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Chlorotris(2,4,6-trimethylphenyl)-tin(IV) and its ethanol hemisolvate

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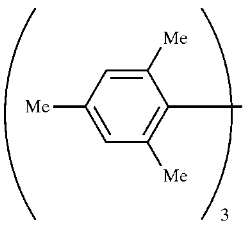
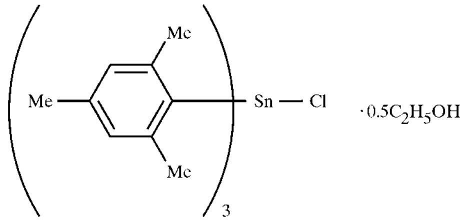
Chlorotris(2,4,6-trimethylphenyl)tin(IV), crystallizes from ethanol as solvent-free needles, [$Sn(C_9H_{11})_3Cl$], (I), and as the hemisolvate, [$Sn(C_9H_{11})_3Cl$]·$0.5C_2H_6O$, (II). The asymmetric unit in (I) has three independent molecules, whereas in (II), there are two [$Sn(C_9H_{11})_3Cl$] molecules together with one ethanol molecule. In the unit cell of (II), the ethanol molecules lie in channels between stacks of $(Mes)_3SnCl$ molecules (Mes is 2,4,6-trimethylphenyl) and each ethanol molecule is disordered (0.50:0.50) over two positions. A comparison of the structures of the title compounds and other $(Mes)_3SnX$ (X = F, Br or I) systems with those of the triphenyltin analogues shows that the steric requirements of the *o*-CH_3 groups are met by a flattening of the SnC_3 skeleton and increases in the average Sn—X and Sn—C values. Comparing Sn—X data for $(Mes)_3SnX$ (X = F, Cl, Br or I) systems with values for the tris(*o*-methoxyphenyl)tin analogues suggests that the Sn—F distance of 1.961 Å in $(Mes)_3SnF$ may well be characteristic of sterically unhindered four-coordinate Ar_3SnF systems.

Comment

Replacement of the phenyl groups in Ph_3SnX by mesityl (mesityl is 2,4,6-trimethylphenyl, hereinafter Mes) produces structural changes that are attributed to the steric effects of the two *ortho*-methyl groups. Thus, while Ph_3SnX compounds with X = OH (Glidewell *et al.*, 2002), F (Tudela *et al.*, 1992) or OAc (Molloy *et al.*, 1984) are polymeric, with five-coordinate Sn and planar C_3Sn units, the mesityl analogues with X = OH or F (Reuter & Puff, 1989) or OAc (Wharf & Simard, 1992) are monomeric, with pyramidal C_3SnX structures. Even when both $(Mes)_3SnX$ and Ph_3SnX are four-coordinate monomers, *e.g.* with X = I (Simard & Wharf, 1994) or Br (Preut & Huber, 1979; Dakternieks *et al.*, 2000), replacement of the *ortho*-H atoms by CH_3 groups still gives small but significant changes in the geometry around Sn, as well as an increase in the mean Sn—X distance of 0.05 Å when phenyl is replaced by mesityl in Ar_3SnX (X = Br or I). We now report the structures of $(Mes)_3SnCl$, (I), and of its ethanol hemisolvate, (II), first for comparison with the structure of Ph_3SnCl (Tse *et al.*, 1986; Ng, 1995), and then to enable the trends in geometry around Sn for the complete $(Mes)_3SnX$ series to be assessed.



(I)



(II)

Two quite different sets of crystals, (I) and (II), were produced by slow evaporation of an ethanol solution of $(Mes)_3SnCl$. Needles, (I), were found to be solvent-free and to have the same space group as $(Mes)_3SnF$, but with three molecules in the asymmetric unit rather than two, as in the fluoride case. The three molecules differ in detail (Table 1 and Fig. 1), but the averaged environment around Sn is almost the same in each case. The molecules in the solvent-free crystals of (I) are closely packed. However, it would appear that, as X in $(Mes)_3SnX$ increases in size from F to I, solvent-free packing

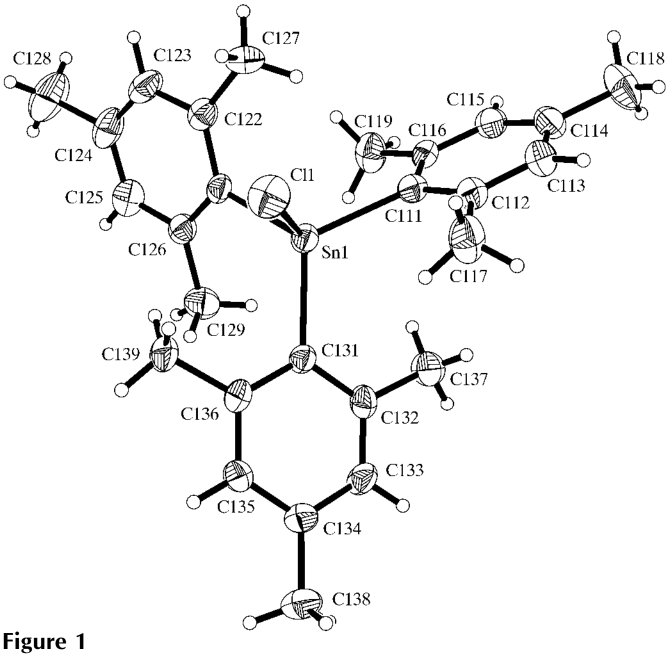


Figure 1
A view of the molecule of [$Sn(C_9H_{11})_3Cl$] in the asymmetric unit of the solvent-free compound, (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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of $(Mes)_3SnX$ units becomes more difficult and has yet to be established with X = Br or I.

In contrast, (II), the solvate $[(Mes)_3SnCl]_2{\cdot}EtOH$ (Table 2), has two molecules in the asymmetric unit, with solvent molecules occupying the channels between stacks of $(Mes)_3SnX$ molecules, as in the isomorphous compounds $[(Mes)_3SnBr]_2{\cdot}$-acetone (Dakternieks *et al.*, 2000) and $[(Mes)_3SnI]_2{\cdot}CDCl_3$ (Simard & Wharf, 1994). However, unlike the trimesityltin iodide solvate, where the $CDCl_3$ molecules are not disordered, the packing of (II) (Fig. 2) requires the ethanol molecules to partially occupy voids in the crystal lattice; they are completely disordered (0.50:0.50) over two positions. There are, in fact, several models possible for the disorder, and that used here was chosen as the most chemically feasible.

The geometries around Sn in various $(Mes)_3SnX$ molecules can be summarized by the average values of the C—Sn—X and C—Sn—C angles, and by the difference [(C—Sn—C) − (C—Sn—X)] (Table 3), as used earlier when comparing Ph_3SnX and $(o\text{-Anis})_3SnX$ structures (o-Anis is o-methoxyphenyl; Wharf *et al.*, 1999).

For the $(Mes)_3SnX$ (X = Cl, Br or I) systems, the SnC_3 pyramid is significantly flatter and the Sn—C distance is longer by ~0.04 Å compared with the Ph_3SnX analogues. Moreover, the Sn environment is essentially the same in all three $(Mes)_3SnX$ (X = Cl, Br or I) molecules, and it would appear that repulsions between the proximal o-CH_3 groups and distal o-$CH_3\cdots X$ interactions give a limiting geometry around Sn. Only when comparing $(Mes)_3SnF$ with $(Mes)_3SnCl$ is a further flattening of the SnC_3 pyramid seen, but the effect is less than was noted earlier for the comparison of $(o\text{-Anis})_3SnF$ with $(o\text{-Anis})_3SnCl$ (Wharf *et al.*, 1999).

The effect of increasing repulsion between X and distal o-CH_3 groups, as Cl is replaced by Br and then I, is shown by increases in Sn—X of 0.03 Å (X = Cl) and 0.05 Å (X = Br or I) when comparing Ph_3SnX with $(Mes)_3SnX$ (Table 4). The effect of distal o-CH_3 groups on Sn—F is less obvious, since monomeric Ph_3SnF does not exist. However, comparison with Sn—X values for $(o\text{-Anis})_3SnX$ provides some insight. For $(o\text{-Anis})_3SnX$ (X = Cl or I), Sn—X distances are longer (by 0.015–0.01 Å) than in the corresponding Ph_3SnX molecules, perhaps due to the weak $Sn\cdots OCH_3$ interaction *trans* to Sn—X in $(o\text{-Anis})_3SnX$, but are still shorter than Sn—X in the corresponding $(Mes)_3SnX$ molecules (Table 4). In contrast, Sn—F in $(o\text{-Anis})_3SnF$ is longer by 0.01 Å than in $(Mes)_3SnF$, which would suggest there is no significant repulsion between F and distal o-CH_3 groups in the latter molecule. Thus, the value for Sn—F of 1.96 Å in $(Mes)_3SnF$ may well be characteristic for sterically unhindered four-coordinate Ar_3SnF systems.

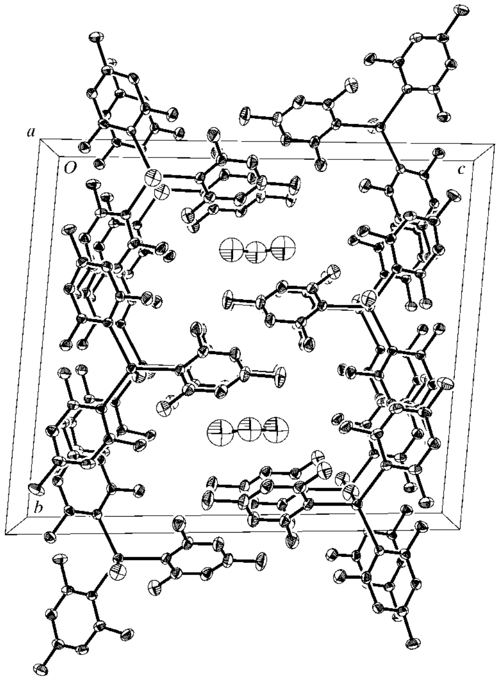

Figure 2
A packing diagram for the hemisolvate, (II). For clarity, only one of the two ethanol conformations is shown.

Experimental

Slow evaporation of an ethanol solution of previously prepared trimesityltin chloride (Wharf & Simard, 1997) produced crystals which could be readily identified visually as two different products, (I) and (II). A suitable crystal of each type was chosen for X-ray study.

Compound (I)

Crystal data

$[Sn(C_9H_{11})_3Cl]$
M_r = 511.67
Monoclinic, $P2_1/n$
a = 8.2337 (1) Å
b = 30.7435 (3) Å
c = 30.3142 (2) Å
β = 93.270 (1)°
V = 7661.02 (13) Å^3
Z = 12
D_x = 1.331 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 39 847 reflections
θ = 2.9–72.9°
μ = 8.97 mm^{-1}
T = 293 (2) K
Needle, colourless
0.64 × 0.05 × 0.02 mm

Data collection

Bruker PLATFORM diffractometer with SMART 2K CCD area-detector
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996*a*)
T_{min} = 0.560, T_{max} = 0.860
92 036 measured reflections
14 917 independent reflections
10 064 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 73°
$h = -9 \rightarrow 7$
$k = -38 \rightarrow 38$
$l = -37 \rightarrow 37$
591 standard reflections
frequency: 2880 min
intensity decay: 0.1%

Table 1
Selected geometric parameters (Å, °) for (I).

Sn1—C131	2.149 (4)	Sn2—C211	2.170 (4)
Sn1—C111	2.155 (5)	Sn2—Cl2	2.3875 (13)
Sn1—C121	2.169 (4)	Sn3—C311	2.148 (5)
Sn1—Cl1	2.3896 (13)	Sn3—C321	2.149 (5)
Sn2—C231	2.160 (5)	Sn3—C331	2.163 (5)
Sn2—C221	2.163 (4)	Sn3—Cl3	2.3824 (16)
C131—Sn1—C111	116.35 (16)	C231—Sn2—Cl2	107.07 (13)
C131—Sn1—C121	116.80 (17)	C221—Sn2—Cl2	100.91 (12)
C111—Sn1—C121	112.96 (17)	C211—Sn2—Cl2	101.61 (12)
C131—Sn1—Cl1	101.83 (12)	C311—Sn3—C321	116.00 (19)
C111—Sn1—Cl1	104.34 (13)	C311—Sn3—C331	114.30 (19)
C121—Sn1—Cl1	101.70 (12)	C321—Sn3—C331	114.95 (19)
C231—Sn2—C221	116.48 (16)	C311—Sn3—Cl3	102.59 (16)
C231—Sn2—C211	110.56 (17)	C321—Sn3—Cl3	101.99 (15)
C221—Sn2—C211	117.89 (17)	C331—Sn3—Cl3	104.47 (15)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.101$
$S = 1.05$
14 917 reflections
811 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.91$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

Compound (II)

Crystal data

$[Sn(C_9H_{11})_3Cl]\cdot 0.5C_2H_6O$
$M_r = 534.71$
Triclinic, $P\bar{1}$
$a = 8.2564$ (1) Å
$b = 16.8363$ (1) Å
$c = 19.5759$ (1) Å
$\alpha = 94.996$ (1)°
$\beta = 96.568$ (1)°
$\gamma = 90.539$ (1)°
$V = 2692.54$ (4) Å^3
$Z = 4$
$D_x = 1.319$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 18 284 reflections
$\theta = 2.3$–72.9°
$\mu = 8.55$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.20 × 0.18 × 0.15 mm

Data collection

Bruker PLATFORM diffractometer with SMART 2K CCD area-detector
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996*a*)
$T_{\min} = 0.160$, $T_{\max} = 0.277$
32 709 measured reflections
10 291 independent reflections
7198 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 72.9°$
$h = -10 \rightarrow 10$
$k = -17 \rightarrow 20$
$l = -24 \rightarrow 24$
240 standard reflections frequency: 2880 min intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.115$
$S = 0.94$
10 291 reflections
565 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.96$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Sn1—C131	2.156 (5)	Sn2—C211	2.149 (4)
Sn1—C121	2.168 (4)	Sn2—C221	2.155 (5)
Sn1—C111	2.169 (4)	Sn2—C231	2.160 (5)
Sn1—Cl1	2.3898 (14)	Sn2—Cl2	2.3884 (14)
C131—Sn1—C121	116.54 (17)	C211—Sn2—C221	117.38 (17)
C131—Sn1—C111	115.60 (18)	C211—Sn2—C231	115.39 (18)
C121—Sn1—C111	115.62 (17)	C221—Sn2—C231	114.82 (19)
C131—Sn1—Cl1	102.75 (13)	C211—Sn2—Cl2	99.92 (13)
C121—Sn1—Cl1	99.96 (12)	C221—Sn2—Cl2	102.14 (13)
C111—Sn1—Cl1	102.74 (13)	C231—Sn2—Cl2	103.65 (14)

For both (I) and (II), H atoms were constrained to the parent site and refined using a riding model, with C—H distances in the range 0.93–0.97 Å and an O—H distance of 0.82 Å. For (I), the H atoms of the methyl groups were located in a difference Fourier map and were allowed to refine by their torsion angles. In (II), the ethanol molecule was disordered over two positions (0.50:0.50); these atoms were refined isotropically using restraints (*DFIX*) to model an ethanol molecule in a crystalline environment (Jonsson, 1976). For (I), a total of 20 peaks of 0.30–0.91 e Å^{-3} were found <1.10 Å from the heavy atoms. The general background was found to be <0.30 e Å^{-3}. A final verification of possible voids in both compounds was performed using the *VOID* routine of *PLATON* (Spek, 1995). In (I), a small hole remained in this structure, accounting for one electron and 84.3 Å^3 of the volume of the cell.

Table 3
Averaged angles (°) around the Sn atom in (Mes)$_3$SnX systems.

Compound	C—Sn—X	C—Sn—C	(C—Sn—C) − (C—Sn—X)
(Mes)$_3$SnF†	303 (1)	349 (1)	46 (2)
(Mes)$_3$SnCl‡	309 (1)	345 (1)	36 (2)
(Mes)$_3$SnCl·0.5C$_2$H$_5$OH‡	306 (1)	348 (1)	42 (2)
(Mes)$_3$SnBr·0.5(CH$_3$)$_2$CO§	306 (1)	348 (1)	42 (2)
(Mes)$_3$SnI·0.5CDCl$_3$¶	308 (1)	346 (1)	38 (2)
(Mes)$_3$SnI·0.5C$_6$H$_5$CH$_3$¶	307 (1)	348 (1)	41 (2)

† Reuter & Puff (1989). ‡ This work. § Dakternieks *et al.* (2000). ¶ Simard & Wharf (1994).

Table 4
Averaged Sn—X distances (Å) for various Ar$_3$SnX complexes.

Ar	X = F	X = Cl	X = Br	X = I
Ph		2.359(8)†	2.495(15)‡	2.70(1)§
Mes	1.96(1)¶	2.388(2)††	2.546(3)‡‡	2.751(3)§
o-Anis	1.972(5)§§	2.371(5)§§		2.713(1)¶¶

† Tse *et al.* (1986) and Ng (1995). ‡ Preut & Huber (1979). § Simard &Wharf (1994). ¶ Reuter & Puff (1989). †† This work. ‡‡ Dakternieks *et al.* (2000). §§ Wharf *et al.* (1999). ¶¶ Howie *et al.* (1994).

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996*b*); molecular graphics: *SHELXTL* (Bruker, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1654). Services for accessing these data are described at the back of the journal.

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