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THE CRYSTAL STRUCTURE OF DICHLOROBIS(*N*-METHYLIMIDAZOLE)DIMETHYLTIN(IV)

RENATO BARDI, ANNAMARIA PIAZZESI,

Centro di Studio sui Biopolimeri del C.N.R., Istituto di Chimica Organica, Università di Padova, Padova (Italy)

RENATO ETTORRE

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione del C.N.R., Istituto di Chimica Analitica, Università di Padova, Padova (Italy)

and GUALTIERO PLAZZOGNA*

Istituto di Chimica Analitica, Università di Padova, Padova (Italy)

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Summary

The structure of the complex dichlorobis(*N*-methylimidazole)dimethyltin(IV), $Me_2SnCl_2(NMiz)_2$, has been determined from three-dimensional X-ray diffraction data. The compound crystallizes in the triclinic space group $P\bar{1}$, and the cell parameters are: a 7.218(2), b 7.441(3), c 7.972(3) Å, α 114.1(1), β 104.05(10), γ 97.8(1)°, $Z = 1$. The coordination geometry about the tin atom is all-*trans* octahedral; the *N*Miz ligands are bonded to the metal through their pyridine-like nitrogen atom. The Sn–C, Sn–Cl and Sn–N bond distances are 2.118(5), 2.571(3) and 2.329(5) Å, respectively. The ^1H NMR spectra are consistent with the presence of a *trans*-octahedral structure for $Me_2SnCl_2(NMiz)_2$ in solution, also.

Introduction

The complexation of dialkyltin dihalides with *N*-donor ligands is a subject of interest in relation to recent findings on the biological activity of these systems [1]. We have previously reported studies on complexes of methyltin halides with 3,5-dimethylpyrazole [2,3]. This paper reports single crystal and solution studies on the structure of a six-coordinate tin(IV) complex of *N*-methylimidazole, $Me_2SnCl_2(N\text{-}Miz)_2$. The study of the coordination of imidazoles can provide a model for the interaction of dialkyltin dihalides with histidyl residues of proteins and with the imidazole ring of purines.

Experimental

Crystals of $Me_2SnCl_2(N\mathrm{Miz})_2$ were obtained upon cooling a mixture of Me_2SnCl_2 and the ligand in the mol ratio of 1/2 in CH_2Cl_2. Precession photographs and single crystal diffractometry showed that the crystals belong to the triclinic system, space group $P\bar{1}$ (after structure determination) with a 7.298(3), b 7.441(3), c 7.972(3) Å, α 114.1(1), β 104.05(10), γ 97.8(1)°, V 369.6 Å^3, D_o 1.72 (by flotation), D_c 1.725 g cm^{-3} for $Z = 1$, $\lambda(\text{Mo-}K_\alpha)$ 0.7107 Å, $\mu(\text{Mo-}K_\alpha)$ 20.85 cm^{-1}.

Intensity data were collected from a crystal of approximate dimensions 0.50 × 0.40 × 0.25 mm on a Philips PW 1100 four-circle diffractometer operating in the $\vartheta/2\vartheta$ scan mode (scan width 1.80°, scan speed 0.045° s^{-1}, total background time 20 s) and using Mo-K_α radiation, monochromatized by a graphite crystal. 1301 independent reflections (2ϑ scan limit 4–50°) were measured, of which 1300 had $I \geqslant 3\sigma(I)$. During the data collection two standard reflections ($2\bar{2}0$ and 222) were measured every 180 min to check the stability of the crystal and the electronics. Intensities were corrected for Lorentz and polarisation effects and put on an absolute scale by Wilson's method. An experimental absorption correction was applied [4].

The structure was determined by the heavy-atom technique. A Patterson synthesis revealed the position of Cl atoms The positions of the remaining non-hydrogen atoms were derived from subsequent difference Fourier maps. The structure was refined by full-matrix least-squares procedure. The function $\Sigma w\Delta^2$ ($\Delta = |F_o| - |F_c|$) was minimized and w was $[\sigma^2(F_o) + 0.00549F_o^2]^{-1}$. Weighting-scheme analysis showed no serious dependence of the mean $w\Delta^2$ as a function of either $|F_o|$ and $\lambda^{-1}\sin\vartheta$. Atomic scattering factors were taken from ref. 5. Allowance was made for the anomalous scattering of tin and chlorine atoms using values of $\Delta f'$ and $\Delta f''$ taken from ref. 5. The refinement was carried out allowing all non-hydrogen atoms to vibrate anisotropically. Hydrogen atoms were located from Fourier difference maps but not refined. The final conventional R value for 1300 observed reflections ($I \geqslant 3\sigma(I)$) was 0.039 ($R_w = 0.036$). The calculations were carried out with an IBM 370/158 computer using the SHELX-76 program for crystal structure determination [6].

TABLE 1

FINAL ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS (Å$^2 \times 10^3$) WITH e.s.d.'s IN PARENTHESES

Atom	x	y	z	$U^\star_{eq}$ ^{a}
Sn	0	0	0	34(1)
Cl(1)	1896(2)	−2679(2)	−1164(2)	54(1)
N(1)	2481(4)	1668(5)	3009(4)	43(1)
N(2)	5342(4)	2568(4)	5215(4)	43(1)
C(1)	1526(5)	1734(5)	−1026(5)	50(1)
C(2)	4319(5)	1557(5)	3324(5)	45(1)
C(3)	4132(6)	3384(6)	6169(6)	53(1)
C(4)	2351(5)	2820(6)	4799(5)	51(1)
C(5)	7447(6)	2791(6)	6092(7)	63(1)

^{a} $U^\star_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a^\star_i a^\star_j a_i a_j$

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

Sn–Cl(1)	2.571(3)	N(1)–Sn–C(1)	89.8(2)
Sn–N(1)	2.329(5)	Cl(1)–Sn–C(1)	88.6(3)
Sn–C(1)	2.118(5)	Cl(1)–Sn–N(1)	89.2(2)
N(1)–C(2)	1.324(5)	Sn–N(1)–C(4)	128.6(5)
N(1)–C(4)	1.367(5)	Sn–N(1)–C(2)	125.4(3)
N(2)–C(2)	1.331(5)	C(2)–N(1)–C(4)	105.9(5)
N(2)–C(3)	1.350(6)	C(3)–N(2)–C(5)	126.5(4)
N(2)–C(5)	1.480(5)	C(2)–N(2)–C(5)	125.6(5)
C(3)–C(4)	1.359(5)	C(2)–N(2)–C(3)	107.8(5)
		N(1)–C(2)–N(2)	110.8(5)
		N(2)–C(3)–C(4)	106.7(5)
		N(1)–C(4)–C(3)	108.7(5)

Final atomic positional parameters are reported in Table 1 and a selection of functions derived from them are presented in the Tables 2–4.

Final atomic thermal parameters and tables of structure factors are available from the authors on request.

The ^1H NMR spectra were measured with a Bruker WP 60 spectrometer.

Results and discussion

A view of the structure of $Me_2SnCl_2(N\text{Miz})_2$ in the solid state is presented in Fig. 1, together with the numbering scheme used in this paper. The coordination geometry about the tin atom is all-*trans* octahedral; the Sn–C, Sn–N, Sn–Cl and ligand bond distances are identical in pairs. The *N*Miz ligands are bonded to the metal through their pyridine-like nitrogen atom. The rings are planar, with no atom deviating from the least-squares plane through the five atoms by more than 0.002(7) Å. The $N-CH_3$ bond is also very close to the ring plane. The bond distances and bond angles of *N*Miz found in this complex are very similar to those observed in other *N*Miz metal complexes [7].

TABLE 3

TORSION ANGLES (°)

Cl(1)–Sn–N(1)–C(2)	24.3(6)
Cl(1)–Sn–N(1)–C(4)	−150.8(6)
C(1)–Sn–N(1)–C(4)	120.7(6)
C(1)–Sn–N(1)–C(2)	−64.2(6)
Sn–N(1)–C(4)–C(3)	175.8(5)
Sn–N(1)–C(2)–N(2)	−175.7(4)
C(2)–N(1)–C(4)–C(3)	0.0(7)
C(4)–N(1)–C(2)–N(2)	0.3(7)
C(3)–N(2)–C(2)–N(1)	−0.5(7)
C(5)–N(2)–C(2)–N(1)	−179.1(6)
C(2)–N(2)–C(3)–C(4)	0.5(7)
C(5)–N(2)–C(3)–C(4)	179.0(6)
N(2)–C(3)–C(4)–N(1)	−0.3(7)

TABLE 4

SOME MEAN PLANES

Plane	Atoms, equation of plane, distance (Å) of atoms from plane			
1	Sn N(1) C(1)			
	$0.7114x - 0.6279y - 0.3157z = 0$			
	Cl(1) ^{a} 2.570(5)			
2	$0.1658x + 0.9815y - 0.0951z = 0.1384$			
	N(1)	−0.001(6)	C(3)	0.002(7)
	N(2)	−0.002(6)	C(4)	−0.001(7)
	C(2)	0.002(7)	C(5) ^{a}	0.019
3	$0.4849x + 0.7954y - 0.3635z = -0.0318$			
	Cl(1)	−0.008(5)	C(2) ^{a}	0.316(6)
	Sn	0.032(5)	C(3) ^{a}	−0.549(7)
	N(1)	−0.077(6)	C(4) ^{a}	−0.625(7)
	N(2)	0.038(6)	C(5) ^{a}	0.354(7)

Dihedral angles between the planes

Planes	Angle (°)
1–2	117.9(2)
1–3	92.3(1)
2–3	26.4(2)

[a] Atom not use in the plane calculation.

The structure of $Me_2SnCl_2(N\text{Miz})_2$ can relevantly be compared with the structurally-related complexes $Me_2SnCl_2(dmp)_2$ [3] and $Me_2SnCl_2(py)_2$ [8] (dmp = 3,5-dimethylpyrazole, py = pyridine). The coordination bond angles between *cis*-ligands in the *N*Miz complex are close to 90°, as found also in the analogous pyridine complex; whereas different N–Sn–Cl bond angles (84 and 96°) are displayed in the

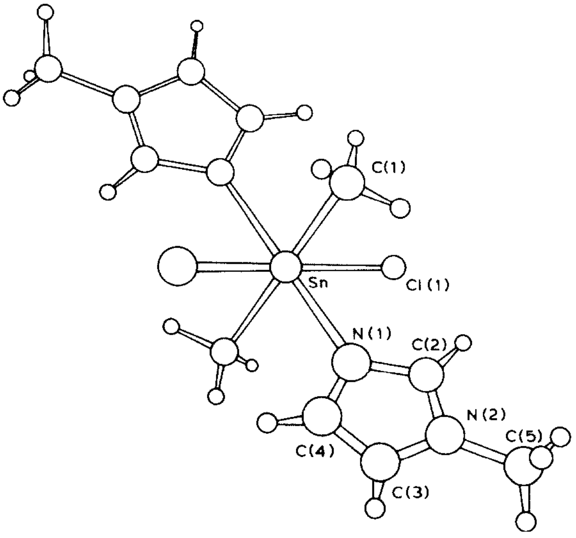

Fig. 1. View of the molecular shape of the complex $Me_2SnCl_2(N\text{Miz})_2$ with the atom numbering scheme.

dmp adduct. The difference of bond angles in the last complex is attributed mainly to non-bonded intramolecular interactions which are due to the presence of a methyl group near to the binding site of dmp.

In the complex $Me_2SnCl_2(N\text{Miz})_2$, the dihedral angle between the imidazole ring and the Sn, N, Cl plane is 26°, while the angle between the ligand ring plane and the Sn, N, Cl plane is 33° in the complex $Me_2SnCl_2(dmp)_2$ and 26° in the complex $Me_2SnCl_2(py)_2$. The somewhat greater dihedral angle observed in the dmp complex is accounted for by non-bonded interactions at the C(3)-methyl group of the ligand and by hydrogen bonding interactions [3].

The Sn–N bond lengths in the analogous 1 : 2 adducts of Me_2SnCl_2 are 2.33 (*N*Miz), 2.38 (dmp) and 2.39 Å (py). Differences of tin–nitrogen bond lengths might be related to the steric requirements and donor abilities of the heterocyclic ligands, as estimated from their basicities (the pK_a values are: 7.1 (*N*Miz), 4.1 (dmp) and 5.2 (py)). However, the observed differences are small, and allowance should also be made for the presence of different pairs of *trans*-ligands in the complexes. It has been noted previously that the relative stabilities of 1 : 1 adducts of Me_3SnCl with dmp and py bear no relationship to the basicities of the ligands [2]. The stability of $Me_3SnCl(dmp)$ towards dissociation of the N-ligand in CCl_4 is an order of magnitude greater than that of $Me_3SnCl(py)$ in the same solvent despite the lower basicity and the greater steric hindrance of dmp. This result can be accounted for by the low degree of covalent character of the Sn–N bonds in the adducts of *N*-donor heterocyclic ligands. This deduction is supported by the observation that the Sn–N bond lengths in the reported complexes of the type *trans*-$Me_2SnCl_2L_2$ significantly exceed the sum of the atomic radii of tin and nitrogen (2.10 Å [9]) and are similar to values found for complexes of the type $R_2SnX_2L_2$ having two donor N atoms in a *cis* arrangement [10].

^1H NMR measurements on the system Me_2SnCl_2-*N*Miz in $CDCl_3$ have been carried out in order to obtain information on the structure of $Me_2SnCl_2(N\text{Miz})_2$ in solution. Coupling constants $J(^{119}Sn-^1H)$ 69.0 and $J(^{117}Sn-^1H)$ 65.5 Hz are measured for the compound Me_2SnCl_2. For the five-coordinated complex $Me_2SnCl_2(N\text{Miz})$ in the same solvent the corresponding *J*-values are 90.0 and 86.5 Hz. The increase of observed coupling constants on going from Me_2SnCl_2 to $Me_2SnCl_2(N\text{Miz})$ is in agreement with a trigonal bipyramidal structure for the 1 : 1 *N*Miz adduct, with the methyl groups in the trigonal plane [11]. A further increase of tin-proton coupling constants is observed for a saturated solution of $Me_2SnCl_2(N\text{Miz})_2$ in the presence of an excess of the ligand. The observed limiting values $J(^{119}Sn-^1H)$ 116.5 and $J(^{117}Sn-^1H)$ 110.0 Hz are even greater than the coupling constants previously reported, for the aqueous Me_2Sn^{2+} cation, as the highest values found in methyltin(IV) derivatives. The magnitude of the observed coupling constants is consistent with an octahedral structure for $Me_2SnCl_2(N\text{Miz})_2$ involving a linear C–Sn–C arrangement being present in solution also [11].

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