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Crystallographic report

Tetraphenylphosphonium nitratobis (chlorodiphenylstannate)methane, $[Ph_4P]^+[(Ph_2ClSn)_2CH_2{\cdot}NO_3]^-$

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The nitrate anion coordinates to the Sn–CH_2–Sn unit of the title phosphonium stannate, $[Ph_4P]^+$ $[(Ph_2ClSn)_2CH_2{\cdot}NO_3]^-$, to give a six-membered ring having the penta-coordinated tin atoms in a trigonal bipyramidal geometry. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; stannate; organotin; C–H···O interactions

COMMENT

The anion comprises two Ph_2SnCl entities that are linked *via* a symmetric methylene bridge, as well as being bridged by a bidentate nitrate. This results in the formation of a buckled six-membered ring, as seen in the Sn1–C1–Sn2–O2 and Sn2–C1–Sn1–O1 torsion angles of −54.3(3) and 69.4(3)° respectively. Each tin atom exists in a distorted trigonal bipyramidal configuration (geometrical goodness[1] $\Delta\Sigma(\theta) =$ 69.3° (Sn1), 67.3° (Sn2)) with chlorine and oxygen atoms in axial positions and carbon atoms in equatorial positions (Fig. 1). The ions are held together in the lattice via C–H···O contacts involving the non-coordinating O3 atom of the nitrate, as shown in Fig. 2. For other organotin nitrate structures see, for instance, Refs 2 and 3.

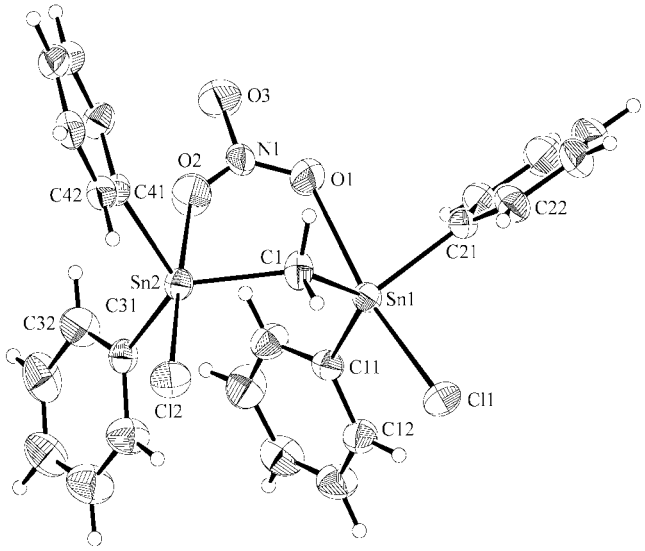

Figure 1. Molecular structure of the anion in $[Ph_4P][(Ph_2ClSn)_2CH_2{\cdot}NO_3]$. Key geometric parameters: Sn1–Cl1 2.4288(16), Sn1–C1 2.093(6), Sn1–O1 2.510(5), Sn2–Cl2 2.4235(16), Sn2–C1 2.101(5), Sn2–O2 2.545(5) Å; Cl1–Sn1–O1 170.53(13), Cl2–Sn2–O2 174.62(14)°.

EXPERIMENTAL

A solution of $(Ph_2ClSn)_2CH_2$[4] (0.252 g, 0.4 mmol) and Ph_4PNO_3 (0.16 g, 0.4 mmol) in CH_2Cl_2 (10 ml) was heated at reflux for 10 min. Hexane was added to the clear reaction mixture. Slow evaporation of the solvent yielded 0.35 g (85%) of the complex as colourless crystals, m.p. 169–172 °C. Anal. Found: C, 57.36; H, 4.24; N, 1.46. Calc. for $C_{49}H_{42}Cl_2NO_3PSn_2$: C, 57.02; H, 4.10; N, 1.36%. ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 1.83$ [s, 2H,

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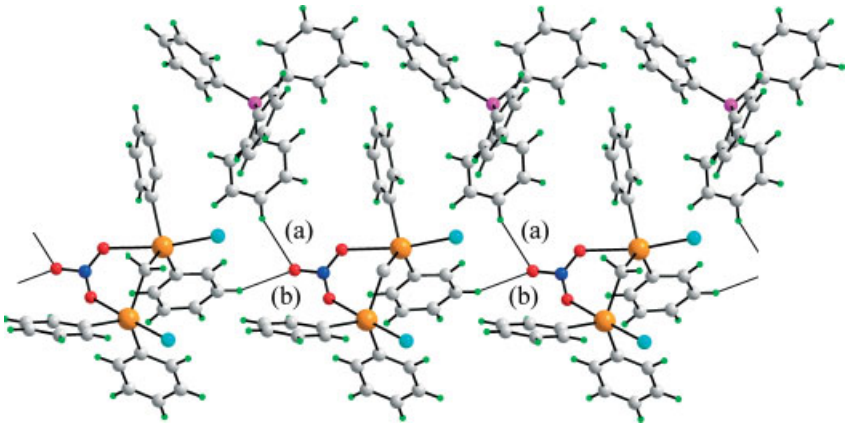

Figure 2. View of the C–H···O hydrogen bonding interactions in the lattice that serve to link ions into a chain. Parameters: (a) C74–H···O3^{i} = 2.47 Å, C74···O3^{i} = 3.290(11) Å, C74–H···O3^{i} = 147°; (b) C13–H···O3^{i} = 2.52 Å, C13···O3^{i} = 3.417(11) Å, C13–H···O3^{i} = 161°; symmetry operation *i*: *x*, *y*, −1 + *z*.

$^{2}J(^{1}H–^{119}Sn) = 77$, CH_2], 7.20 (complex pattern, 12H, $H_{m,p}$), 7.6 (complex pattern, 20H, Ph_4P), 7.75 ppm (complex pattern, 8H, H_o); $^{13}C\{^{1}H\}$ NMR (125.697 MHz, $CDCl_3$): $\delta = 11.5$ (broad, CH_2), 128.0 [$^{3}J(^{13}C–^{119/117}Sn) = 69$, SnC_m], 128.7 (SnC_p), 136.3 [$^{2}J(^{13}C–^{119/117}Sn) = 50$, SnC_o], 143.1 [$^{1}J(^{13}C–^{119/117}Sn) = 725$, SnC_i], 117.4 [$^{1}J(^{13}C–^{31}P) = 90$, PC_i], 134.3 [$^{2}J(^{13}C–^{31}P) = 10$, PC_o], 130.7 [$^{3}J(^{13}C–^{31}P) = 13$, PC_m], 135.7 ppm (PC_p); ^{119}Sn NMR (186.409 MHz, $CDCl_3$): −102 ppm. Intensity data were collected at 293 K on a Rigaku AFC6R diffractometer for a colourless block 0.13 × 0.15 × 0.45 mm^3. $C_{49}H_{42}Cl_2NO_3PSn_2$, $M = 1032.14$, triclinic, $P\bar{1}$, $a = 13.3586(18)$, $b = 16.397(2)$, $c = 10.1652(8)$ Å, $\alpha = 103.231(8)$, $\beta = 92.962(9)$, $\gamma = 92.032(11)°$, $V = 2162.0(4)$ Å^3, $Z = 2$, 10 328 unique data (θ_{max} 27.9°), 6138 data with $I \geq 2\sigma(I)$, $R = 0.044$ (obs. data), $wR = 0.148$ (all data). Programs used: teXsan, DIFABS, SHEXLS-86, SHELXL-97, ORTEP. CCDC deposition number: 210954.

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