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Synthesis, Spectroscopic Studies (Mössbauer and Infrared), and the Crystal and Molecular Structure of the Organotin(IV)–pyrazine Adducts [$Sn(CH_3)_2Cl_2$]$_2$pyz and [$Sn(CH_3)_2Br_2$pyz]

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Abstract

Two adducts [$Sn(CH_3)_2Cl_2$]$_2$pyz (**Ia**) and [$Sn(CH_3)_2Br_2$pyz] (**Ib**) (pyz = pyrazine) have been synthesized and characterized in the solid state. Infrared and Mössbauer spectroscopies suggest a five-coordinated species for the **Ia** complex with an angular C–Sn–C bond and a six-coordinated compound with a linear C–Sn–C bond for the **Ib** complex. X-ray diffraction studies confirm a distorted trigonal bipyramidal geometry with N, Cl axial atoms and Cl and methyls in the equatorial plane for **Ia** where the Cl_{ax}–Sn–N bond angle is the lowest one reported to date and the Cl_{eq}–Sn bond distance the longest one with regard to similar complexes. This molecule has a short contact of 3.47 Å between the tin and the axial chlorine atoms. The molecular structure of complex **Ib** points out all equivalent bonds in the *trans* position arising from a polymeric chain with bridged pyrazine ligand. The complex **Ib** is centrosymmetric at the tin atom.

Introduction

Organotin complexes have many interactions with biological systems such as bactericides, fungicides, acaricides and industrial biocides [1]. In recent years investigations to test their antitumor activity have been carried out [2]. A statistical study on organotin(IV) derivatives has shown that R_2SnX_2 species, complexed or not, are favoured against the P 388 lymphocytic leukaemia tumor *in vivo* [3]. As a part of a program of investigation on the biological interaction of organotin(IV) complexes [4] we present here an infrared, Mössbauer and X-ray structural study of two complexes: [$Sn(CH_3)_2Cl_2$]$_2$pyz (**Ia**) and [$Sn(CH_3)_2Br_2$pyz]$_n$ (**Ib**) (pyz = pyrazine) in order to obtain further information on structure–activity relationships for more complex systems involving tin atoms.

Experimental

Organotin reagents were gifts from Schering AG (Bergkamen) and Ciba Geigy (Marienberg) and were used as received. The pyrazine ligand was purchased from Merck-Schuchardt. The solvents (C. Erba, Milano) were dried with molecular sieves prior to use.

The **Ia** and **Ib** adducts have been obtained as white crystalline solids at room temperature by mixing cyclohexane solutions of the reagents in the appropriate amounts. Several preparations with different molar proportions organotin/ligand yielded solids of the same composition. The compounds were crystallized from a dichloromethane–cyclohexane mixture. Analytical data are reported in Table I. Melting points were obtained by Mettler TA 3000 System and are reported in Table I. Infrared spectra were obtained using a Perkin-Elmer 983 IR spectrometer in the 4000–200 cm^{-1} region on nujol mulls between CsI disks. Relevant assignments are reported in Table I.

The Mössbauer spectra were determined on solid samples of the products, with the apparatus and procedures described elsewhere [5], at liquid N_2 temperature, with a $Ca^{119}SnO_3$ source (10 mCi, Radiochemical centre, Amersham) moving at room temperature with constant acceleration in a triangular waveform. The measured parameters are reported in Table I.

Collection and Reduction of X-ray Intensity Data

Preliminary Weissemberg studies showed that the crystals of the two compounds are sensitive to X-ray radiation, so the crystals of **Ia** and **Ib** were sealed in thin-walled capillaries before X-ray analysis.

A Nicolet R3 automatic diffractometer was used for the measurement of cell constants and the data

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TABLE I. Analytical Data, Mössbauer Parameters and IR Assignments

Compound	Melting point (°C)	Analysis, found (calc.) (%)			IS[a] (mm s^{-1})	QS[b] (mm s^{-1})	ν[c] (cm^{-1})	Assignments
		C	H	N				
Ia $[Sn(CH_3)_2Cl_2]_2pyz$	183.5	18.37 (18.50)	3.11 (3.11)	5.31 (5.39)	1.41	3.36	573m	$\nu(SnC_2)_{as}$
							524m	$\nu(SnC_2)_s$
							330s	$\nu(SnCl_2)_{as}$
							286s	$\nu(SnCl_2)_s$
Ib $Sn(CH_3)_2Br_2pyz$	143.1	18.38 (18.54)	2.56 (2.59)	7.08 (7.21)	1.49	4.10	568m	$\nu(SnC_2)_{as}$

[a]Isomer shift with respect to room temperature $Ca^{119}SnO_3$. [b]Nuclear quadrupole splitting. [c]Wavenumbers: m = medium, s = strong.

TABLE II. Summary of Crystal Data and Intensity Measurements

Compound	**Ia**	**Ib**
Formula	$Sn_2Cl_4N_2C_8H_{16}$	$SnBr_2N_2C_6H_{10}$
F_w	519.40	388.66
a (A)	6.924(8)	10.701(4)
b (Å)	10.334(8)	7.586(3)
c (A)	11.968(6)	7.550(3)
α (°)	90.	90.
β (°)	87.5(1)	118.40(2)
γ (°)	90.	90.
V (A^3)	855(1)	539.1(3)
Z	2	4
Space group	$P2_1/n$	$C2/m$
Radiation	Mo Kα graphite monochromated	
Crystal dimensions (mm)	0.40 × 0.30 × 0.30	0.40 × 0.20 × 0.10
Diffractometer	Nicolet R3	
Scan mode	$\theta-2\theta$	
2θ limits (°)	3, 56	3, 60
Observations	2292	904
No. unique data with $F_o^2 > 3\sigma(F_o^2)$	1616	721
Final number of variables	73	31
Final R (R_w)	0.058 (0.076)	0.067 (0.084)

collection. A summary of the crystal parameters along with details of the data collection is given in Table II. The collected intensities were processed to give structure factor amplitudes with standard deviations.

Solution and Refinement of the Structures

The compounds were solved with CAOS Program [6]. The solution of the two structures was carried out using a three-dimensional Patterson function to determine the position of Sn and halogen atoms in **Ia**, and Fourier methods to localize other atoms. Patterson and Fourier functions coincide for the Br complex due to the special position of the metal atom. Refinement by least-square procedures was applied subsequently.

*$[Sn(CH_3)_2Cl_2]_2pyz$ (**Ia**)*

After the isotropic refinement converged at $R = 0.109$, the refinement was continued allowing all the non-hydrogen atoms to vibrate anisotropically. The fixed contribution of the H atoms was included in the calculation (d(C–H) = 1 Å). Convergence was reached at $R = 0.058$ ($R_w = 0.073$).

Refinement was by full matrix and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights of the type $w = (a + F_o + bF_o^2)$, where a and b are of the order of $2F_o$ (min) and $2/F_o$ (max) respectively [7].

*$Sn(CH_3)_2Br_2pyz$ (**Ib**)*

The isotropic refinement converged at $R = 0.151$ after which the refinement was continued as for the **Ia** complex (see above). Convergence was reached at

$R = 0.067$ ($R_w = 0.084$). Weights were of the type $w = (1/\lambda)\sin\theta$.

Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography. The calculations were performed on the Eclipse Data General computer of the CNR Research Area of Rome. See also 'Supplementary Material'.

Results and Discussion

Mössbauer and IR Spectra

The two $Sn(CH_3)_2X_2$ adducts, **Ia** and **Ib**, were initially examined by Mössbauer and IR spectroscopy. Their composition suggests a possible different coordination of the tin atom and this supposition is confirmed by Mössbauer parameters listed in Table I. The isomer shift (IS) values are typical of quadrivalent tin in inorganic and organometallic compounds, the very close values for **Ia** and **Ib** compounds do not allow discrimination. In fact the IS, which is proportional to s-electron density, depends on both the coordination number and the nature of the ligands, decreases on going from four to six-coordinated species but increases as much as the tin atom is covalently bound to the coordinated atoms. The two effects seem to self compensate with a little predominance of the second [8].

The quadrupole splitting parameter (QS) permits a better differentiation. The 4.10 mm/s QS value for $[Sn(CH_3)_2Br_2pyz]$ (**Ib**) is unambiguously indicative of a octahedral configuration of the tin atom with *trans* methyl groups [9]. A polymeric structure with bridged pyrazine can be deduced in consonance with a series of $SnRCl_3pyz$ (R = alkyl, phenyl or Cl) adducts previously investigated [10].

The 3.36 mm/s QS value for the chloride complex (**Ia**) suggests a possible five-coordinate species with the $Sn^{IV}(CH_3)_2$ moiety surrounded by two chlorine atoms and one nitrogen atom in a trigonal bipyramidal structure with a non-linear C–Sn–C skeleton in consonance with a relation between QS values and C–Sn–C bond angles in a series of five and six-coordinated Me_2Sn^{IV} and Ph_2Sn^{IV} systems [9].

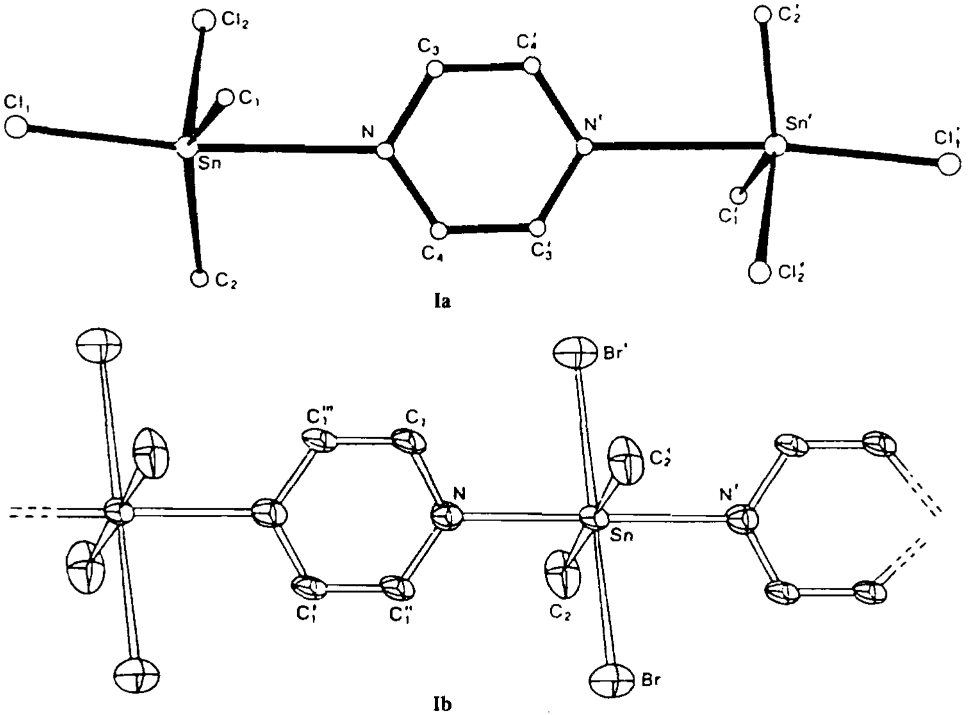
IR spectra show a single stretching at 568 cm^{-1} assigned to $\nu(Sn-CH_3)_{as}$ for the bromide complex (**Ib**) instead both ν_{as} and ν_s at 573 cm^{-1} and 524 cm^{-1} respectively are present for the chloride adduct (**Ia**) [11].

Two Sn–Cl stretchings at 330 cm^{-1}, ν_{as}, and 286 cm^{-1}, ν_s, show the non-linearity of the Cl–Sn–Cl bond angle as for the C–Sn–C bond angle in **Ia**. These structural hypotheses have been confirmed by X-ray molecular resolution.

Crystallographic Study

$[Sn(CH_3)_2Cl_2]_2pyz$ (Ia)

A computer generated drawing of this molecule is shown in Fig. 1, Table III shows relevant geometrical features around the tin atom and positional atomic



Ia

Ib

Fig. 1. Computer generated drawings of compounds **Ia** and **Ib**.

TABLE III. Selected Interatomic Distances (Å) and Interbond Angles (°) for **Ia** and **Ib**

	Ia	**Ib**
Distances		
Sn–N	2.746(8)	2.40(1)
Sn–X(1)	2.438(3)	2.723(3)
Sn–X(2)	2.363(3)	
Sn–C(1)	2.10(1)	2.10(2)
Sn–C(2)	2.10(1)	
Angles		
X(1)–Sn–X(2)	92.7(1)	180.
X(1)–Sn–C(1)	101.1(3)	90.9(9)
X(1)–Sn–C(2)	100.5(3)	90.
X(1)–Sn–N	173.2(2)	90.
X(2)–Sn–C(1)	107.7(3)	90.
X(2)–Sn–C(2)	108.5(3)	90.
X(2)–Sn–N	81.1(2)	90.
C(1)–Sn–C(2)	136.5(5)	180.
C(1)–Sn–N	83.6(4)	90.
C(2)–Sn–N	79.0(3)	90.

X denotes Cl or Br for **Ia** and **Ib** complexes, respectively. Standard deviations are given in parenthesis.

TABLE IV. Positional Atomic Parameters in **Ia**

Atom	*x/a*	*y/b*	*z/c*
Sn(1)	0.09176(8)	0.21069(5)	0.06294(4)
Cl(1)	−0.14174(36)	0.04582(24)	0.12386(19)
Cl(2)	−0.00261(46)	0.35113(26)	0.21125(25)
N(1)	0.3529(12)	0.4065(7)	0.0203(6)
C(1)	−0.0338(19)	0.2798(11)	−0.0830(10)
C(2)	0.3524(14)	0.1193(10)	0.1026(9)
C(3)	0.4480(20)	0.4619(11)	0.1016(8)
C(4)	0.4103(16)	0.4469(11)	−0.0835(7)
H(1)	−0.1635	0.3219	−0.0856
H(2)	0.0601	0.3446	−0.1155
H(3)	−0.0394	0.2033	−0.1339
H(4)	0.3880	0.0927	0.1793
H(5)	0.3579	0.0382	0.0570
H(6)	0.4574	0.1795	0.0754
H(7)	0.4144	0.4356	0.1805
H(8)	0.3469	0.4088	−0.1494

parameters are given in Table IV. The crystals of **Ia** are composed of binuclear units. The two $Sn(CH_3)_2Cl_2$ groups are bridged by a pyrazine ring. The center of the pyrazine ligand coincides with the center of symmetry of the adduct. The coordination around the tin atom, consisting of two methyl groups, two Cl atoms and one N atom, is trigonal bipyramidal. One Cl and one N atom are bound in axial positions of the pentacoordinated tin atoms. The same type of compound has been found recently [12] in $[SnPh_2Cl_2]_2pyz$. A comparison of geometrical data between the two compounds shows:

(a) The Sn–N bond distance is longer in our complex, that is 2.746(8) Å *versus* 2.696(12) Å for the phenyl derivative. However the difference between them lies below 3σ of the bond distance.

(b) The $Sn-Cl_{ax}$ bond distance is significantly longer for the methyl complex (2.438(3) Å and 2.402 Å).

(c) The $Sn-Cl_{eq}$ bond length is also longer but as in (a) the difference is within the standard deviations, *i.e.* 2.363(3) and 2.340(5) Å for the methyl and phenyl complexes respectively.

(d) The organometallic bonds (Sn–C) are equivalent in both complexes; this feature is characteristic of organotin compounds [13] since this bond is less sensitive to substituent changes (2.10(1) and 2.106(6) Å).

(e) The C–Sn–C bond angle is larger, 136.5(5)° compared to 133.1(2)°, and the $C-Sn-Cl_{eq}$ angles are lower than for the phenyl adduct. The sum of the three equatorial angles is similar for the two compounds, *i.e.* 352.7° and 353.3° respectively.

(f) The $N-Sn-Cl_{ax}$ bond angle is markedly lower in our complex (173.5(3)° and 178.5(3)°).

We can consider two effects on the metal atom dependent on the organic substituents:

(1) Hindrance effect. Tolman [14] has shown through the cone angle parameter that methyl groups have less steric requirements than phenyl groups. Thus a lower C–Sn–C bond angle for the methyl complex should be expected. On the contrary we have found a higher angle.

(2) Electronic effect. In spite of the fact that methyl is a better electron donating group than phenyl we observe that the Sn–C bond distance is the same in both complexes (see above).

We can conclude from this comparison that the structural changes are difficult to explain and, probably, more complexes are necessary in order to see any systematic trends.

Looking at the metal–metal axis we observe that the equatorial ligands tend to approach the heterocyclic ring; unfortunately Cunningham *et al.* [12] have not published the related angles that in our case have the following values: N–Sn–C = 83.6(4)° and 79.0(3)° and $N-Sn-Cl_{eq}$ = 81.1(2)°. This feature is also evidenced by the distance between the metal atom and the plane defined by Cl_{eq} and the two C atoms of the methyl groups; this distance is 0.33 Å. Another compound reported with a similar configuration is $SnPh_2Cl_2(BT)$, BT = benzothiazole [15]. From this comparison we see that the effect of the equatorial ligands approaching to the N atom is more marked in our methyl complex. The reported angles values are N–Sn–C = 85.4° and 81.1° and $N-Sn-Cl_{eq}$ = 84.6°. The $Cl_{ax}-Sn-N$ bond angle is 176.1(7)° for the BT complex whereas our value is lower at 173.2(2)°. The $Sn-Cl_{ax}$ bond lengths are similar since in the BT complex it is 2.446(1) Å whereas the $Sn-Cl_{eq}$ bond distance in our compound is the longest one, the reported value being 2.336(1) Å. Short contacts of 3.47 Å between the tin and the axial chlorine atoms are shown in Fig. 2.

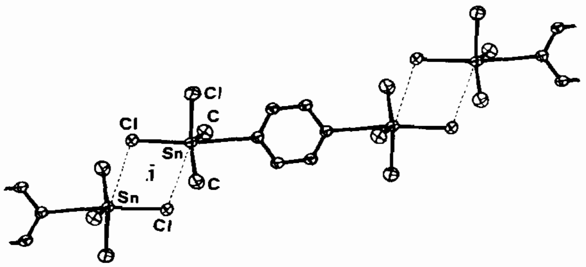


Fig. 2. Short contacts in **Ia**.

$[Sn(CH_3)_2Br_2(pyz)]$ (Ib)

Figure 1 shows a partial view of this molecule, the main geometrical data are in Table III and positional atomic coordinates are presented in Table V. The Sn atoms are surrounded by two methyl groups, two nitrogen atoms belonging to two different pyrazine rings and two bromine atoms in an octahedral arrangement. These octahedra form endless chains of formula $[Sn(CH_3)_2Br_2(pyz)]_n$ and the crystalline structure is built up by the packing of these infinite one-dimensional chains. Cunningham *et al.* have found another stereoisomer compound, a complex formed when chlorine atoms and phenyl groups substitute bromine and methyl groups of our compound and the polymer develops through *cis* –N–Sn–N– bonds. Curiously their complex crystallizes together with the binuclear five-coordinated tin complex $[SnPh_2Cl_2]_2pyz$ (see above). Both of these complexes seem difficult to separate either by synthesis with excess of the reagents or by crystallization [12]. In the **Ib** complex there are two independent centers of symmetry, a first one at the metal atom and the other one at the center of the pyrazine ring so that all the ligands are *trans*. This complex has high symmetry since Sn is in a special position (0, 0, 0), the axis –N–Sn–N– coincides with the crystallographic binary axis and the normal mirror plane contains the other ligands on the metal atom, *i.e.* two bromine and two carbon atoms. This symmetry requires that one of the hydrogen atoms of every methyl group lies on the mirror plane.

TABLE V. Positional Atomic Parameters in **Ib**

Atom	*x/a*	*y/b*	*z/c*
Sn(1)	0.0000	0.0000	0.0000
Br(1)	0.28016(20)	0.0000	0.27857(26)
N(1)	0.0000	0.3163(16)	0.0000
C(1)	−0.0724(13)	0.4092(14)	−0.1722(13)
C(2)	−0.0588(24)	0.0000	0.2289(27)
H(1)	0.0088	0.0000	0.3767
H(2)	−0.1187	0.1077	0.2045
H(3)	−0.1272	0.3446	−0.3022

Our values of the Sn–C and Sn–N bond distances, 2.10(2) and 2.40(1) Å, can be compared with published results, for instance $Sn(CH_3)_2Cl_2(pyridine)_2$ has the values of 2.15 Å and 2.39 Å [16] or $Sn(CH_3)_2Cl_2(dmp)_2$, dmp = dimethylpyrazole, with values of 2.12 Å and 2.38 Å [13] or $Sn(CH_3)_2Cl_2(NMiz)_2$, NMiz = N-methylimidazole, which has the values of 2.12 Å and 2.33 Å [17].

Conclusions

The **Ia** complex is a rare example of a $Sn(CH_3)_2Cl_2$ adduct with N donor ligand, with the tin atom at the center of a distorted trigonal bipyramidal geometry, which structure has been crystallographically detected. The **Ib** complex is a very regular octahedral complex with six-coordinated tin *trans* Me, N, Br, which develops a polymeric chain with bridged bis monodentate pyrazine.

Supplementary Material

Tables of observed and calculated structure factors are available upon request.

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