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Dichlorobis(3,5-dimethylpyrazole-*N*^{2})-methylphenyltin(IV)

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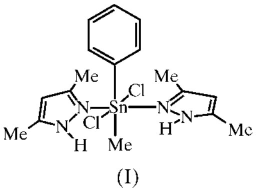
The title compound, $[SnCl_2(CH_3)(C_6H_5)(C_5H_8N_2)_2]$, was obtained by reaction of dichloromethylphenyltin(IV) and 3,5-dimethylpyrazole (dmpz) in chloroform, and was recrystallized from acetone. The structure consists of octahedral all-*trans* $[SnMePhCl_2(dmpz)_2]$ molecules, with the Sn atom coordinated to two C [Sn—C 2.127 (5) and 2.135 (4) Å], two Cl [Sn—Cl 2.5753 (8) Å] and two N atoms [Sn—N 2.357 (3) Å]. The dmpz ligands, bound to the metal through their unprotonated N atoms, form weak intra- and intermolecular hydrogen bonds with the Cl ligands *via* their NH groups, giving rise to a polymeric chain along the *c* axis.

Comment

Although the coordination chemistry of $[SnMe_2]^{2+}$ and $[SnPh_2]^{2+}$ derivatives has received some attention from a structural point of view, few structural studies have been carried out on compounds containing the mixed organometallic ion $[SnMePh]^{2+}$. In fact, a survey of the Cambridge Structural Database (Allen & Kennard, 1993) showed X-ray structures for only five such compounds: two complexes with ligands coordinating *via* deprotonated –SH groups (Drager, 1985; Doidge-Harrison *et al.*, 1996), $[SnMePhCl_2]$ (Amini *et al.*, 1987) and two adducts of the latter, $[SnMePhCl_2(H_2O)]_2\cdot$18-crown-6 (Amini *et al.*, 1994) and $[SnMePhCl_2(phen)]$ (Buntine *et al.*, 1998). As part of our work on structural and biological aspects of dihalodiorganotin(IV) derivatives, we have prepared some new complexes of $[SnMePhCl_2]$, one of which, $[SnMePhCl_2(dmpz)_2]$, (I), was studied by X-ray diffraction (Fig. 1).



(I)

The C1, Sn1, C11 and C14 atoms lie on a crystallographic twofold axis of symmetry. The Sn atom is six-coordinated in a slightly distorted all-*trans* octahedral environment. The Sn—C$_{Ph}$ and Sn—C$_{Me}$ bond lengths (Table 1) are similar to those found in the other two $SnMePhCl_2$ adducts that have been described, $[SnMePhCl_2(H_2O)]_2\cdot$18-crown-6 [Sn—C$_{Ph}$ = 2.103 (6) and Sn—C$_{Me}$ = 2.124 (3) Å] (Amini *et al.*, 1994) and $[SnMePhCl_2(phen)]$ [Sn—C$_{Ph}$ = 2.146 (5) and Sn—C$_{Me}$ = 2.130 (6) Å; Buntine *et al.*, 1998]. The Sn1—Cl1 bond length, 2.5753 (8) Å, is significantly longer than the range of 2.335 (9)–2.39 (1) Å found in the free acceptor $[SnMePhCl_2]$ (Amini *et al.*, 1987), in which the Sn atom is basically in a tetrahedral environment, and is also slightly longer than the 2.438 (2) and 2.500 (2) Å found in $[SnMePhCl_2(phen)]$, in which the Sn atom is in a *trans*-C$_2$ *cis*-Cl$_2$N$_2$ octahedral environment. The greater length of Sn1—Cl1 in $[SnMePhCl_2(dmpz)_2]$ may be due to the hydrogen bonds in which Cl1 is involved (see below). The Sn1—N1 distances are shorter than in the phenanthroline complex [2.386 (4) and 2.410 (4) Å].

The coordination of the dmpz ligand to the Sn atom mainly affects the N—N distance, which is longer than in the free ligand (N—N = 1.334 Å; Smith *et al.*, 1989). The dmpz ligands are essentially planar, their planes making angles of ±38.2 (1)° with the equatorial plane Sn1/Cl1/Cl1^i/N1/N1^i. These angles place the C6 methyl groups near the phenyl ring, the plane of which almost exactly bisects the Cl1—Sn1—N1 angle. This arrangement of the phenyl and pyrazole rings is stabilized by weak bifurcated intra- and intermolecular hydrogen bonds between N2 and Cl1 and Cl1^{ii} (Fig. 1 and Table 2). The

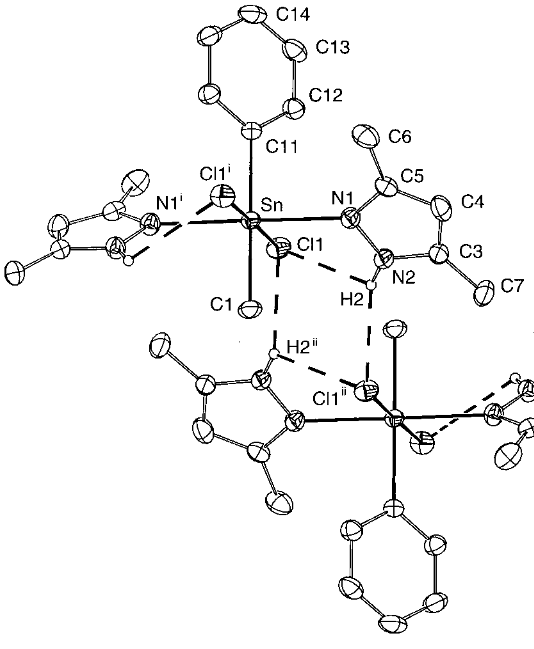


Figure 1
The crystal structure of $[SnMePhCl_2(dmpz)_2]$ with the atom-numbering scheme and ellipsoids drawn at the 30% probability level.

intermolecular hydrogen bonding links the molecules in a chain along the *c* axis. Additionally, C6, C7 and C12 are involved in weak intra- and intermolecular C—H···Cl interactions (Table 2).

It is worth comparing [SnMePhCl$_2$(dmpz)$_2$] with [SnMe$_2$Cl$_2$(dmpz)$_2$] (Graziani *et al.*, 1982). In both compounds, the Sn atoms lie at a special position on a C_2 symmetry axis with two independent Sn—C bonds, and the two Sn—Cl and Sn—N bond lengths are identical. However, in keeping with the expected greater Lewis acidity of the methylphenyltin(IV) unit, Sn—Cl and Sn—N are slightly shorter in [SnMePhCl$_2$(dmpz)$_2$]. The presence of the phenyl group also slightly modifies the angle between each dimethylpyrazole ring and the equatorial plane, which in [SnMe$_2$Cl$_2$(dmpz)$_2$] is 33.3°, and elongates the N2—H2···Cl1 hydrogen bond and all the intermolecular interactions.

Experimental

Dichloromethylphenyltin(IV) was prepared by reaction of trichlorophenyltin(IV) and tetramethyltin(IV) using a published method (Kuivila *et al.*, 1968). The title complex was obtained by reacting dmpz (0.068 g, 0.71 mmol) with SnMePhCl$_2$ (0.1 g, 0.35 mmol) dissolved in chloroform (2 ml). A white solid formed after a few minutes of stirring and was recrystallized from acetone, affording crystals suitable for X-ray diffraction (m.p. 457–458 K). The same compound was obtained when the reactants were used in a 1:1 mole ratio.

Crystal data

[SnCl$_2$(CH$_3$)(C$_6$H$_5$)(C$_5$H$_8$N$_2$)$_2$]
M_r = 473.99
Monoclinic, $C2/c$
a = 15.590 (2) Å
b = 10.889 (2) Å
c = 11.8700 (10) Å
β = 95.982 (10)°
V = 2004.1 (5) Å^3
Z = 4
D_x = 1.571 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 17.62–36.40°
μ = 1.548 mm^{-1}
T = 293 (2) K
Prism, colourless
0.25 × 0.25 × 0.15 mm

Data collection

Enraf–Nonius MACH3 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.698, $T_{\rm max}$ = 0.801
2131 measured reflections
2028 independent reflections
1617 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016
$\theta_{\rm max}$ = 26.28°
$h = -19 \rightarrow 19$
$k = -13 \rightarrow 0$
$l = -14 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Table 1
Selected geometric parameters (Å, °).

Sn1—C1	2.127 (5)	Sn1—N1	2.357 (3)
Sn1—C11	2.135 (4)	Sn1—Cl1	2.5753 (8)
C1—Sn1—C11	180	C1—Sn1—Cl1	89.12 (2)
C1—Sn1—N1	89.64 (7)	C11—Sn1—Cl1	90.88 (2)
C11—Sn1—N1	90.36 (7)	N1—Sn1—Cl1	84.99 (7)
N1$^{\rm i}$—Sn1—N1	179.28 (14)	Cl1—Sn1—Cl1$^{\rm i}$	178.24 (4)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 2
Hydrogen-bonding and short contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···N1	0.93	2.93	3.335 (4)	108
C12—H12···Cl1	0.93	2.94	3.420 (4)	113
N2—H2···Cl1	0.86	2.86	3.310 (3)	115
C6—H6*C*···Cl1$^{\rm i}$	0.96	2.78	3.643 (4)	151
N2—H2···Cl1$^{\rm ii}$	0.86	2.57	3.342 (3)	150
C7—H7*A*···Cl1$^{\rm ii}$	0.96	3.26	3.726 (4)	112

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-x, -y, -z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.063
S = 1.020
2028 reflections
114 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 1.9268P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.38 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.27 e Å^{-3}

The H atoms on C1 were included with an occupancy of 0.5.

Data collection and cell refinement: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); data reduction: *HELENA* (Spek, 1993); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zolsnai & Huttner, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1001). Services for accessing these data are described at the back of the journal.

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