of 115.9 and 127.8°, and a Sn–N–N angle of 173.8°. There is a close parallel to this type of distortion evident in the structure of $Cu(O_3SMe)_2{\cdot}2pyz$.[13] Half of the pyrazine molecules within this structure provide normal Cu–N bond lengths and link copper atoms into infinite chains with collinear copper and nitrogen atoms. Other pyrazine molecules link these chains, with abnormally long Cu–N bonds. Each copper atom lies within the plane of neighbouring pyrazine molecules providing the abnormal bonds, and in-plane twisting of the pyrazine molecules about their inversion centres provide Cu–N–N angles of 171.6°. The second type of distortion is seen in the polymeric chains $(SnPh_2Cl_2{\cdot}pyz)_n$. In this case tin and nitrogen atoms sit in the crystallographic mirror plane, while the pyrazine groups are perpendicular to the plane, so that the non-linearity of the Sn–N–N–Sn system results from tin atoms being removed from the pyrazine planes. In the case of the pyrazine groups giving the shorter Sn–N bond lengths, the Sn–N–N angle is 171.9°, and each tin is removed from the least-squares plane defined by its neighbouring pyrazine molecule (it is virtually planar) by 0.387 Å. In the case of the pyrazine groups giving the longer Sn–N bonds, the Sn–N–N angle is 173.8°, and each tin is displaced from the least-squares plane defined by its neighbouring pyrazine molecule (which also is virtually planar) by 0.338 Å. The non-linearity of the Sn–N–N–Sn system in the structure of $(SnMe_2Cl_2)_2{\cdot}pyz$ results from a combination of the effects described above. Thus, the Sn–N–C(pyrazine) bond angles are 123.4 and 120.9°, and tin is removed from the least-squares plane defined by the virtually planar pyrazine molecule by 0.231 Å. As a result, the Sn–N–N angle becomes 175.1°.

In view of the inability of ^{119}Sn Mössbauer spectroscopy to distinguish between the two tin environments in the structure of $SnPh_2Cl_2{\cdot}0.75pyz$[17,18] [due to the very similar C–Sn–C bond angles of 133.1(2) and 137.7(3)°], the solid-state ^{119}Sn n.m.r. spectrum assumes particular interest. The solid-state spectrum (proton decoupled), recorded under c.p.m.a.s. (cross polarisation magic angle sample spinning) conditions, is shown in Figure 7. The spectrum consists of a series of resonance envelopes, each with fine structure, within the range 100 to −600 p.p.m. (with respect to $SnMe_4$). However, only two of these signals, centred at *ca.* −130 and −153 p.p.m., are not shifted at higher spinning rates, and are thus true resonances,* the remaining part of the observed spectrum being due to spinning side-bands. This type of observation is not uncommon in the solid-state spectra of heavy nuclei.[32] The fine structure, and broad lines (*ca.* 200 Hz) within each component section of the spectrum, may arise from coupling to ^{35}Cl and ^{37}Cl ($I = \frac{3}{2}$) and ^{14}N ($I = 1$), but cannot be unambiguously assigned at present. The solid-state ^{119}Sn n.m.r. spectrum of $[SnPh_3Cl_2]^-$, which is currently under further study, shows a similar appearance.[33] Thus, unlike the ^{119}Sn Mössbauer spectrum, the ^{119}Sn n.m.r. spectrum reveals the presence of the two tin sites confirmed by the crystallographic study. However, the shifts of the two resonance signals are very similar, and are more typical of five- than six-co-ordinate tin. This suggests that the influence of the nitrogen at 2.961 Å from tin on the shielding of the metal nucleus is very small.

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* The assignment of centre bands is based upon the fact that within each of the resonance envelopes at *ca.* −130 and −153 p.p.m. three resonances (−130.6, −134.3, −136.7, and −153.3, −156.6, −159.1) are not shifted with change in spinning rate. The situation is, however, complicated by the fact that separation between these two sets of resonances (*ca.* 2 500 Hz) is comparable with the spinning rates used, and thus, side-bands from one site underly the adjacent centre band.

Table 3. Crystallographic data[a]

Compound	$SnPh_2Cl_2$·0.75pyz	$(SnMe_2Cl_2)_2$·pyz
Crystal system	*Pbam*	$P2_1/n$
a/Å	14.935(2)	6.855(1)
b/Å	13.409(3)	10.344(2)
c/Å	14.959(3)	12.014(3)
β/°		92.590(7)
U/Å^3	3 196.00	851.05
Z	4 $SnPh_2Cl_2$·pyz 2 $(SnPh_2Cl_2)_2$·pyz	2
D_c/g cm^{-3}	1.68	2.03
F(000)	1 580	492
Crystal dimensions (mm)	0.5 × 0.3 × 0.3	0.4 × 0.3 × 0.3
μ(Mo-K_α)/cm^{-1}	17.72	32.93
Data collected	$+h, +k, +l$	$\pm h, +k, +l$
Unique reflections	1 876	811
Reflections with $I > 3\sigma(I)$	1 478	727
R[b]	0.047	0.0299
R'[c]	0.056	0.0328
g	0.007 59	0.002 05
Max. shift/e.s.d.	0.02	0.001
Residual density max. (min.), e A^{-3}	0.35 (−0.32)	0.37 (−0.39)
Goodness of fit	0.79	0.85

[a] All measurements performed on a Hilger and Watts Y290 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å), scan range θ—2θ with $\theta_{max.} = 24°$. [b] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. [c] $R' = \Sigma(|F_o - F_c|\cdot w^{\frac{1}{2}})/\Sigma(|F_o|\cdot w^{\frac{1}{2}})$, $w = 1/[\sigma^2(F) + gF_o^2]$.

Table 4. Fractional atomic co-ordinates for $SnPh_2Cl_2$·0.75pyz

Atom	x	y	z
Sn(1)	0.243 70(6)	0.152 29(6)	0.000 00
Cl(3)	0.357 0(2)	0.279 7(3)	0.0000
Cl(4)	0.128 8(3)	0.275 1(3)	0.0000
Sn(2)	0.102 19(7)	0.218 86(7)	0.500 00
Cl(1)	0.242 7(3)	0.296 1(4)	0.5000
Cl(2)	0.153 1(3)	0.048 8(3)	0.5000
C(1)	0.250 8(4)	0.096 4(4)	0.122 7(3)
C(2)	0.250 4(4)	−0.005 6(4)	0.140 1(3)
C(3)	0.257 6(4)	−0.038 7(4)	0.222 7(3)
C(4)	0.265 2(4)	0.030 0(4)	0.287 9(3)
C(5)	0.265 6(4)	0.132 0(4)	0.270 5(3)
C(6)	0.258 5(4)	0.165 2(4)	0.187 9(3)
C(7)	0.045 7(5)	0.223 0(5)	0.378 9(3)
C(8)	0.070 3(5)	0.297 1(5)	0.322 2(3)
C(9)	0.038 4(5)	0.294 3(5)	0.240 1(3)
C(10)	−0.018 3(5)	0.217 3(5)	0.214 7(3)
C(11)	−0.043 0(5)	0.143 1(5)	0.271 5(3)
C(12)	−0.011 0(5)	0.146 0(5)	0.353 6(3)
N(1)	0.041 0(8)	0.407 0(8)	0.5000
C(13)	−0.046 4(10)	0.417 1(11)	0.5000
C(14)	−0.087 8(11)	0.510 4(13)	0.5000
N(2)	0.085 7(7)	0.042 3(8)	0.0000
C(15)	0.041 5(6)	0.020 7(7)	0.068 7(6)
N(3)	0.415 3(7)	0.041 7(7)	0.0000
C(16)	0.457 8(6)	0.020 1(7)	0.069 0(6)

Experimental

Preparation of Adducts.—The pyrazine adduct of diphenyltin dichloride was prepared in benzene and crystallized from petroleum spirit as described in the literature.[16] The same adduct (confirmed by *X*-ray powder diffractometry, i.r. spectroscopy, and analytical data) was obtained when the acid to base ratio was both 1:10 and 10:1 (Found: C, 44.50; H, 3.00; Cl, 17.55; N, 5.45. $SnPh_2Cl_2$·0.75pyz requires C, 44.60; H, 3.20; Cl, 17.55; N, 5.20. $SnPh_2Cl_2$·pyz requires C, 45.35; H, 3.30; Cl, 16.75; N, 6.60%).

The pyrazine adduct of dimethyltin dichloride is conveniently prepared in warm light petroleum (b.p. 40—60 °C) under nitrogen. The acid to base ratio does not influence the composition of the product, which has low solubility in cold solvent. Crystallization of the adduct from the same solvent under ambient conditions resulted in the formation of two types of crystals. A crystal-structure determination of the first crystal chosen for study revealed it to be the distannoxane $(SnMe_2Cl)_2O$; the structure of this complex has previously been determined[34] [Found: C, 18.35; H, 3.15; Cl, 27.35; N, 5.35. $(SnMe_2Cl_2)_2$·pyz requires C, 18.50; H, 3.10; Cl, 27.30; N, 5.40%].

X-Ray Crystallography.—Crystallographic details are in Table 3. In the case of the diphenyltin dichloride adduct absences were compatible with either of the space groups *Pbam* or *Pba*2. Since the structure refined satisfactorily only in the former it was taken to be the correct one. Both structures were solved by a combination of Patterson search and direct methods, and refined by full-matrix least-squares using SHELX 76.[35] Data were corrected for Lorentz, polarization, and extinction effects, but not for absorption. Hydrogen atoms were included in calculated positions. In the case of the diphenyltin dichloride adduct phenyl groups were treated as regular hexagons (C–C = 1.395 Å), and tin and chlorine atoms were refined anisotropically. In the case of the dimethyltin dichloride pyrazine adduct all non-hydrogen atoms were refined anisotropically. The atomic scattering factors for all atoms, and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature.[36–38] Calculations were performed on a DEC20 computer. Final atomic co-ordinates for $SnPh_2Cl_2$·0.75pyz are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, remaining atomic co-ordinates, and remaining bond lengths and angles.

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