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Note

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Molecular Stannatelluroxanes

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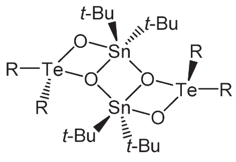
*Summary: The syntheses and structures are described of the molecular stannatelluroxanes 2,4,6-t-$Bu_3C_6H_2TeO_2Sn$-t-Bu_2Cl (**4**), 8-$Me_2NC_{10}H_6TeO_2Sn$-t-Bu_2Cl (**5**), and (2,6-$Mes_2C_6H_3Te)_2O_5(Sn$-t-$Bu_2)_2$ (**6**), which were obtained by the reaction of (t-$Bu_2SnO)_3$ with the respective aryltellurium trichlorides $RTeCl_3$ (R = 2,4,6-t-$Bu_3C_6H_2$, 8-$Me_2NC_{10}H_6$, 2,6-$Mes_2C_6H_3$). Compounds **4**−**6** were characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{119}Sn, ^{125}Te), ESI-TOF MS spectrometry, osmometric molecular weight determination, and X-ray crystallography.*

Organostannoxane clusters and polymers have been the focus of extensive research due to their fascinating structural diversity and applications in catalysis and material science.[1] Attempts to incorporate a second heavy element into the structure of organostannoxanes are motivated by the possibility to develop more advanced catalysts with multiple active centers. However, so far only very few compounds containing Sn−O−E linkages (E = heavy element) are known. We recently reported that the reaction of (t-$Bu_2SnO)_3$ with (p-$MeOC_6H_4)_2TeO$ using a Sn/Te ratio of 1:1 quantitatively provides the hypervalent stannatelluroxane [p-$MeOC_6H_4)_2TeOSn$$t$-$Bu_2O]_2$ (**1**).[2,3] Solutions of **1** rapidly absorb gaseous CO_2, giving a tetranuclear stannatelluroxane carbonate cluster [(p-$MeOC_6H_4)_2TeOSn$$t$-$Bu_2CO_3]_2$ (**2**).[2] Unlike most metal carbonates, **2** possesses three unevenly long C−O bonds due to the different coordination modes with the Sn and Te atoms, a useful characteristic when pursuing bond activation within carbonates. While salt-like carbonates are often thermally very stable, **2** liberates CO_2 upon heating above 90 °C. These properties make **2** a promising candidate for applications in the fixation and activation of CO_2. Another stannatelluroxane, [(p-$MeOC_6H_4)_2Te(OSn$-t-$Bu_2OH)_2$] (**3**), was obtained by the reaction of (t-$Bu_2SnO)_3$ with (p-$MeOC_6H_4)_2TeO$ using a Sn/Te ratio of 2:1 in the presence of moisture.[3] Two molecules of **3** interacted to give dimers in the solid state. The structural characterization of **2** and **3** has revealed the importance of hypervalent and secondary bonding for the fixation of CO_2, the degree of aggregation, and the supramolecular association.



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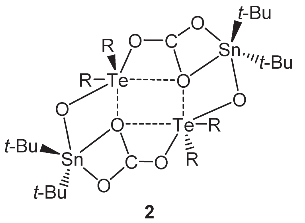
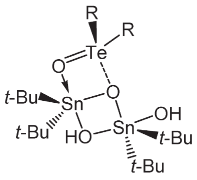


2

R = p-$MeOC_6H_4$



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In an effort to obtain deeper insight into the formation of stannatelluroxanes and their ability to absorb CO_2, we have now studied the reaction of di-*tert*-butyltin oxide with known aryltellurium trichlorides at various stoichiometric ratios (Scheme 1). The reaction of (t-$Bu_2SnO)_3$ with 2,4,6-t-$Bu_3C_6H_2TeCl_3$ and 8-$Me_2NC_{10}H_6TeCl_3$, respectively, using a Sn/Te ratio of 2:1 exclusively provided the dinuclear stannatelluroxanes 2,4,6-t-$Bu_3C_6H_2TeO_2Sn$$t$-$Bu_2Cl$ (**4**) and 8-$Me_2NC_{10}H_6TeO_2Sn$-t-Bu_2Cl (**5**), respectively, and t-Bu_2SnCl_2. Under the same conditions, the reaction of (t-$Bu_2SnO)_3$ with 2,6-$Mes_2C_6H_3TeCl_3$ proceeded with complete oxide transfer and produced the dimeric aryltellurium oxo chloride [2,6-$Mes_2C_6H_3Te(O)Cl]_2$[4] and t-Bu_2SnCl_2. At a Sn/Te ratio of 5:2 the reaction of (t-$Bu_2SnO)_3$ with 2,6-$Mes_2C_6H_3TeCl_3$ afforded the tetranuclear stannatelluroxane (2,6-$Mes_2C_6H_3Te)_2O_5$(Sn-t-$Bu_2)_2$ (**6**). Further variation of the Sn/Te ratios provided no other stannatelluroxane products. Alternatively, **6** also was obtained by the condensation reaction of (t-$Bu_2SnO)_3$ with the aryltellurinic acid [2,6-$Mes_2C_6H_3Te(O)OH]_2$. Compounds **4**−**6** were isolated as colorless crystals in high yields and are rare examples of molecular oxides incorporating two heavy main group elements.

The molecular structures of **4**−**6** are shown in Figures 1− 3, and selected bond parameters are collected in the captions of the figures. The spatial arrangement of the Sn atoms is

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(1) Reviews and references cited therein: (a) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190. (b) Jain, V. K. *Coord. Chem. Rev.* **1994**, *135*−*136*, 809. (c) Beckmann, J.; Jurkschat, K. *Coord. Chem. Rev.* **2001**, *215*, 267. (d) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1. (e) Chandrasekhar, V.; Gopal, K.; Thilagar, P. *Acc. Chem. Res.* **2007**, *40*, 420.

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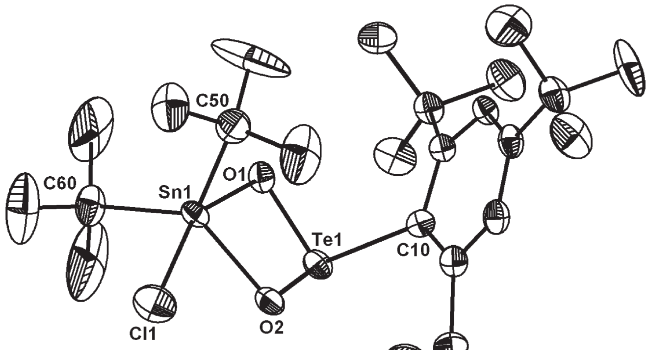
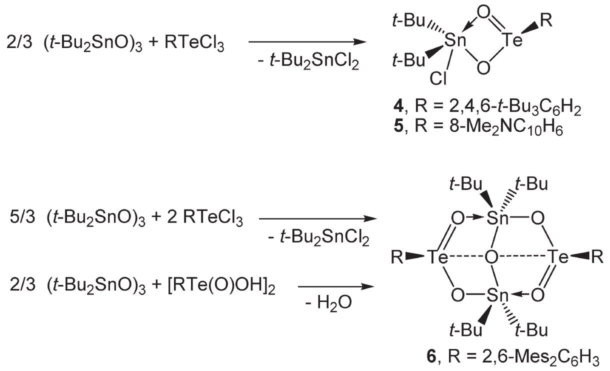


Figure 1. Molecular structure of **4** showing 30% probability displacement ellipsoids and the atom numbering. Selected bond parameters [Å, deg]: Sn1−O1 2.247(6), Sn1−O2 2.084(7), Sn1−Cl1 2.461(3), Sn1−C50 2.17(1), Sn1−C60 2.178(1), Te1−O1 1.855(6), Te1−O2 1.886(7), Te1−C10 2.138(9), O1−Sn1−O2 72.4(3), O1−Sn1−Cl1 155.0(2), O1−Sn1−C50 97.3(4), O1−Sn1−C60 90.4(4), O2−Sn1−Cl1 82.8(2), O2−Sn1−C50 118.6(4), O2−Sn1−C60 118.0(4), Cl1−Sn1−C50 96.4(3), Cl1−Sn1−C60 99.6(4), C50−Sn1−C60 122.5(4), O1−Te1−O2 86.4(3), O1−Te1−C10 97.2(3), O2−Te1−C10 100.0(3), Sn1−O1−Te1 98.1(3), Sn1−O2−Te1 103.0(3).

Scheme 1



distorted trigonal bipyramidal, and the Sn−O bond lengths are in the expected range for single bonds. The axial Sn−Cl bond lengths of **4** (2.461(3) Å) and **5** (2.517(3) Å) are somewhat longer than those in $t\text{-Bu}_2\text{SnCl}_2$ (2.334(1) and 2.335 Å).[5] Taking into account the stereochemically active lone pair, the spatial arrangement of the Te atoms is distorted tetrahedral for **4** (CO_2 donor set), distorted octahedral for **5** ($\text{CO}_2 + \text{NO}$ donor set), and distorted trigonal bipyramidal for **6** ($\text{CO}_2 + \text{O}$ donor set), respectively. The primary Te−O bond lengths of **4** (1.855(6), 1.886(7) Å), **5** (1.900(6), 1.944(5) Å), and **6** (1.857(6)−1.874(7) Å) are significantly shorter than the standard Te−O single bond of $[(4\text{-MeOC}_6\text{H}_4)_2\text{TeO}]_n$ (2.025(2) and 2.100(2) Å),[6] pointing to a bond order of approximately 1.5. The intramolecular Te···N contact of **5** (2.533(8) Å) is longer than that in $8\text{-Me}_2\text{NC}_{10}\text{H}_6\text{TeCl}_3$ (2.420(3) Å),[7] suggesting a reduced Lewis acidity of the Te atom. Besides the primary coordination sphere, **5** reveals two symmetry-related intermolecular secondary Te···O contacts (2.650(6) Å), which link two molecules into a centrosymmetric dimer in the crystal lattice. Compound **6** shows two intramolecular Te···O contacts (2.581(7) and 2.588(7) Å) to the Sn−O−Sn linkage (146.9(3)°). Compound **4** lacks any secondary interactions due to the confined space around the Te atom. Due to servere repulsion of the inorganic moiety with the *tert*-butyl groups in *ortho*-positions, the Te atom is not coplanar with the phenyl ring of the 2,4,5-tri-*tert*-butylphenyl substituent (largest deviation from the ideal plane 0.299(5) Å).[8]

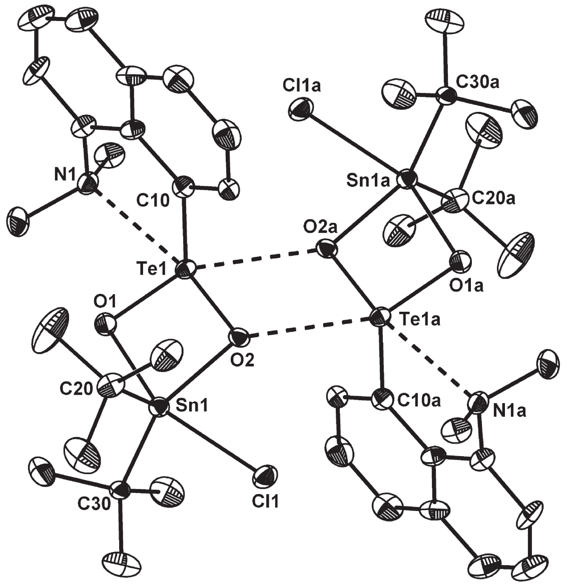


Figure 2. Molecular structure of **5** showing 30% probability displacement ellipsoids and the atom numbering. Symmetry code used to generate equivalent atoms: $a = 2-x,\ 1-y,\ 1-z$. Selected bond parameters [Å, deg]: Sn1−O1 2.165(6), Sn1−O2 2.075(5), Sn1−C20 2.210(8), Sn1−C30 2.160(8), Sn1−Cl1 2.517(4), Te1−O1 1.900(6), Te1−O2 1.944(5), Te1···O2a 2.650(6), Te1···N1 2.533(8), Te1−C10 2.123(8), O1−Te1−O2 82.8(2), O1−Te1−C10 99.6(3), O2−Te1−C10 95.8(3), O1−Sn1−O2 73.6(2), O1−Sn1−Cl1 155.8(2), O1−Sn1−C20 99.3(3), O1−Sn1−C30 92.0(3), O2−Sn1−Cl1 82.7(2), O2−Sn1−C20 117.1(3), O2−Sn1−C30 120.1(3),Cl1−Sn1−C30 95.9(2), Cl1−Sn1−C20 95.6(2), C20−Sn1−C30 122.6(3), Sn1−O1−Te1 100.9(2), Sn1−O2−Te1 102.6(2).

Compounds **4** and **6** are reasonably soluble in polar solvents such as CHCl_3 and THF, whereas **5** is only poorly soluble in most solvents. The ^{125}Te NMR spectrum (CDCl_3) of $2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{TeO}_2\text{Sn-}t\text{-Bu}_2\text{Cl}$ (**4**) shows a signal at $\delta = 1748.6$ with unresolved Sn satellites ($^2J(^{125}\text{Te}-^{119/117}\text{Sn}) = 196$ Hz), which is only slightly shifted compared to the parent compound $2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{TeCl}_3$ ($\delta = 1791.0$).[8] The ^{119}Sn NMR spectrum (CDCl_3) of **4** displays a signal at $\delta = -128.3$ with Te satellites ($^2J(^{119}\text{Sn}-^{125}\text{Te}) = 196$ Hz), which agrees well with the spatial arrangement of the pentacoordinated Sn atom and the $\text{C}_2\text{O}_2\text{Cl}$ donor set. The ^1H and ^{13}C NMR spectra of **4** show that the two *tert*-butyl groups are magnetically inequivalent, which is in good agreement with the molecular structure established by X-ray crystallography. The ^{125}Te NMR spectrum (CDCl_3) of $8\text{-Me}_2\text{N-C}_{10}\text{H}_6\text{TeO}_2\text{Sn-}t\text{-Bu}_2\text{Cl}$ (**5**) shows a signal at $\delta = 1529.3$

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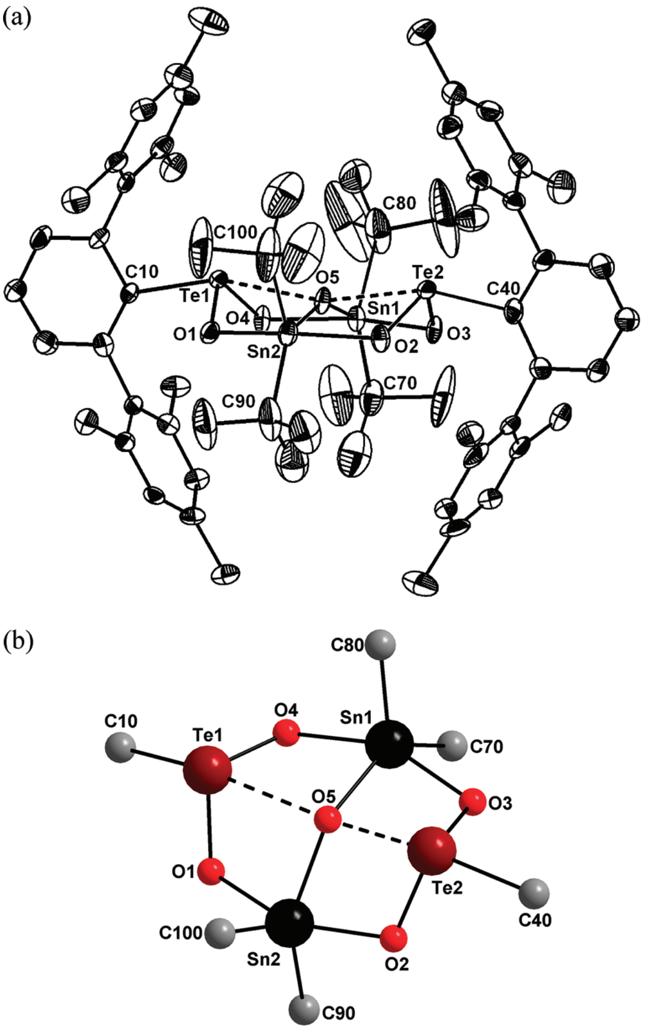

Figure 3. (a) Molecular structure of **6** showing 30% probability displacement ellipsoids and the atom numbering scheme and (b) inorganic core of **6**. Selected bond parameters [Å, deg]: Sn1−O3 2.165(6), Sn1−O4 2.174(6), Sn1−O5 1.997(5), Sn1−C70 2.10(1), Sn1−C80 2.21(1), Sn2−O1 2.162(7), Sn2−O2 2.142(7), Sn2−O5 2.016(5), Sn2−C90 2.07(1), Sn2−C100 2.24(2), Te1−O1 1.869(7), Te1−O4 1.857(6), Te1...O5 2.588(7), Te1−C10 2.199(6), Te2−O2 1.874(7), Te2−O3 1.858(7), Te2···O5 2.581(7), Te2−C40 2.169(7), O3−Sn1−O4 155.5(2), O3−Sn1−O5 79.3(2), O4−Sn1−O5 79.4(2), O3−Sn1−C70 93.1(3), O3−Sn1−C80 98.7(4), O4−Sn1−C70 92.8(3), O4−Sn1−C80 98.2(4), O5−Sn1−C70 133.1(4), O5−Sn1−C80 104.7(5), C70−Sn1−C80 122.1(6), O1−Sn2−O2 156.3(3), O1−Sn2−O5 79.6(2), O2−Sn2−O5 79.5(2), O1−Sn2−C90 91.6(3),O1−Sn2−C100 99.6(3), O2−Sn2−C90 94.2(3), O2−Sn2−C100 96.7(3), O5−Sn2−C90 132.2(4), O5−Sn2−C100 105.9(4), C90−Sn2−C100 121.9(5), O1−Te1−O4 105.1(3), O1−Te1−C10 96.5(3), O4−Te1−C10 98.1(3), O2−Te2−O3 105.6(3), O2−Te2−C40 98.6(3), O3−Te2−C40 97.1(3), Sn1−O5−Sn2 146.9(3), Sn1−O4−Te1 111.8(3), Sn1−O3−Te2 111.5(3), Sn2−O1−Te1 111.4(3), Sn2−O2−Te2 112.5(4).

($\omega_{1/2} = 42$ Hz), which is shifted to higher frequencies compared to the parent compound 8-$Me_2NC_{10}H_6TeCl_3$ ($\delta = 1317.1$ ($CDCl_3$)).[7] The ^{119}Sn NMR spectrum ($CDCl_3$) of **5** exhibits a signal at $\delta = -149.1$ ($\omega_{1/2} = 89$ Hz), which is also consistent with the spatial arrangement of the pentacoordinated Sn atom and the C_2O_2Cl donor set. No satellites were observed due to the poor signal-to-noise ratio (acquisition time for each spectrum 24 h). Like the ^{119}Sn NMR signal, the ^{1}H and ^{13}C NMR chemical shifts of **5** were slightly broad, which is explained by a dynamic exchange process, namely, a monomer−dimer equilibrium in solution. This is supported by an osmometric molecular weight determination, which reveals a degree of association of 1.64 in $CHCl_3$. An attempt to measure a reasonable ^{125}Te and ^{119}Sn NMR spectrum of **5** at −20 °C failed due to the poor solubility. The ^{125}Te NMR ($CDCl_3$) of (2,6-$Mes_2C_6H_3Te)_2O_5(Sn$-*t*-$Bu_2)_2$ (**6**) shows a signal at $\delta = 1613.5$ ($\omega_{1/2} = 42$ Hz), which is shifted to higher frequencies when compared to [2,6-$Mes_2C_6H_3Te(O)OH]_2$ ($\delta = 1403$).[4] The ^{119}Sn NMR spectrum ($CDCl_3$) of **6** shows a signal at $\delta = -253.3$ with Sn ($^2J(^{119}Sn-^{117}Sn) = 528$ Hz) and Te satellites ($^2J(^{119}Sn-^{125}Te) = 32$ Hz) that are consistent with the spatial arrangement of the pentacoordinated Sn atoms and the C_2O_3 donor set. While the magnitude of the $^2J(^{119}Sn-^{117}Sn)$ coupling agrees well with the wide Sn−O−Sn angle,[9] no explanation can be given for the small $^2J(^{119}Sn-^{125}Te)$ coupling at this point in time. The ^{1}H and ^{13}C NMR spectra show two sets of signals for the magnetically inequivalent *tert*-butyl groups, confirming that the molecular structure is retained in solution. Stannatelluroxanes **4**−**6** were also characterized by ESI-TOF MS spectrometry, a method that allows the detection of (trace amounts of) ionic species formed by autoionization in solution. For **4** and **5**, significant mass clusters were detected in the positive mode of the cations $[(RTe)_3t\text{-}Bu_2SnO_5]^+$, $[(RTe)_2t\text{-}Bu_2SnO_3(OH)]^+$, $[(RTe)t\text{-}Bu_2SnO(OH)Cl]^+$, and $[(RTe)t\text{-}Bu_2SnO_2]^+$ (R = 2,4,6-*t*-$Bu_3C_6H_2$, 8-$Me_2NC_{10}H_6$), respectively, whereas **6** showed a mass cluster for the cation $[(RTe)_2(t\text{-}Bu_2Sn)_2O_4(OH)]^+$ (R = 2,6-$Mes_2C_6H_3$).

In an effort to investigate their ability to fix carbon dioxide, solid and liquid samples of **4** and **6** in $CDCl_3$ were treated with gaseous CO_2 at room temperature. No reaction was observed by means of IR and NMR spectroscopy. Thus, unlike $[p\text{-}MeOC_6H_4)_2TeOSn\text{-}t\text{-}Bu_2O]_2$ (**1**),[2,3] no evidence for the formation of stannatelluroxane carbonates was found.

Experimental Section

General Considerations. The starting compounds (*t*-$Bu_2SnO)_3$,[10] 2,4,6-*t*-$Bu_3C_6H_2TeCl_3$,[8] 8-$Me_2NC_{10}H_6TeCl_3$,[7] 2,6-$Mes_2C_6H_3TeCl_3$, and [2,6-$Mes_2C_6H_3Te(O)OH]_2$[4] were prepared according to a literature procedure. The solution ^{1}H, ^{13}C, ^{119}Sn, and ^{125}Te NMR spectra were collected using a Jeol JNM-LA 400 FT spectrometer and a Jeol Eclipse + 500 FT spectrometer and are referenced against Me_4Si, Me_4Sn, and Me_2Te. Electrospray ionization time-of-flight ESI-TOF mass spectra were measured on an Agilent 6210 mass spectrometer (Agilent Technologies, Santa Clara, CA). Solvent flow rate was adjusted to 4 μL/min. The spray voltage and skimmer voltage were set to 4 kV and 150 V, respectively. Molecular weights were determined using a Knauer vapor pressure osmometer. Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of 4−6. A solution or suspension of the appropriate aryltellurium trichloride (240 mg of 2,4,6-*t*-$Bu_3C_6H_2TeCl_3$, 202 mg of 8-$Me_2NC_{10}H_6TeCl_3$, 273 mg of 2,6-$Mes_2C_6H_3TeCl_3$; 0.50 mmol) and (*t*-$Bu_2SnO)_3$ (246 mg, 0.33 mmol for **4** and **5**; 620 mg, 0.83 mmol for **6**) in THF (60 mL) was stirred at rt for 6 h. The volume of the solution was reduced to

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Table 1. Crystal Data and Structure Refinement of 4−6

	4	5·THF	6
formula	$C_{26}H_{47}ClO_2SnTe$	$C_{24}H_{38}ClNO_3SnTe$	$C_{64}H_{86}O_5Sn_2Te_2$
fw, g mol^{-1}	673.38	670.29	1427.91
cryst syst	monoclinic	triclinic	monoclinic
cryst size, mm	0.31 × 0.18 × 0.07	0.25 × 0.21 × 0.08	0.50 × 0.13 × 0.05
space group	$P2_1/n$	$P\bar{1}$	$C2/c$
a, Å	11.949(2)	8.56(1)	21.52(1)
b, Å	10.2751(8)	12.65(1)	21.417(5)
c, Å	25.423(3)	12.90(2)	29.85(1)
α, deg	90	100.4(1)	90
β, deg	91.64(1)	92.4(1)	96.22(4)
γ, deg	90	90.39(9)	90
V, Å^3	3120.1(7)	1373(3)	13676(9)
Z	4	2	8
ρ_{calcd}, Mg m^{-3}	1.433	1.622	1.387
T, K	150	150	150
μ(Mo Kα), mm^{-1}	1.839	2.093	1.608
F(000)	1352	664	5712
θ range, deg	1.86 to 25.25	2.08 to 29.20	2.22 to 29.29
index ranges	$-14 \le h \le 14$	$-11 \le h \le 11$	$-29 \le h \le 29$
	$0 \le k \le 12$	$-17 \le k \le 17$	$-29 \le k \le 24$
	$0 \le l \le 30$	$-17 \le l \le 17$	$-40 \le l \le 40$
no. of reflns collected	5643	14 890	65 721
completeness to θ_{max}	99.8%	98.2%	97.7%
no. indep reflns	5643	7303	18 258
no. obsd reflns with ($I > 2\sigma(I)$)	3258	2371	5397
no. refined params	275	280	730
GooF (F^2)	0.866	0.994	0.958
R_1 (F) ($I > 2\sigma(I)$)	0.0530	0.0375	0.0570
wR_2 (F^2) (all data)	0.1543	0.0844	0.1149
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001	< 0.001
largest diff peak/hole, e Å^{-3}	0.972/−1.600	0.602/−0.940	0.900/−0.713

10 mL under vacuum. Colorless single crystals of **4**, **5**·THF, and **6** were obtained within 12 h. The crystals of **5**·THF were dried for 2 h at 40 °C under vacuum to give an analytical sample of **5**.

2,4,6-*t*-Bu$_3$C$_6$H$_2$TeO$_2$Sn-*t*-Bu$_2$Cl (4). Yield: 272 mg, 0.41 mmol; 81%. ^{1}H NMR (CDCl$_3$): δ 7.37 (s, 2H; Ar), 1.49 (s, 18H; CH$_3$), 1.38 (s, 9H; CH$_3$), 1.24 (s, 18H; CH$_3$). ^{13}C NMR (CDCl$_3$): δ 156.7, 152.3, 149.8, 141.5, 125.5, 119.39 (Ar), 45.1, 42.1, 39.7, 34.7, 33.8, 31.5, 31.4, 30.4 (CMe$_3$). ^{119}Sn NMR (CDCl$_3$): δ −128.3 ($^2J(^{119}Sn-^{125}Te)$=196 Hz). ^{125}Te NMR (CDCl$_3$): δ 1748.6 ($^2J(^{125}Te-^{119/117}Sn)$ = 196 Hz). Anal. Calcd for $C_{26}H_{47}ClO_2SnTe$ (673.41): C, 46.37; H, 7.03. Found: C, 46.25; H, 6.78. ESI-TOF MS: m/z 1433.4 [$C_{62}H_{105}O_5Te_3Sn$]$^+$, 1044.1 [$C_{44}H_{77}O_4Te_2Sn$]$^+$, 675.1 [$C_{26}H_{48}O_2SnTeCl$]$^+$, 639.2 [$C_{26}H_{47}O_2SnTe$]$^+$.

8-Me$_2$NC$_{10}$H$_6$TeO$_2$Sn-*t*-Bu$_2$Cl (5). Yield: 147 mg, 0.25 mmol; 50%. ^{1}H NMR (CDCl$_3$): δ 8.68 (d, 2H; Ar), 8.05 (d, 2H; Ar), 7.87−7.81 (m, 4H; Ar), 7.59−7.57 (m, 4H; Ar), 3.34 (s, 12 H, NCH$_3$), 1.03 (s, 36 H, CCH$_3$). ^{13}C NMR (CDCl$_3$): δ 148.6, 140.9, 134.9, 131.9, 131.6, 131.3, 127.6, 127.4, 126.8, 119.7 (Ar), 47.9 (NMe$_2$), 40.9 (*C*Me$_3$), 29.8 (C*Me$_3$*). ^{119}Sn NMR (CDCl$_3$): δ −149.1 ($\omega_{1/2}$ = 89 Hz). ^{125}Te NMR (CDCl$_3$): δ 1529.3 ($\omega_{1/2}$ = 42 Hz). Anal. Calcd for $C_{20}H_{30}ClNO_2TeSn$ (598.22): C, 40.15; H, 5.05; N, 2.34. Found: C, 39.99; H, 4.84; N, 2.28. ESI-TOF MS: m/z 1208.0 [$C_{44}H_{54}N_3O_5SnTe_3$]$^+$, 895.0 [$C_{32}H_{43}N_2O_4SnTe_2$]$^+$, 600.0 [$C_{20}H_{31}NO_2SnTeCl$]$^+$, 564.0, [$C_{20}H_{30}NO_2SnTe$]$^+$. MW: 981 g mol^{-1} (c 10−25 mg/g CHCl$_3$).

(2,6-Mes$_2$C$_6$H$_3$Te)$_2$O$_5$(Sn*t*-Bu$_2$)$_2$ (6). Yield: 550 mg, 0.39 mmol, 77%. ^{1}H NMR (CDCl$_3$): δ 7.47 (t, 1H; Ar), 7.03 (d, 2H; Ar), 6.82 (s, 4H; Ar), 2.29 (s, 6H; CH$_3$), 2.0 (s, 12H; CH$_3$), 0.95 (s, 9H; CH$_3$), 0.88 (s, 9H; CH$_3$). ^{13}C NMR (CDCl$_3$): δ 146.3, 146.1, 137.5, 136.7, 136.4, 130.9, 129.3, 128.1 (Ar), 41.5, 35.5 (*C*Me$_3$), 30.2, 29.9 (C*Me$_3$*), 21.4, 21.0 (Ar*Me*). ^{119}Sn NMR (CDCl$_3$): δ −253.3 ($^2J(^{119}Sn-^{117}Sn)$ = 528 Hz, $^2J(^{119}Sn-O-^{125}Te)$ = 32 Hz). ^{125}Te NMR (CDCl$_3$): δ 1613.5 ($\omega_{1/2}$ = 42 Hz). Anal. Calcd for $C_{64}H_{86}O_5Sn_2Te_2$ (1427.98): C, 53.83; H, 6.07. Found: C, 53.86; H, 5.91. ESI-TOF MS: m/z 1429.3 [$C_{64}H_{87}O_5Sn_2Te_2$]$^+$.

Alternative Synthesis of 6. A solution of [2,6-Mes$_2$C$_6$H$_3$Te(O)-OH]$_2$ (474 mg; 0.50 mmol) and (t-Bu$_2$SnO)$_3$ (246 mg; 0.33 mmol) in toluene (50 mL) was heated under reflux in a Dean−Stark apparatus for 2 h. The volume of the solution was reduced to 10 mL under vacuum. Colorless single crystals of **6**, which were obtained within 12 h, were isolated by filtration. Yield: 542 mg, 0.38 mmol, 76%.

X-ray Crystallography. Intensity data of **4**−**6** were collected on a STOE IPDS 2T area detector with graphite-monochromated Mo Kα (0.7107 Å) radiation. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 and SHELXL-97 implemented in the program WinGX 2002.[11] Full-matrix least-squares refinements were done on F^2, using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Disorder of the inorganic core of **6** was resolved with split occupancies of 0.75 (Te1, Te2, Sn1, Sn2, and O1−O5) and 0.25 (Te1′, Te2′, Sn1′, Sn2′, and O1′−O5′). Crystal and refinement details are collected in Table 1. Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 733996 (**4**), 733997 (**5**), and 733998 (**6**). 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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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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