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Short Communication

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Crystal structure of polymeric triphenyltin triflate

Abstract: The crystal structure of the previously known title compound, $Ph_3SnO_3SCF_3$, was determined by single-crystal X-ray diffraction; it comprises a one-dimensional polymeric structure and pentacoordinated Sn atoms.

Keywords: cation; hypercoordination; tin; triflate; X-ray crystallography.

The preparation of the first tricoordinated triaryltin cation, $[(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3Sn]B(C_6F_5)_3$, using three bulky aryl substituents and a weakly coordinating anion marked a significant breakthrough in organotin chemistry (Lambert et al., 2003). Previous attempts using smaller organic groups and/or counterions with a higher donor capacity gave rise to tetra- and pentacoordinated triorganotin cations $(R_3SnL_n)A$ [R=alkyl, aryl; L=neutral donor molecules, e.g., H_2O, DMSO, DMF, DMA, MeCN, NH_3, Ph_3PO, Ph_3AsO; n=0–2; A=anion, e.g., BPh_4, $N(SO_2Me)_2$, $N(SO_2CF_3)_2$, SbF_6, SO_3CF_3] in which the neutral donor molecule L and/or the anion A increases the coordination number of the Sn atoms to 3+1 or 3+2 (Zharov and Michl, 2002).

A few years ago, we reviewed the literature on hypercoordinated organotin triflates (Beckmann, 2005) and noted that simple triorganotin triflates without σ-donor ligands that are characterized by X-ray crystallography are very rare. In fact, a literature search brought forward only a single example, namely, $[(Me_3Si)_2CH]_3SnO_3SCF_3$ (Westerhausen and Schwarz, 1997), which prompted us to study the title compound $Ph_3SnO_3SCF_3$, one of the first reported members of this compound class (Schmeisser et al., 1970). The crystal structure of $Ph_3SnO_3SCF_3$ is shown in Figure 1. Selected bond parameters are shown in the caption of the figure. Crystal and refinement details are listed in Table 1. The spatial arrangement of the Sn atoms is distorted trigonal bipyramidal [geometrical goodness $\Delta\Sigma(\theta)=\Sigma(\theta_{eq})-\Sigma(\theta_{ax})=94.1°$] (Kolb et al., 1991, 1994). The occupancy of the C_3O_2 donor set is consistent with Bent's rule. The Sn−O bond lengths of 2.375(4) and 2.310(4) Å are substantially longer than those of the tetracoordinated Mes_3SnOH (1.999(6) Å) (Reuter and Puff, 1989) and $[(Me_3Si)_2CH]_3SnO_3SCF_3$ [2.139(4) Å] (Westerhausen and Schwarz, 1997) as well as of the pentacoordinated Ph_3SnOH [2.180(2) and 2.250(2) Å] (Glidewell et al., 2002). It is worthwhile to compare these different Sn−O bond lengths with Pauling bond orders [definition: $\log BO=-c(d-d_{st})$ with c=1.41 and $d_{st}=2.00$] (Pauling, 1960; Zickgraf et al., 1998), which decreases in the order Mes_3SnOH (1.00)<$[(Me_3Si)_2CH]_3SnO_3SCF_3$ (0.64)<Ph_3SnOH (0.56/0.44, Σ 1.00)<$Ph_3SnO_3SCF_3$ (0.30/0.37, Σ 0.67). Interestingly, the sum of the two bond orders of the pentacoordinated species Ph_3SnOH and $Ph_3SnO_3SCF_3$ compares quite well with the single bond orders of the tetracoordinated species Mes_3SnOH and

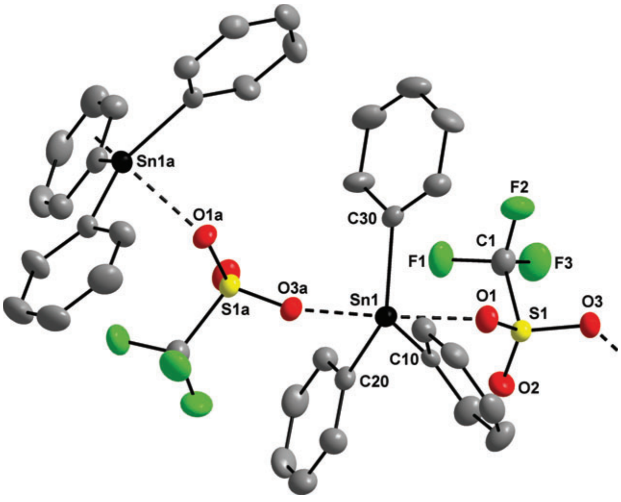

Figure 1 Crystal structure of $Ph_3SnO_3SCF_3$ showing 50% probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: a=0.5+x, 0.5-y, 0.5+z). Selected bond parameters [Å]: Sn1-O1 2.375(4), Sn1-O3a 2.310(4), Sn1-C10 2.118(5), Sn1-C20 2.104(6), Sn1-C30 2.117(6), C10-Sn1-O1 86.9(2), C10-Sn1-O3a 90.8(2), C20-Sn1-O1 93.0(2), C20-Sn1-O3a 91.5(2), C30-Sn1-O1 85.9(2), C30-Sn1-O3a 91.7(2), C10-Sn1-C20 117.4(2), C10-Sn1-C30 116.2(2), C20-Sn1-C30 126.3(2), O1-Sn1-O3a 175.6(1).

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Formula	$C_{19}H_{15}F_3O_3SSn$
Formula weight, g/mol	499.06
Crystal system	Monoclinic
Crystal size, mm	0.50×0.20×0.20
Space group	$P2_1/n$
a, Å	8.720(1)
b, Å	18.356(3)
c, Å	12.143(1)
α, °	90
β, °	102.68(1)
γ, °	90
V, Å^3	1896.3(4)
Z	4
ρ_{calcd}, Mg/m^3	1.748
T, K	173
μ (Mo Kα), mm^{-1}	1.502
F(000)	984
θ range, °	2.22–27.51
Index ranges	$-9 \le h \le 11$
	$-23 \le k \le 17$
	$-15 \le l \le 15$
No. of reflections collected	5585
Completeness to θ_{max}	99.3%
No. of independent reflections	4339
No. of observed reflections with ($I > 2\sigma(I)$)	2963
No. of refined parameters	244
Goodness of fit (F^2)	1.014
R_1 (F) ($I > 2\sigma(I)$)	0.0529
wR_2 (F^2) (all data)	0.1141
$(\Delta/\sigma)_{max}$	<0.001
Largest diffraction peak/hole, e/Å^3	0.811/-0.778

Table 1 Crystal data and structure refinement of $Ph_3SnO_3SCF_3$.

$[(Me_3Si)_2CH]_3SnO_3SCF_3$ regardless of the steric demand of the organic substituents.

Experimental

The title compound, $Ph_3SnO_3SCF_3$, was prepared by the reaction of Ph_4Sn with triflic acid (Schmeisser et al., 1970). Single crystals were obtained by slow evaporation of a CH_2Cl_2/hexane under inert conditions of a glove box.

X-ray crystallography

The intensity data of $Ph_3SnO_3SCF_3$ were collected on a Siemens P4 difractometer (Siemens, Germany) with graphite-monochromated Mo-Kα (0.7107 Å) radiation. The data were reduced and corrected for absorption (Walker and Stuart, 1983). The structure was solved by direct methods and difference Fourier synthesis with subsequent Full-matrix least-squares refinements on F^2, using all data (Sheldrick, 2008). All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Crystal and refinement data are shown in Table 1. Figures were created using the Diamond visualization software (Brandenburg and Putz, 2006). Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 898394. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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