

Indazole complexes of diorganotin(IV) dihalides. The crystal structures of dichloro and dibromodimethylbis(indazole) tin(IV)

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Abstract

Reaction of indazole (HInd) with diorganotin(IV) dihalides yielded compounds of the type $[\text{SnR}_2\text{X}_2(\text{HInd})_2]$ (R = Me, Et, Bu and Ph; X = Cl, Br). The structures of the dihalodimethylbis(indazole)tin(IV) complexes were determined by X-ray crystallography. These are trans-octahedral centrosymmetric compounds with the following bond lengths (Å) around the tin atom: Sn–Cl 2.590(2), Sn–N 2.377(6), Sn–C 2.12(1) in the chloride; and Sn–Br 2.733(1), Sn–N 2.370(5) and Sn–C 2.12(1) in the bromide. Mössbauer and vibrational spectra suggest similar trans stereochemistry for the other complexes prepared. The behaviour of these compounds in solution was studied by conductimetry and NMR techniques.

Keywords: Tin; Indazole; Organotin; Complexes; Preparation; Crystal structure

1. Introduction

In previous work [1–5], several dialkyltin(IV) complexes of the type $[\text{SnR}_2\text{X}_2\text{L}_2]$ were prepared (R = Me, Et or Bu; X = Cl or Br; L = imidazole, pyrazole or thiazole), and some were studied crystallographically; this study was recently extended to diaryltin(IV) derivatives [5,6]. The L ligands used were chosen so as to allow analysis of the structural influence of the presence and position of an N–H group: imidazole and pyrazole have N–H groups capable of forming N–H···X hydrogen bonds, but thiazole does not.

We have now further extended our study of hydrogen bonding in diorganotin(IV) dihalide azole complexes by investigating the influence of a more voluminous, bicyclic ligand with the donor atom at one end. Specifically, we prepared the complexes $[\text{SnR}_2\text{X}_2(\text{HInd})_2]$ (HInd = indazole; R = Me, Et, Bu, Ph; X = Cl, Br). This paper describes their synthesis, their solid-state vibrational and Mössbauer spectra and their NMR spec-

tra in CDCl_3 , together with the crystal structures of $[\text{SnMe}_2\text{Cl}_2(\text{HInd})_2]$ and $[\text{SnMe}_2\text{Br}_2(\text{HInd})_2]$.

2. Experimental section

2.1. Materials

Dimethyltindichloride (Ventron), dimethyltindibromide (Ventron), diethyltindichloride (Ventron), diethyltindibromide (Ventron), dibutyltindichloride (Aldrich), dibutyltindibromide (Aldrich), diphenyltindichloride (Aldrich) and indazole (Aldrich) were used as supplied. Diphenyltindibromide was prepared by reacting diphenyltindichloride with sodium bromide. Solvents were purified by the usual methods.

2.2. Preparation of compounds

2.2.1. General procedure

A solution of SnR_2X_2 in 3 ml of CH_2Cl_2 (10 ml for the phenyl compounds) was added dropwise to a solu-

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tion of indazole in 10 ml of the same solvent. After stirring, the white solid formed was filtered off and dried in vacuo.

2.2.2. $[\text{SnMe}_2\text{Cl}_2(\text{HInd})_2]$

As above, from 0.274 g (1.25 mmol) of SnMe_2Cl_2 and 0.295 g (2.5 mmol) of indazole. Anal. Found: C, 42.7; H, 3.9; N, 6.0. $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{N}_4\text{Sn}$. Calc.: C, 43.1; H, 3.9; N, 6.5%. M.p. 140 °C, Λ_M (MeCN, 10^{-3} M) $6.9 \text{ S cm}^2 \text{ mol}^{-1}$.

2.2.3. $[\text{SnMe}_2\text{Br}_2(\text{HInd})_2]$

From 0.471 g (1.5 mmol) of SnMe_2Br_2 and 0.354 g (3.0 mmol) of indazole. Anal. Found: C, 35.2; H, 3.1; N, 9.9. $\text{C}_{16}\text{H}_{18}\text{Br}_2\text{N}_4\text{Sn}$. Calc.: C, 35.2; H, 3.3; N, 10.3%. M.p. 137 °C, Λ_M (MeCN, 10^{-3} M) $7.8 \text{ S cm}^2 \text{ mol}^{-1}$.

2.2.4. $[\text{SnEt}_2\text{Cl}_2(\text{HInd})_2]$

From 0.520 g (2.1 mmol) of SnEt_2Cl_2 and 0.495 g (4.2 mmol) of indazole. Anal. Found: C, 48.9; H, 4.8; N, 12.0. $\text{C}_{18}\text{H}_{22}\text{Cl}_2\text{N}_4\text{Sn}$. Calc.: C, 49.2; H, 4.5; N, 11.6%. M.p. 120 °C, Λ_M (MeCN, 10^{-3} M) $7.6 \text{ S cm}^2 \text{ mol}^{-1}$.

2.2.5. $[\text{SnEt}_2\text{Br}_2(\text{HInd})_2]$

From 0.714 g (2.1 mmol) of SnEt_2Br_2 and 0.495 g (4.2 mmol) of indazole. Anal. Found: C, 38.0; H, 3.7; N, 10.0. $\text{C}_{18}\text{H}_{22}\text{Br}_2\text{N}_4\text{Sn}$. Calc.: C, 37.7; H, 3.8; N, 9.8%. M.p. 110 °C, Λ_M (MeCN, 10^{-3} M) $8.6 \text{ S cm}^2 \text{ mol}^{-1}$.

2.2.6. $[\text{SnBu}_2\text{Cl}_2(\text{HInd})_2]$

From 0.380 g (1.25 mmol) of SnBu_2Cl_2 and 0.295 g (2.5 mmol) of indazole. Anal. Found: C, 48.3; H, 10.3; N, 5.6. $\text{C}_{22}\text{H}_{30}\text{Cl}_2\text{N}_4\text{Sn}$. Calc.: C, 48.9; H, 10.3; N, 5.5%. M.p. 106 °C, Λ_M (MeCN, 10^{-3} M) $7.5 \text{ S cm}^2 \text{ mol}^{-1}$.

2.2.7. $[\text{SnBu}_2\text{Br}_2(\text{HInd})_2]$

From 1.218 g (3.1 mmol) of SnBu_2Br_2 and 0.732 g (6.2 mmol) of indazole. Anal. Found: C, 41.8; H, 8.6; N, 5.7. $\text{C}_{22}\text{H}_{30}\text{Br}_2\text{N}_4\text{Sn}$. Calc.: C, 42.0; H, 8.9; N, 4.8%. M.p. 135 °C, Λ_M (MeCN, 10^{-3} M) $13.8 \text{ S cm}^2 \text{ mol}^{-1}$.

2.2.8. $[\text{SnPh}_2\text{Cl}_2(\text{HInd})_2]$

From 0.584 g (1.7 mmol) of SnPh_2Cl_2 and 0.401 g (3.4 mmol) of indazole. Anal. Found: C, 53.1; H, 3.8; N, 9.1. $\text{C}_{28}\text{H}_{26}\text{Cl}_2\text{N}_4\text{Sn}$. Calc.: C, 53.8; H, 3.8; N, 9.7%. M.p. 102 °C, Λ_M (MeCN, 10^{-3} M) $11.4 \text{ S cm}^2 \text{ mol}^{-1}$.

2.2.9. $[\text{SnPh}_2\text{Br}_2(\text{HInd})_2]$

From 0.465 g (1.1 mmol) of SnPh_2Br_2 and 0.248 g (2.1 mmol) of indazole. Anal. Found: C, 46.0; H, 3.6;

N, 8.5. $\text{C}_{28}\text{H}_{26}\text{Br}_2\text{N}_4\text{Sn}$. Calc.: C, 46.7; H, 3.3; N, 8.4%. M.p. 95 °C, Λ_M (MeCN, 10^{-3} M) $49.4 \text{ S cm}^2 \text{ mol}^{-1}$.

2.3. Physical measurements

Elemental analyses were performed with a Carlo-Erba 1108 apparatus. Melting points were measured on a Büchi apparatus. IR spectra were recorded in Nujol mulls or KBr discs, and Raman spectra in capillary tubes, on a Bruker IFS-66 V FT-IR apparatus equipped with an FRA-106 Raman module. Conductivities were measured in a WTW-LF3 conductimeter. Mössbauer spectra were determined at 80.0 K in a constant acceleration apparatus with a $\text{Ca}^{119\text{m}}\text{SnO}_3$ source, with δ referred to SnO_2 . ^1H (250.13 MHz) and ^{13}C (62.83 MHz) NMR spectra were recorded in CDCl_3 at room temperature on a Bruker WM-250 spectrometer, and were referred to TMS.

2.4. Determination of the structure of $[\text{SnMe}_2\text{X}_2(\text{HInd})_2]$

Well-formed crystals of maximum dimension 0.2 mm were selected and used for the X-ray analysis. Data were collected on a Philips PW 1100 diffractometer

Table 1
Crystal and intensity data for the complexes $[\text{SnMe}_2\text{Cl}_2(\text{HInd})_2]$ and $[\text{SnMe}_2\text{Br}_2(\text{HInd})_2]$

	$[\text{SnMe}_2\text{Cl}_2(\text{HInd})_2]$	$[\text{SnMe}_2\text{Br}_2(\text{HInd})_2]$
Formula	$\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{N}_4\text{Sn}$	$\text{C}_{16}\text{H}_{18}\text{Br}_2\text{N}_4\text{Sn}$
Fw	455.6	544.5
Cell constants		
a (Å)	7.277(3)	7.276(3)
b (Å)	10.106(4)	10.176(4)
c (Å)	6.597(3)	6.844(3)
α (deg)	102.77(3)	103.41(3)
β (deg)	93.73(3)	93.04(3)
γ (deg)	107.97(3)	108.82(3)
V (Å ³)	$V = 445$	462
Density (calc.) (g cm^{-3})	1.70	1.96
Molecules per cell, Z	1	1
System	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Absorption	16	55
$\mu(\text{Mo K}\alpha)$ (cm^{-1})		
Wavelength	0.7107	0.7107
$\lambda(\text{Mo K}\alpha)$ (Å)		
Scan method	$\theta - 2\theta$	$\theta - 2\theta$
2θ limits (deg)	$6 < 2\theta < 64$	$6 < 2\theta < 54$
Scan speed (deg min^{-1})	2	2
Data collected	3081	2065
Data with $F > 6\sigma(F)$	2872	1859
Corrections applied	Lp, absorption [8]	Lp, absorption [8]
Discrepancy factor R	0.084	0.050

Table 2
Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for $[\text{SnMe}_2\text{Cl}_2(\text{HInd})_2]$

Atom	x	y	z	U_{eq}^a
Sn(1)	0.0	0.0	0.0	0.0320(2)
Cl(1)	0.2552(3)	0.0899(3)	-0.2380(3)	0.0482(8)
N(1)	0.104(1)	0.2345(7)	0.230(1)	0.036(2)
N(2)	0.177(1)	0.2665(7)	0.437(1)	0.037(2)
C(1)	0.236(1)	0.4110(8)	0.519(1)	0.036(2)
C(2)	0.323(1)	0.495(1)	0.726(1)	0.050(3)
C(3)	0.366(1)	0.641(1)	0.756(2)	0.062(4)
C(4)	0.328(2)	0.706(1)	0.602(2)	0.065(4)
C(5)	0.247(1)	0.624(1)	0.396(2)	0.056(4)
C(6)	0.199(1)	0.4740(8)	0.358(1)	0.038(2)
C(7)	0.117(1)	0.3570(8)	0.181(1)	0.040(3)
C(8)	-0.214(1)	0.0537(9)	-0.168(1)	0.043(3)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

using MoK α radiation. Cell dimensions were determined by least squares refinement of 25 medium-angle settings. The crystals were stable under irradiation. The structures were solved by Patterson and Fourier methods alternated with cycles of least squares refinement of the atomic parameters.

Even though most hydrogen atoms were clearly located on the Fourier difference maps, they were generally introduced in calculated positions with a fixed C–H distance (1.08 \AA) and isotropic temperature factor ($U_{\text{iso}} = 0.08 \text{\AA}^2$). Only the coordinates of the H atoms bound to C(2) and N(2) in the bromo complex were directly obtained from the electron density map. Anisotropy was introduced for all non-hydrogen atoms. Scale factors and positional and thermal parameters were refined by minimizing the function $\sum w(\Delta F)^2$, with $w = 1$. At convergence, the largest parameter shift of the refined parameters of the non-hydrogen atoms was 0.01 times the standard deviation of the parameter.

No significant residual was observed in the final

Table 3
Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for $[\text{SnMe}_2\text{Br}_2(\text{HInd})_2]$

Atom	x	y	z	U_{eq}^a
Sn(1)	0.0	0.0	0.0	0.0336(2)
Br(1)	0.2703(1)	0.09401(9)	-0.2447(1)	0.0489(3)
N(1)	0.1056(9)	0.2346(6)	0.2226(9)	0.040(2)
N(2)	0.172(1)	0.2667(6)	0.423(1)	0.041(2)
C(1)	0.232(1)	0.4117(8)	0.506(1)	0.041(2)
C(2)	0.312(1)	0.4923(9)	0.707(1)	0.057(3)
C(3)	0.359(1)	0.641(1)	0.743(2)	0.073(4)
C(4)	0.325(1)	0.7044(9)	0.594(2)	0.074(4)
C(5)	0.249(1)	0.6254(9)	0.395(2)	0.061(4)
C(6)	0.201(1)	0.4738(7)	0.353(1)	0.045(3)
C(7)	0.121(1)	0.3582(8)	0.179(1)	0.047(3)
C(8)	-0.212(1)	0.0533(9)	-0.160(1)	0.046(3)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Bond lengths (\AA) and angles (deg) in $[\text{SnMe}_2\text{Cl}_2(\text{HInd})_2]$ and $[\text{SnMe}_2\text{Br}_2(\text{HInd})_2]$. E.s.d.'s (in parentheses) refer to the last significant digit

Atom	X = Cl	X = Br	
Sn–X	2.590(3)	2.733(2)	
Sn–C(8)	2.12(1)	2.12(1)	
Sn–N(1)	2.377(6)	2.370(5)	
N(1)–N(2)	1.359(9)	1.358(9)	
N(1)–C(7)	1.32(1)	1.33(1)	
N(2)–C(1)	1.36(1)	1.364(9)	
C(7)–C(6)	1.41(1)	1.41(1)	
C(1)–C(6)	1.41(1)	1.39(1)	
C(1)–C(2)	1.42(1)	1.41(1)	
C(2)–C(3)	1.38(2)	1.40(1)	
C(3)–C(4)	1.38(2)	1.38(2)	
C(4)–C(5)	1.41(1)	1.39(2)	
C(5)–C(6)	1.41(1)	1.42(1)	
X–Sn–C(8)	91.5(2)	91.1(2)	
X–Sn–N(1)	89.9(2)	90.1(2)	
C(8)–Sn–N(1)	89.5(3)	89.1(3)	
Sn–N(1)–C(7)	127.5(5)	128.3(5)	
Sn–N(1)–N(2)	124.5(5)	124.4(5)	
N(2)–N(1)–C(7)	107.8(6)	107.2(6)	
N(1)–N(2)–C(1)	109.8(6)	110.2(6)	
N(2)–C(1)–C(6)	107.6(7)	107.3(7)	
N(2)–C(1)–C(2)	130.3(8)	129.6(7)	
C(2)–C(1)–C(6)	122.2(8)	123.1(7)	
N(1)–C(7)–C(6)	110.5(7)	110.1(7)	
C(1)–C(6)–C(7)	104.4(7)	105.2(7)	
C(1)–C(6)–C(5)	120.8(8)	120.2(8)	
C(5)–C(6)–C(7)	134.8(9)	134.5(8)	
C(1)–C(2)–C(3)	114.9(9)	115.2(8)	
C(2)–C(3)–C(4)	124(1)	123(1)	
C(3)–C(4)–C(5)	121(1)	122.2(9)	
C(4)–C(5)–C(6)	117(1)	116.7(9)	
Hydrogen bonds			
Cl \cdots H(22 ¹)	2.29	Br \cdots H(22 ¹)	2.45
Cl \cdots N(2 ¹)	3.20	Br \cdots N(2 ¹)	3.35

$i = x, y, 1 + z.$

electron density map of the bromine compound, but some residuals not attributable to atom positions were found in that of the chlorine compound.

Form factors for neutral atoms were supplied internally by the SHELX program system [7]. Crystal and intensity data, final atomic parameters and bond distances and angles are listed in Tables 1–4.

3. Results and discussion

3.1. Description of the structures

The two $[\text{SnMe}_2\text{X}_2(\text{HInd})_2]$ compounds are isomorphous and essentially isostructural. Their structures are shown in Figs. 1 and 2, together with the adopted numbering scheme. In both compounds the Sn atom lies

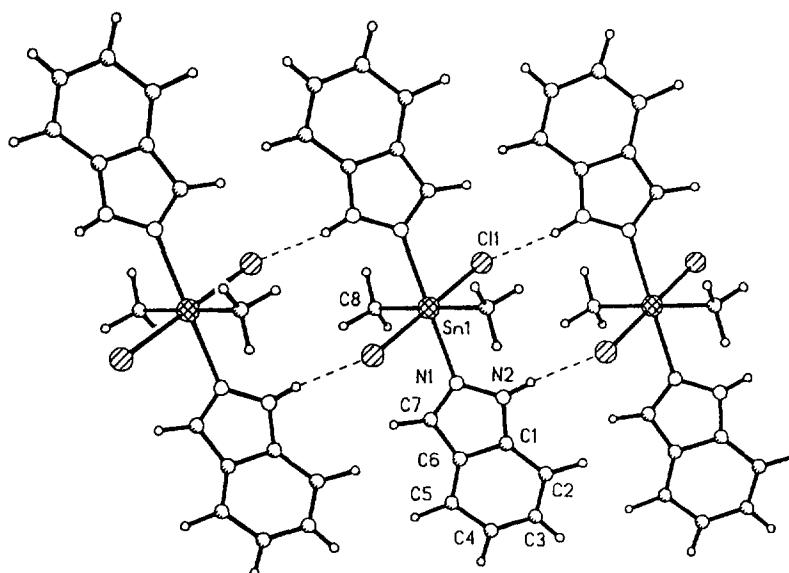


Fig. 1. Perspective view of $[\text{SnMe}_2\text{Cl}_2(\text{HInd})_2]$, showing the atom numbering scheme and the coordination geometry about the tin atom.

in a special position at a crystallographic inversion centre. Comparison of the numbers of observed and collected reflections, greatest map residuals and final R factors (Table 1) suggests that the sample of the chlorine compound was of poorer quality, and probably less crystalline, than the bromine compound, but their structures are nevertheless very similar, with practically undistorted trans-octahedral $\text{SnC}_2\text{X}_2\text{N}_2$ coordination kernels. All the Sn bond lengths are close or very close (Sn–C in both compounds, Sn–N in the bromide) to the mean Sn–X, Sn–C and Sn–N distances reported in a recent review of diorganodihalotin complexes with all-trans $\text{SnR}_2\text{X}_2\text{N}_2$ kernels [9]; 2.579 Å, 2.123 Å and 2.355 Å respectively for chlorides, and 2.715 Å, 2.115 Å and 2.37 Å respectively for bromides. The Sn bond length farthest from the corresponding mean is that of

Sn–N in the chloride; in spite of the different acceptor capacities of the two SnR_2X_2 species, this bond is practically the same length as Sn–N in the bromide, probably because of the hydrogen bond described below.

In both compounds, each indazole ligand is virtually planar; in particular, the atoms of the penta-atomic ring are coplanar to within 0.02 Å in the chlorine compound and 0.004 Å in the bromine compound. The observed N–N and N–C bond lengths are typical of heterocyclic compounds; C(7)–N(1) has the greatest degree of double bond character.

As shown in the figures, each halogen atom is involved in a hydrogen bond with one of the N(2) atoms of an adjacent molecule, with the result that the individual molecules are linked in polymeric chains along the

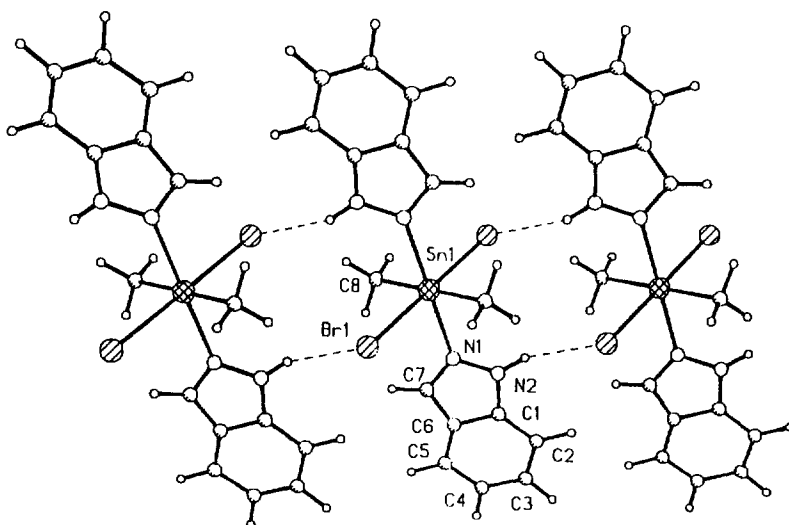


Fig. 2. Perspective view of $[\text{SnMe}_2\text{Br}_2(\text{HInd})_2]$, showing the atom numbering scheme and the coordination geometry about the tin atom.

Table 5
Significant IR and Raman bands of the compounds prepared in the range 700–1000 cm⁻¹

Compound	$\nu_{\text{as}}(\text{Sn}-\text{C})$	$\nu_{\text{sym}}(\text{Sn}-\text{C})$	$\nu_{\text{as}}(\text{Sn}-\text{X})$
[SnMe ₂ Cl ₂ (HInd) ₂]	IR 575 m	—	235 s
	R —	504 s	—
[SnMe ₂ Br ₂ (HInd) ₂]	IR 572 m	500 w	140 s
	R —	500 s	—
[SnEt ₂ Cl ₂ (HInd) ₂]	IR 530 s	482 m ^a	230 s
	R —	477 s	—
[SnEt ₂ Br ₂ (HInd) ₂]	IR 530 s	475 m ^a	130 s,b
	R —	475 s	—
[SnBu ₂ Cl ₂ (HInd) ₂]	IR 617 m	—	231 s
	R —	595 s	226 m
[SnBu ₂ Br ₂ (HInd) ₂]	IR 617 m	—	130 s,b
	R —	595 s	130 m
[SnPh ₂ Cl ₂ (HInd) ₂]	IR 292 m	260 m	263 m
	R —	255 s	—
[SnPh ₂ Br ₂ (HInd) ₂]	IR 290 m	250 sh	170 m
	R —	254 m	—

b = broad; s = strong; m = medium; w = weak; ^a contributed to by an indazole band.

c axis of the crystallographic cell. These bonds, the geometry of which is similar to that of N–H ··· Cl and N–H ··· Br bonds in other complexes [1–5,10], probably influence the angles between the ligand and SnN₂X₂ planes (66.5° in [SnMe₂Cl₂(HInd)₂] and 55.5° in

Table 6
Mössbauer spectral data at 80.0 K

Compound	δ^a	ΔE_Q	Γ	A_2/A_1^b
[SnMe ₂ Cl ₂ (HInd) ₂]	1.53	4.19	0.88	1.15
[SnMe ₂ Br ₂ (HInd) ₂]	1.60	4.16	0.85	1.15
[SnEt ₂ Cl ₂ (HInd) ₂]	1.75	4.24	0.86	0.81
[SnEt ₂ Br ₂ (HInd) ₂]	1.78	4.15	0.93	0.96
[SnBu ₂ Cl ₂ (HInd) ₂]	1.69	4.20	0.87	1.03
[SnBu ₂ Br ₂ (HInd) ₂]	1.82	4.35	0.84	1.05
[SnPh ₂ Cl ₂ (HInd) ₂]	1.39	3.73	0.92	0.94
[SnPh ₂ Br ₂ (HInd) ₂]	1.47	3.73	0.91	0.98

^a Relative to room temperature SnO₂. ^b Area ratio between the high and low velocity components.

[SnMe₂Br₂(HInd)₂]) and the values of the Sn–N bond lengths; also, this is probably the cause of the asymmetry between the bond angles at N(1), where the Sn–N(1)–C(7) angle is 3–4° wider than Sn–N(1)–N(2).

3.2. Vibrational spectra

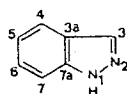
The three ring stretching bands involving $\nu(\text{C}=\text{N})$, which lie at 1504, 1486 and 1443 cm⁻¹ in the spectrum of the free ligand [11], are slightly shifted in those of all the compounds prepared (e.g. to 1512, 1478 and 1451 cm⁻¹ in [SnMe₂Cl₂(HInd)₂] and 1509, 1473 and

Table 7
¹H NMR parameters (δ ppm, J Hz) of [SnR₂X₂(HInd)₂] complexes in CDCl₃

Compound ^a	$\delta\text{H}(\text{C1})$	$\delta\text{H}(\text{C2})$	$\delta\text{H}(\text{C3})$	$\delta\text{H}(\text{C4})$	$\delta(\text{Ligand})$
HInd					10.90(N–H), 8.14(H3,s), 7.53(H4,d), 7.40(H5,t), 7.19(H6,t), 7.79(H7,d)
[SnMe ₂ Cl ₂ (HInd) ₂] ^b	1.27(s)				—(N–H), 8.17(H3,s), 7.54(H4,d), 7.45(H5,t), 7.22(H6,t), 7.79(H7,d)
[SnMe ₂ Br ₂ (HInd) ₂] ^c	1.43(s)				10.50(N–H), 8.15(H3,s), 7.51(H4,d), 7.43(H5,t), 7.20(H6,t), 7.79(H7,d)
[SnEt ₂ Cl ₂ (HInd) ₂] ^d	1.87(q)	1.27(t)			10.10(N–H), 8.29(H3,s), 7.58(H4,d), 7.47(H5,t), 7.23(H6,t), 7.80(H7,d)
[SnEt ₂ Br ₂ (HInd) ₂] ^e	1.97(q)	1.28(t)			9.10(N–H), 8.29(H3,s), 7.56(H4,d), 7.46(H5,t), 7.22(H6,t), 7.81(H7,d)
[SnBu ₂ Cl ₂ (HInd) ₂]	1.83(m)	1.75(m)	1.38(m)	0.91(t)	10.10(N–H), 8.15(H3,s), 7.54(H4,d), 7.43(H5,t), 7.21(H6,t), 7.79(H7,d)
[SnBu ₂ Br ₂ (HInd) ₂]	1.91(m)	1.78(m)	1.41(m)	0.94(t)	9.60(N–H), 8.13(H3,s), 7.54(H4,d), 7.43(H5,t), 7.20(H6,t), 7.78(H7,d)
	$\delta\text{H}(\text{Cm}, \text{Cp})$	$\delta\text{H}(\text{Co})$			
[SnPh ₂ Cl ₂ (HInd) ₂]	7.43–7.52(m)	7.71–7.78(m)			—(N–H), 8.14(H3,s), 7.43–7.52(H4,H5,m), 7.20(H6,t), 7.71–7.78(H7,m)
[SnPh ₂ Br ₂ (HInd) ₂] ^f	7.41–7.52(m)	7.69–7.72(m)			—(N–H), 8.16(H3,s,b), 7.41–7.52(H4,H5,m), 7.20(H6,t), 7.76(H7,d)

s = singlet; b = broad; d = doublet; t = triplet; q = quadruplet; m = multiplet.

^a Numbering scheme: Sn–C1–C2–C3–C4 Ligand.



^b ²J(¹¹⁹Sn–¹H) = 78.6; ^c ²J(¹¹⁹Sn–¹H) = 71.4; ^d ²J(¹¹⁹Sn–¹H) = 71.9, ³J(¹¹⁹Sn–¹H) = 162.3; ^e ²J(¹¹⁹Sn–¹H) = 64.4, ³J(¹¹⁹Sn–¹H) = 160.2; ^f ³J(¹¹⁹Sn–¹H) = 83.8.

Table 8
 ^{13}C NMR parameters (δ ppm, J Hz) of $[\text{SnR}_2\text{X}_2(\text{HInd})_2]$ complexes in CDCl_3

Compound	$\delta(\text{C1})$	$\delta(\text{C2})$	$\delta(\text{C3})$	$\delta(\text{C4})$	$\delta(\text{Ph})$	$\delta(\text{Ligand})$
HInd						135.2(C3), 121.4(C4), 121.3(C5), 127.2(C6) 110.2(C7), 123.6(C3a), 140.5(C7a)
$[\text{SnMe}_2\text{Cl}_2(\text{HInd})_2]$	11.7					134.8(C3), 121.9(C4), 121.3(C5), 128.1(C6) 110.4(C7), 123.4(C3a), 140.3(C7a)
$[\text{SnMe}_2\text{Br}_2(\text{HInd})_2]$	11.5					135.1(C3), 121.8(C4), 121.5(C5), 127.8(C6) 110.3(C7), 123.5(C3a), 140.3(C7a)
$[\text{SnEt}_2\text{Cl}_2(\text{HInd})_2]^a$	10.3	28.1				134.9(C3), 122.1(C4), 121.7(C5), 128.4(C6) 110.6(C7), 123.3(C3a), 140.2(C7a)
$[\text{SnEt}_2\text{Br}_2(\text{HInd})_2]^b$	10.8	28.1				135.2(C3), 122.0(C4), 121.6(C5), 128.2(C6) 110.5(C7), 123.3(C3a), 140.3(C7a)
$[\text{SnBu}_2\text{Cl}_2(\text{HInd})_2]^c$	29.9	27.5	26.6	13.9		135.5(C3), 121.8(C4), 121.4(C5), 127.7(C6) 110.3(C7), 123.5(C3a), 140.3(C7a)
$[\text{SnBu}_2\text{Br}_2(\text{HInd})_2]^d$	28.5	28.0	26.4	13.9		135.3(C3), 121.6(C4), 121.4(C5), 127.5(C6) 110.2(C7), 123.6(C3a), 140.4(C7a)
$[\text{SnPh}_2\text{Cl}_2(\text{HInd})_2]^e$					141.0(Ci), 135.4(Co), 131.6(Cp), 129.8(Cm)	135.4(C3), 121.9(C4), 121.6(C5), 128.0(C6) 110.4(C7), 123.3(C3a), 140.1(C7a)
$[\text{SnPh}_2\text{Br}_2(\text{HInd})_2]^f$					140.2(Ci), 134.9(Co), 131.8(Cp), 129.9(Cm)	135.3(C3), 121.6(C4), 121.4(C5), 127.6(C6) 110.2(C7), 123.5(C3a), 139.0(C7a)

^a $^nJ(^{119}\text{Sn}-^{13}\text{C})$: $n=1$, 49.4; $n=2$, 679.2; ^b $^nJ(^{119}\text{Sn}-^{13}\text{C})$: $n=1$, 46.3; $n=2$, 594.3; ^c $^nJ(^{119}\text{Sn}-^{13}\text{C})$: $n=1$, 509.4; $n=2$, 36.0; ^d $^nJ(^{119}\text{Sn}-^{13}\text{C})$: $n=2$, 33.5; $n=3$, 86.4; ^e $^nJ(^{119}\text{Sn}-^{13}\text{C})$: $n=2$, 65.0; $n=3$, 90.2; $n=4$, 18.5; ^f $^nJ(^{119}\text{Sn}-^{13}\text{C})$: $n=2$, 63.2; $n=3$, 87.8; $n=4$, 17.9.

1445 cm^{-1} in $[\text{SnEt}_2\text{Cl}_2(\text{HInd})_2]$, suggesting that all these compounds have similar coordination. The positions of $\nu(\text{N-H})$ (e.g. 3210 cm^{-1} in $[\text{SnMe}_2\text{Cl}_2(\text{HInd})_2]$ and 3304 cm^{-1} in $[\text{SnEt}_2\text{Cl}_2(\text{HInd})_2]$, as against 3523 cm^{-1} in indazole vapour [11]) suggest that the $\text{N-H} \cdots \text{X}$ bond identified in the two methyl derivatives by X-ray diffraction is also present in the other compounds. Table 5 shows the chief vibrational bands of the SnR_2X_2 fragment, which are located at positions close to those found for other complexes in which the presence of an all-trans octahedral $\text{SnR}_2\text{X}_2\text{N}_2$ fragment has been confirmed by X-ray diffraction [1–5].

3.3. Mössbauer spectra

The Mössbauer data listed in Table 6 are typical of all-trans octahedral $\text{SnR}_2\text{X}_2\text{L}_2$ compounds in which the ligand L is coordinated via a nitrogen atom, and so support the hypothesis that the ethyl, butyl and phenyl derivatives synthesized in this work have the same configuration as the methyl compounds. ΔE_Q values similar to those of Table 6 have been reported for the bis pyridine adducts of SnR_2X_2 [12,13], while the thiazole derivatives have somewhat lower values (which has led to calculation of a slightly negative p.q.s. (-0.2 mm s^{-1}) attributable to its sulphur atom [5]). By the point charge model for the crystal structures of $[\text{SnMe}_2\text{X}_2(\text{HInd})_2]$ ($\text{X} = \text{Cl}$ and Br), the mean ΔE_Q value for the dialkyl complexes prepared in this work, 4.21 mm s^{-1} , implies that the contributions of the two X and two HInd ligands to the electric field gradient are virtually zero, and hence that the p.q.s. of the indazole nitrogen is zero.

The isomer shift values are in full accord with the electronegativities of the various substituents, and it is worth noting that the replacement of Me with Et or Bu has a larger effect than the replacement of chlorine with bromine. Closely similar values have been reported for the thiazole adducts, while those for the pyridine adducts, though showing the same trends, are about 0.2 mm s^{-1} smaller [12]. This is due to the s electron density at the tin nucleus being less after complexation with indazole or thiazole than after complexation with pyridine.

3.4. Studies in solution

The molar conductivities of 10^{-3} M solutions of the complexes in MeCN show them all to be non-ionogenic in this solvent [14]. Tables 7 and 8 list the significant parameters of the ^1H and ^{13}C NMR spectra in CDCl_3 . The free indazole signals are only very slightly shifted in the spectra of the complexes, showing that, as in other systems [1–6], donor–acceptor interaction only partially persists in solution. For the methyl derivatives the values of $^2J(^{119}\text{Sn}-^1\text{H})$ are only slightly greater than

those of the free acceptors (69.82 Hz for the chloride and 68.92 Hz for the bromide [15]), again suggesting that extensive dissociation of the indazole ligand occurs. For the SnMe_2Cl_2 derivative the $^2J(^{119}\text{Sn}-^1\text{H})$ value is intermediate between the 80.5 Hz of the pyrazole analogue [2] and the 73.8 Hz of the thiazole analogue [5], showing that the extent of dissociation is also intermediate. Similar dissociation behaviour by the ethyl derivatives is shown by comparison of their 2J and $^3J(^{119}\text{Sn}-^1\text{H})$ values with those of the pyrazole [1] and thiazole [5] complexes.

The corresponding $^nJ(^{119}\text{Sn}-^1\text{H})$ constants of the butyl complexes could not be determined under the experimental conditions used, and the ^{13}C data are no more informative, except that a slight deshielding of the C(1) signal with respect to its position in the SnBu_2Cl_2 spectrum [4] indicates partial preservation of coordination to indazole. The ^1H spectra of the phenyl complexes show two multiplets attributed to H(Co) and H(Cm, Cp); comparison of their positions in the spectra of the chloro derivative and SnPh_2Cl_2 [16] shows only very slight shielding of H(Co) upon coordination, which again suggests extensive dissociation of the indazole ligand, and this dissociation is confirmed by the slight shift of the ^{13}C signal of Ci [16,17].

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