

Synthesis and crystal structure of $\text{Me}_2\text{SnCl}_2 \cdot (2\text{-MeOC}_6\text{H}_4\text{N=CHC}_5\text{H}_4\text{N-2})$

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Abstract

The reaction between Me_2SnCl_2 and the ligand $2\text{-MeOC}_6\text{H}_4\text{N=CHC}_5\text{H}_4\text{N-2}$ in ethanol affords the monomeric (1:1) complex $\text{Me}_2\text{SnCl}_2 \cdot (2\text{-MeOC}_6\text{H}_4\text{N=CHC}_5\text{H}_4\text{N-2})$. An X-ray diffraction study has shown that the tin atom has a distorted octahedral co-ordination with *trans*-methyl groups. The methoxy oxygen of the ligand remains uncoordinated. The Sn–N bond lengths are $> 2.39 \text{ \AA}$.

Introduction

A variety of metal complexes are now known to show antitumour activity. These include the organotin compounds of the type $\text{R}_2\text{SnCl}_2 \cdot (\text{L})$ (L = phenanthroline or N-N type chelating ligands [1–3]) and some tin and other metal derivatives of biologically important species [4–15]. It has been suggested [2] that organotin complexes having Sn–N bond lengths $> 2.39 \text{ \AA}$ may show anti-tumour activity, whereas those with average Sn–N bond lengths $< 2.39 \text{ \AA}$ are inactive. This suggests that more stable complexes have lower activities. As a part of a study of structure-activity relationship of these types of compounds, we describe below the synthesis and crystal structure of the title compound $\text{Me}_2\text{SnCl}_2 \cdot (2\text{-MeOC}_6\text{H}_4\text{N=CHC}_5\text{H}_4\text{N-2})$.

Experimental

Preparation

The ligand $2\text{-MeOC}_6\text{H}_4\text{N=CHC}_5\text{H}_4\text{N-2}$ was prepared by the slow addition of 1.60 g (14.01 mmol) of 2-pyridine carboxyaldehyde to a stirred solution of 1.72 g (13.98 mmol) of *o*-anisidine in the minimum volume of ethanol. Stirring was continued for a further 30 min, the ethanol then removed under vacuum and the residual liquid was distilled (0.1 Torr and 110°C) to give 1.8 g (8.49 mmol) of the

product. Analytical results (Found: C, 73.95; H, 6.00; N, 12.65%) show that the compound is $C_{13}H_{12}N_2O$ (calcd.: C, 73.58; H, 5.66; N, 13.21%). IR: $\nu(C=N)$ 1629 cm^{-1} . 1H NMR: δ 9.10–6.82 (m, 8 phenyl and pyridine ring protons); δ 8.90 (d, 1, protons adjacent to N(1) on C(6) of pyridine ring); δ 8.80 (s, 1, H–C=N); δ 3.97 (s, 3, OCH_3).

The organotin complex was prepared by addition of a solution of 0.3 g (1.36 mmol) of dimethyltin dichloride in CH_2Cl_2 (10 cm^3) to a stirred solution of the ligand (0.32 g, 1.50 mmol) in a mixture of CH_2Cl_2 (100 cm^3) and CCl_4 (50 cm^3) at room temperature. The product was filtered off, washed with CH_2Cl_2 (10 cm^3) and dried *in vacuo* (0.5 g, 98.4%), m.p. 166 °C. Recrystallisation from 30 ml CH_2Cl_2 give bright yellow crystals suitable for the X-ray study. Analytical results (found: C, 41.2; H, 4.26; N, 6.22; Sn, 27.6%) correspond to the molecular formula $C_{15}H_{18}Cl_2N_2OSn$ (calcd.: C, 41.69; H, 4.16; N, 6.48; Sn, 27.5%). IR: $\nu(C=N)$ 1635, $\nu(Sn-C)$ 573 and 532, $\nu(Sn-Cl)$, 305 and 275 cm^{-1} . 1H NMR: δ 8.8–7.1 (m, 8, phenyl and pyridine ring protons); δ 8.67 (s, 1, H–C=N); δ 9.38 (d, 1, protons adjacent to N(1) on C(6) pyridine ring); δ 3.91 (s, 3, OCH_3); δ 1.05 (s, 6, $Sn(CH_3)_2$, $^2J(^1H-^{119}Sn)$ 112.50, $^2J(^1H-^{117}Sn)$ 107.51 (all shifts relative to $SiMe_4$). ^{119}Sn Mössbauer at 80 K: IS 1.46 $mm\ s^{-1}$; QS 4.32 $mm\ s^{-1}$. The IR band assignments were based on previous analyses [10,16].

Structural studies

The X-ray diffraction data were obtained with a Syntex P2₁ four circle computer-controlled diffractometer (using graphite-monochromated $Mo-K_{\alpha}$ 0.7017 Å) at room temperature. All calculations were performed with an Eclipse S/200 computer using INEXTL programs [17]. The unit cell parameters were calculated from the setting angles of 16 reflections with $26 \leq 2\theta \leq 28^\circ$. Crystal data: $C_{15}H_{18}Cl_2N_2OSn$, M 431.7, monoclinic, $a = 17.268(5)$, $b = 7.049(2)$, $c = 15.839(4)$

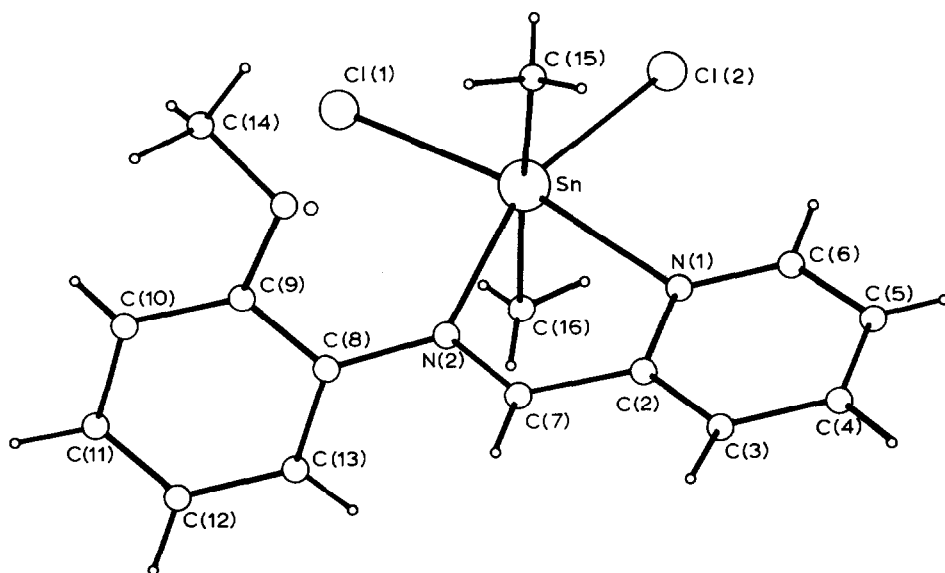


Fig. 1. A view of $Me_2SnCl_2 \cdot (2-MeOC_6H_4N=CHC_5H_4N-2)$ showing the atom labelling.

Table 1

Bond lengths (Å) for $\text{Me}_2\text{SnCl}_2 \cdot (2\text{-MeOC}_6\text{H}_4\text{N}=\text{CHC}_5\text{H}_4\text{N-2})$ with esd's in parentheses

Sn...Cl(1)	2.496(2)	C(2)...C(3)	1.372(9)
Sn...Cl(2)	2.519(2)	C(2)...C(7)	1.454(9)
Sn...N(1)	2.456(5)	C(3)...C(4)	1.40(1)
Sn...N(2)	2.459(5)	C(4)...C(5)	1.37(1)
Sn...C(15)	2.103(9)	C(5)...C(6)	1.38(1)
Sn...C(16)	2.108(9)	C(8)...C(9)	1.390(9)
O...C(9)	1.358(8)	C(8)...C(13)	1.374(9)
O...C(14)	1.42(1)	C(9)...C(10)	1.38(1)
N(1)...C(2)	1.359(7)	C(10)...C(11)	1.38(1)
N(1)...C(6)	1.326(8)	C(11)...C(12)	1.36(1)
N(2)...C(7)	1.274(9)	C(12)...C(13)	1.38(1)
N(2)...C(8)	1.425(8)		

α , $\beta = 114.56(2)^\circ$, $V = 1753(1) \text{ \AA}^3$, space group $P2_1/c$, $Z = 4$, $D_{\text{calcd}} = 1.64 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 17.7 \text{ cm}^{-1}$. The intensities of 2264 independent reflections with $I \geq 2\sigma(I)$ and $2\theta \leq 53^\circ$ were measured by the $\theta/2\theta$ scan technique. The structure was solved by conventional Patterson and Fourier methods. Full-matrix least-squares refinement of all non-hydrogen atoms anisotropically and all hydrogens (initially in calculated positions) isotropically converged to $R = 0.040$ ($R_w = 0.047$). The atomic coordinates and thermal parameters are listed in Table 4. A table of thermal parameters and a list of observed and calculated structure factors are available from the authors.

Results and discussion

The molecular structure of the complex $\text{Me}_2\text{SnCl}_2 \cdot (2\text{-MeOC}_6\text{H}_4\text{N}=\text{CHC}_5\text{H}_4\text{N-2})$ (I) was determined by X-ray crystallography (see Fig. 1, and bond lengths and

Table 2

Bond angles ($^\circ$) with esd's in parentheses

Cl(1)SnCl(2)	100.17(6)	SnN(2)C(8)	123.0(4)
Cl(1)SnN(1)	167.0(1)	C(7)N(2)C(8)	119.3(5)
Cl(1)SnN(2)	98.9(1)	N(1)C(2)C(3)	122.1(6)
Cl(1)SnC(15)	94.2(3)	N(1)C(2)C(7)	116.7(5)
Cl(1)SnC(16)	90.9(3)	C(3)C(2)C(7)	121.2(6)
Cl(2)SnN(1)	92.8(1)	C(2)C(3)C(4)	119.2(6)
Cl(2)SnN(2)	160.1(1)	C(3)C(4)C(5)	118.2(7)
Cl(2)SnC(15)	92.5(3)	C(4)C(5)C(6)	119.6(7)
Cl(2)SnC(16)	91.5(3)	N(1)C(6)C(5)	122.9(6)
N(1)SnN(2)	68.1(2)	N(2)C(7)C(2)	122.2(6)
N(1)SnC(15)	85.8(3)	N(2)C(8)C(9)	118.9(5)
N(1)SnC(16)	88.1(3)	N(2)C(8)C(13)	121.6(6)
N(2)SnC(15)	91.7(3)	C(9)C(8)C(13)	119.5(6)
N(2)SnC(16)	82.6(3)	OC(9)C(8)	114.3(5)
C(15)SnC(16)	172.8(4)	OC(9)C(10)	125.9(6)
C(9)OC(14)	117.6(7)	C(8)C(9)C(10)	119.7(6)
SnN(1)C(2)	116.2(4)	C(9)C(10)C(11)	119.6(7)
SnN(1)C(6)	125.6(4)	C(10)C(11)C(12)	121.1(8)
C(2)N(1)C(6)	117.9(5)	C(11)C(12)C(13)	119.2(8)
SnN(2)C(7)	116.2(4)	C(8)C(13)C(12)	121.0(7)

Table 3

Average bond distances ($\text{\AA}$) and angles ($^\circ$) in the complexes R_2SnCl_2 with π -N-chelating ligands ^a

Complex	$\text{Me}_2\text{SnCl}_2 \cdot (\text{L}^1)$ (I)	$\text{Ph}_2\text{SnCl}_2 \cdot (\text{bipy})$ (II)	$\text{Et}_2\text{SnCl}_2 \cdot (\text{bipy})$ (III)	$\text{Et}_2\text{SnCl}_2 \cdot (\text{L}^2)$ (IV)
Reference	This work	19	20	21
<i>Distances</i>				
Sn—Cl	2.508	2.510	2.542	2.477
Sn—N	2.458	2.360	2.375	2.52
Sn—C	2.106	2.152	2.137	2.14
<i>Angle</i>				
C—Sn—C	172.8	173.5	175.8	163

^a $\text{L}^1 = 2\text{-MeOC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{N}-2$, $\text{L}^2 = 3\text{-(2-pyridyl)-5,5-diphenyl-1,2,4-triazine}$.

Table 4

Atomic coordinates ($\text{Sn} \times 10^5$, $\text{H} \times 10^3$, rest $\times 10^4$)

Atom	x	y	z	$B_{\text{eq}}/B_{\text{iso}}$
Sn	21408(2)	19521(5)	39472(2)	2.67(1)
Cl(1)	3093(1)	4031(3)	3521(1)	5.01(6)
Cl(2)	1148(1)	773(3)	2363(1)	5.31(6)
O	4288(3)	2467(7)	5773(3)	4.8(2)
N(1)	1399(3)	169(6)	4722(3)	2.9(1)
N(2)	2705(3)	2687(7)	5614(3)	2.9(1)
C(2)	1682(3)	444(8)	5652(4)	2.9(2)
C(3)	1370(4)	−574(10)	6180(5)	3.8(2)
C(4)	750(5)	−1954(9)	5756(5)	4.3(2)
C(5)	467(4)	−2216(10)	4818(5)	3.8(2)
C(6)	804(4)	−1136(9)	4328(5)	3.5(2)
C(7)	2331(4)	1892(9)	6064(4)	3.2(2)
C(8)	3276(4)	4219(8)	6028(4)	3.1(2)
C(9)	4091(4)	4145(9)	6057(4)	3.5(2)
C(10)	4628(5)	5681(11)	6387(4)	4.2(2)
C(11)	4357(5)	7263(11)	6707(5)	5.1(3)
C(12)	3565(6)	7334(11)	6697(6)	5.4(3)
C(13)	3027(5)	5795(10)	6363(5)	4.5(2)
C(14)	5103(7)	2302(23)	5759(9)	7.1(4)
C(15)	2931(6)	−443(11)	4199(7)	4.6(3)
C(16)	1333(6)	4264(12)	3849(7)	4.9(3)
H(3)	162(5)	−41(10)	681(5)	5(2)
H(4)	55(4)	−266(9)	616(5)	4(1)
H(5)	13(4)	−307(9)	457(4)	2(2)
H(6)	62(4)	−129(9)	368(4)	4(1)
H(7)	248(3)	220(7)	664(4)	2.3(9)
H(10)	515(4)	556(7)	643(4)	3(1)
H(11)	472(4)	837(8)	689(4)	4(1)
H(12)	337(5)	853(12)	691(6)	8(2)
H(13)	248(5)	584(12)	628(5)	5(2)
H(14)	507(7)	121(15)	548(7)	8(3)
H(14)'	561(7)	266(15)	639(9)	11(3)
H(14)''	504(8)	205(15)	524(9)	5(3)
H(15)	298(8)	−69(19)	376(9)	11(4)
H(15)'	233(9)	−242(23)	444(9)	22(4)
H(15)''	343(8)	−16(18)	460(9)	17(4)
H(16)	132(7)	514(15)	340(8)	9(3)
H(16)'	135(6)	456(15)	430(8)	7(3)
H(16)''	88(8)	383(19)	332(9)	15(5)

angles in Tables 1 and 2). The tin atom has a slightly distorted octahedral coordination with a *cis* arrangement of the chloro ligands and a *trans* arrangement of the methyl groups, like the previously studied organotin complexes with $\overline{\text{N N}}$ -chelating ligands (see Table 3). It is noteworthy that the oxygen atom does not participate in the coordination ($\text{Sn} \cdots \text{O}$ 3.651(6) Å).

The Sn–C(Me) distances in I are slightly shorter than the Sn–C(Et) distances in III and IV, but the difference is probably overestimated, as the structures of III and IV were refined without inclusion of the ethyl hydrogens. The present structure provides more evidence for Sn–C(sp^3) bonds being shorter than Sn–C(sp^2) bonds, probably because the tin 5s electron density is predominantly concentrated in bonds with less electronegative ligands, and the electronegativity of C(sp^3) is 2.6 vs 2.8 for C(sp^2) [18].

In I the Sn–N bonds with chemically non-equivalent N(1) and N(2) atoms have the same Sn–N bond lengths of 2.458 Å, but are almost 0.1 Å longer than these in the bipyridyl complexes II and III, and ca. 0.06 Å shorter than those in pyridyl-triazene derivative complex IV, thus revealing the sensitivity of Sn–N distance to electronic effects. The Sn–N bond length in I, 2.458 Å, is significantly greater than 2.39 Å and thus the compound is suitable for anti-tumour screening tests.

The five-membered metallacycle in I is planar within ± 0.04 Å. The pyridine and benzene rings form a dihedral angle of 66° . The N(2)=C(7) bond is almost co-planar with the pyridine ring, and the methoxy group with the benzene ring, the torsion angles being N(1)C(2)C(7)N(2) $-9.5(5)$, C(7)N(2)C(8)C(13) $-54.7(8)$, and C(10)C(9)OC(14) $-4(1)^\circ$.

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References

- 1 A.J. Crowe, P.J. Smith and G. Atassi, *Chem. Biol. Interact.*, **32** (1980) 171.
- 2 A.J. Crowe, P.J. Smith, C.J. Cardin, H.E. Parge and F.E. Smith, *Cancer Let.*, **24** (1984) 45.
- 3 A.K. Saxena and F. Huber, *Coord. Chem. Rev.*, **95** (1989) 109.
- 4 W. Saenger, *Principles of Nucleic Acid structure*, Springer-Verlag, Berlin 1983 and refs. therein.
- 5 J.R. Rubin, M. Sabat and M. Sundaralingam, in B. Pullman and J. Jortner (Eds.), *Nucleic Acids: The Vectors of Life*, Reidel, Dordrecht, 1983 and refs. therein.
- 6 K. Aoki and H. Yamajaki, *J. Am. Chem. Soc.*, **106** (1984) 3691.
- 7 H. Köpf and P. Köpf-Maier, in S.J. Lippard (Ed.), *Platinum, Gold and Other Metal Chemotherapeutic Agents*, A.C.S. Symposium Series No. 209, 1983.
- 8 P. Köpf-Maier, H. Köpf and E.W. Neuse, *Angew. Chem., Int. Ed. Engl.*, **23** (1984) 456.
- 9 L.S. Hollis, A.R. Amundsen and E.W. Stern, *J. Am. Chem. Soc.*, **107** (1985) 274.
- 10 C.J. Cardin and A. Roy, *Inorg. Chim. Acta*, **107** (1985) 57.
- 11 C.J. Cardin and A. Roy, *Inorg. Chim. Acta*, **107** (1985) L33.
- 12 C.J. Cardin and A. Roy, *Inorg. Chim. Acta*, **107** (1985) L37.
- 13 C.J. Cardin and A. Roy, *Inorg. Chim. Acta*, **125** (1986) 63.
- 14 G. Arena, R. Purello, E. Rizzarelli, A. Gianuguzza and L. Pellerito, *J. Chem. Soc., Dalton Trans.*, (1989) 773.
- 15 G. Valle, A. Sanchez Gonzalez, R. Ettorre and G. Plazzogna, *J. Organomet. Chem.*, **348** (1988) 49.
- 16 C. Carini, G. Peaizzi, P. Tarasconi, C. Pelizzi, K.C. Molloy and P.C. Waterfield, *J. Chem. Soc., Dalton Trans.*, (1989) 289.

- 17 R.G. Gerr, A.I. Yanovskii and Yu.T. Struchkov, *Kristallografiya*, 28 (1983) 1029.
- 18 S.S. Batsanov, *Uspekhi Khimii*, 36 (1968) 778 (In Russian).
- 19 A.J. Edwards and R.J. Sills, *J. Chem. Soc., Dalton Trans.*, (1974) 1723.
- 20 S.L. Chadha, P.G. Harrison and K.C. Molloy, *J. Organomet. Chem.*, 202 (1980) 247.
- 21 L. Prasad, Y. Le Page and F.E. Smith, *Inorg. Chim. Acta*, 68 (1983) 45.