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Crystallographic report

Bis(tetraphenylphosphonium) bis(dichloronitratophenylstannate)methane, $[Ph_4P^+]_2$ $[(PhCl_2(NO_3)Sn)_2CH_2]^{2-}$

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Each tin atom of the title compound is five-coordinate, defined by 2C, 2Cl and 1O atoms, and shows a distorted square pyramidal configuration stabilized by intramolecular Sn···O or Sn···Cl interactions. Both nitrate anions coordinate the tin atoms in a monodentate mode. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; organotin; diorganostannate

COMMENT

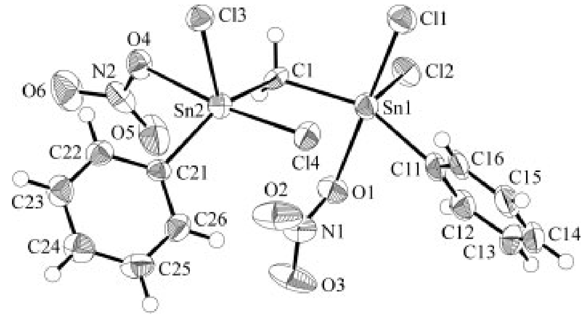

Figure 1. Molecular structure of the anion in $[Ph_4P]_2[(PhCl_2(NO_3)Sn)_2CH_2]$. Key geometric parameters: Sn1–Cl1 2.4535(12), Sn1–Cl2 2.3952(13), Sn1–O1 2.448(3), Sn1–C1 2.105(5), Sn1–C11 2.126(5), Sn2–Cl3 2.3874(12), Sn2–Cl4 2.5076(14), Sn2–O4 2.332(3), Sn2–C1 2.094(5), Sn2–C21 2.128(5) Å; Cl1–Sn1–Cl2 100.77(15), Cl1–Sn1–O1 176.60(9), C1–Sn1–C11 153.24(18), Cl3–Sn2–Cl4 92.64(4), Cl4–Sn2–O4 171.91(9), C1–Sn2–C21 148.24(16)°.

The molecular structure of the dianion (Fig. 1) features two five-coordinate tin atoms each having a C_2Cl_2O substituent pattern and that are linked by a methylene group. There are also close intramolecular interactions such that Sn1···Cl4 is 3.2291(14) Å, Sn1···O2 is 3.141(4) Å and Sn2···O2 is 3.005(4) Å. Although these do not represent significant bonding interactions, they exert an influence upon the coordination geometries such that these are best described as distorted square pyramidal with the loosely associated atoms occupying the vacant site opposite the Cl2 and Cl3 atoms. Taken to an extreme, if the weaker interactions were considered bonding, then the coordination geometry about each tin atom would be described as distorted octahedral. In contrast to $[Ph_4P]^+$ $[(Ph_2Cl(NO_3)Sn)_2CH_2]^-$ with the nitrate anion bridging the two tin atoms,[1] in the title compound the nitrate anions coordinate the tin atoms in a monodentate mode. The lattice comprises alternate layers of cations and anions, stacked along the *a*-direction, with the primary interactions between layers being of the type C–H···O.

EXPERIMENTAL AND RESULTS

A solution of $(PhCl_2Sn)_2CH_2$[2] (0.200 g, 3.7 mmol) and Ph_4PNO_3 (0.293 g, 7.3 mmol) in CH_2Cl_2 (10 ml) was heated at reflux for 10 min.

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Hexane was added to the clear reaction mixture. Slow evaporation of the solvent yielded 0.13 g (38%) of the complex as colourless crystals, m.p. 220–222 °C. Anal. Found: C, 54.1; H, 3.5; N, 2.2. Calc. for $C_{61}H_{52}Cl_4N_2O_6P_2Sn_2$: C, 54.3; H, 3.9; N, 2.1%. ^{1}H NMR (400.13 MHz, DMSO-d_6): $\delta = 2.28$ [s, 2H, $^2J(^1H-^{119}Sn) = 109$ Hz, CH_2], 7.27–7.44 [complex pattern, 4H, H_o], 7.65–7.84 [complex pattern, 40H, Ph_4P], 7.86–7.98 ppm [complex pattern, 6H, $H_{m,p}$]; $^{13}C\{^1H\}$ NMR (125.697 MHz, DMSO-d_6): $\delta = 35.8$ [broad, CH_2], 117.3 [SnC_m], 118.1 (SnC_p), 128.0 [SnC_o], 129.0 [SnC_i], 130.5 [$^3J(^{13}C-^{31}P) = 12$ Hz, PC_m], 134.6 [$^2J(^{13}C-^{31}P) = 10$ Hz, PC_o], 135.4 ppm ($^4J(^{13}C-^{31}P) = 2.9$ Hz, PC_p); ^{31}P NMR (161.99 MHz, $CDCl_3$): 23.1 ppm; ^{119}Sn NMR (149.18 MHz, DMSO-d_6): −291 (integral 75), −312 ppm (integral 25). Intensity data were collected at 173 K on a Nonius Kappa CCD for a colourless block 0.05 × 0.05 × 0.07 mm^3. $C_{61}H_{52}Cl_4N_2O_6P_2Sn_2$, $M = 1350.17$, monoclinic, $P2_1/c$, $a = 22.3821(9)$, $b = 14.2729(11)$, $c = 18.1313(12)$ Å, $\beta = 95.993(4)^\circ$, $V = 5760.5(6)$ Å^3, $Z = 4$, 10 119 unique data (θ_{max}25.0°), 4615 data with $I \geq 2\sigma(I)$, $R = 0.037$ (obs. data), $wR = 0.068$ (all data). Programs used: teXsan, SHEXLS-97, SHELXL-97 and ORTEP. CCDC deposition number: 212 295.

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