Crystal Structure of Dichlorobis(3,5-dimethylpyrazole-N^2)dimethyltin(IV)

By **Rodolfo Graziani,** Istituto di Chimica Generale, Università di Padova, Padova, Italy
Umberto Casellato, Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., 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
Gualtiero Plazzogna,* Istituto di Chimica Analitica, Università di Padova, Padova, Italy

The structure of the title compound, $SnMe_2Cl_2(dmp)_2$, has been determined by single-crystal *X*-ray techniques using diffractometer data. The compound crystallizes in the monoclinic space group *C*2/*c* with four molecules in a cell of dimensions a = 13.62(1), b = 10.42(1), c = 12.34(1) Å, and β = 92.76(5)°. Least-squares refinement of the structure has led to a final *R* value of 0.045 using 1 122 observed intensities. The complex consists of discrete *trans*-$SnMe_2Cl_2(dmp)_2$ units held together by intermolecular Cl ··· H bonds to form infinite linear chains along the *c* axis. The tin and the metal-bonded methyl carbon atoms lie on a crystallographic two-fold axis of symmetry. The 3,5-dimethylpyrazole ligands are bonded to the metal through their pyridine-like nitrogen atom. The Sn–C, Sn–Cl, and Sn–N bond distances are 2.11(1), 2.581(2), and 2.379(6) Å respectively.

THE co-ordination chemistry of the dialkyltin dihalides is of interest in relation to the biological activity displayed by these compounds.[1] We have previously reported spectroscopic and thermodynamic studies on complexes of methyltin halides with 3,5-dimethylpyrazole (dmp).[2] This paper describes the crystal and molecular structure of the six-co-ordinate tin complex $SnMe_2Cl_2(dmp)_2$.

EXPERIMENTAL

The complex $SnMe_2Cl_2(dmp)_2$ was prepared as described previously.[2] A well formed prismatic crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm was used to determine the cell dimensions and to measure the intensity data.

The crystal was coated with cyanoacrylate adhesive and mounted in a Lindemann glass capillary tube on the goniostat of a Philips PW 1100 diffractometer. Accurate cell parameters were obtained by least-squares refinement of 25 medium angle settings.

Crystal Data.—$C_{12}H_{22}Cl_2N_4Sn$, $M = 411$, Monoclinic, $a = 13.62(1)$, $b = 10.42(1)$, $c = 12.34(1)$ Å, $\beta = 92.76(5)°$, $U = 1\,750$ Å^3, $D_m = 1.56(1)$, $Z = 4$, $D_c = 1.56$ g cm^{-3}, $F(000) = 824$, μ(Mo-K_α) = 34.5 cm^{-1}, space group *C*2/*c* from systematic absences hkl, $h + k = 2n + 1$; $h0l$, $h = 2n + 1$ and $l = 2n + 1$; $0k0$, $k = 2n + 1$.

Data Collection.—Data, up to $\theta = 25°$, were collected by the θ—2θ step-scan method using Mo-K_α radiation (λ = 0.7107 Å). Each reflection was scanned over 1.2° in 2θ for 30 s and the associated two background counts for 10 s. The intensities of two standard reflections monitored every hour showed no significant variations during data collection. All reflections with an intensity less than three times the estimated standard deviation of the total counts were considered as non-observed, reducing the total number of reflections from 1 710 to 1 122. The intensities were corrected for Lorentz and polarization effects. No absorption correction was made.

Structure Determination.—The fact that only four molecules per unit cell are present in space group *C*2/*c* having eight general positions implies that the tin atoms lie on special positions and that the asymmetric unit corresponds to a half molecule. It was found that the tin atoms are on two-fold axes in the equipoints $(0\ 0\ 0;\ \tfrac{1}{2}\ \tfrac{1}{2}\ 0) + (0\ y\ \tfrac{1}{4};\ 0\ \bar{y}\ \tfrac{3}{4})$ of the cell. Attempts to locate these atoms on inversion centres gave no positive results. The positions of all the non-hydrogen atoms were then determined by successive Fourier syntheses. Full-matrix least-squares refinement with isotropic thermal parameters converged to an *R* value of 0.072. The function minimized was $\Sigma w \Delta F^2$ and each reflection was assigned unit weight. Refinement was continued with anisotropic thermal parameters to an *R* factor of 0.053. At this point, an electron-density difference map allowed determination of most hydrogen-atom co-ordinates, which were varied in subsequent refinement with fixed thermal parameters of 8 Å^2. Location of the hydrogens of the two methyl groups directly bonded to tin is complicated by the fact that their carbon atoms also lie on the two-fold axis. However, the molecule itself does not possess two-fold symmetry along the C–Sn–C axis due to the presence of the methyl hydrogen atoms. Therefore, these hydrogens must be statistically distributed in two positions related by the binary axis and should be introduced with occupancy factors of 0.5. Because of the uncertainty in their positions and of the little interest in them in this structure, these atoms were not included. At convergence the conventional *R* value was 0.045. A final electron-density difference map had no unusual features.

TABLE 1

Atomic parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Sn	0	0.162 4(1)	0.2500
Cl	−0.057 4(2)	0.159 6(3)	0.047 7(2)
N(1)	0.160 3(5)	0.158 6(8)	0.181 7(6)
N(2)	0.175 1(5)	0.091 0(7)	0.089 6(6)
C(1)	0	0.364 9(13)	0.2500
C(2)	0	0.958 4(14)	0.2500
C(3)	0.260 9(10)	0.284 2(13)	0.313 2(12)
C(4)	0.249 2(6)	0.202 4(8)	0.215 1(8)
C(5)	0.318 7(6)	0.163 8(11)	0.142 9(8)
C(6)	0.270 4(6)	0.092 4(9)	0.064 3(8)
C(7)	0.305 3(10)	0.024 8(20)	−0.032 8(14)
H(1)	0.124 3(88)	0.041 7(117)	0.050 0(99)
H(31)	0.317 6(94)	0.283 3(123)	0.358 4(104)
H(32)	0.211 1(92)	0.277 6(117)	0.377 0(103)
H(33)	0.266 5(106)	0.361 3(128)	0.295 3(117)
H(71)	0.331 9(112)	−0.000 5(208)	−0.018 7(158)
H(72)	0.353 3(90)	0.095 5(116)	−0.096 9(100)
H(73)	0.261 4(93)	0.021 3(149)	−0.081 7(112)
H(51)	0.383 6(88)	0.188 4(119)	0.164 9(96)

Scattering factors for the tin atom were taken from Cromer and Waber,[3] with corrections for anomalous dispersion;[4] those for the other non-hydrogen atoms were from Cromer and Mann,[5] while those for hydrogen were from ref. 6.

TABLE 2

Bond and contact distances (Å) with estimated standard deviations in parentheses

(*a*) Bond distances			
(*i*) Co-ordination sphere			
Sn–Cl	2.581(2)	Sn–C(1)	2.11(1)
Sn–N(1)	2.379(6)	Sn–C(2)	2.12(1)
(*ii*) Ligand			
N(1)–N(2)	1.36(1)	N(2)–H(1)	0.97(12)
N(1)–C(4)	1.34(1)	C(5)–H(51)	0.95(12)
N(2)–C(6)	1.35(1)	C(3)–H(31)	0.93(13)
C(4)–C(5)	1.39(1)	C(3)–H(32)	1.06(13)
C(5)–C(6)	1.37(1)	C(3)–H(33)	0.84(14)
C(3)–C(4)	1.48(2)	C(7)–H(71)	
C(6)–C(7)	1.49(2)	C(7)–H(72)	1.08(13)
		C(7)–H(73)	0.83(13)
(*b*) Contact distances *			
Cl ··· H(1)	2.76(12)	Cl ··· H(31^{II})	2.88(12)
Cl ··· H(1^{I})	2.56(12)	Cl ··· H(32^{III})	2.64(12)
Cl ··· Cl^{I}	3.883(5)		

* Roman numeral superscripts refer to the symmetry transformations: I $\bar{x}, \bar{y}, \bar{z}$; II $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; III, $\bar{x}, y, \frac{1}{2} - z$.

TABLE 3

Bond angles (°) with estimated standard deviations in parentheses *

(*a*) Co-ordination sphere			
Cl–Sn–N(1)	84.1(2)	Cl–Sn–C(2)	89.3(1)
Cl–Sn–N(1^{II})	95.8(2)	N(1)–Sn–C(1)	91.0(2)
Cl–Sn–C(1)	90.7(1)	N(1)–Sn–C(2)	89.0(2)
(*b*) Ligand			
Sn–N(1)–N(2)	118.7(5)	C(7)–C(6)–N(2)	122.3(6)
Sn–N(1)–C(4)	135.8(6)	C(6)–N(2)–N(1)	111.7(7)
N(2)–N(1)–C(4)	105.4(6)	N(1)–N(2)–H(1)	124(7)
N(1)–C(4)–C(5)	109.7(8)	C(6)–N(2)–H(1)	124(8)
N(1)–C(4)–C(3)	120.4(9)	N(2)–H(1) ··· Cl^{I}	153(9)
C(3)–C(4)–C(5)	129.8(9)	N(2)–H(1) ··· Cl	113(8)
C(4)–C(5)–C(6)	107.0(8)	Sn–Cl ··· H(1)	76(2)
C(5)–C(6)–N(2)	106.1(8)	Sn–Cl ··· H(1^{I})	123(3)
C(5)–C(6)–C(7)	131.9(9)	H(1) ··· Cl ··· H(1^{I})	86(4)

* Roman numeral superscripts refer to the symmetry transformations: I $\bar{x}, \bar{y}, \bar{z}$; II $\bar{x}, y, \frac{1}{2} - z$.

TABLE 4

Least-squares planes and deviations (Å) of atoms from the planes; X, Y, and Z are fractional co-ordinates in the direct cell *

Plane 1: Sn, Cl, N(1)

$$0.166X + 10.421Y - 0.191Z = 1.644$$

Plane 2: N(1), N(2), C(4), C(5), C(6)

$$-1.896X + 8.642Y - 6.592Z = -0.135$$

[N(1) 0.004, N(2) −0.001, C(4) −0.006, C(5) 0.005, C(6) −0.003, *Sn* −0.109, *C*(3) 0.032, *C*(7) −0.013]

Plane 3: Cl, Cl^{I}, H(1)

$$-3.370X - 4.988Y + 10.533Z = -0.100$$

Plane 4: Cl, N(2), H(1)

$$3.370X + 4.988Y - 10.533Z = 0.100$$

Angles (°) between the planes

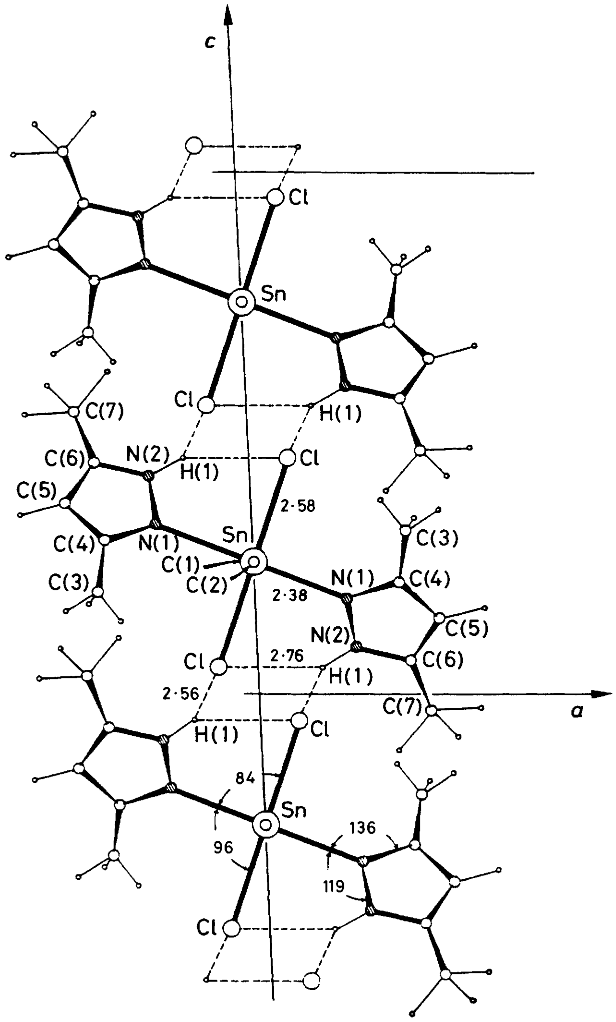
Planes	Angle	Planes	Angle
1—2	33.3	2—3	37.5
1—3	64.3	2—4	35.1
1—4	60.4	3—4	4.5

* Atoms not used in the plane calculation are italicized.

All calculations were performed on a CDC 7600 computer using the '*X*-Ray '72 ' program system.[7] Final positional parameters are listed in Table 1, bond lengths and angles in Tables 2 and 3, and details of planes in Table 4. Thermal parameters and observed and calculated structure factors are deposited as Supplementary Publication No. SUP 23227 (11 pp.).*

RESULTS AND DISCUSSION

A view of the structure of $SnMe_2Cl_2(dmp)_2$ down the *b* axis is shown in the Figure. In each molecule the tin atom is bonded to two methyl groups, two chlorine atoms, and two dmp ligands through their pyridine-like imino-nitrogen. The tin and the metal-bonded methyl carbon atoms lie on a crystallographic two-fold axis of symmetry. Hence, the Sn–Cl, Sn–N, and ligand bond distances are in identical pairs, while the two Sn–C bonds are independent.



View of the structure of $SnMe_2Cl_2(dmp)_2$ down the *b* axis showing the atom-labelling scheme, bond lengths (Å), and angles (°)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

The bond lengths and angles of the pyrazole ring in the Sn–dmp complex are very close to the values reported for pyrazole, 5-methylpyrazole, and pyrazolylborato-metal complexes.[8] The five-membered ring is strictly planar and the C(3)–C(4) and C(6)–C(7) bonds are close to the ring plane. It should be noted that both C–C–C external angles are *ca.* 10° larger than the external N–C–C angles. This asymmetry in bond angles, also observed for 5-methylpyrazole,[8] can be ascribed to electronic effects within the ligand, where the ring carbon atoms bearing a methyl group are bonded to the more electronegative nitrogen atom.[9]

The Sn–dmp complex has the same *trans* configuration as the related complex $SnMe_2Cl_2(NC_5H_5)_2$,[10] with very similar Sn–C, Sn–Cl, and Sn–N bond distances [2.12, 2.58, and 2.38 Å (dmp); 2.15, 2.57, and 2.39 Å (pyridine) respectively]. However, significant differences between the complexes are observed as far as distortion in the co-ordination octahedron (bond angles) and intermolecular interactions are concerned.

Each chlorine atom of $SnMe_2Cl_2(dmp)_2$ makes an intramolecular contact of 2.76 Å with a hydrogen atom at N(2) and a closer intermolecular contact of 2.56 Å with a hydrogen atom at N(2) in a nearby molecule. Since both Cl · · · H contact distances are shorter than the van der Waals radii of 3.0 Å,[11] it could be inferred that the amine hydrogen of each dmp ligand is involved in two N–H · · · Cl bonds. Evidence for hydrogen bonding in solid $SnMe_2Cl_2(dmp)_2$ has been previously shown by i.r. measurements.[2] However, the rather long contact distance of 2.76 Å and the rather small N(2)–H · · · Cl angle (113°) suggest only a weak interaction, whereas the Cl^I · · · H contact distance of 2.56 Å and the observed N(2)–H · · · Cl^I angle (153°) are consistent with the presence of intermolecular hydrogen bonds. As shown in the Figure, each pair of adjacent molecules of $SnMe_2Cl_2(dmp)_2$ makes two such interactions, so that the molecules along the *c* axis of the cell are held together to form infinite linear chains.

The structure of $SnMe_2Cl_2(dmp)_2$ can be compared with the structures of complexes of the type *trans*-$[ML_4X_2]$ [8] ($M = Mn^{II}$, L = 5-methylpyrazole, X = Br; $M = Ni^{II}$, L = pyrazole, X = Cl or Br). In these complexes a parallel orientation of the pyrazole rings with respect to the M–X direction is found. This orientation differs greatly from that observed in analogous pyridine complexes, where the heterocyclic rings are inclined by *ca.* 45° to the M–X direction due to the formation of internal N–H · · · X hydrogen bonds.

In the complex $SnMe_2Cl_2(dmp)_2$ the dihedral angle between the pyrazole ring and the Sn, Cl, N(1) plane is 33°, while in the related complex $SnMe_2Cl_2(NC_5H_5)_2$ the angle between the pyridine ring and the Sn, Cl, N plane is 26°. Therefore, it appears that, in the Sn–dmp complex, non-bonded intramolecular intractions are the determining factors for the ligand orientation about the Sn–N bond, although hydrogen bonding may also play a part. Moreover, intramolecular non-bonded interactions at the C(3) methyl group of dmp are largely responsible for the differences between the N(1)–Sn–Cl bond angles (84.1 and 95.8°) and between the Sn–N(1)–N(2) and Sn–N(1)–C(4) angles (118.7 and 135.8°). For the complex $SnMe_2Cl_2(NC_5H_5)_2$ a Cl–Sn–N angle of 90.2° is reported.[10] Differences between M–N–N and M–N–C angles of *ca.* 10° are observed for the pyrazole and 5-methylpyrazole complexes of the type $[ML_4X_2]$ mentioned above.[8]

The C–Sn bond distances of $SnMe_2Cl_2(dmp)_2$ have similar values (2.11 and 2.12 Å) which agree with those found for other organotin complexes.[12] It is observed that in most cases the C–Sn bond distances are independent of the co-ordination number of tin and the nature of the ligands. On the contrary, Sn–Cl bond distances in octahedral organotin complexes are spread over a wide range of values. These distances appear to depend on the number of co-ordinated chlorine atoms and on their relative positions. Thus, Sn–Cl bond distances examined in several *cis*-$Sn^{IV}Cl_2$ six-co-ordinate complexes are in the range 2.41—2.53 Å, with a mean value of 2.49 Å,[12] while the following values have been found for *trans*-$Sn^{IV}Cl_2$ six-co-ordinate complexes: $SnMe_2Cl_2(dmp)_2$, 2.581 Å; $SnMe_2Cl_2(NC_5H_5)_2$, 2.570 Å;[10] $SnMe_2Cl_2(ONC_5H_5)_2$, 2.584 Å;[13] $SnMe_2Cl_2(H_2salen)$ [H_2salen = *NN'*-ethylenebis(salicylideneimine)], 2.59 and 2.64 Å.[14] It appears that Sn–Cl bond distances in *trans*-$Sn^{IV}Cl_2$ complexes are very similar and invariably longer than in *cis*-$Sn^{IV}Cl_2$ complexes. The Sn–N bond distance of 2.38 Å in $SnMe_2Cl_2(dmp)_2$ exceeds the sum of the atomic radii (2.10 Å, ref. 15) and is similar to the values found for $SnMe_2Cl_2(NC_5H_5)_2$ (2.39 Å, ref. 10), $SnPh_2Cl_2$(bipy) (2.34 and 2.38 Å ref. 16) (bipy = 2,2'-bipyridyl), $Sn(CHCH_2)_2(O_2CCF_3)_2$(bipy) (2.34 Å, ref. 17), and *cis*-$SnMe_2$(quin)$_2$ (quin = quinolin-8-olate) (2.31 and 2.38 Å).[18]

We thank Mrs. M. Magnabosco for valuable technical assistance. One of us (G. P.) also thanks C.N.R. for financial support.

[1/1237 *Received*, 6*th August*, 1981]

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