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Complexes of diethyldihalotin(IV) with imidazole and pyrazole. The crystal structure of dibromobis(pyrazole)diethyltin(IV) *

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Abstract

Imidazole and pyrazole reacts with diethyltin(IV) dihalides to yield adducts of the type $Et_2SnX_2L_2$ (X = Cl, Br). The structure of dibromobis(pyrazole)diethyltin(IV) has been determined by X-ray diffraction. (Crystal data: $C_{10}H_{18}Br_2N_4Sn$, $M = 472.79$, monoclinic, $C2/c$, a 1426.6(3), b 888.4(1) c 1393.9(6) pm, β 114.83(3)°, V 1603.3×10^6 pm^3, $Z = 4$, $R = 0.035$). The crystal consists of discrete *trans*-$SnEt_2Br_2(HPz)_2$ units with the metal atom octahedrally coordinated to two Br atoms (Sn–Br: 274.6(1) pm, Br–Sn–Br: 180°), two ethyl carbons (Sn–C: 209.3(7) pm, C–Sn–C: 180°), and two pyrazole groups (Sn–N: 235.6(4) pm, N–Sn–N: 180°). The pyrazole ligands are intramolecularly and intermolecularly hydrogen bonded to the bromine atoms. The IR data are consistent with this *trans*-stereochemistry for all the compounds prepared. The ^1H NMR data indicate that the pyrazole compounds dissociate fully in DMSO-d_6 and partially in $CDCl_3$.

Introduction

In recent years there have been a considerable number of structural studies on Me_2SnX_2 or methyl derivative complexes (1, 2, 3 and ref. therein), but Et_2SnX_2 complexes have received less attention [4,5]. We previously described the isolation and characterization of $Me_2SnX_2L_2$ for L = imidazole (HIm) and L = pyrazole (HPz) [6]; with the aim of establishing the molecular structures of the analogous Et_2SnX_2 complexes we treated Et_2SnX_2 (X = Cl, Br) with the same ligands. We

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Table 1

Analytical and some physical data of the compounds prepared

		Analysis (Found (calcd.) (%))			Colour	M.P. (°C)	Λ_m [a]	M.W. (F.W.)
		C	N	H				
I	$Et_2SnCl_2(HPz)_2$	31.9 (31.3)	15.0 (14.6)	4.8 (4.7)	White	153	8.0	249.5 [b] (383.9) 268.2 [c]
II	$Et_2SnBr_2 (HPz)_2$	25.2 (25.4)	11.7 (11.9)	3.9 (3.8)	White	165	9.2	247.4 [b] (472.8) 333.2 [c]
III	$Et_2SnCl_2(HIm)_2$	30.5 (31.3)	14.9 (14.6)	4.6 (4.7)	White	160	26.2	
IV	$Et_2SnBr_2(HIm)_2$	25.5 (25.4)	12.1 (11.9)	3.9 (3.8)	White	209	44.6	

[a] 10^{-3} *M* in MeCN. [b] In $CHCl_3$. [c] In C_6H_6.

describe below the results of this study, including the crystal structure of $Et_2SnBr_2(HPz)_2$.

Experimental

Reagent and preparations

Diethyltin dichloride (Ventron), diethyltin dibromide (Ventron), pyrazole (Ega) and imidazole (Ega) were used as supplied. Solvents were purified by the usual methods. Adducts were prepared by slow addition of a solution of the ligand in methylene chloride to a stirred solution of Et_2SnX_2 in the same solvent. In a typical preparation a solution of pyrazole (5.12×10^{-3} mol) in 20 cm^3 of CH_2Cl_2 was added dropwise to a solution of Et_2SnBr_2 (2.56×10^{-3} mol) in 20 cm^3 of CH_2Cl_2 and the mixture was stirred for two days. The white powder formed was filtered off and dried under vacuum. Crystals suitable for the X-ray analysis were obtained by slow evaporation of the filtrate. Analyses for the complexes are shown in Table 1.

Measurements

Elemental analyses were performed with a Perkin–Elmer 240B apparatus. Melting points were determined with an Electrothermal apparatus. Infrared spectra were recorded with Nujol mulls or KBr discs on a Perkin–Elmer 180 spectrometer. Molecular weights were measured in a Knauer vapour-pressure osmometer in benzene or $CHCl_3$.

Only the pyrazole derivatives were sufficiently soluble in $CDCl_3$ for recording of the ^1H NMR spectra, which were obtained at 250 MHz on a Bruker WM 250 spectrometer for freshly prepared solutions. Table 5 shows the main parameters obtained from first-order analysis of the spectra; the similarity between our data for Et_2SnCl_2 and those reported by Barbieri and Taddei [7] confirm the validity of this approach.

Crystal structure determination

A colourless prismatic crystal of $Et_2SnBr_2(HPz)_2$ measuring approximately $0.50 \times 0.35 \times 0.10$ mm was used. Data for structure determination were obtained at room temperature with a CAD-4 Enraf–Nonius automated four-circle diffractome-

Table 2

Crystal data for $Et_2SnBr_2(HPz)_2$

Molecular formula	$C_{10}H_{18}Br_2N_4Sn$
Molecular weight	472.79
Crystal class	monoclinic
Space group	$C2/c$
Lattice constants	a 1426.6(3) pm b 888.4(1) pm c 1393.9(6) pm β 114.83(3)°
Cell volume	V 1603.3 10^6 pm^3
Formula units	$Z = 4$
Density	ρ_x 1.959 g. cm^{-3}
Absorption coefficient	$\mu(Mo\text{-}K_\alpha)$ 65.258 cm^{-1}

Table 3

Atomic coordinates and isotropic equivalent thermal parameters B_{eq} ($pm^2 \times 10^4$) for $Et_2SnBr_2(HPz)_2$ with esd in parentheses; parameters for the tin atoms were fixed by symmetry

Atom	x	y	z	B_{eq} [a]
Sn	0.500	0.500	0.500	2.88(2)
Br	0.42535(6)	0.7203(1)	0.58748(6)	4.50(2)
N(1)	0.6611(4)	0.5187(9)	0.6470(4)	4.0(2)
N(2)	0.6745(5)	0.5785(9)	0.7418(5)	4.9(2)
C(3)	0.7709(7)	0.559(1)	0.8120(7)	5.9(3)
C(4)	0.8220(6)	0.490(1)	0.7618(7)	6.2(3)
C(5)	0.7517(5)	0.464(1)	0.6606(6)	4.5(2)
C(6)	0.4587(8)	0.339(1)	0.5849(8)	6.8(3)
C(7)	0.407(1)	0.209(3)	0.536(1)	17.6(8)

[a] $B_{eq} = 4/3\ (B_{11}a^{\star 2} \ldots + B_{12}a^{\star}b^{\star} \cos\gamma \ldots)$

ter with Mo-K_α radiation and graphite monochromator. Cell constants were determined from the setting angles of 25 reflections (Table 2). The systematic absences observed suggested the space group to be either Cc or $C2/c$. With the ω/θ scan mode, 1698 reflections were collected in the range θ 3–30°. Of 1494 symmetry-independent reflections ($R_{int} = 0.014$), 1052 with $|F_o| > 3\sigma(|F_o|)$ were considered as observed and used for refinement. Absorption corrections were applied at a later stage in the refinements [8]. For the calculations the centrosymmetric space group $C2/c$ was assumed, a choice later confirmed by successful refinement of the structure. The structure was solved by Patterson and Fourier methods [9] and the hydrogen atoms of the ethyl groups were fixed at calculated positions. In the final refinement all atoms other than H were assigned anisotropic temperature parameters. The positions of hydrogen atoms in the pyrazole ring were used only for structure factor calculations. The final refinement converged at $R = 0.035$, $R_w = 0.038$. Positional and thermal parameters are given in Table 3 *.

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* Further details of the structure determination have been deposited as Supplementary Publication No. CSD 52949. Copies may be obtained through the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen.

Results and discussion

Table 1 shows the elemental analyses and some relevant physical properties of the complexes. The conductivities show that the complexes are unionised in solution in MeCN, and the molecular weights found indicate dissociation.

Description of the structure

The atomic numbering scheme is show in Fig. 1. Atomic coordinates are given in Table 3 and selected bond distances and angles in Table 4.

The Sn atom is octahedrally coordinated to two Br atoms, two ethyl groups, and two pyrazole groups in an all-*trans* configuration with the Sn atom at a centre of symmetry. The pyrazole ligand binds to the metal through the pyridine-like nitrogen, and the bond lengths in the ring are close to those in pyrazole-Me_2SnX_2 complexes [2,6]. The rings are essentially planar, with negligible deviation from the best least-squares plane. The Sn–N bond length is similar to those in $Me_2SnX_2(HPz)_2$ [2,6] and Et_2SnCl_2(bipy) [4], but slightly shorter than that in dichlorodiethyl[3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine]tin(IV) [5]. The Sn–C distance is close to those in the two diethyldichlorotin(IV) compounds [4,5].

The dihedral angle between the pyrazole ring and the SnN(1)Br plane is 18°, smaller than those found in the all-*trans* complexes $Me_2SnX_2L_2$ for imidazole, pyrazole and pyridine ligands [2 and ref. therein, 6].

The presence of intermolecular and intramolecular hydrogen bonds of similar intensities is suggested by the following distances and angles: N(2)–Br, 352.5(6) pm; H(N(2))–Br, 278(5) pm; N(2)–H–Br, 136.5(5)°; N(2)–Br^{ii}, 348.3(8) pm; H(N(2))–Br^{ii}, 281(7) pm; N(2)–H–Br^{ii}, 129(4)°, (symmetry code: (*ii*) $1-x$, y, $1/2-z$). Although such bonds have been detected in other R_2SnX_2 azole com-

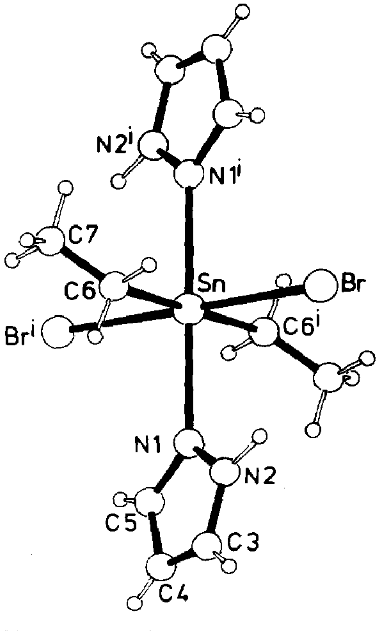

Fig. 1. The molecular structure of $Et_2SnBr_2(HPz)_2$ with the atom numbering scheme.

Table 4

Important bond lengths (pm) and angles (deg) for $Et_2SnBr_2(HPz)_2$

Bond lengths	
Sn–Br	274.6(1)
Sn–N(1)	235.6(4)
Sn–C(6)	209.3(7)
Bond angles	
Br–Sn–Br$^{i\,a}$	180
Br–Sn–N(1)	89.0(1)
Br–Sn–N(1^i)	91.0(1)
Br–Sn–C(6)	89.0(2)
Br–Sn–C(6^i)	91.0(2)
N(1)–Sn–N(1^i)	180
N(1)–Sn–C(6)	87.7(2)
N(1)–Sn–C(6^i)	92.3(2)
C(6)–Sn–C(6^i)	180

[a] Symmetry code: (*i*) $-x, -y, -z$.

plexes [2 and ref. therein, 6], we know of no other examples of these systems for which inter- and intra-molecular bonds of similar intensity has been observed. Figure 2 shows stereoscopically these hydrogen bonds.

IR Spectra

The coordination-induced frequency shifts of the most significant ring stretching vibrations and the NH stretching vibration are similar to those observed in the complexes of these ligands with Me_2SnX_2 [6]. The asymmetric Sn–C bands (540, 530, 535 and 525 cm^{-1} for compounds I, II, III and IV, respectively) and the asymmetric Sn–Cl bands (very strong broad bands at 200 cm^{-1} for I and III) lie at positions close to those detected in $Et_2SnCl_2(Py)_2$ [10]. The similarity of these IR data for compounds I–IV seems to indicate that all have identical *trans*-stereochemistry.

^1H NMR

Owing to solubility problems. ^1H NMR spectra, in $CDCl_3$ and DMSO-d_6, were only recorded for the pyrazole complexes (Table 5). The chemical shifts and the $^2J(^{117/119}Sn-^1H)$ coupling constants in DMSO-d_6 are similar to those observed for the free donor and free acceptor in this solvent. This indicates that, as for $Me_2SnX_2(HPz)_2$ [6], the high donor ability and high concentration of the solvent lead to the formation of Et_2SnX_2 (DMSO-d_6)$_n$ compounds, the pyrazole ligand being displaced from the tin coordination sphere. In the weaker donor solvent $CDCl_3$ the chemical shifts and the $^2J(^{117/119}Sn-^1H)$ coupling constants differ from those observed for the free donor and acceptor; the methyl group signals are strongly shielded and those of the methylene groups slightly deshielded, and the $^2J(^{117/119}Sn-^1H)$ coupling constants are larger than those for the free acceptors. These observations indicate that some tin–pyrazole coordination remains in $CDCl_3$ solution.

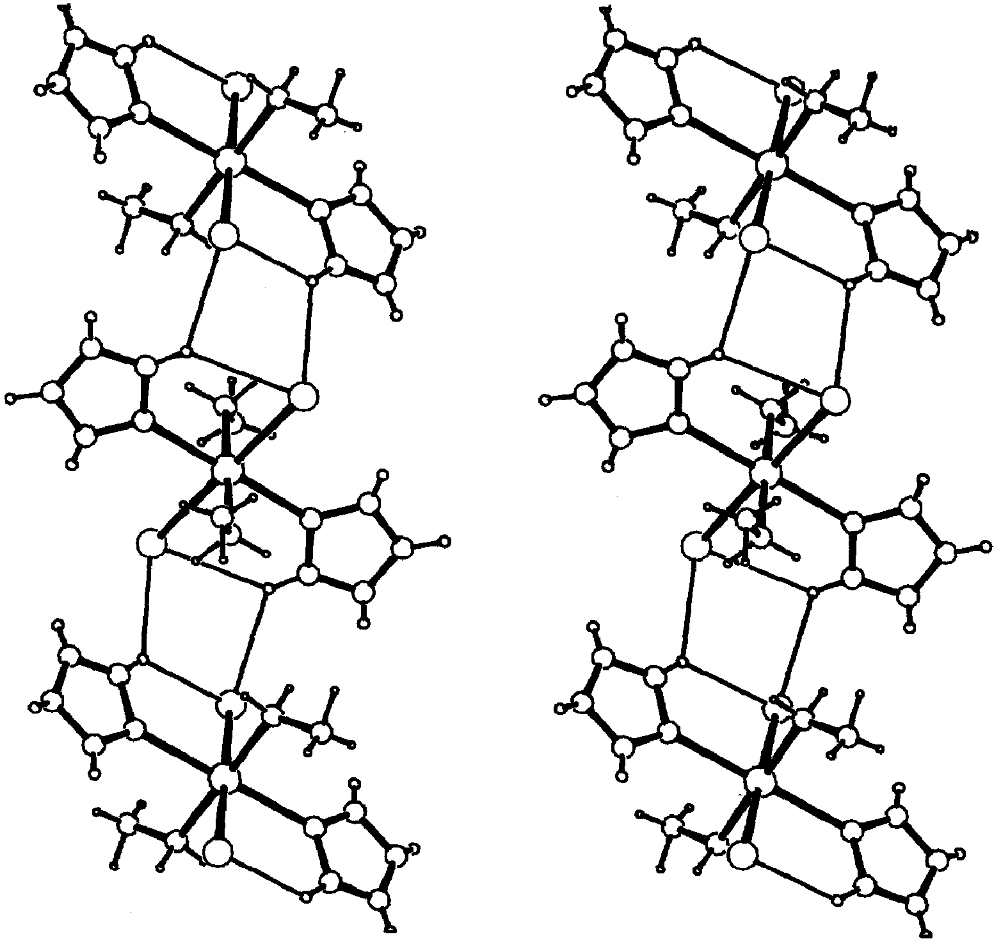

Fig. 2. A stereoview of the molecular packing and the hydrogen bonds for $Et_2SnBr_2(HPz)_2$.

The $^2J(^{119}Sn-^1H)$ coupling constant has been related to the C–Sn–C angle ϕ for dimethyltin(IV) compounds [11], dibutyltin(IV) compounds [12], and other diorganotin(IV) derivatives with various ligands [13]. For all these species the coupling constant was positively correlated with ϕ. As previously pointed out [6,12], however, this relationship must be used with caution when attempting to establish the stereochemistry of the tin atom in compounds which can undergo partial dissociation. Thus although substitution of the value of $^2J(^{119}Sn-^1H)$ in the equation of Howard et al. [13] yields a C–Sn–C angle of ca. 124° for the chlorine derivative, apparently implying, distortion of the octahedral structure adopted by $Et_2SnCl_2(HPz)_2$ in the solid state, this value probably reflects partial dissociation to give a 1/1 adduct whose R groups are probably in a *cis* disposition [14,15]:

$$R_2SnX_2L_2 \rightleftharpoons R_2SnX_2L + L \qquad (1)$$

Two arguments support this hypothesis: (i) the molecular weight measurements (see Table 1) indicate dissociation; and (ii) if equilibrium 1 holds, then an increase in the excess of L should shift the system to the left, thus increasing the value of

Table 5

^{1}H NMR parameters (δ in ppm from TMS and J in Hz) for $Et_2SnX_2(HPz)_2$ complexes and related compounds

Compound	Solvent	$\delta(CH_3)$	$\delta(CH_2)$	$J(CH_2$ $-CH_3)$	$^2J(^{117/119}Sn$ $-^1H)$	$^3J(^{117/119}Sn$ $-^1H)$	δ(ligand) [a]
HPz	$CDCl_3$	–	–	–	–	–	5.83 (H(4),t) [b] 7.12 (H(3), H(5),d) 12.12 (NH,s,b)
Et_2SnCl_2	$CDCl_3$	1.43(t)	1.79(q)	7.7	47.9/50.3 [7]	130.3/135.9	–
Et_2SnBr_2	$CDCl_3$	1.40(t)	1.85(q)	7.9	43.7/45.6	131.0/137.1	–
Et_2SnCl_2-$(HPz)_2$	$CDCl_3$	1.22(t)	1.80(q)	7.8	71.5/74.8	157.0/164.3	6.46 (H(4),t) 7.78 (H(3),H(5),d) 10.82 (NH,s)
Et_2SnBr_2-$(HPz)_2$	$CDCl_3$	1.22(t)	1.92(q)	7.8	67.1 [c]	156.1/163.2	6.44 (H(4),t) 7.78 (H(3),H(5),d) 10.30 (NH,s)
HPz	DMSO-d_6						6.25 (H(4)s,b) 7.60 (H(3),H(5),s,b) 12.83 (NH,s,vb)
Et_2SnCl_2	DMSO-d_6	1.28(t)	1.58(q)	7.8	93.6/98.1 [7]	169.8/177.8	–
Et_2SnBr_2	DMSO-d_6	1.23(t)	1.65(q)	7.8	96.7/101.0	178.2/186.4	–
Et_2SnCl_2-$(HPz)_2$	DMSO-d_6	1.25(t)	1.53(q)	7.7	97.2/101.5	170.8/178.7	6.24 (H(4),t) 7.59 (H(3),H(5),s) 12.80 (NH,s,b)
Et_2SnBr_2-$(HPz)_2$	DMSO-d_6	1.24(t)	1.66(q)	7.8	96.7/100.5	178.1/186.3	6.23 (H(4),s) 7.58 (H(3),H(5),s) 12.80 (NH,s,b)

[a] Numberig scheme $\overline{\mathrm{NC(3)C(4)C(5)N}}$. [b] t, triplet; d, doublet; s, singlet; b, broad; vb, very broad; q, quartet. [c] ^{117}Sn–^{119}Sn satellites not resolvable under our experimental conditions.

$^2J(^{119}Sn-^1H)$ until only $R_2SnX_2L_2$ species with *trans* R groups are present; when HPz is added to an $Et_2SnCl_2(HPz)_2$ solution in $CDCl_3$ until a 1/3 molar ratio of complex to ligand is reached, the coupling constant does, in fact, rise to 92.4 Hz.

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