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THE STRUCTURE OF DICHLORODIMETHYLBIS(PYRAZOLE-N^2)TIN(IV)

G. VALLE,

Centro di Studio sui Biopolimeri del C.N.R.,
Department of Organic Chemistry, University of Padua (Italy)

R. ETTORRE,

Centro di Studio sulla Stabilita' e Reattivita' dei Composti di Coordinazione del C.N.R., Department of Inorganic, Organometallic and Analytical Chemistry, University of Padua (Italy)

V. PERUZZO* and G. PLAZZOGNA

Department of Inorganic, Organometallic and Analytical Chemistry, University of Padua,
Via Marzolo, 1, 35131 Padua (Italy)

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Summary

The structure of the complex $Sn(CH_3)_2Cl_2 \cdot 2C_3H_4N_2$ has been determined by single crystal X-ray diffraction methods. The compound crystallizes in the monoclinic system, space group $C2/c$ (no. 15), with unit cell dimensions a 14.010(4), b 7.906(3), c 13.617(4) Å, β 114.7(3)°, and $Z = 4$. The configuration about the tin atom is all-*trans*-octahedral. The pyrazole ligands, coordinated through the imino nitrogen atom, are intramolecularly and intermolecularly hydrogen bonded to the chloride ligands, the N(1)–H ··· Cl distances being 3.480 and 3.297 Å, respectively. Structural features of the complex are compared with those of other complexes of *N*-bonded heterocyclic ligands of the type $Sn(CH_3)_2Cl_2 \cdot 2L$.

Hydrogen bonding is an important feature of the structure of several organotin(IV) complexes [1]. Outer sphere coordination and intramolecular interactions through hydrogen bonds are exemplified by the structures of the complexes diaquadichlorodimethyltin(IV)/purine (1/4) [2] and dichlorodimethylbis[2(1*H*)-pyridinethione-*S*] [3], respectively. Formation of N–H ··· Cl bonds is also displayed by the title compound. Its crystals structure, reported here, is compared with that of the closely related complex dichlorodimethylbis(3,5-dimethylpyrazole)tin(IV) [4] and those of other *trans* octahedral adducts of $Sn(CH_3)_2Cl_2$ with *N*-bonded heterocyclic ligands.

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TABLE 1

FRACTIONAL COORDINATES

Atom	x/a	y/b	z/c
Sn	0.0	0.0	0.0
Cl	0.0737(2)	0.2178(4)	−0.0903(2)
N(1)	0.1749(6)	−0.0590(12)	0.2503(7)
N(2)	0.1611(5)	−0.0166(12)	0.1512(6)
C(3)	0.2568(7)	0.0256(17)	0.1569(8)
C(4)	0.3308(8)	0.0082(18)	0.2641(10)
C(5)	0.2774(9)	−0.0471(17)	0.3229(9)
C(6)	0.0501(8)	−0.1976(15)	−0.0720(9)

Experimental

Crystals of $Sn(CH_3)_2Cl_2 \cdot 2C_3H_4N_2$ were obtained by diffusion of cyclohexane into a solution of the complex in dichloromethane. A well formed crystal of approximate dimensions 0.25 × 0.25 × 0.7 mm was used for X-ray analysis.

The compound $C_8H_{14}Cl_2N_4Sn$, $M = 356$, crystallizes in the monoclinic system, space group $C2/c$ (no. 15), a 14.010(4), b 7.906(3), c 13.617(4) Å, β 114.7(3)°, $Z = 4$, D_c 1.725 g cm^{-3}, $F(000) = 696$. Intensity data were collected using a Philips PW 1100 four-circle diffractometer in the range $4 < 2\theta < 50$, with Mo-K_α monochromatized radiation. Reflections with $I \geqslant 3\sigma(I)$ were considered as observed (1058 out of 1214). The intensities were collected for Lorentz and polarization effects, but not for absorption.

The position of the non-hydrogen atoms were obtained from a three-dimensional Fourier synthesis with the tin atom in the special position 1. The hydrogen atoms were located from a Fourier difference map. Final refinements were carried out with anisotropic thermal parameters for all the non-hydrogen atoms. The final conventional R factor was 0.0438. The function minimized was $\Sigma w \Delta F^2$, with $w = 1$. Scattering factors for all atoms were those incorporated in the program SHELX [5]. Positional parameters of non-hydrogen atoms are listed in Table 1.

Results and discussion

The structure of $Sn(CH_3)_2Cl_2 \cdot 2C_3H_4N_2$ is shown in Fig. 1 together with the atom-numbering scheme. Selected bond lengths and angles are reported in Table 2. The tin atom is at a centre of symmetry. The Sn–C, Sn–N and Sn–Cl distances are similar to those in other *trans* octahedral adducts of dimethyltin dichloride. The H atom on the N(1) atom of each pyrazole takes part in an intramolecular hydrogen bond with a chloride ligand and in an intermolecular hydrogen bond with a chloride in a neighboring molecule at x; $\bar{y}$; $\frac{1}{2} + z$. Values of N–H...Cl distances in $Sn(CH_3)_2Cl_2 \cdot 2C_3H_4N_2$ and in other methylchlorotin(IV) derivatives are compared in Table 3.

The IR spectrum of the title compound is consistent with relatively weak hydrogen bonding. The N–H stretching mode absorption is characteristically shifted to lower frequency by ca. 180 cm^{-1} with respect to the uncomplexed monomeric ligand, but the bandwidth is only increased from 20 to 120 cm^{-1}. By comparison,

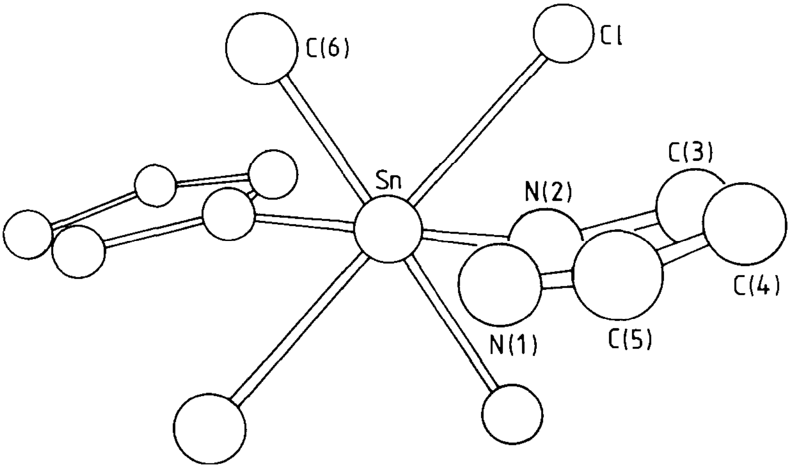

Fig. 1. Structure of $Sn(CH_3)_2Cl_2 \cdot 2C_3H_4N_2$.

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°)

Sn–Cl	2.570(3)	N(2)–C(3)	1.352(13)
Sn–N(2)	2.338(6)	C(3)–C(4)	1.400(14)
Sn–C(6)	2.114(13)	C(4)–C(5)	1.376(21)
N(1)–N(2)	1.324(12)	C(5)–N(1)	1.364(12)
Cl–Sn–Cl	180	Sn–N(2)–C(3)	127.3(7)
N(2)–Sn–N(2)	180	N(1)–N(2)–C(3)	106.6(7)
C(6)–Sn–C(6)	180	N(2)–C(3)–C(4)	108.7(11)
N(2)–Sn–Cl	91.5(2), 88.5(2)	C(3)–C(4)–C(5)	107.0(9)
C(6)–Sn–Cl	89.7(4), 90.3(4)	C(4)–C(5)–N(1)	105.3(10)
C(6)–Sn–N(2)	88.9(3), 91.1(3)	C(5)–N(1)–N(2)	112.5(10)
Sn–N(2)–N(1)	126.0(6)		

TABLE 3

HYDROGEN BONDS N–H ··· Cl IN METHYLTIN(IV) COMPLEXES

Compound	Distance N–H ··· Cl (Å)
$[C_5H_5NH]_2[(CH_3)SnCl_4]$ [a]	3.243, 3.312
$[C_9H_7NH][(CH_3)_2SnCl_3]$ [a]	3.181, 3.599
$[2\text{-}H_3NC_6H_4C(O)NH_2][(CH_3)_2SnCl_4](H_2O)_2$ [a]	3.211
$Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$ [b]	3.199
$Sn(CH_3)_2Cl_2 \cdot 2C_5H_8N_2$ [c]	3.264 [d], 3.452 [e]
$Sn(CH_3)_2Cl_2 \cdot 2C_3H_4N_2$	3.297 [e]; 3.480 [d]

[a] F.A.K. Nasser, M.B. Hossain, D. van der Helm, and J.J. Zuckerman, Inorg. Chem., 23 (1984) 606 and ref. therein. [b] Ref. 3. [c] Ref. 4. [d] Intramolecular. [e] Intermolecular.

the complex dichlorodimethylbis[2(1*H*)pyridinethione-*S*]tin(IV), where much shorter N–H · · · Cl contacts are found, displays an N–H stretching band extending over several hundreds of cm^{-1}. Formation of intra- and inter-molecular N–H · · · Cl bonds is also a feature of dichloromethylbis(3,5-dimethylpyrazole)tin(IV) [4]. However, the intramolecular N · · · Cl distances in this complex are shorter than the intermolecular N · · · Cl distances, whereas the opposite is observed in the pyrazole complex (Table 3). The closer intramolecular N · · · Cl contact in the dimethylpyrazole complex is the result of the presence of an exocyclic methyl group near to the binding site of the ligand. In this complex there are significant differences between the N–Sn–Cl bond angles (84.1 and 95.8°) and between the Sn–N–N and Sn–N–C bond angles (118.7 and 135.8°). Hydrogen bonding in both complexes is not strong enough to make the pyrazole ring nearly coplanar with the metal–halide bond, as was observed for other metal complexes of pyrazoles [6]. This can be accounted for in terms of the relatively large metal–nitrogen bond length.

The orientation of the pyrazole ligands in $Sn(CH_3)_2Cl_2 \cdot 2C_3H_4N_2$ is comparable with that observed for other *N*-bonded heterocyclic ligands in all-*trans*-octahedral complexes of the type $Sn(CH_3)_2Cl_2 \cdot 2L$, showing that the conformation about the tin–nitrogen bond in these compounds is determined by similar intramolecular interactions. The following values for the angle between the normals to the plane (Sn, Cl, N) and to the plane of the heterocyclic ligand are calculated: 24° (L = pyrazole), 33° (L = 3,5-dimethylpyrazole), 24° (L = *N*-methylimidazole [7]) and 26° (L = pyridine [8]). The fact that the angles are significantly less than 45° is not ascribed to the bulkiness of the ligands (CH_3, Cl), since the highest angle is observed for the most hindered base. The conformation of these complexes arises from the difference of the polarities of the coordination bonds, which favour a closer approach of the hydrogen atoms of the heterocyclic ligand to the more negatively charged chloride ligands.

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