

Imidazole and pyrazole complexes of phenyltin(IV) halides: The crystal structures of dichlorodiphenyl bis(pyrazole)tin(IV) and trichlorophenylbis(pyrazole)tin(IV)

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Abstract

The reaction of diphenyltin(IV) dichloride with imidazole (HIm) and pyrazole (HPz) afforded $[\text{SnPh}_2\text{Cl}_2(\text{HIm})_2]$ and $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ respectively. The crystal structure of $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ was determined by X-ray analysis. The crystal consists of discrete all-*trans* $\text{SnPh}_2\text{Cl}_2(\text{HPz})_2$ units with the tin atom octahedrally coordinated to two phenyl carbons, two Cl atoms and two pyrazole N atoms. The pyrazole ligands are also bound intramolecularly via hydrogen bonds to the chlorine atoms. Recrystallization of this compound in hot chloroform afforded $[\text{SnPhCl}_3(\text{HPz})_2]$, the structure of which was likewise determined by X-ray analysis as consisting of discrete *mer*- $\text{SnPhCl}_3(\text{HPz})_2$ units with the tin atom octahedrally coordinated to a phenyl carbon, three Cl atoms and two pyrazole N atoms. Both pyrazole ligands are bound intramolecularly via hydrogen bonds to the chlorine atoms, and one of them is also bound intermolecularly to a chlorine atom of a neighbouring molecule.

All three compounds were studied in the solid state by vibrational spectroscopy, and the formation of $[\text{SnPhCl}_3(\text{HPz})_2]$ from $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ was investigated by means of ^1H and ^{119}Sn NMR spectroscopy.

Keywords: Tin; Phenyltin chlorides complexes; Pyrazole complexes; X-ray structure; Vibrational spectroscopy; ^{119}Sn NMR spectroscopy

1. Introduction

The coordination compounds of diorganotin derivatives SnR_2X_2 (R-alkyl) with the azole ligands imidazole (HIm), pyrazole (HPz) and their substituted derivatives have been extensively studied to determine how their structures depend on ligand substitution, the bulk of R and N–H...X hydrogen bonds [1]. With no similar study having been carried out for the aryl analogues, in this work we prepared and spectroscopically characterized (IR, Raman, ^1H and ^{119}Sn NMR) the diphenyltin complexes $[\text{SnPh}_2\text{Cl}_2(\text{HIm})_2]$ and $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$. Recrystallization of the latter in CH_2Cl_2 afforded crystals suitable for X-ray analysis, but a pre-

vious attempt at recrystallization from hot chloroform afforded which were characterized as $[\text{SnPhCl}_3(\text{HPz})_2]$. We investigated this conversion process by NMR spectroscopy.

This paper describes this work and reports the crystal structures of $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ and $[\text{SnPhCl}_3(\text{HPz})_2]$. As far as we are aware, the SnCCl_3N_2 kernel, present in the latter, has not previously been studied crystallographically in complexes with monodentate N-donor ligands.

2. Experimental details

2.1. Materials and measurements

Diphenyltin dichloride (Aldrich), phenyltin trichloride (Aldrich), triphenyltin chloride (Aldrich), HIm

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(Ega) and HPz (Ega) were used as supplied. The solvents were purified by the usual methods.

Elemental analysis was performed with a Carlo Erba 1108 microanalyser. IR (KBr pellet or Nujol mull) and Raman (polycrystalline solid) spectra were recorded on a Bruker IFS66V FT-IR apparatus equipped with an FRA 106 accessory. Thermoanalytical data were obtained from TG, DTG and DSC curves. These were recorded on a Mettler TA-4000 system with a Mettler TG 50 thermobalance and a Mettler DSC 20 differential scanning calorimeter. The atmospheres used for TG and DSC were air (flow, 200 ml min⁻¹) or nitrogen (flow, 200 ml min⁻¹; purity, 99.99% v/v). The heating rate was 10°C min⁻¹, with sample weights around 10 mg for TG and 3 mg for DSC. The temperature range investigated was 35–600°C. Room temperature ¹H (300.14 MHz) NMR spectra were recorded on a Bruker AMX300 spectrometer, and ¹¹⁹Sn (186.43 MHz) NMR spectra on a Bruker AMX500 spectrometer, in the solvents CDCl₃ or (CD₃)₂SO, in 5 mm o.d. tubes. Chemical shifts, in ppm, are referred to TMS in ¹H NMR spectra (via the solvent peaks: 7.26 ppm for CDCl₃ and 2.49 ppm for (CD₃)₂SO) and to external pure tetramethyltin in ¹¹⁹Sn NMR spectra. The temperature-dependence of the ¹H and ¹¹⁹Sn NMR spectra of [SnPh₂Cl₂(HPz)₂] in CDCl₃ in the range 294–329 K was investigated on a Bruker AMX500, spectra being recorded at 5 K intervals under temperature control by the spectrometer temperature unit.

2.2. Synthesis of the complexes

2.2.1. [SnPh₂Cl₂(HIm)₂]

A solution of HIm (0.182 g, 2.7 mmol) in CH₂Cl₂ (10 ml) was added dropwise with continuous stirring to a solution of SnPh₂Cl₂ (0.459 g, 1.3 mmol) in the same solvent (10 ml). After 2 days stirring the solvent was partially evaporated and the white solid obtained was filtered out and dried under vacuum. M.p. 204°C. (Found: C, 44.2; H, 3.8; N, 11.6. C₁₈H₁₈Cl₂N₄Sn requires C, 45.1; H, 3.8; N, 11.7%).

2.2.2. [SnPh₂Cl₂(HPz)₂]

A solution of HPz (0.195 g, 2.9 mmol) in CH₂Cl₂ (10 ml) was added dropwise with continuous stirring to a solution of SnPh₂Cl₂ (0.492 g, 1.4 mmol) in the same solvent (10 ml). After 2 days stirring the solvent was partially evaporated and the white solid obtained was filtered out and dried under vacuum. M.p. 143°C. (Found: C, 45.1; H, 3.9; N, 11.4. C₁₈H₁₈Cl₂N₄Sn requires C, 45.1; H, 3.8; N, 11.7%.) Crystals suitable for X-ray analysis were obtained upon recrystallization in CH₂Cl₂.

2.2.3. [SnPhCl₃(HPz)₂]

A solution of HPz (0.410 g, 6.0 mmol) in CH₂Cl₂ (12 ml) was added dropwise with continuous stirring to a solution of SnPhCl₃ (500 μl, 3.0 mmol) in the same

Table 1
Crystallographic data ^a

| | [SnPh ₂ Cl ₂ (HPz) ₂] | [SnPhCl ₃ (HPz) ₂] |
|---|---|---|
| Molecular formula | C ₁₈ H ₁₈ Cl ₂ N ₄ Sn | C ₁₂ H ₁₃ Cl ₃ N ₄ Sn |
| <i>M</i> | 479.97 | 438.31 |
| <i>a</i> (Å) | 9.283(2) | 8.750(1) |
| <i>b</i> (Å) | 13.846(3) | 13.152(1) |
| <i>c</i> (Å) | 15.824(4) | 14.051(2) |
| <i>β</i> (deg) | 105.94(1) | 97.72(1) |
| <i>U</i> (Å ³) | 1955.6(6) | 1602.3(6) |
| <i>D_c</i> (g cm ⁻³) | 1.63 | 1.81 |
| <i>μ</i> (mm ⁻¹) | 15.94 (Mo K _α) | 176.99 (Cu K _α) |
| <i>F</i> (000) | 952 | 856 |
| Crystal dimensions (mm) | Irregular (max. 0.50; min. 0.15) | Irregular (max. 0.38; min. 0.08) |
| Min., max. absorpt. correct. | 0.88, 1.06 | 0.81, 1.52 |
| <i>h</i> ; <i>k</i> ; <i>l</i> range | -11 → 10; 0 → 16; 0 → 18 | -9 → 9; 0 → 14; 0 → 15 |
| Reflections measured | 3429 | 1668 |
| <i>θ</i> range (deg) | 0–26 | 0–60 |
| Unique reflections, <i>R</i> _{int} | 3318, 0.020 | 1600, 0.030 |
| Reflections above 3σ(<i>I</i>) | 2278 | 1349 |
| Weighting scheme | 1/[σ ² (<i>F</i> _o) + 0.0002 <i>F</i> _o ²] | 1/[σ ² (<i>F</i> _o) + 0.0015 <i>F</i> _o ²] |
| <i>R</i> ^b | 0.044 | 0.032 |
| <i>R</i> ' ^c | 0.042 | 0.035 |

^a Details in common: monoclinic, space group *P*2₁/*n*, scan technique ω-2θ, *Z* = 4, *T* = 293 K. ^b *R* = Σ(|*F*_o - *F*_c|)/Σ|*F*_o|. ^c *R*' = [Σw(|*F*_o - *F*_c|)²/Σw|*F*_o|²]^{1/2}.

Table 2
Fractional atomic coordinates for $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$, and equivalent isotropic temperature factors (\AA^2)

| Atom | x | y | z | B_{iso}^a |
|-------|-----------|------------|-----------|--------------------|
| Sn | 0.9942(1) | 0.1384(1) | 0.2571(1) | 3.03(1) |
| Cl(1) | 0.7641(2) | 0.0936(2) | 0.1358(1) | 4.11(6) |
| Cl(2) | 1.2200(2) | 0.1866(2) | 0.3811(1) | 4.58(7) |
| N(1) | 0.9042(9) | -0.0863(6) | 0.2865(5) | 5.0(3) |
| N(2) | 0.9835(7) | -0.0098(5) | 0.3229(4) | 3.4(2) |
| C(3) | 1.055(1) | -0.0387(7) | 0.4019(5) | 4.5(3) |
| C(4) | 1.021(1) | -0.1336(8) | 0.4156(7) | 6.9(4) |
| C(5) | 0.925(1) | -0.1604(6) | 0.3414(8) | 5.7(4) |
| N(3) | 0.9263(9) | 0.3103(6) | 0.1084(5) | 5.4(3) |
| N(4) | 1.0065(7) | 0.2866(5) | 0.1882(4) | 3.2(2) |
| C(5') | 1.1022(9) | 0.3567(6) | 0.2162(5) | 3.4(2) |
| C(6) | 1.082(1) | 0.4274(7) | 0.1554(7) | 6.1(4) |
| C(7) | 0.972(1) | 0.3986(7) | 0.0861(6) | 5.6(4) |
| C(8) | 1.1370(8) | 0.0782(5) | 0.1846(4) | 2.7(2) |
| C(9) | 1.274(1) | 0.1208(6) | 0.1893(5) | 4.3(3) |
| C(10) | 1.3676(9) | 0.0803(8) | 0.1424(6) | 5.0(3) |
| C(11) | 1.325(1) | 0.0010(7) | 0.0921(5) | 4.4(3) |
| C(12) | 1.186(1) | -0.0408(6) | 0.0841(5) | 4.0(3) |
| C(13) | 1.0927(9) | -0.0022(6) | 0.1326(5) | 3.7(3) |
| C(14) | 0.8523(8) | 0.1974(6) | 0.3302(5) | 3.1(2) |
| C(15) | 0.7291(9) | 0.1472(6) | 0.3383(5) | 3.8(3) |
| C(16) | 0.639(1) | 0.1858(8) | 0.3878(6) | 5.3(4) |
| C(17) | 0.671(1) | 0.2752(8) | 0.4276(6) | 5.5(4) |
| C(18) | 0.790(1) | 0.3252(7) | 0.4179(6) | 5.0(3) |
| C(19) | 0.882(1) | 0.2859(6) | 0.3700(5) | 3.7(3) |

$$^a B_{\text{iso}} = 4/3 \sum_{i,j} B_{ij} a_i a_j.$$

solvent (10 ml). On the following day the white solid obtained was filtered out and dried under vacuum. M.p. > 300°C. (Found: C, 32.4; H, 3.0; N, 12.4. $\text{C}_{12}\text{H}_{13}\text{Cl}_3\text{-N}_4\text{Sn}$ requires C, 32.9; H, 3.0; N, 12.8%.) Crystals of this compound that were suitable for X-ray analysis had already been obtained when trying to recrystallize $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ in hot chloroform.

2.3. X-ray data collection and structure refinement

All X-ray crystallographic measurements were carried out using an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) for $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ or graphite monochromated Cu K_{α} radiation ($\lambda = 1.54053 \text{ \AA}$) for

Table 3
Fractional atomic coordinates for $[\text{SnPhCl}_3(\text{HPz})_2]$, and equivalent isotropic temperature factors (\AA^2)

| Atom | x | y | z | B_{iso}^a |
|-------|------------|-----------|-----------|--------------------|
| Sn | 0.1405(1) | 0.1688(1) | 0.8487(1) | 2.60(2) |
| Cl(1) | 0.0230(2) | 0.0072(1) | 0.7989(2) | 4.43(6) |
| Cl(2) | 0.0189(2) | 0.2628(2) | 0.7070(1) | 3.78(5) |
| Cl(3) | 0.2272(2) | 0.1003(2) | 1.0093(1) | 4.07(6) |
| N(1) | 0.288(1) | 0.3447(6) | 0.9991(6) | 4.9(3) |
| N(2) | 0.2098(7) | 0.3248(5) | 0.9117(4) | 3.0(2) |
| N(3) | -0.1352(9) | 0.1456(6) | 0.9712(6) | 5.0(2) |
| N(4) | -0.0740(7) | 0.2068(5) | 0.9099(4) | 3.4(2) |
| C(3) | 0.190(1) | 0.4144(6) | 0.8685(6) | 4.3(2) |
| C(4) | 0.313(2) | 0.448(1) | 1.0094(7) | 6.9(4) |
| C(5) | 0.245(2) | 0.4887(8) | 0.9224(7) | 7.2(4) |
| C(5') | -0.172(1) | 0.2821(7) | 0.8950(7) | 5.5(3) |
| C(6) | -0.294(1) | 0.2705(8) | 0.9470(7) | 5.5(3) |
| C(7) | -0.270(1) | 0.1839(8) | 0.9936(7) | 5.2(3) |
| C(8) | 0.3564(8) | 0.1483(5) | 0.7940(5) | 2.9(2) |
| C(9) | 0.4447(8) | 0.0640(6) | 0.8221(5) | 3.4(2) |
| C(10) | 0.5868(8) | 0.0499(6) | 0.7858(5) | 3.8(2) |
| C(11) | 0.6340(9) | 0.1187(8) | 0.7261(6) | 4.5(3) |
| C(12) | 0.547(1) | 0.2076(9) | 0.7009(7) | 5.2(3) |
| C(13) | 0.4058(9) | 0.2197(7) | 0.7340(6) | 4.1(3) |

$$^a B_{\text{iso}} = 4/3 \sum_{i,j} B_{ij} a_i a_j.$$

[SnPhCl₃(HPz)₂]. In each case, the intensity of one standard reflection was essentially constant throughout the measurements. Crystal data and experimental conditions are listed in Table 1.

Both structures were solved by the standard heavy-atom Patterson method followed by normal difference Fourier techniques. Blocked matrix least squares refinement was performed with all non-H atoms anisotropic; H atoms in [SnPh₂Cl₂(HPz)₂] were included as fixed contributors at positions calculated on stereochemical grounds (all with an overall isotropic temperature factor of 0.05 Å²), whereas H atoms in [SnPhCl₃(HPz)₂] were included at positions found by combining stereochemical considerations with difference synthesis results (all with a common isotropic temperature factor that refined to $U_{iso} = 0.078(8)$ Å²). The final difference Fourier maps showed no features of chemical significance. Empirical absorption corrections were applied [2]. The programs used were SHELXS76 [3] and ORTEP [4]. Scattering factors were taken from Ref. [5] for non-H atoms (with corrections for anomalous dispersion from Ref. [6]), and from Ref. [7] for H atoms. The final atomic

coordinates for [SnPh₂Cl₂(HPz)₂] and [SnPhCl₃(HPz)₂] are listed in Tables 2 and 3 respectively. Bond distances and angles are listed in Tables 4 and 5.

3. Results and discussion

3.1. X-ray structures

3.1.1. Description of the structure of [SnPh₂Cl₂(HPz)₂]

Fig. 1 shows a drawing of the [SnPh₂Cl₂(HPz)₂] molecule showing the atom numbering. The Sn atom is octahedrally coordinated to two Cl atoms, two phenyl C atoms and two HPz N atoms in an all-*trans* configuration. Each HPz ligand is essentially planar (the deviation from the least-squares plane is negligible) and binds to the metal through the pyridine-like nitrogen. The bond lengths in the ring are close to those found in HPz complexes with dialkyltindihalides [1d, e, g, h]. The Sn–Cl and Sn–C bond lengths are similar to those found in other octahedral dichlorodiphenyltin complexes [8,9], while the Sn–N bond lengths, though in

Table 4
Selected interatomic distances (Å) and angles (deg) for [SnPh₂Cl₂(HPz)₂], with e.s.d.s in parentheses

| | | | |
|-----------------------|-----------|-------------------|----------|
| <i>Sn environment</i> | | | |
| Sn–Cl(1) | 2.526(2) | Sn–Cl(2) | 2.536(2) |
| Sn–N(2) | 2.315(6) | Sn–N(4) | 2.341(6) |
| Sn–C(8) | 2.146(7) | Sn–C(14) | 2.140(8) |
| Cl(1)–Sn–Cl(2) | 178.18(7) | Cl(1)–Sn–N(2) | 89.6(2) |
| Cl(1)–Sn–N(4) | 90.0(2) | Cl(1)–Sn–C(8) | 90.9(2) |
| Cl(1)–Sn–C(14) | 89.2(2) | Cl(2)–Sn–N(2) | 90.8(2) |
| Cl(2)–Sn–N(4) | 89.7(2) | Cl(2)–Sn–C(8) | 90.9(2) |
| Cl(2)–Sn–C(14) | 89.0(2) | N(2)–Sn–N(4) | 178.8(2) |
| N(2)–Sn–C(8) | 90.3(2) | N(2)–Sn–C(14) | 89.2(3) |
| N(4)–Sn–C(8) | 88.6(2) | N(4)–Sn–C(14) | 91.9(3) |
| C(8)–Sn–C(14) | 179.5(3) | | |
| <i>Ligands</i> | | | |
| N(1)–N(2) | 1.33(1) | N(1)–C(5) | 1.32(1) |
| N(2)–C(3) | 1.31(1) | C(3)–C(4) | 1.38(1) |
| C(4)–C(5) | 1.32(2) | N(3)–N(4) | 1.32(1) |
| N(3)–C(7) | 1.37(1) | N(4)–C(5') | 1.31(1) |
| C(5')–C(6) | 1.35(1) | C(6)–C(7) | 1.34(2) |
| C(8)–C(9) | 1.39(1) | C(8)–C(13) | 1.38(1) |
| C(9)–C(10) | 1.41(1) | C(10)–C(11) | 1.35(1) |
| C(11)–C(12) | 1.39(1) | C(12)–C(13) | 1.41(1) |
| C(14)–C(15) | 1.37(1) | C(14)–C(19) | 1.37(1) |
| C(15)–C(16) | 1.40(1) | C(16)–C(17) | 1.38(1) |
| C(17)–C(18) | 1.35(2) | C(18)–C(19) | 1.40(1) |
| N(2)–N(1)–C(5) | 111.7(8) | N(1)–N(2)–C(3) | 104.3(7) |
| N(2)–C(3)–C(4) | 111.3(8) | C(3)–C(4)–C(5) | 105(1) |
| N(1)–C(5)–C(4) | 108(1) | N(4)–N(3)–C(7) | 109.6(7) |
| N(3)–N(4)–C(5') | 107.0(7) | N(4)–C(5')–C(6) | 110.4(8) |
| C(5')–C(6)–C(7) | 107.1(9) | N(3)–C(7)–C(6) | 106.0(9) |
| C(9)–C(8)–C(13) | 119.7(7) | C(8)–C(9)–C(10) | 119.6(8) |
| C(9)–C(10)–C(11) | 120.8(9) | C(10)–C(11)–C(12) | 120.5(9) |
| C(11)–C(12)–C(13) | 119.1(8) | C(8)–C(13)–C(12) | 120.2(7) |
| C(15)–C(14)–C(19) | 118.5(7) | C(14)–C(15)–C(16) | 120.0(8) |
| C(15)–C(16)–C(17) | 120.7(9) | C(16)–C(17)–C(18) | 119(1) |
| C(17)–C(18)–C(19) | 120.2(9) | C(14)–C(19)–C(18) | 121.4(8) |

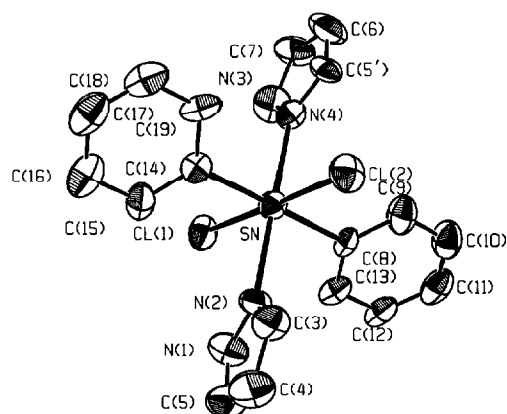


Fig. 1. Perspective view of [SnPh₂Cl₂(HPz)₂], showing the numbering scheme used (the H atoms have been omitted).

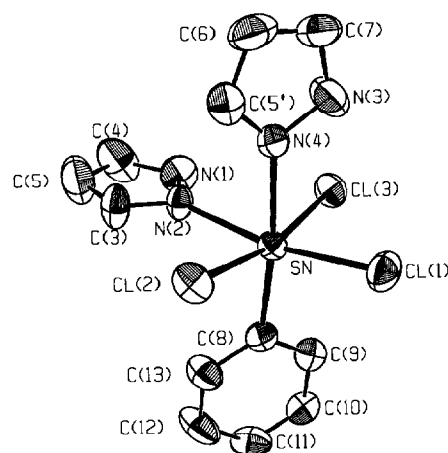


Fig. 2. Perspective view of [SnPhCl₃(HPz)₂], showing the numbering scheme used (the H atoms have been omitted).

the range found for other azole complexes of diorganotin(IV) dihalides [1], are slightly shorter than those found in [SnPh₂Cl₂(Tz)₂] [9] (Tz = thiazole), the only known diphenyltin(IV) derivative with an all-*trans* SnC₂Cl₂N₂ kernel [10]. The bond angles at the tin atom deviate very little from those of the perfect octahedron. Similar all-*trans* stereochemistry has previously been found in other HPz complexes of formula [SnR₂X₂L₂] [1a, c–e, h]. The presence of intramolecular hydrogen bonds is suggested by the following distances and an-

gles: N(1)–Cl(1), 3.447(8) Å; N(1)–H ⋯ Cl(1), 118.5(5)°; N(3)–Cl(1), 3.437(9) Å; N(3)–H ⋯ Cl(1), 119.6(5)°. The two N–H groups are hydrogen-bonded to the same halogen atom, as in [SnR₂X₂L₂] complexes with R = Bu [1g] or Cy [1h], although in both these latter cases there are also intermolecular hydrogen bonds that are not present in [SnPh₂Cl₂(HPz)₂]. In keeping with the hydrogen bond pattern, the dihedral angle between the pyrazole rings, 10(2)°, is also similar

Table 5

Selected interatomic distances (Å) and angles (deg) for [SnPhCl₃(HPz)₂], with e.s.d.s in parentheses

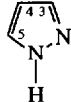
| | | | |
|-----------------------|----------|-------------------|-----------|
| <i>Sn environment</i> | | | |
| Sn–Cl(1) | 2.423(2) | Sn–Cl(2) | 2.461(2) |
| Sn–Cl(3) | 2.453(2) | Sn–N(2) | 2.284(6) |
| Sn–N(4) | 2.224(6) | Sn–C(8) | 2.150(7) |
| Cl(1)–Sn–Cl(2) | 94.96(6) | Cl(1)–Sn–Cl(3) | 90.59(7) |
| Cl(1)–Sn–N(2) | 168.6(2) | Cl(1)–Sn–N(4) | 87.8(2) |
| Cl(1)–Sn–C(8) | 98.4(2) | Cl(2)–Sn–Cl(3) | 167.24(6) |
| Cl(2)–Sn–N(2) | 85.7(2) | Cl(2)–Sn–N(4) | 84.5(2) |
| Cl(2)–Sn–C(8) | 94.5(2) | Cl(3)–Sn–N(2) | 86.6(2) |
| Cl(3)–Sn–N(4) | 84.2(2) | Cl(3)–Sn–C(8) | 96.0(2) |
| N(2)–Sn–N(4) | 80.9(2) | N(2)–Sn–C(8) | 92.9(2) |
| N(4)–Sn–C(8) | 173.8(2) | | |
| <i>Ligands</i> | | | |
| N(1)–N(2) | 1.35(1) | N(1)–C(4) | 1.38(2) |
| N(2)–C(3) | 1.33(1) | N(3)–N(4) | 1.34(1) |
| N(3)–C(7) | 1.36(1) | N(4)–C(5') | 1.31(1) |
| C(3)–C(5) | 1.29(1) | C(4)–C(5) | 1.39(2) |
| C(5')–C(6) | 1.38(1) | C(6)–C(7) | 1.32(2) |
| C(8)–C(9) | 1.38(1) | C(8)–C(13) | 1.37(1) |
| C(9)–C(10) | 1.42(1) | C(10)–C(11) | 1.34(1) |
| C(11)–C(12) | 1.41(1) | C(12)–C(13) | 1.39(1) |
| N(2)–N(1)–C(4) | 109.9(8) | N(1)–N(2)–C(3) | 105.3(7) |
| N(4)–N(3)–C(7) | 111.1(7) | N(3)–N(4)–C(5') | 104.3(7) |
| N(2)–C(3)–C(5) | 112.9(8) | N(1)–C(4)–C(5) | 104(1) |
| C(3)–C(5)–C(4) | 108(1) | N(4)–C(5')–C(6) | 111.6(9) |
| C(5')–C(6)–C(7) | 106.0(9) | N(3)–C(7)–C(6) | 106.9(9) |
| C(9)–C(8)–C(13) | 121.1(7) | C(8)–C(9)–C(10) | 119.1(7) |
| C(9)–C(10)–C(11) | 119.8(7) | C(10)–C(11)–C(12) | 121.0(8) |
| C(11)–C(12)–C(13) | 119.0(8) | C(8)–C(13)–C(12) | 119.8(8) |

Table 6
 ^1H and ^{119}Sn NMR parameters in CDCl_3 (δ in ppm and J in Hz)

| Compound | Temperature (K) | Ph | | | HPz | | | $\delta(^{119}\text{Sn})$ |
|--|-----------------|-----------------------|-------------------------|-----------------------------|-----------------------|---------------------|-----------------------------|---------------------------|
| | | $\delta(\text{H}2,6)$ | $\delta(\text{H}3,4,5)$ | $^3J(^1\text{H}-\text{Sn})$ | $\delta(\text{H}3,5)$ | $\delta(\text{H}4)$ | $\delta(\text{N}-\text{H})$ | |
| HPz | – | – | – | – | 7.63d | 6.36t | 10.77s,b | – |
| $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ | 294 | 7.70m | 7.37m | 99.1 | 7.70m | 6.40t | 8.90s,vb | –258.0 |
| $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ | 329 | 7.72m | 7.49m | 85.5 | 7.63s,b | 6.36s,b | 8.30s,vb | –130.9 |
| SnPh_2Cl_2 | – | 7.70m | 7.56m | 81.7 | – | – | – | –26.5 |
| $[\text{SnPhCl}_3(\text{HPz})_2]$ | – | 7.77m | 7.32m | – | 7.90s,b | 6.47t | – | – |
| SnPhCl_3 | – | 7.62m | – | 119.1 | – | – | – | -63 ± 0.5^a |
| SnPh_3Cl | – | 7.67m | 7.47m | 60.4 | – | – | – | -48 ± 1^a |

^a Ref. [17] (spectra in CD_2Cl_2).

Numbering scheme:



to those found when $\text{R} = \text{Bu}$ (10.4°) [1g] or Cy (0° in molecule A and 7.3° in B) [1h].

The dihedral angle between the planar phenyl groups is $12(1)^\circ$, and one of these groups [C(8)C(9)C(10)C(11)C(12)C(13)] makes an angle of $31.4(3)^\circ$ with the Cl(1)Cl(2)SnC(8) plane. These angles, and that between the pyrazole rings, show that each pair of like rings is less coplanar than in the Tz compound $[\text{SnPh}_2\text{Cl}_2(\text{Tz})_2]$ [9], probably as a result of the one-sided hydrogen bonding.

3.1.2. Description of the structure of $[\text{SnPhCl}_3(\text{HPz})_2]$

Fig. 2 shows a drawing of the $[\text{SnPhCl}_3(\text{HPz})_2]$ molecule showing the numbering scheme. The tin atom is coordinated with distorted octahedral geometry to three Cl atoms in *mer* arrangement, to one phenyl C and to two HPz N atoms. In contrast with the alkyl complex $[\text{SnMeBr}_3(\text{Py})_2]$ (Py = pyridine) [11], in which the two Py ligands are mutually *trans*, this complex has the two non-aryl organic ligands *cis* to each other, as in $[\text{SnMeCl}_3(\text{DMF})_2]$ (DMF = dimethylformamide) [12] and compounds of the type $[\text{SnRCl}_3 \cdot \text{L}_2]$ ($\text{R} = \text{Et}$, ^iPr , L an O-donor ligand) (see Ref. [13] and references cited therein).

The Sn–C bond length is similar to, and the Sn–N and Sn–Cl bonds are shorter than, those found in $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$. Of the two Sn–N bond lengths, that of the HPz *cis* to R is the greater, and the shortest Sn–Cl bond is the one that is *trans* to this HPz. The bond angles at the Sn atom also deviate from the ideal octahedral values; in particular, all the C(8)–Sn–X angles ($\text{X} = \text{Cl}(1), \text{Cl}(2), \text{N}(2)$ or $\text{Cl}(3)$) are greater than 90° . This pattern of distances and angles is the same as in other $[\text{SnRCl}_3\text{L}_2]$ compounds in which the Cl atoms are *mer* and the L ligands *cis* [13].

As in $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$, the HPz ligands are essentially planar, but in $[\text{SnPhCl}_3(\text{HPz})_2]$ there are more pronounced differences between the structural parameters of these two rings. The orientation of all the rings

can be referred to the plane SnCl(1)N(4)C(8) ($\chi^2 = 128$): this plane makes an angle of $53.8(2)^\circ$ with the planar phenyl ring ($\chi^2 = 16.6$) (which is practically coplanar (dihedral angle = $2(6)^\circ$) with its *trans*-HPz ring ($\chi^2 = 1.1$) and an angle of $88.7(3)^\circ$ with the other HPz ring ($\chi^2 = 3.5$).

The orientation of the HPz ring *trans* to the phenyl group enables it to form an intramolecular hydrogen bond with Cl(3) (N(3)–Cl(3) = $3.197(8)$ Å, N(3)–H...Cl(3) = $121.4(4)^\circ$), and the N(1)–Cl(3) distance ($3.264(8)$ Å) and N(1)–H...Cl(3) angle ($113.0(4)^\circ$) suggest [14] the existence of a second intramolecular hydrogen bond between Cl(3) and the HPz *cis* to the phenyl group (which is practically coplanar with the N(2)SnCl(3) plane). Furthermore, the Cl(3)¹–N(3) distance ($3.353(8)$ Å) and the N(3)–H...Cl(3)¹ angle ($112.9(3)^\circ$) (symmetry operation $i: -x, -y, 2-z$) suggest [14] the formation of an intermolecular hydro-

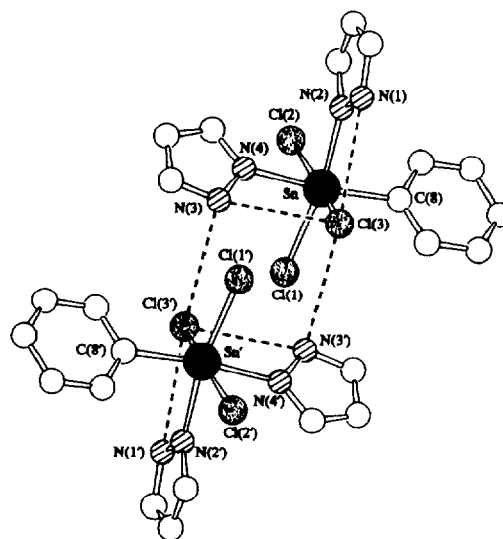


Fig. 3. A perspective view of $[\text{SnPhCl}_3(\text{HPz})_2]$, showing the hydrogen bond scheme (the H atoms have been omitted).

gen bond, so that the N(3)–H unit is involved [15] in a bifurcated hydrogen bond with the Cl(3) and Cl(3)' atoms, and each Cl(3) atom is involved in a total of three hydrogen bonds. Fig. 3 shows a SCHAKAL [16] representation of these bonds and the dimeric arrangement resulting from the intermolecular bonds.

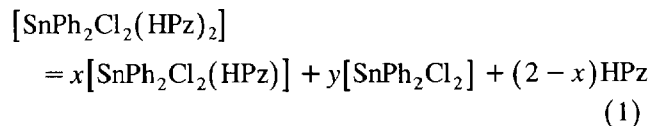
3.2. Vibrational spectra

As expected for coordination via a Py-like nitrogen atom, the significant IR ring stretching frequencies of the free azole ligands, which lie in the ranges 1540–1360 cm^{-1} for HPz and 1575–1325 cm^{-1} for HIm, are slightly shifted in all three complexes, as in all-*trans* dialkyldihalotin(IV) complexes, of these ligands [1g]. The new compounds also show the IR bands typical of phenyltin complexes near 1060, 1020, 730, 700 and 460 cm^{-1} . In the range 400–200 cm^{-1} , $[\text{SnPh}_2\text{Cl}_2(\text{HIm})_2]$ shows bands for $\nu_{\text{as}}(\text{Sn}-\text{C})$ (290m(IR)), $\nu_{\text{sym}}(\text{Sn}-\text{C})$ (230s, b(IR); 238s(R)) and $\nu_{\text{as}}(\text{Sn}-\text{Cl})$ (230s, b(IR)); $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ bands for $\nu_{\text{as}}(\text{Sn}-\text{C})$ (290m(IR)), $\nu_{\text{sym}}(\text{Sn}-\text{C})$ (248s,b(IR); 248s(R)) and $\nu_{\text{as}}(\text{Sn}-\text{Cl})$ (248s,b(IR)); and $[\text{SnPhCl}_3(\text{HPz})_2]$ bands for $\nu(\text{Sn}-\text{Cl})$ (290s,b(IR); 260m(IR, R)) and $\nu(\text{Sn}-\text{C})$ (290s,b(IR) 293(R)). The similarity between the patterns of the two diphenyl compounds suggests that the HIm complex too has an all-*trans* octahedral structure.

3.3. NMR spectra

The fortuitous preparation of $[\text{SnPhCl}_3(\text{HPz})_2]$ by recrystallization of $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ in hot CHCl_3 prompted us to study the temperature dependence of the NMR spectra of solutions of $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ in CDCl_3 . Table 6 shows the data for 294 and 329 K; intermediate temperatures were also examined (see Experimental details). At 294 K the HPz proton signals are shifted to low field with respect to the free ligand, $^3J(\text{H}-\text{Sn})$ is greater than in SnPh_2Cl_2 and the ^{119}Sn signal lies upfield of its position in the SnPh_2Cl_2 spec-

trum. When the temperature was increased to 329 K, the multiplet at 7.70 ppm split into a signal at 7.72 ppm and a broad second signal at higher field (7.63 ppm), and the multiplet at 7.37 ppm shifted to lower field (7.49 ppm). The signals at 6.36 and 7.63 ppm may be attributed to the existence in solution of free HPz, showing that the dissociation equilibrium (1) is significant at this temperature:



This equilibrium is confirmed by the fact that $\delta(^{119}\text{Sn})$ increased almost linearly with temperature (at a rate of approximately 3.6 ppm K^{-1}), which may be attributed to a steadily increasing degree of dissociation.

HPz was also lost when solid $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ was heated: TG curves show a weight loss of approximately 29.5% over the range 90–160°C, and a sharp endothermic process at 143°C ($\Delta H = 65.5 \text{ kJ mol}^{-1}$) is clearly reflected in DSC curves. Integration of the ^1H NMR spectrum of the residue left at 160°C confirms the loss of HPz.

In view of the above findings, we hypothesized that $[\text{SnPh}_2\text{Cl}_2]$ produced by the forward reaction of equilibrium (1) (or by further dissociation of $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ produced by the same reaction) might undergo a redistribution reaction [18,19], and that the resulting $[\text{SnPhCl}_3]$ might then afford the observed $[\text{SnPhCl}_3(\text{HPz})_2]$ by complexation with HPz. This sequence of reactions (dissociation, redistribution and complexation) would be maintained if the final product, $[\text{SnPhCl}_3(\text{HPz})_2]$, were of low solubility in chloroform.

That $[\text{SnPhCl}_3(\text{HPz})_2]$ is indeed very poorly soluble in chloroform was confirmed using $[\text{SnPhCl}_3(\text{HPz})_2]$ prepared as described in the Experimental section. Encouraged by this, we set about substantiating the hypothesized process by preparing $[\text{SnPhCl}_3(\text{HPz})_2]$ directly from $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ dissolved in hot chloro-

Table 7
 ^1H and ^{119}Sn NMR parameters in $(\text{CD}_3)_2\text{SO}$ (δ in ppm and J in Hz)

| Compound | Ph | | | HPz | | | $\delta(^{119}\text{Sn})$ |
|---|-----------------------|-------------------------|---------------------------|-----------------------|---------------------|-----------------------------|---------------------------|
| | $\delta(\text{H}2,6)$ | $\delta(\text{H}3,4,5)$ | $^3J(\text{H}-\text{Sn})$ | $\delta(\text{H}3,5)$ | $\delta(\text{H}4)$ | $\delta(\text{N}-\text{H})$ | |
| HPz | – | – | – | 7.60d | 6.25t | 12.83s,vb | – |
| $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ | 7.89m | 7.35m | 115.2 | 7.60s,b | 6.25t | 12.82s,vb | –399.9 |
| SnPh_2Cl_2 | 7.89m | 7.35m | 114.9 | – | – | – | –399.6 |
| $[\text{SnPhCl}_3(\text{HPz})_2]$ | 7.70m | 7.28m | 137.7 | 7.59s,b | 6.24t | 12.81s,vb | –496.7 ^a |
| SnPhCl_3 | 7.70m | 7.28m | 138.3 | – | – | – | –498.2 ^a |
| SnPh_3Cl | 7.83m | 7.43m | 65.5 | – | – | – | –223.7 |
| Refluxed $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$: | 7.71 ^b | 7.28 ^b | – | 7.59s,b | 6.25t | 12.81s,vb | –224.0 ^c |
| | 7.84 ^c | 7.35 ^d | – | | | | –399.9 ^d |
| | 7.89 ^d | 7.42 ^c | – | | | | –497.1 ^{a,b} |

^a Three additional signals: –508, –518 and –542 ppm. ^b SnPhCl_3 ; ^c SnPh_3Cl ; ^d SnPh_2Cl_2 .

form. When $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ was heated for 15 min in refluxing CHCl_3 and then left to stand at room temperature, the crystalline solid that first formed was shown by its ^1H NMR spectrum to be almost pure HPz; but the ^1H spectrum of the oily residue obtained upon concentrating the mother liquors to dryness, though too crowded for unequivocal interpretation when run in CDCl_3 , showed the presence of SnPh_2Cl_2 , SnPhCl_3 and SnPh_3Cl when run in $(\text{CD}_3)_2\text{SO}$ (Table 7, 'Refluxed $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ '). The absence of distinctive signals for unreacted $[\text{SnPh}_2\text{Cl}_2(\text{HPz})_2]$ or $[\text{SnPhCl}_3(\text{HPz})_2]$ from this spectrum was explained when the $(\text{CD}_3)_2\text{SO}$ ^1H NMR spectra of samples of these compounds (prepared as described in the Experimental section) were found to show total removal of the HPz ligands by this solvent (Table 7).

The presence of all three $\text{SnPh}_n\text{Cl}_{4-n}$ compounds in the oily residue, and hence the occurrence of the key redistribution step of the hypothesized mechanism, was finally confirmed by the ^{119}Sn spectrum of the same $(\text{CD}_3)_2\text{SO}$ solution, which showed three strong signals at -224.0 , -399.9 and -497.1 ppm (Table 7; the three weak additional signals in the neighbourhood of -500 ppm are attributed to the hydrolysis products of SnPhCl_3).

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