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The crystal structure of dichlorobis(imidazole)dimethyltin(IV)

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Abstract

The structure of dichlorobis(imidazole)dimethyltin(IV) has been determined by X-ray diffraction. The crystal consists of discrete *trans*-$Me_2SnCl_2(HIm)_2$ units with the metal atom octahedrally coordinated to two Cl atoms (Sn–Cl, 2.5955(7) Å; Cl–Sn–Cl, 180°), two methyl carbons (Sn–C, 2.110(3) Å; C–Sn–C, 180°), and two imidazole groups (Sn–N, 2.312(2) Å; N–Sn–N, 180°). The imidazole ligands are bound to the metal through their pyridine-like nitrogen atom, and intermolecularly hydrogen-bonded to the chlorine atoms.

Introduction

Knowledge of the participation of imidazole (HIm) in biological processes has stimulated study of its interactions with other systems, especially those involving the formation of hydrogen bonds through the N–H group, and of the influence of such hydrogen bonds on such biological processes [1, 2 and references therein]. At the same time, the wide spread industrial use of organotin(IV) compounds [3] and the antitumour activity of some of their complexes [4] have prompted investigation of their aqueous coordination chemistry [5] and of their hydrates and hydrolysates [6,7]. We previously described the interaction of Me_2SnCl_2 with imidazole in a non-aqueous solvent [8]. Here we describe the structure of the compound $Me_2SnCl_2(HIm)_2$, which was isolated as a secondary product during a study of the reaction of Me_2SnCl_2 with imidazole in water.

Experimental

Preparation

A solution of Me_2SnCl_2 (2.85 mmoles) in 20 cm^3 of water was slowly added to a solution of HIm (5.70 mmoles) in 20 cm^3 of water. The mixture was stirred for 3 d

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and the white solid formed was then filtered off, washed and vacuum dried. The analytical results (C, 14.4; H, 3.8%) show that the solid is Me_2SnO (calcd.: C, 14.6; H, 3.8%), the yield from the hydrolysis being approximately 68%. Crystals of $Me_2SnCl_2(HIm)_2$ suitable for the X-ray study were obtained by slow evaporation of the filtrate.

Crystal structure determination

A colourless crystal having approximate dimensions $0.50 \times 0.25 \times 0.45$ mm was mounted in an Enraf Nonius CAD-4 four-circle diffractometer. All constants were determined from setting angles for 25 reflections in the range $5.8 < \theta < 10.4°$ (Table 1). The systematic absences observed suggested the space group to be $I2$ or $I2/a$. Reflections were measured by the ω–θ scan technique. The hkl range was $h < 16$, $k < 8$ and $-17 < l < 17$, with θ varying between 3 and 25°. Of 2600 reflections measured, 1250 were unique with $R_{int} = 0.014$, and 1086 with $I_o > 2\sigma(I_o)$ were considered as observed and used for the refinement. Lorentz polarization corrections and an empirical absorption correction [9] were made (max. and min. transmission factors 1.1761 and 0.6710). For the refinement, the centrosymmetric space group $I2/a$ was assumed, and this choice was confirmed by successful resolution of the structure.

The structure was solved by Patterson techniques, which revealed the positions of all non-H atoms. Refinement was carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o)$. The difference maps revealed the positions of all H atoms.

In final least squares cycles all non-H atoms were treated anisotropically. Inspection of F_c and F_o values indicated that a correction for secondary extinction was required: $F_{corr} = F_c(1.0 + kF_c^2/\sin 2\theta)^{0.25}$, where k refined to 2.22×10^{-7} in the final run. A total of 99 parameters were refined (max. shift/error 0.01). At that stage, the R factors were $R = 0.021$ and $Rw = 0.023$. A final difference map showed maxima of electron density of 0.625 eÅ^{-3}. Scattering factors and corrections for anomalous dispersion were taken from International Tables [10]. Calculations were performed with SHELX-86 [11] and the SDP program system [12] on a DEC micro VAX II computer.

Table 1

Crystal data for $Me_2SnCl_2(HIm)_2$

Molecular formula	$C_8Cl_2H_{14}N_4Sn$
Molecular weight	355.82
Crystal class	Monoclinic
Space group	$I2/a$ (No. 15)
Lattice constants	a 13.795(3) Å
	b 7.361 (2) Å
	c 14.770(6) Å
	β 119.85(2)°
Cell volume	1300.85 Å^3
Formula units	$Z = 4$
$D_{calcd.}$	1.817 g cm^{-3}
Absorption coefficient	μ(Mo-K_α)23.63 cm^{-1}
T	296 K

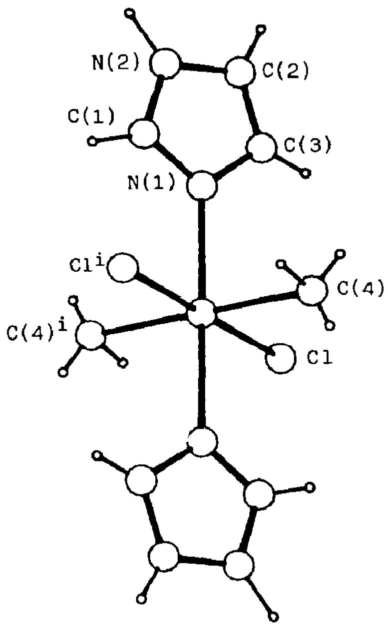

Fig. 1. The molecular structure of $Me_2SnCl_2(HIm)_2$, with the atom numbering.

Tables of thermal parameter and a list of observed and calculated structure factors are available from the authors.

Results and discussion

The crystals obtained consist of discrete $Me_2SnCl_2(HIm)_2$ units (see Fig. 1 for atom numbering; atomic coordinates are given in Table 2 and interatomic bond lengths and angles in Table 3). In these units the Sn atom is octahedrically coordinated to two Cl atoms, two methyl groups, and two imidazole groups, in an all-*trans* configuration with the Sn atom at a centre of symmetry. The imidazole ligands bind to the metal through the pyridine-like nitrogen, and the bond lengths and angles in the ring are close to those in other imidazole complexes [13,14]. The rings are essentially planar, with negligible deviation from the best least-squares plane.

Table 2

Positional parameters for $Me_2SnCl_2(HIm)_2$ with esd's in parentheses

Atom	*x*	*y*	*z*
Sn	0.500	0.000	0.000
Cl	0.35669(7)	0.2636(1)	−0.05431(6)
N(1)	0.5186(2)	−0.0032(4)	0.1644(2)
N(2)	0.5897(3)	−0.0385(5)	0.3316(2)
C(1)	0.6100(3)	−0.0413(6)	0.2521(3)
C(2)	0.4808(3)	0.0033(7)	0.2931(3)
C(3)	0.4371(3)	0.0250(6)	0.1900(3)
C(4)	0.6316(3)	0.1898(6)	0.0507(3)

Table 3

Bond distances (Å) and angles (°) for $Me_2SnCl_2(HIm)_2$

Bond distances		Bond angles	
Sn–Cl	2.5955(7)	Cl–Sn–Cl [a]	180
Sn–N(1)	2.312(2)	Cl–Sn–N(1)	90.08(6)
Sn–C(4)	2.110(3)	Cl–Sn–N(1) [a]	89.92(6)
N(1)–C(1)	1.311(4)	Cl–Sn–C(4)	90.2(1)
N(1)–C(3)	1.368(4)	Cl–Sn–C(4) [a]	89.8(1)
N(2)–C(1)	1.336(4)	N(1)–Sn–N(1) [a]	180
N(2)–C(2)	1.351(5)	N(1)–Sn–C(4)	90.5(1)
C(2)–C(3)	1.340(5)	N(1)–Sn–C(4) [a]	89.5(1)
		C(4)–Sn–C(4) [a]	180
		C(1)–N(1)–C(3)	106.1(3)
		C(1)–N(2)–C(2)	108.0(3)
		N(1)–C(1)–N(2)	110.2(4)
		N(2)–C(2)–C(3)	106.3(4)
		N(1)–C(3)–C(2)	109.3(3)

[a] Symmetry code: $1-x, -y, -z$.

The hydrogen atom at N(2) makes an intermolecular contact of 2.52 Å with a chlorine atom of a neighbouring molecule (Fig. 2). This distance, the Cl–N(2) distance [3.327(3) Å] and the Cl–H–N(2) angle [134(3)°] are similar to those in similar systems with intermolecular hydrogen bonds (e.g., ref. 15). Figure 2 shows how the hydrogen bonding determines a packing structure in which hydrogen-bonded molecules form layers. In the unit cell these layers are parallel to the bc plane.

Although a similar *trans* configuration has been observed in the molecular units of the related complexes $Me_2SnCl_2(HPz)_2$ (HPz = pyrazole) [15], $Me_2SnCl_2(py)_2$,

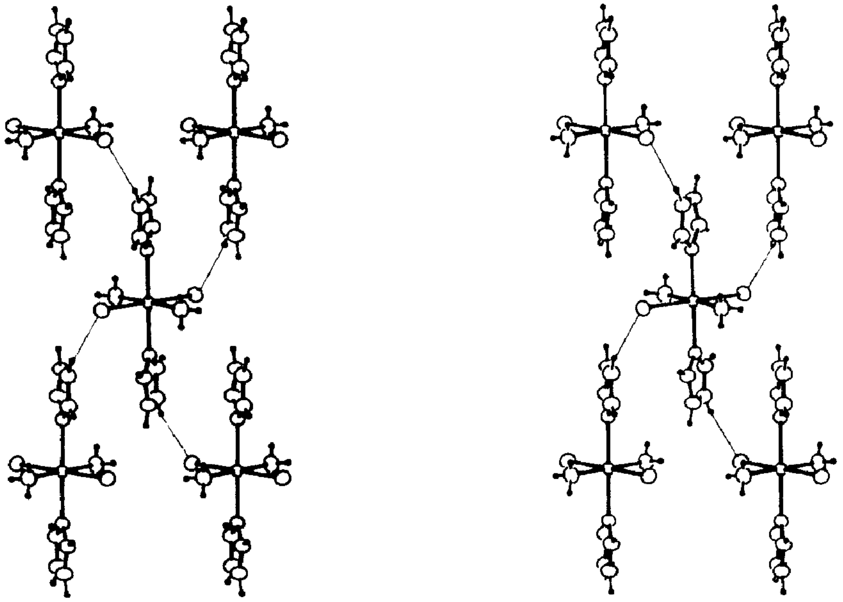

Fig. 2. A stereoview of the intermolecular hydrogen bonding in $Me_2SnCl_2(HIm)_2$.

(py = pyridine) [16], $Me_2SnCl_2(HDMPz)_2$ (HDMPz = 3,5-dimethylpyrazole) [17] and $Me_2SnCl_2(NMIm)_2$ (NMim = (*N*)-methylimidazole) [18], there are several structural differences, especially in respect of bond lengths, and, as has been pointed out previously [17], the distortion of the coordination octahedron and other features resulting from the intra- and inter-molecular interactions.

The Sn–C and Sn–Cl bond lengths [2.110(3) Å and 2.5955(7) Å respectively] are consistent with those found for the above mentioned $Me_2SnCl_2 \cdot L_2$ complexes (2.11(1)–2.114(13) and 2.570(3)–2.58(2), respectively) [15–18], while the Sn–N bond length (2.312(2) Å) is slightly shorter than those in the pyridine and dimethylpyrazole complexes (2.39(2) Å, 2.379(6) Å) and close to those in the (*N*)-methylimidazole and pyrazole complexes (2.329(5) Å, 2.338(6) Å).

Like the closely related complexes dichlorodimethylbis(pyrazole)tin(IV) [15] and dichlorobis(*N*)-methylimidazole)dimethyltin(IV) [18], $Me_2SnCl_2(HIm)_2$ has near 90° coordination bond angles. This shows that the NCH_3 group in (*N*)-methylimidazole, the intra and inter-molecular N–H–Cl hydrogen bonds in the pyrazole complex, and the intermolecular hydrogen bond in the compound studied here, have little influence on the coordination polyhedron. Similarly, the smallness of the difference between the Sn–N(1)–C(3) and Sn–N(1)–C(1) angles in $Me_2SnCl_2(HIm)_2$ (1.6°) and $Me_2SnCl_2(NMIm)_2$ (3.2°) [18] shows that the NCH_3 group has little influence on this distortion.

The two imidazole rings are located in a single plane, making a dihedral angle of 35.2(2)° with the Sn–N(1)–Cl plane. The analogous angles in the above mentioned related systems are 26° (L = pyridine), 24° (L = pyrazole), 33° (L = dimethylpyrazole) and 26° (L = (*N*)-methylimidazole). This angle is thus the structural parameter most influenced by substituents on the ligand ring and by hydrogen bonding.

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