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Bis[tetrakis(triphenylphosphine-κP)silver(I)] di-μ-trifluoroacetato-κ^4O:O'-bis[bis(trifluoroacetato-κO)stannate(IV)]

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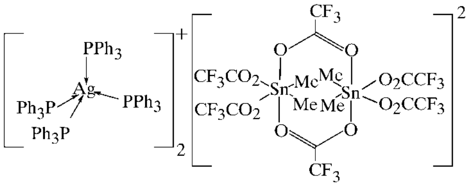
The crystal structure of the title compound, $[Ag(C_{18}H_{15}P)_4]_2[Sn_2(CH_3)_4(CF_3CO_2)_6]$, consists of discrete tetrahedral cations and *trans*-C_2SnO_4 octahedral dianions [C—Sn—C = 154.6 (2)°]. The dianion lies about a center of inversion and the two Sn atoms are linked unevenly by the carboxylate unit [Sn—O = 2.291 (3) Å and Sn←O = 2.818 (3) Å].

Comment

Tetrakis(triphenylphosphine)silver(I) bis(trifluoroacetato)triphenylstannate (Ng & Rae, 2003) illustrates the use of an extremely bulky metal-bearing counter-ion to stabilize the dicarboxylatotriorganostannate anion. Such an anion, which was first synthesized in expectation of enhanced aqueous solubility owing to the ionic nature of the complex, was documented as the tetramethylammonium bis(trifluoroacetato)triphenylstannate salt (Ng & Kumar Das, 1997); other ammonium stannates have also been characterized (Ng, 1998; Ng & Hook, 1999). The trifluoroacetate group is a strong electron-withdrawing group that can bind to a neutral triorganotin fluoroacetate molecule; the nature of the organic radical is probably not important, as a bis(trifluoroacetato)tricyclohexylstannate is also known (Ng, 1999). In these stannates, the carboxylate anion behaves as a monodentate group that bonds covalently to the Sn atom, but the Sn—O bond is weaker than the covalent Sn—O bonds found in neutral triorganotin carboxylates (Ng *et al.*, 1988). Apart from the trifluoroacetate anion, a limited number of carboxylate anions also display this property of affording organostannates (Ng & Kumar Das, 1999). In contrast, the related dioxalatodiorganostannate dianion does not require special assistance, as stability is conferred by the chelating nature of the dicarboxylate group (Xu *et al.*, 2003). Investigations of the dicarboxylatotriorganostannates have now been extended to the analogous tricarboxylatodiorganostannates.

The structural chemistry of organotin carboxylates (Tiekink, 1991, 1994; Holloway & Melnik, 2000) lists only one example of a stannate, *viz.* tetramethylammonium triacetatodimethylstannate, which crystallizes as an air-sensitive chloroform solvate (Lockhart *et al.*, 1987). This sole example contrasts with the numerous examples of neutral diorganotin dicarboxylates, which, with the possible exceptions of dimethyltin diformate (Mistry *et al.*, 1990) and dimethyltin bis(trifluoroacetate) (Mistry *et al.*, 1995), exist as monomeric molecules, having the chelated Sn atom in a skew-trapezoidal environment.



(I)

Tetraammonium triacetatodimethylstannate possesses two chelating acetate groups [Sn—O = 2.291 (1) and 2.525 (3) Å, and 2.271 (8) and 2.520 (9) Å]; the third acetate group is monodentate [Sn—O = 2.113 (9) Å], the double-bonded carbonyl O atom being ∼3.5 Å from the Sn atom (Lockhart *et al.*, 1987). In the trifluoroacetate analog, *viz.* the title compound, (I), the negative charge of the stannate group is balanced by the positive charge of the tetrakis(triphenylphosphine)silver cation. The three carboxylate groups of the stannate ion are monodentate, but the carbonyl O atom of one of the groups widens the $(CH_3)_2Sn$ skeleton [C—Sn—C = 154.6 (2)°; Table 1] across a center of inversion, so that the Sn atoms in the dianionic entity are formally six-coordinate in

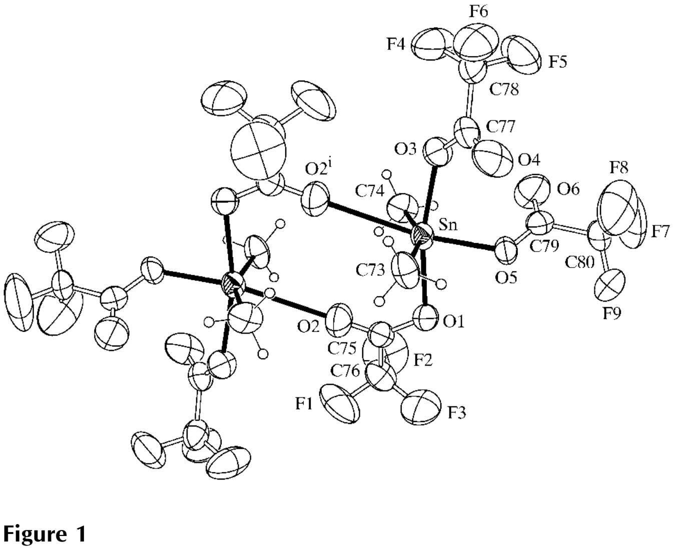


Figure 1
*ORTEP*II (Johnson, 1976) plot of the $[Sn(CH_3)_2(O_2CCF_3)_3]_2^{2-}$ dianion, with displacement ellipsoids drawn at the 50% probability level. Only one set of F atoms of the disordered trifluoromethyl group is shown. H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

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a distorted octahedral geometry (Fig. 1). The dianion features an eight-membered $\rightarrow$Sn—O—C=O$\rightarrow$Sn—O—C=O$\rightarrow$ ring, but the carboxylate bridge [Sn$\leftarrow$O = 2.818 (3) Å] is weak and is much longer than those found in the six-coordinate polymeric parent Lewis acid [Sn$\leftarrow$O = 2.619 (4) and 2.700 (4) Å; Mistry *et al.*, 1995]. Such a ring has only been documented previously in tetranuclear $(OH)_2(Cl_3CCO_2)_6[Sn(C_6H_5)_2]_4$, in which the covalent and dative Sn—O bonds [2.185 (6) and 2.361 (7) Å, respectively] are similar to one another (Alcock & Roe, 1989). There are no significant interactions between the cation and anion in the unit cell. The ability of two trifluoroacetatodimethylstannate ions to aggregate into a dianion can be attributed to enhanced Lewis acidity brought about by the electron-withdrawing trifluoroacetate group. Evidence of enhanced Lewis acidity of diorganotin bis(fluoroacetates) comes from the isolation of stable complexes with α,α'-diimine ligands (Garner *et al.*, 1975; Ng *et al.*, 1999). The trifluoroacetate group is probably comparable in its electron-withdrawing ability to, for example, the chloride ion; several trichlorodimethylstannates that are doubly chlorine bridged into dianions are known (Matsubayashi *et al.*, 1985; Lanfranchi *et al.*, 1986; Teoh *et al.*, 1992).

Experimental

The title compound was obtained as prismatic crystals from the reaction of silver trifluoroacetate, triphenylphosphine, bis(trifluoroacetic) anhydride and dimethyltin oxide in a 1:4:2:1 ratio. Silver trifluoroacetate (0.22 g, 1 mmol) and triphenylphosphine (1.05 g, 4 mmol) were heated in ethanol (25 ml). Bis(trifluoroacetic) anhydride (0.42 g, 2 mmol) and dimethyltin oxide (0.16 g, 1 mmol) were also heated in ethanol (25 ml) until the oxide dissolved completely. The two hot solutions were mixed. The filtered mixture was allowed to cool over a period of 1 d, furnishing the silver stannate. The resulting large prisms were not suitable for diffraction, as all had a milky portion in the middle. An irregularly shaped specimen suitable for X-ray diffraction was therefore cut from a large prism.

Crystal data

$[Ag(C_{18}H_{15}P)_4]_2[Sn_2(CH_3)_4(C_2F_3O_2)_6]$
$M_r = 3289.54$
Triclinic, $P\overline{1}$
$a = 12.9439 (6)$ Å
$b = 14.0499 (6)$ Å
$c = 20.7267 (9)$ Å
$\alpha = 100.370 (1)^\circ$
$\beta = 99.429 (1)^\circ$
$\gamma = 95.899 (1)^\circ$
$V = 3623.6 (3)$ Å^3
$Z = 1$
$D_x = 1.507$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5859 reflections
$\theta = 2.3$–27.7°
$\mu = 0.78$ mm^{-1}
$T = 223 (2)$ K
Irregular block, colorless
0.31 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.672$, $T_{max} = 0.837$
31 408 measured reflections
16 043 independent reflections
11 658 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.5^\circ$
$h = -16 \rightarrow 16$
$k = -18 \rightarrow 18$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.113$
$S = 0.92$
16 043 reflections
939 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.39$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn—C73	2.081 (4)	Sn—O2^i	2.818 (3)
Sn—C74	2.065 (4)	Sn—O3	2.155 (3)
Sn—O1	2.291 (3)	Sn—O5	2.082 (3)
C73—Sn—C74	154.6 (2)	C74—Sn—O5	109.2 (2)
C73—Sn—O1	92.9 (2)	O1—Sn—O2^i	114.0 (1)
C73—Sn—O2^i	77.3 (1)	O1—Sn—O3	164.2 (1)
C73—Sn—O3	99.5 (2)	O1—Sn—O5	79.7 (1)
C73—Sn—O5	95.5 (1)	O2^i—Sn—O3	78.7 (1)
C74—Sn—O1	86.2 (1)	O2^i—Sn—O5	164.6 (1)
C74—Sn—O2^i	79.9 (2)	O3—Sn—O5	89.3 (1)
C74—Sn—O3	86.9 (1)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

A 2θ-dependent absorption was applied by assuming 2θ × diameter = 0.24. The final difference Fourier map had a large peak ~1 Å from the Sn and Ag atoms. One of the three trifluoromethyl groups is disordered over two sites, and the disorder was refined as a 50:50 disorder. The six C—F distances for this group were restrained to 1.32 (1) Å and the F···F distance was restrained to 2.16 (1) Å. Additionally, the six F atoms of the disordered group were restrained to lie in a plane. All H atoms were placed at calculated positions and were included in the refinements in the riding-model approximation (C—H = 0.94 Å for aromatic H atoms and 0.97 Å for aliphatic H atoms). The H-atom displacement parameters were set at $1.2U_{eq}$ of the C atoms. The torsion angles of the methyl groups were refined.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); 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: TA1433). Services for accessing these data are described at the back of the journal.

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