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Tris(4-*tert*-butylphenyl)chlorotin(IV)

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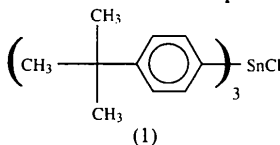
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Abstract

The structure of tris(4-*tert*-butylphenyl)chlorotin(IV), [Sn(C₁₀H₁₃)₃Cl], has been determined by single-crystal X-ray diffraction. It crystallizes in a space group (*C2/c*) which differs from those usually found for triaryltin halides. The structure comprises molecules forming ladders using overlapping aryl or *tert*-butyl groups. This relatively open but organized arrangement contrasts with the more closely packed but random one found for Ph₃SnCl and may account for the differences in physical properties of these two triaryltin chlorides.

Comment

Triaryltin halides show only trivial space-group changes (*P2₁/a* or *P2₁/c* or *P2₁/n*) when phenyl ring substituents are varied (Wharf & Simard, 1991), examples being the recently reported structures of (*o*-CH₃OC₆H₄)₃SnI (Howie, Ross, Wardell & Low, 1994) and its *para* analogue (Simard & Wharf, 1994). Our interest in the title compound arose from its apparently anomalous melting point for Ar₃SnCl compounds [Ar = *p*-ZC₆H₄; Z = H, m.p. = 379 K; Z = CH₃, m.p. = 371 K; Z = CH₃CH₂, m.p. = 302 K; Z = (CH₃)₂C, m.p. = 492–496 K]. Crystals of the title compound, (1), were obtained from acetone but preliminary X-ray study of one crystal showed a very large unit cell with molecules of both Ar₃SnCl and Ar₂SnCl₂ present, as indicated by the analytical data (see below). Another crystal gave the data reported here for the title compound.



The structure has four 'chains' of Ar₂Sn [Ar = *p*-(CH₃)₃CC₆H₄] units formed by overlapping of *tert*-butyl groups on neighbouring molecules and which parallel the *a* axis of the unit cell (Fig. 1). This structure resembles that found earlier for (Mes)₃SnI.0.5S (*S* = CDCl₃, C₆H₅CH₃) (Simard & Wharf, 1994) but in the present case, the third aryl group on each tin completely overlaps the equivalent phenyl ring attached to an Sn atom in an adjacent 'chain' creating 'ladders' across the unit cell. This relatively open structure may well account for the lower density compared with that of Ph₃SnCl (1.544 Mg m⁻³). The latter compound has a more tightly packed structure (*P2₁/c*) with the molecules relatively randomly arranged (Bokii, Zakharova & Struchkov, 1970; Tse, Lee & Gabe, 1986). For both the title compound and Ph₃SnCl, intermolecular interatomic distances are of van der Waals magnitude or greater, showing that the bulky *tert*-butyl group is well accommodated by the change in crystal structure.

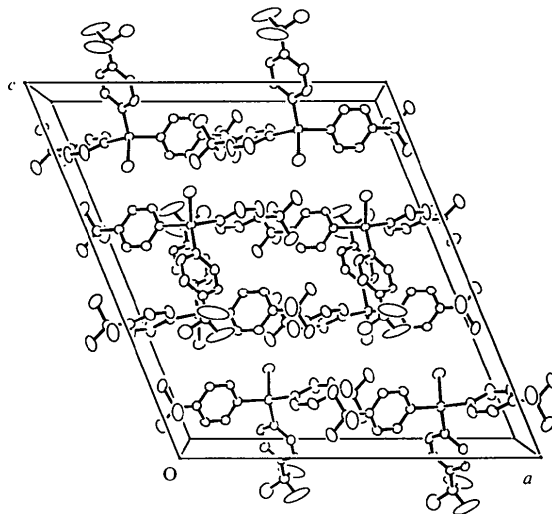


Fig. 1. Packing diagram of the unit cell.

At first sight, the more open structure of the title compound appears inconsistent with the change in physical properties from those noted for Ph₃SnCl. However, crystals taken from the bulk sample, m.p. 490–491 K, have almost the same density (1.23 Mg m⁻³ by flotation) as that found for the crystal used for the structure determination. Perhaps it is the more organized nature of this relatively open structure which accounts for the increased lattice rigidity required for the higher melting point and lower solubility when compared with other triaryltin chlorides. Molecular-mechanics calculations may well be required to shed light on the effects of changes in crystal structures on the properties of triaryltin halides.

Like those of Ph_3SnCl , molecules of the title compound (Table 2, Fig. 2) have no symmetry, but the distortion from the 'ideal' tetrahedral angles is a little less. In addition, the Sn—Cl and Sn—C distances are slightly smaller than those in triphenyltin chloride (Tse, Lee & Gabe, 1986).

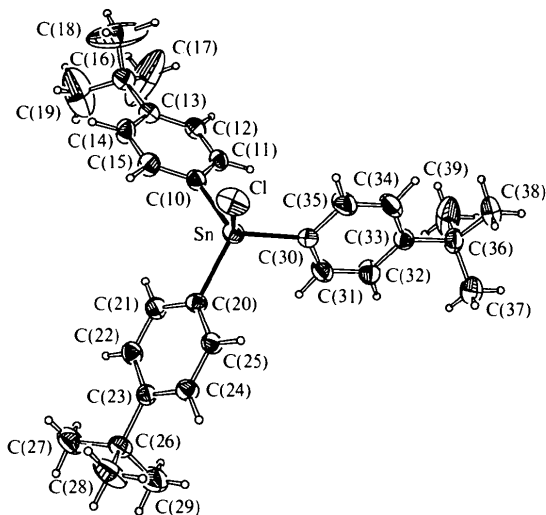


Fig. 2. ORTEP (Johnson, 1965) view of the molecule forming the asymmetric unit with the numbering scheme adopted. Ellipsoids are drawn at the 30% probability level. H atoms are represented by spheres of arbitrary size.

Experimental

All experimental procedures were as given earlier (Wharf, 1989). Tetra(4-*tert*-butylphenyl)tin(IV) was prepared by the literature method (Neville, 1963), m.p. 647–649 K (literature 568 K). Chlorotris(4-*tert*-butylphenyl)tin(IV) was obtained by refluxing a xylene (100 ml) solution of tin tetrachloride (1.97 g) and Ar_4Sn (15.2 g) for 48 h, followed by evaporation to dryness under reduced pressure. The residue was extracted with boiling acetone (Ar_4Sn is insoluble) to give colourless needles: yield 11%, m.p. 492–496 K. Analysis: found, C 63.8, H 7.4%; calculated for $\text{C}_{30}\text{H}_{39}\text{ClSn}$, C 65.1, H 7.1%. Slow evaporation of an acetone solution gave the larger crystals used here. NMR data [CDCl_3 ; $(\text{CH}_3)_4\text{Sn}$ (ext.); $(\text{CH}_3)_4\text{Si}$ (int.); Ar = *p*-(CH_3)₃CC₆H₄; δ (p.p.m.); J (Hz)]: for Ar_4Sn , $\delta(^{119}\text{Sn})$ –129.11, $\delta(^{13}\text{C})$ 134.70 (*i*-C), 137.00 (*o*-C), 125.42 (*m*-C), 151.65 (*p*-C), 34.62 (—C—), 31.24 (CH_3), $^nJ_{119\text{Sn}-^{13}\text{C}}$, 536.3 ($n = 1$), 38.2 ($n = 2$), 51.4 ($n = 3$), 11.5 ($n = 4$); for Ar_3SnCl , $\delta(^{119}\text{Sn})$ –38.44, $\delta(^{13}\text{C})$ 134.06 (*i*-C), 135.93 (*o*-C), 126.05 (*m*-C), 153.41 (*p*-C), 34.80 (—C—), 31.17 (CH_3), $^nJ_{119\text{Sn}-^{13}\text{C}}$, 622.5 ($n = 1$), 50.5 ($n = 2$), 64.3 ($n = 3$), 13.0 ($n = 4$).

Crystal data

$[\text{Sn}(\text{C}_{10}\text{H}_{13})_3\text{Cl}]$
 $M_r = 553.77$

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$

Monoclinic
 $C2/c$
 $a = 20.503 (3) \text{ \AA}$
 $b = 13.436 (2) \text{ \AA}$
 $c = 22.916 (4) \text{ \AA}$
 $\beta = 112.357 (14)^\circ$
 $V = 5838.3 (16) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.260 \text{ Mg m}^{-3}$

Cell parameters from 25 reflections
 $\theta = 40.0\text{--}50.0^\circ$
 $\mu = 8.07 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
Parallelepiped
 $0.30 (111, \bar{1}\bar{1}1) \times 0.28$
 $(\bar{1}11, 1\bar{1}\bar{1}) \times 0.13$
 $(011, 00\bar{1}) \text{ mm}$
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans [$\Delta\omega = (1.00 + 0.14\tan\theta)^\circ$]
Absorption correction: Gaussian by integration from crystal shape (20×20)
 $T_{\min} = 0.16$, $T_{\max} = 0.43$
21 189 measured reflections
5530 independent reflections

3647 observed reflections
 $[I \geq 3\sigma(I)]$
 $R_{\text{int}} = 0.037$
 $\theta_{\max} = 70.0^\circ$
 $h = -24 \rightarrow 23$
 $k = 0 \rightarrow 16$
 $l = 0 \rightarrow 27$
5 standard reflections
frequency: 60 min
intensity decay: 6.5 to 9.5%

Refinement

Refinement on F
 $R = 0.051$
 $wR = 0.054$
 $S = 2.94$
3647 reflections
290 parameters
 $w = 1/[\sigma^2(F) + 0.0001F^2]$
 $(\Delta/\sigma)_{\max} = 0.13$
 $\Delta\rho_{\max} = 0.56 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.88 \text{ e \AA}^{-3}$

Extinction correction: secondary (Zachariasen, 1967)
Extinction coefficient: 0.25 (3)
Atomic scattering factors from Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Sn	0.79476 (2)	0.36542 (3)	0.12076 (2)	6.16 (2)
Cl	0.83105 (11)	0.47425 (15)	0.20750 (9)	10.11 (12)
C(10)	0.7767 (3)	0.4563 (4)	0.0417 (3)	5.9 (3)
C(11)	0.8103 (3)	0.4365 (4)	–0.0002 (3)	6.1 (3)
C(12)	0.7980 (3)	0.4926 (4)	–0.0530 (3)	6.2 (3)
C(13)	0.7514 (3)	0.5720 (4)	–0.0693 (2)	5.8 (3)
C(14)	0.7173 (3)	0.5916 (5)	–0.0287 (3)	7.4 (4)
C(15)	0.7301 (3)	0.5347 (4)	0.0257 (3)	7.3 (4)
C(16)	0.7366 (4)	0.6322 (4)	–0.1275 (3)	7.2 (4)
C(17)	0.7572 (11)	0.5858 (11)	–0.1725 (5)	29.1 (17)
C(18)	0.7677 (10)	0.7293 (10)	–0.1110 (5)	28.5 (14)
C(19)	0.6615 (7)	0.6479 (13)	–0.1629 (6)	25.1 (15)
C(20)	0.7016 (3)	0.2938 (4)	0.1183 (2)	5.5 (3)
C(21)	0.6405 (3)	0.2994 (5)	0.0645 (3)	6.6 (3)
C(22)	0.5795 (3)	0.2499 (5)	0.0609 (3)	6.9 (3)
C(23)	0.5765 (3)	0.1948 (4)	0.1103 (3)	5.8 (3)
C(24)	0.6383 (3)	0.1874 (5)	0.1642 (3)	6.6 (3)
C(25)	0.6992 (3)	0.2366 (4)	0.1672 (3)	6.4 (3)
C(26)	0.5096 (3)	0.1389 (4)	0.1071 (3)	7.7 (4)
C(27)	0.4451 (4)	0.1753 (7)	0.0531 (4)	11.2 (5)
C(28)	0.4984 (4)	0.1537 (7)	0.1680 (4)	12.1 (7)
C(29)	0.5195 (4)	0.0300 (6)	0.0981 (5)	12.7 (7)
C(30)	0.8796 (3)	0.2675 (4)	0.1350 (3)	6.0 (3)
C(31)	0.8697 (3)	0.1729 (5)	0.1144 (3)	7.5 (4)

C(32)	0.9245 (3)	0.1095 (4)	0.1192 (3)	7.9 (4)
C(33)	0.9936 (3)	0.1394 (4)	0.1452 (3)	6.4 (3)
C(34)	1.0037 (3)	0.2339 (5)	0.1656 (4)	10.1 (5)
C(35)	0.9494 (3)	0.2980 (5)	0.1622 (4)	10.2 (5)
C(36)	1.0533 (3)	0.0697 (5)	0.1489 (3)	7.8 (4)
C(37)	1.0410 (4)	-0.0332 (6)	0.1660 (5)	12.8 (7)
C(38)	1.1233 (4)	0.1055 (6)	0.1979 (5)	12.3 (6)
C(39)	1.0595 (6)	0.0698 (9)	0.0849 (5)	16.8 (9)

Table 2. Selected geometric parameters (Å, °)

Sn—Cl	2.349 (2)	Sn—C(20)	2.119 (5)
Sn—C(10)	2.098 (6)	Sn—C(30)	2.106 (5)
		Sn—C (average)	2.108 (5)
Cl—Sn—C(10)	105.30 (16)	C(10)—Sn—C(20)	112.3 (2)
Cl—Sn—C(20)	107.29 (14)	C(10)—Sn—C(30)	111.2 (2)
Cl—Sn—C(30)	106.31 (16)	C(20)—Sn—C(30)	113.80 (19)
Cl—Sn—C (average)	106.30 (15)	C—Sn—C (average)	112.4 (2)

The full-matrix least-squares refinement was based on *F*, with all non-H atoms anisotropic and H atoms isotropic. H atoms were initially calculated at idealized positions (C—H = 0.95 Å, *sp*² or *sp*³ hybridization), with *U*_{iso} initially refined then fixed in the last cycles [*U*_{iso} = 0.10 (phenyl), 0.36 (*tert*-butyl, 1×) and 0.18 Å² (*tert*-butyl, 2× and 3×)]. The final Fourier map showed eight peaks of 0.56–0.36 e Å⁻³ at 0.58–1.48 Å from tin or chlorine, and three peaks of 0.43–0.36 e Å⁻³ corresponding to local disorder at *tert*-butyl (1×), not introduced in the refined model.

The structure was solved by direct methods using *SHELX86* (Sheldrick, 1985) and difference Fourier synthesis using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The graphics were produced using *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Dinitrato(diphenylphenanthroline)-palladium(II) Complex

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Abstract

The crystal structure of di(nitrato-*O*)(4,7-diphenyl-1,10-phenanthroline-*N,N'*)palladium(II) dimethyl sulfoxide solvate, [Pd(NO₃)₂(C₂₄H₁₆N₂)]·C₂H₆OS, contains two unidentate O-bonded nitrato groups, and the bidentate 4,7-diphenyl-1,10-phenanthroline molecule in almost square-planar coordination around the Pd atom. The phenanthroline ring system is non-planar, exhibiting a bow-shaped deformation likely originating from the metal coordination. The coordinated ligand, as a consequence, exhibits geometrical deformations compared with the free ligand molecule. The crystals have channels which host the disordered solvate molecules. The geometrical results are compared with those for related compounds.

Comment

This paper reports the structure of a mixed-ligand complex, (I), of 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline = Bphen) and nitrate ions, with palladium(II) as the coordinating metal (Fig. 1). The low affinity of Pd^{II} for oxygen ligands is well known, and in addition to this, the reactivity of the nitrate groups and susceptibility to substitution by water molecules renders such complexes rather unstable.

