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Complexes of dimethyldihalotin(IV) with imidazole and pyrazole: the crystal structure of dibromobis(pyrazole)dimethyltin(IV)

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Abstract

A series of neutral adducts of dimethyltin(IV) dihalides of general formula $Me_2SnX_2L_2$ (where L = imidazole, pyrazole) has been prepared. The structure of the complex dibromobis(pyrazole)dimethyltin(IV) has been determined by X-ray diffraction. (Crystal data: $Br_2C_8H_{14}N_4Sn$, $M = 444.7$; orthorhombic, *Pbca*, *a* 7.644(1), *b* 13.955(7), *c* 26.249(4) Å, *V* 2800(2) Å^3, $Z = 8$, $R = 0.041$). The compound consists of discrete *trans*-$SnMe_2Br_2(HPz)_2$ units with the metal atom octahedrally coordinated to two Br atoms (Sn–Br 2.703(2), 2.766(2) Å; Br–Sn–Br 178.78(7)°), to two methyl carbons (both Sn–C 2.13(2) Å; C–Sn–C 179.0(6)°), and to two pyrazole groups (Sn–N 2.34(1), 2.36(1) Å; N–Sn–N 175.8(4)°). The dihedral angle between the two pyrazole rings is 8.9°. The IR data are consistent with this *trans*-stereochemistry for all the complexes. The ^1H NMR data indicate that the pyrazole compounds dissociate in DMSO-d_6 solution but in $CDCl_3$ solution the *trans*-configuration can be also present if an excess of the ligand is present.

Introduction

The biological activity of the dialkyltin(IV) dihalide complexes [1] has stimulated considerable research into the chemistry of these compounds in the last years. The study of complexes with monodentate nitrogen donor ligands could be very useful in increasing understanding of the interaction of the complexes with DNA (where N-atoms of nucleic acid bases could be involved) [2,3] and also of the effect on the reactivity of $R_2SnX_2(L–L)$ systems (where L–L is a nitrogen donor bidentate ligand) of the Sn–N bond distance. We have therefore prepared a series of diorganotin (IV) complexes derived from such ligands with the aim of studying their molecular structures. We describe here the reactions between Me_2SnX_2 (X = Cl, Br) and imidazole (HIm) or pyrazole (HPz) and the crystal structure of the compound $Me_2SnBr_2(HPz)_2$.

Experimental

Preparations. Dimethyltin dichloride (Ventron), dimethyltin dibromide (Ventron), pyrazole (Ega), and imidazole (Ega) were used as supplied. The solvents were purified by usual methods. Adducts were prepared by adding solutions of the appropriate ligand in methylene chloride slowly with stirring to Me_2SnX_2 in the same solvent. In a typical preparation, a solution of pyrazole (6.4×10^{-3} mol) in 20 cm^3 CH_2Cl_2 was added dropwise to a solution of Me_2SnBr_2 (3.2×10^{-3} mol) in 20 cm^3 CH_2Cl_2. The mixture was stirred for seven days then cooled, and the crystalline product was filtered and dried in vacuo.

Measurements. Analytical data were obtained with a Perkin–Elmer 240B apparatus. Melting points were determined in a Electrothermal apparatus. Infrared spectra were recorded as Nujol or KBr discs with a Perkin–Elmer 180 spectrometer. ^1H NMR spectra were recorded with a Bruker WM 250 spectrometer.

Crystal structure determination. A hygroscopic, prismatic, colourless crystal, $0.40 \times 0.20 \times 0.28$ mm, sealed in a ⌀ 0.5 mm Lindemann capillary; Enraf Nonius CAD-4 diffractometer, graphite monochromated Mo-K_α radiation; cell parameters by least squares on setting angles from 25 reflections, $10.3 < \theta < 18.9°$, ω–2θ scans, scan width $(0.70 + 0.35 \tan(\theta))°$, max. scan speed 10 min^{-1}, *hkl* range: $h < 9$, $k < 15$, $-1 < l < 29$, θ_{max} 23°; standard $10\overline{14}$ varied $\pm 3.5\%$ of mean intensity over data collection; 2044 reflections measured, 1947 unique, R_{int} 2.3%, 940 observed with $I > 3\sigma(I)$, Lp and absorption corrections (max. and min. transmission factors 0.3000, 0.143); structure solved by Patterson techniques. In final cycles of full matrix least squares refinement all non-H atoms anisotropic. Pyrazole rings-H atoms included at fixed positions (C–H 1.00(1) Å) based on those found in difference synthesis, all with fixed isotropic temperature factor U 0.05 $Å^2$; methyl-H atoms not found and not included in the model. Function minimized $\Sigma w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0.0025\ F_o^2]^{-1}$, 137 parameters refined. Inspection of F_c and F_o values indicated that a correction for secondary extinction was required: $F_{corr} = F_c\ [1.0 - \chi F_c^2/\sin\theta]$, where χ refined to 4.4×10^{-8} in the final run; $R = 0.041$, R_w 0.044; max.shift/error 0.01, $\Delta\rho$ excursions within 0.80 and -1.00 $eÅ^{-3}$. Scattering factors for non-H atoms from [6] with corrections for anomalous dispersion from [7] and for H-atoms from [8]. Programs used: SHELX-76 [9] and ORTEP [10]. Calculations were performed on a VAX 11/780 computer.

Crystal data: $Br_2C_8H_{14}N_4Sn$, M 444.7, orthorhombic, *Pbca*, a 7.644(1), b 13.955(7), c 26.249(4) Å, V 2800(2) $Å^3$, Z 8, D_x 2.110 g cm^{-3}, λ(Mo-K_α) 0.71073 Å, μ 7.27 mm^{-1}, $F(000) = 1680$, T 296 K.

A table of thermal parameters and lists of structure factors are available from the authors.

Results and discussion

The analyses, colours, melting points and molar conductivities of the complexes are shown in Table 1. The conductivities show that the complexes are unionised in CH_3CN.

Table 1

Analytical and some physical data for the compounds prepared

	Analysis (Found (calcd.) (%))			Colour	M.p. (°C)	Λ_M [a]
	C	N	H			
I $Me_2SnCl_2(HPz)_2$	26.6	16.7	3.7	White	138	8.9
	(27.0)	(15.8)	(4.0)			
II $Me_2SnBr_2(HPz)_2$	21.4	12.9	3.2	Colourless	130	2.8
	(21.6)	(12.6)	(3.2)			
III $Me_2SnCl_2(HIm)_2$	26.7	16.1	4.1	White	186	17.1
	(27.0)	(15.8)	(4.0)			
IV $Me_2SnBr_2(HIm)_2$	21.4	12.6	3.3	White	191	25.9
	(21.6)	(12.6)	(3.2)			

[a] 10^{-3} *M* in CH_3CN.

Description of the structure. Figure 1 presents a drawing of the molecule showing the atom numbering. Atomic coordinates are given in Table 2 and interatomic bond distances and angles in Tables 3 and 4, respectively. The scattering is heavily dominated by the Sn and Br atoms, which results in a rather low accuracy in the fractional coordinates and consequently in the calculated bond distances and angles between the lighter atoms.

The Sn atom is octahedrally coordinated to two Br atoms, two methyl carbons and two pyrazole groups in a *trans* configuration; the pyrazole ligand bonds to the metal through the pyridine-like nitrogen atom, and the bond lengths in the ring *d*(N(1)–N(2)) 1.34(2) Å) are very close to those in free pyrazole [11] (*d*(N(1)–N(2)) 1.35 Å in pyrazole). The pyrazole rings are essentially planar, with a negligible deviation from the best least-squares plane.

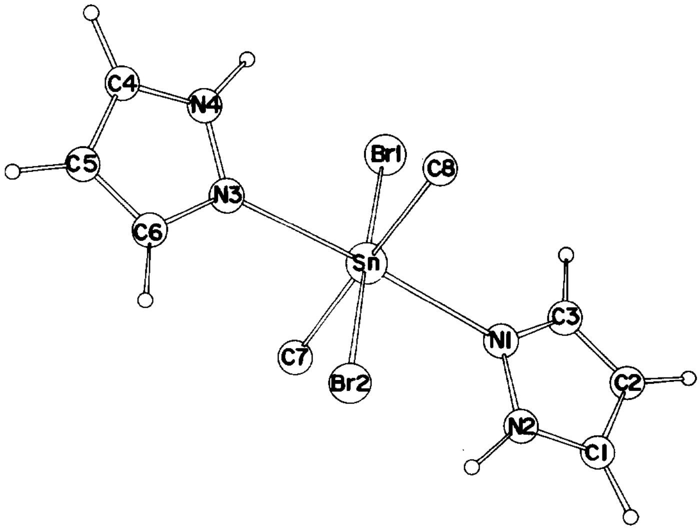


Fig. 1. The molecular structure of $Me_2SnBr_2(HPz)_2$ with the atom numbering scheme.

Table 2

Final atomic parameters with e.s.d.s in parentheses

Atom	x/a	y/b	z/c	B_{eq} ^{a}
Sn	−0.7210(1)	0.1068(1)	0.6257(0)	2.92(4)
Br(1)	−0.4756(2)	0.2255(1)	0.6646(1)	4.30(7)
Br(2)	−0.9765(2)	−0.0140(1)	0.5877(1)	3.85(6)
N(1)	−0.754(2)	0.0220(9)	0.7029(5)	3.7(5)
N(2)	−0.809(2)	−0.069(1)	0.7069(5)	3.9(5)
C(1)	−0.803(2)	−0.101(1)	0.7549(6)	3.9(6)
C(2)	−0.738(3)	−0.027(1)	0.7830(6)	4.8(7)
C(3)	−0.704(2)	0.044(1)	0.7485(5)	4.0(6)
N(3)	−0.702(2)	0.1827(9)	0.5464(5)	3.7(5)
N(4)	−0.667(2)	0.275(1)	0.5377(6)	4.4(6)
C(4)	−0.680(2)	0.299(2)	0.4890(7)	6.1(9)
C(5)	−0.714(3)	0.216(2)	0.4633(7)	6.0(9)
C(6)	−0.735(2)	0.147(1)	0.4993(6)	4.0(6)
C(7)	−0.526(2)	0.008(1)	0.6018(6)	4.2(6)
C(8)	−0.920(2)	0.204(1)	0.6499(5)	3.5(6)

^{a} $B_{eq} = \frac{4}{3}\Sigma_{ij}B_{ij}(a_i \cdot a_j)$

The structure of $Me_2SnBr_2(HPz)_2$ can be compared with those of $Me_2SnBr_2(py)_2$ (py = pyridine) [12] and $[Sn(CH_3)_2Br_2pyz]$, (pyz = pyrazine) [13] in both of which the moiety *trans*-$SnC_2Br_2N_2$ is present. The Sn–Br, Sn–C, and Sn–N bond distances in our complex are close to those in these complexes, and the Sn–C and Sn–N bonds are close to those reported for $Me_2SnCl_2(dmp)_2$ (dmp = dimethylpyrazole) [14], $Me_2SnCl_2(Py)_2$ [12], and $Me_2SnCl_2(NMIz)_2$ (NMIz = N-methylimidazole) [15].

The dihedral angles between the pyrazole ring 1 (N(1),N(2),C(1),C(2),C(3)). and the Sn,N(1),Br(1) plane and between the ring 2 (N(2),N(3),C(4),C(5),C(6)) and the Sn,N(2),Br(2) plane are, respectively, 21.6 and 32.5°, the latter value close to the

Table 3

Interatomic bond distances (Å) for $Me_2SnBr_2(HPz)_2$

Sn–Br(1)	2.703(2)
Sn–Br(2)	2.766(2)
Sn–N(1)	2.36(1)
Sn–N(3)	2.34(1)
Sn–C(7)	2.13(2)
Sn–C(8)	2.13(2)
N(1)–N(2)	1.34(2)
N(1)–C(3)	1.29(2)
N(2)–C(1)	1.34(2)
C(1)–C(2)	1.36(2)
C(2)–C(3)	1.37(2)
N(3)–N(4)	1.34(2)
N(3)–C(6)	1.36(2)
N(4)–C(4)	1.33(2)
C(4)–C(5)	1.37(3)
C(5)–C(6)	1.36(3)

Table 4

Bond angles (°) for $Me_2SnBr_2(HPz)_2$

Br(1)–Sn–Br(2)	178.78(7)
Br(1)–Sn–N(1)	93.3(3)
Br(1)–Sn–N(3)	90.9(3)
Br(1)–Sn–C(7)	91.3(4)
Br(1)–Sn–C(8)	89.6(4)
Br(2)–Sn–N(1)	85.9(3)
Br(2)–Sn–N(3)	89.9(3)
Br(2)–Sn–C(7)	89.6(4)
Br(2)–Sn–C(8)	89.5(4)
N(1)–Sn–N(3)	175.8(4)
N(1)–Sn–C(7)	90.2(5)
N(1)–Sn–C(8)	89.3(5)
N(3)–Sn–C(7)	89.3(5)
N(3)–Sn–C(8)	91.2(5)
C(7)–Sn–C(8)	179.0(6)
Sn–N(1)–N(2)	125.0(1)
Sn–N(1)–C(3)	130.0(1)
N(2)–N(1)–C(3)	104.0(1)
N(1)–N(2)–C(1)	112.0(1)
N(2)–C(1)–C(2)	106.0(1)
C(1)–C(2)–C(3)	105.0(1)
N(1)–C(3)–C(2)	113.0(1)
Sn–N(3)–N(4)	127.0(1)
Sn–N(3)–C(6)	129.0(1)
N(4)–N(3)–C(6)	104.0(1)
N(3)–N(4)–C(4)	113.0(1)
N(4)–C(4)–C(5)	106.0(1)
C(4)–C(5)–C(6)	106.0(1)
N(3)–C(6)–C(5)	111.0(1)

33° found in the $Me_2SnCl_2(dmp)_2$ structure [14]. On the other hand, the differences between the N–Sn–X bond angles are 7.4 and 1.0° for the two ligands and those for and between the the Sn–N–N and Sn–N–C angles are 5° and 2° for the two ligands. The data seem to confirm that the intramolecular non-bonded interactions at the methyl group of 3,5-dimethylpyrazole are responsible [14] for larger differences in $Me_2SnCl_2(dmp)_2$ but that they have a smaller influence on the orientation of the rings with respect to the Sn–N–X plane.

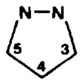
The short intermolecular contacts N(2)–Br(1) 3.49(2) Å, $H(N_2)$–Br(1) 2.64(2) Å and the value of the angle N(2)–H–Br(1) 131.5(8)° suggest the presence of a hydrogen bond similar to those found in $Me_2SnCl_2(dmp)_2$ [14] and $Me_2SnCl_2(NMI_2)_2$ [15], and generally in complexes in which the coordinated pyrazole ring is present [16–18].

IR Spectra. The small frequency shifts of the more significant ring stretching vibrations (in the range 1540–1360 cm^{-1} for HPz and 1575–1325 cm^{-1} for HIm) upon coordination, are similar to those previously reported [19,20], and are in accordance with bonding through the pyridine-like nitrogen and with the small observed structural modifications in the HPz ligand. The position of the N–H stretching band is consistent with the presence of the hydrogen bond observed in the crystal.

Table 5

^{1}H NMR parameters (δ in ppm from TMS and J in Hz) for Me_2SnX_2 $(HPz)_2$ complexes and related compounds

Compound	Solvent	$\delta(Sn-CH_3)$	$^2J(^{117}Sn-H/$ $^{119}Sn-H)$	δ(Ligand) [a]
HPz	DMSO-d_6			6.25 (H_4,s,b) [b] 7.60 (H_3,H_5,b) 12.83 (N-H,s,vb)
Me_2SnCl_2	DMSO-d_6	1.03	108.5/113.5	
Me_2SnBr_2	DMSO-d_6	1.23	108.7/112.9	
Me_2SnCl_2 $(HPz)_2$	DMSO-d_6	1.02	107.5/112.4	6.25 (H_4,t) 7.60 (H_3,H_5,d)
Me_2SnBr_2 $(HPz)_2$	DMSO-d_6	1.28	108.3/113.3	6.40 (H_4,t) 7.68 (H_3,H_5,d) 9.42 (N-H,s,b)
HPz	$CDCl_3$			5.83 (H_4,t) 7.12 (H_3,H_5,d) 12.12 (N-H,s,b)
Me_2SnCl_2	$CDCl_3$	1.23	66.82/69.82	– [c]
Me_2SnBr_2	$CDCl_3$	1.44	65.70/68.92	– [c]
Me_2SnCl_2 $(HPz)_2$	$CDCl_3$	1.22	77.0/80.5	6.40 (H_4,t) 7.68 (H_3,H_5,d) 9.42 (NH,s,b)
Me_2SnBr_2 $(HPz)_2$	$CDCl_3$	1.43	79.1/82.6	6.41 (H_4, t) 7.74 (H_3,H_5,d) 9.98 (N-H,s)

[a] 

. [b] t = triplet, d = doublet, s = singlet, b = broad. [c] G. Barbieri and F. Taddei, J. Chem. Soc. Perkin Trans. II, (1972) 1327.

In the IR spectrum, the asymmetric Sn–C stretching bands (570, 560, 560 and 565 cm^{-1} for compound I, II, III and IV, respectively) have frequencies close to the corresponding bands for other similar systems [21,22]. The symmetric Sn–C stretching mode is observed in the IR spectrum of compound I only as a weak band at 520 cm^{-1}. Strong bands at 240 cm^{-1} (I) and at 225 cm^{-1} (III) can be assigned to the Sn–Cl asymmetric stretching mode and those at 200, 190, 210 and 200 cm^{-1} (compounds I to IV respectively) can be tentatively assigned to the Sn–N stretching modes. The similarity of these data for compounds I, III and IV with those observed for $Me_2SnBr_2(HPz)_2$, seems to indicate an identical *trans* stereochemistry for all the complexes prepared.

^{1}H NMR. Table 5 shows the most relevant ^{1}H NMR spectra parameters of the donor, acceptors, and complexes in DMSO-d_6 and $CDCl_3$. In DMSO-d_6 the chemical shifts and the ^2J(Sn–H) constants of the Me_2Sn fragment are practically the same as those for the acceptors in the same solvent, and the signals of the ligands also appear at the same positions observed for free pyrazole. It can thus be concluded that in DMSO-d_6 solution the adducts dissociate, according to eq. 1.

$$Me_2SnX_2(HPz)_2 + n\ \text{DMSO-}d_6 \rightleftarrows Me_2SnX_2(\text{DMSO-}d_6)_n + 2HPz \qquad (1)$$

When a less donating solvent ($CDCl_3$) was used a somewhat different situation was observed. The coupling constants ^2J(Sn–H) (now slightly sensitive to the adduct concentration) are clearly larger for the adducts than for the free acceptors, and the ligand protons are deshielded with respect to those in the free donor. These data suggest that the donor–acceptor interaction between Me_2SnX_2 and HPz is maintained in the solution. The ^2J(Sn–H) constants are, however, lower than those expected for compounds with coordination number six around the tin atom, suggesting, instead, coordination number five [15,23]. In fact, use of the Lockhart and Manders equation for Me_2SnX_2 [24] indicates C–Sn–C angles of 126.1° (X = Cl) and 128° (X = Br), values consistent with a trigonal bypiramidal structure with the two methyl groups in equatorial positions, a normal situation for 1/1 adducts [25]. Consequently, it can be concluded that in $CDCl_3$ the compounds undergo partial dissociation (eq. 2).

$$Me_2SnX_2(HPz)_2 \rightleftarrows Me_2SnX_2(HPz) + HPz \qquad (2)$$

This conclusion is confirmed by the spectra of the complexes in the presence of an excess of the ligand. In this case, the ^2J(Sn–H) increases by 90 to 110 Hz, depending on the amount of ligand added. The new values indicate a coordination of six around the tin atom, and show that equilibrium 2 is displaced to the left. The greater extent of dissociation of these adducts compared with those of 3,5-dimethylpyrazole may be due to the inductive effect of the methyl groups which increases the donor ability of the ring [26] and so stabilizes the 1/2 adduct.

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