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Methyl Tin(IV) Derivatives of $HOTeF_5$ and $HN(SO_2CF_3)_2$: A Solution Multinuclear NMR Study and the X-ray Crystal Structures of $(CH_3)_2SnCl(OTeF_5)$ and $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$[†]

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The new tin(IV) species $(CH_3)_2SnCl(OTeF_5)$ was prepared via either the solvolysis of $(CH_3)_3SnCl$ in $HOTeF_5$ or the reaction of $(CH_3)_3SnCl$ with $ClOTeF_5$. It was characterized by NMR and vibrational spectroscopy, mass spectrometry, and single crystal X-ray diffraction. $(CH_3)_2SnCl(OTeF_5)$ crystallizes in the monoclinic space group $P2_1/n$ ($a = 5.8204(8)$ Å, $b = 10.782(1)$ Å, $c = 15.493(2)$ Å, $\beta = 91.958(2)°$, $V = 971.7(2)$ Å^3, $Z = 4$). NMR spectroscopy of $(CH_3)_3SnX$, prepared from excess $Sn(CH_3)_4$ and HX (X = $OTeF_5$ or $N(SO_2CF_3)_2$), revealed a tetracoordinate tin environment using $(CH_3)_3SnX$ as a neat liquid or in dichloromethane-d_2 (CD_2Cl_2) solutions. In acetone-d_6 and acetonitrile-d_3 (CD_3CN) solutions, the tin atom in $(CH_3)_3SnOTeF_5$ was found to extend its coordination number to five by adding one solvent molecule. In the strong donor solvent DMSO, the Sn—$OTeF_5$ bond is broken and the $(CH_3)_3Sn(O{=}S(CH_3)_2)_2^+$ cation and the $OTeF_5^-$ anion are formed. $(CH_3)_3SnOTeF_5$ and $(CH_3)_3SnN(SO_2CF_3)_2$ react differently with water. While the Te—F bonds in the $OTeF_5$ group of $(CH_3)_3SnOTeF_5$ undergo complete hydrolysis that results in the formation of $[(CH_3)_3Sn(H_2O)_2]_2SiF_6$, $(CH_3)_3SnN(SO_2CF_3)_2$ forms the stable hydrate salt $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$. This salt crystallizes in the monoclinic space group $P2_1/c$ ($a = 7.3072(1)$ Å, $b = 13.4649(2)$ Å, $c = 16.821(2)$ Å, $\beta = 98.705(1)°$, $V = 1636.00(3)$ Å^3, $Z = 4$) and was also characterized by NMR and vibrational spectroscopy.

Introduction

The solvolytic reactions of alkyltin(IV) chlorides in strong protonic acids, such as HF,[1] $HOSO_2F$, $HOSO_2CF_3$, and $HOPOF_2$,[2−4] and the superacid HF−MF_5 (M = Sb, Nb, or Ta) systems[5] are convenient preparative routes to the corresponding organotin(IV) derivatives. The cleavage of Sn−Cl as well as Sn−C bonds has been observed in these acidolysis reactions, with a preferential cleavage of the Sn−Cl bond. Alkyl tin(IV) derivatives of acids are commonly polymeric due to vacant coordination sites on tetracoordinate tin(IV). The bridging occurs through halogen atoms or the oxoacid ligands. In the solid state, methyl tin halides $(CH_3)_3SnF$[6,7] and $(CH_3)_3SnCl$[8] form extended halogen-bridged chains with pentacoordinate tin, while $(CH_3)_2SnF_2$ has a sheetlike polymeric structure with hexacoordinate tin.[9] The crystal structures of $(CH_3)_2Sn(SO_3F)_2$,[10] $(CH_3)_3SnOOCCF_3$,[11] $(C_6H_{12})_3SnOOCC_3H_7$,[12] and $(CH_3)_2SnCl(OOCCH_3)$[13] contain

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tin centers that are bridged by the oxoacid ligands. However, due to steric crowding, tricyclohexyltin(IV) trifluoroacetate contains only a four-coordinate tin.[14] While chlorodimethyltin(IV) species, such as $(CH_3)_2SnCl(OOCCH_3)$, contain a five-coordinate tin with bridging acetate groups,[13] the corresponding diethyl species exhibit a distorted trigonal bipyramidal structure involving chlorine bridges.[15]

Alternative synthetic routes to such alkyltin(IV) derivatives involve metathetical reactions of alkyltin(IV) chlorides with Ag^+ salts of the corresponding acids[5,16−19] and reactions with chloro derivatives of the acids.[18] Alkyltin(IV) derivatives of the nitrogen acids $HN(SO_2X)_2$ (X = F or CF_3) have been prepared by the metathetical reaction of $(CH_3)_3SnCl$ with $[Ag][N(SO_2X)_2]\cdot C_6H_6$[17] and by the reaction of $(CH_3)_3SnCl$ with $ClN(SO_2X)_2$.[18] Solutions of $R_3SnN(SO_2X)_2$ (R = alkyl; X = F or CF_3) have been studied by multinuclear NMR spectroscopy in various solvents, showing that these species contain highly electron deficient tin centers.[17,18]

The extreme case of an electron deficient tin center is exemplified by a tricoordinate stannyl cation. Recently, the Mes_3Sn^+ cation (Mes = mesityl) has been prepared in solution by Lambert et al. and characterized by its highly deshielded ^{119}Sn resonance at 806 ppm.[20] The closest approximation to a stannyl cation in the solid state is the $[n\text{-}Bu_3Sn][CB_{11}(CH_3)_{12}]$ salt that has been characterized by X-ray crystallography.[21]

The only report of the $Sn-OTeF_5$ compound $(CH_3)_3SnOTeF_5$ was published in 1973,[19] but no detailed structural characterization was carried out. The acid strength of $HOTeF_5$, which was found to lie between that of HNO_3 and HCl,[22] is greater than that determined for nitrogen acids $HN(SO_2X)_2$, that is, $pK_a = 1.3$ (X = F)[23] or 1.7 (X = CF_3).[24] The exceptionally high group electronegativity of the $OTeF_5$ group (3.87)[25] has been commented on by Schrobilgen et al.,[25] Seppelt,[26] and Christe[27] and lies slightly above those of the $N(SO_2X)_2$ groups (∼3.6 on the Pauling scale).[23] This property of the $OTeF_5$ group can be employed to synthesize highly electron deficient organotin(IV) species. The present study was undertaken to investigate the synthesis and structural studies of trimethyltin(IV) derivatives containing the strongly electronegative $OTeF_5$ and $N(SO_2CF_3)_2$ groups and study their Lewis acidity by multinuclear NMR.

Results and Discussion

Syntheses and Properties of $(CH_3)_2SnCl(OTeF_5)$ and $(CH_3)_3SnOTeF_5$. The reaction of $(CH_3)_3SnCl$ with a slight excess of $HOTeF_5$ in the absence of solvent yielded the colorless solid $(CH_3)_2SnCl(OTeF_5)$ as the major Sn(IV) product, according to eq 1. The byproduct methane was

$$(CH_3)_3SnCl + HOTeF_5 \xrightarrow{\sim 25\ °C} (CH_3)_2SnCl(OTeF_5) + CH_4 \quad (1)$$

identified by infrared spectroscopy. Solid $(CH_3)_2SnCl(OTeF_5)$ can be sublimed at 50 °C (0.01 Torr). This result is in contrast to the previously reported preparation of $(CH_3)_3SnOTeF_5$ via the reaction of $(CH_3)_3SnCl$ with $HOTeF_5$ at room temperature.[19] Under our experimental conditions, only a minor amount of $(CH_3)_3SnOTeF_5$ was detected by ^{119}Sn NMR spectroscopy and the major product was $(CH_3)_2SnCl(OTeF_5)$. The formation of $(CH_3)_2SnCl(OTeF_5)$ indicates that either the Sn−C bond is cleaved preferentially compared to the Sn−Cl bond or the Sn−Cl bond is initially cleaved forming $(CH_3)_3SnOTeF_5$ and HCl as intermediates, followed by attack of HCl, thereby forming $(CH_3)_2SnCl(OTeF_5)$ and CH_4. The propensity of hydrogen halides to cleave as many as two Sn−C bonds has been well established.[28] The reaction of $(CH_3)_3SnCl$ with trifluoroacetic acid has also been reported to result in the replacement of a methyl group.[29]

Surprisingly, $(CH_3)_3SnCl$ also reacts with $ClOTeF_5$ in $CFCl_3$ solvent to form $(CH_3)_2SnCl(OTeF_5)$, according to eq 2, where chloromethane was identified as the reaction byproduct. A byproduct was also identified by ^{119}Sn NMR

$$(CH_3)_3SnCl + ClOTeF_5 \rightarrow (CH_3)_2SnCl(OTeF_5) + CH_3Cl \quad (2)$$

spectroscopy and is assigned to $[(CH_3)_2SnO(OTeF_5)]_n$ based upon X-ray diffraction analysis. Investigation of three separate crystals yielded twinned samples, and so far, we have not been able to refine the structure satisfactorily. The formation of this product can be explained by the hydrolysis of one $OTeF_5$ group in $(CH_3)_2Sn(OTeF_5)_2$, probably formed by the disproportionation of $(CH_3)_2SnCl(OTeF_5)$, followed by polymerization via formation of Sn−O−Sn bonds.

Pure $(CH_3)_3SnOTeF_5$ can be prepared in quantitative yield by the solvolysis of $HOTeF_5$ in a large excess of $Sn(CH_3)_4$ with the elimination of methane, as previously reported[19] (eq 3).

$$\text{excess } Sn(CH_3)_4 + HOTeF_5 \rightarrow (CH_3)_3SnOTeF_5 + CH_4 \quad (3)$$

The clear, colorless, mobile liquid $(CH_3)_3SnOTeF_5$ is far less viscous than the fluidlike $(CH_3)_3SnN(SO_2X)_2$ (X = F or CF_3).[17,18] In the presence of donor solvents such as $(CH_3)_2$-

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CO (donor number, DN = 17.0)[30] and CH_3CN (DN = 14.1),[30] $(CH_3)_3SnOTeF_5$ forms adducts in solution (eq 4), which were characterized by NMR spectroscopy (see NMR Spectroscopy (a)).

$$(CH_3)_3SnOTeF_5 + Dn \rightarrow (CH_3)_3SnOTeF_5{\cdot}Dn \quad (4)$$
$$Dn = (CD_3)_2CO,\ CD_3CN$$

The even stronger donor solvent DMSO (DN = 29.8)[30] causes a solvent assisted dissociation of the Sn−O bond, yielding the $(CH_3)_3Sn(DMSO)_2^+$ cation and the $OTeF_5^-$ anion in solution (eq 5), which were characterized by NMR spectroscopy.

$$(CH_3)_3SnOTeF_5 + 2DMSO \rightarrow [(CH_3)_3Sn(DMSO)_2][OTeF_5] \quad (5)$$

Unlike $(CH_3)_3SnN(SO_2CF_3)_2$, which forms adducts with water (vide infra), $(CH_3)_3SnOTeF_5$ reacts with water in CH_3CN and DMSO solvents, resulting in hydrolytic degradation of the $OTeF_5$ group, as evidenced by the appearance of numerous signals in the ^{125}Te and ^{19}F NMR spectra. Similar results were obtained using methylene chloride solutions saturated with water. The formation of the hydrolyzed product $[(CH_3)_3Sn(H_2O)_2]_2SiF_6$, characterized by single crystal X-ray diffraction studies,[31] can be explained on the basis of formation of HF due to hydrolysis of $OTeF_5$,[32] followed by its reaction with glass to form the SiF_6^{2-} anion.

Synthesis and Properties of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$. The reaction of $(CH_3)_3SnN(SO_2CF_3)_2$ with water in a mixture of $CH_2Cl_2/CHCl_3$ resulted in the dissociation of $(CH_3)_3SnN(SO_2CF_3)_2$ and the formation of colorless crystals of $[(CH_3)_2Sn(H_2O)_2][N(SO_2CF_3)_2]$, according to eq 6. No degradation of the $[N(SO_2CF_3)_2]^-$ anion was observed.

$$(CH_3)_3SnN(SO_2CF_3)_2 + 2H_2O \xrightarrow{CH_2Cl_2/CHCl_3} [(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2] \quad (6)$$

Vibrational Spectroscopy. The vibrational spectroscopic data of $(CH_3)_2SnCl(OTeF_5)$, $(CH_3)_3SnOTeF_5$, and $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ together with their tentative assignments are listed in the Experimental Section.

(a) $(CH_3)_2SnCl(OTeF_5)$ and $(CH_3)_3SnOTeF_5$. The frequencies of the Te−O stretching vibration in the $OTeF_5$ derivatives lie in the range 868−613 cm^{-1}.[33a,b] This variation in the ν(Te−O) band is attributed to the partial double bond character in the $OTeF_5^-$ anion.[33c] The ν(Te−O) bands for $(CH_3)_2SnCl(OTeF_5)$ and $(CH_3)_3SnOTeF_5$ lie both at 860 cm^{-1} in the infrared spectrum and at 856 cm^{-1} in the Raman spectrum, indicating a similar bonding situation in both tin pentafluorotellurate species.

(b) $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$. The infrared spectrum of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ shows additional bands attributable to the coordinated water molecules when compared to that of its parent compound, $(CH_3)_3SnN(SO_2CF_3)_2$.[18] The infrared bands associated with the $N(SO_2CF_3)_2$ group are slightly shifted. The most significant shift is found for the antisymmetric SO_2 stretch of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ which appears at a lower frequency (1346 cm^{-1}) relative to that of $(CH_3)_3SnN(SO_2CF_3)_2$ (1378 cm^{-1}).[18] The $\nu_{as}(SO_2)$ stretching band is diagnostic of sulfonamide groups and is lowered by about 100 cm^{-1} upon going from covalent to ionic derivatives as a consequence of the delocalization of the negative charge of sulfonamide anions onto the sulfonyl oxygen atoms, resulting in weaker S=O bonds.[17,34] For ionic $N(SO_2CF_3)_2$ groups, $\nu_{as}(SO_2)$ frequencies of 1345 cm^{-1} have been reported which is in excellent agreement with that observed for $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$, corroborating its ionic nature that was observed by X-ray crystallography (see Crystal Structures (b)).

NMR Spectroscopy. The multinuclear NMR spectroscopic data of $(CH_3)_3SnOTeF_5$ as a neat liquid and in various solvents as well as those of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ in CD_3CN and DMSO-d_6, are listed in Tables 1 and 2, together with the literature data for $(CH_3)_3SnN(SO_2CF_3)_2$[18] and $(CH_3)_3SnN(SO_2F)_2$.[17]

(a) $(CH_3)_3SnOTeF_5$. The ^{119}Sn chemical shift of $(CH_3)_3SnOTeF_5$ is highly dependent upon the nature of the solvent. The ^{119}Sn resonances for $(CH_3)_3SnOTeF_5$ in CH_2Cl_2 solvent (272.4 ppm) and as a neat liquid (270.8 ppm) are ~20 ppm more deshielded than those of the $N(SO_2X)_2$ (X = F or CF_3) substituted trimethyl tin derivatives[17,18] and are at significantly higher chemical shifts compared to the previously suggested range of 200 to −60 ppm for tetracoordinated organotin(IV) derivatives.[35,36] This indicates a highly ionic Sn−O bond and a highly electron deficient tin center in $(CH_3)_3SnOTeF_5$. In donor solvents such as $(CH_3)_2CO$, CD3CN, and DMSO-d_6, the ^{119}Sn resonance is shifted to significantly lower δ values, as previously reported for dialkyl and trialkyl tin(IV) species.[17,18,35,36] This increase in shielding is indicative of an increase in coordination number from four to five upon adduct formation with the donor solvent.

Lockhart[37,38] suggested empirical correlations between the $^2J(^{119}Sn-^1H)$ and $^1J(^{119}Sn-^{13}C)$ coupling constants in methyltin compounds and the average C−Sn−C angles (eqs 7 and 8). The C−Sn−C angles calculated using both equations

$$\theta = 0.0161|^2J(^{119}Sn-^1H)^2| - 1.32|^2J(^{119}Sn-^1H)| + 133.4 \quad (7)$$

$$|^1J(^{119}Sn-^{13}C)| = 11.4\theta - 875 \quad (8)$$

are listed in Table 1. The C−Sn−C angles calculated for

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(31) Crystals of $[(CH_3)_3Sn(H_2O)_2]_2SiF_6$ belong to the monoclinic space group *I*2/*a* with cell constants a = 11.104(2) Å, b = 13.013(2) Å, c = 12.898(2) Å, β = 91.698(2)°, and V = 1863.4(7) Å^3. These crystals show rotational twinning, and solution of the twinned structure shows that the SiF_6^{2-} anion is highly disordered with the hydrated trimethyltin(IV) cation in a TBP geometry. Details of this experiment are being published elsewhere.
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Table 1. ^{1}H and ^{13}C NMR Spectroscopic Data[a] and Calculated[b,c] C−Sn−C Angles for $(CH_3)_3SnX$ (X = $OTeF_5$ or $N(SO_2F/CF_3)_2$)

solute	solvent[d]	$\delta(^{1}H)$ (ppm)	$^{2}J(^{119(117)}Sn-^{1}H)$ (Hz)	θ(C−Sn−C)[b] (deg)	$\delta(^{13}C)$ (ppm)	$^{1}J(^{119(117)}Sn-^{13}C)$ (Hz)	θ(C−Sn−C)[c] (deg)	ref
$(CH_3)_3SnOTeF_5$	neat	0.84	59.2[e]	111.7	0.84	376.9 (360.3)	109.8	this work
	CD_2Cl_2	0.79	58.5 (55.9)	111.3	0.90	374.0 (357.4)	109.6	this work
	acetone-d_6	0.69	68.8 (65.8)	118.8	1.55	480.4 (459.3)	118.9	this work
	CD_3CN	0.66	69.2 (66.2)	119.2	1.49	484.6 (463.1)	119.3	this work
	DMSO-d_6	0.50	69.5 (66.6)	119.4	1.05	511.4 (490.0)	121.6	this work
$(CH_3)_3SnOTeF_5$	CD_3CN/D_2O	0.46	69.6 (66.7)	119.5	0.10	508.5 (486.0)	121.4	this work
	DMSO-d_6/D_2O	0.43	70.1 (68.5)[e]	120.0	0.84	515.5 (492.5)	122.0	this work
$(CH_3)_3SnN(SO_2F)_2$	neat	0.91	63.8 (61.6)	114.7	1.6	416.8 (400.3)	113.3	17
	CD_2Cl_2	0.96	62.3 (59.9)	113.6	1.4	404.1 (387.7)	112.2	17
	DMSO-d_6	0.83	72.4 (70.0)	122.2	−0.2	528.3 (509.9)	123.1	17
$(CH_3)_3SnN(SO_2CF_3)_2$	neat	0.84	64.2 (61.6)	115.0	2.1	412.6 (394.1)	113.0	18
	CD_2Cl_2	0.81	64.4 (61.8)	115.2	0.8	414.8 (395.2)	113.0	18
	CD_3CN	0.82	70.2 (67.1)	120.1	−1.7	489.5 (467.6)	119.7	18
	DMSO-d_6	0.48	69.0 (67.4)	119.0	0.7	512.2 (499.0)	121.6	18
$[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$	CD_3CN	0.61	69.7 (66.7)	119.6	0.10	491.8 (470.0)	120.0	this work
	DMSO-d_6	1.18	69.8 (66.7)	119.7	0.92	512.9 (497.2)	121.8	this work

[a] NMR spectroscopic data were recorded at 300 K. [b] Calculated from the relation $\theta = 0.0161|^{2}J(^{119}Sn-^{1}H)|^2 - 1.32|^{2}J(^{119}Sn-^{1}H)| + 133.4$. [c] Calculated from the relation $|^{1}J(^{119}Sn-^{13}C)| = 11.4\theta - 875$. [d] Acetone-$d_6$ = $(CD_3)_2CO$, DMSO-d_6 = $(CD_3)_2SO$. [e] Calculated from the center of unresolved ^{119}Sn and ^{117}Sn satellites ($|J_{obs}|$1.023).[28]

Table 2. ^{19}F, ^{119}Sn, and ^{125}Te NMR Spectroscopic Data[a] of $(CH_3)_3SnX$ (X = $OTeF_5$ or $N(SO_2F/CF_3)_2$)

solute	solvent[b]	$\delta(^{19}F)$ (ppm) F_{ax}	$\delta(^{19}F)$ (ppm) F_{eq}	$\delta(^{19}F)$ (ppm) CF_3/SO_2F	$^{2}J(^{19}F_{ax}-^{19}F_{eq})$ (Hz)	$\delta(^{119}Sn)$ (ppm)	$\delta(^{125}Te)$	$\delta(^{13}CF_3)$ (ppm)	$^{1}J(^{125}Te-^{19}F)$ (Hz) F_{ax}	$^{1}J(^{125}Te-^{19}F)$ (Hz) F_{eq}	$^{1}J(^{13}C-^{19}F)$ (Hz)	ref
$(CH_3)_3SnOTeF_5$	neat	−32.9	−41.9		182.5	270.8	569.5		3112	3540		this work
	CD_2Cl_2	−30.3	−38.5		183.0	272.4	564.6		3188	3550		this work
	acetone	−29.1	−40.6		180.0	96.0	574.9		3020	3558		this work
	CD_3CN	−29.2	−40.8		179.0	84.2	575.0		3032	3556		this work
	DMSO-d_6	−16.2	−33.8		170.0	40.0	598.7		2712	3666		this work
$(CH_3)_3SnN(SO_2F)_2$	neat			55.5		242.5						16
	CD_2Cl_2			55.6		248.6						16
	DMSO-d_6			52.5		32.9						16
$(CH_3)_3SnN(SO_2CF_3)_2$	neat			−78.5		240.2		118.7			320.4	17
	CD_2Cl_2			−78.8		251.0		118.1			319.8	17
	CD_3CN			−78.9		44.9		119.4			320.7	17
	DMSO-d_6			−78.6		37.4		120.0			321.7	17
$[(CH_3)_3Sn(H_2O)_2]$-$[N(SO_2CF_3)_2]$	CD_3CN			−79.0		59.0						this work
	DMSO-d_6			−79.1		42.8						this work

[a] NMR spectroscopic data were recorded at 300 K. [b] Acetone-d_6 = $(CD_3)_2CO$, DMSO-d_6 = $(CD_3)_2SO$.

the neat $(CH_3)_3SnOTeF_5$ or the CH_2Cl_2 solution are close to the tetrahedral angle of 109.5°. In donor solvents, $^{2}J(^{119}Sn-^{1}H)$ and $^{1}J(^{119}Sn-^{13}C)$ are larger by ∼10 and ∼120 Hz, respectively, reflecting an increase in the s-electron density in the orbitals of tin involved in bonding to the methyl groups. As a consequence, the calculated C−Sn−C angles are close to 120° which is consistent with a trigonal bipyramidal geometry with the three methyl groups in the equatorial positions.

The ^{19}F NMR spectra of the $OTeF_5$ derivatives also provide information about the extent of bond polarization. An increase in electron density on the oxygen atom reaching a maximum for the $OTeF_5^-$ anion increases the O−Te back-bonding. This causes a weakening of the Te−F_{ax} bond and results in increased shielding of the axial fluorine resonance and a decrease in $^{1}J(^{125}Te-^{19}F_{ax})$.[33] The NMR spectroscopic parameters for the $OTeF_5$ group in $(CH_3)_3SnOTeF_5$ dissolved in CH_2Cl_2, $(CH_3)_2CO$, and CD3CN and as a neat liquid are in the same range ($^{19}F_{ax}$, ∼ −30 ppm; $^{19}F_{eq}$, ∼ −40 ppm; ^{125}Te, 565−575 ppm; $^{1}J(^{125}Te-^{19}F_{ax})$, 3020−3188 Hz; and $^{1}J(^{125}Te-^{19}F_{eq})$, ∼3550 Hz), reflecting only slight changes to the electronic structure of the $OTeF_5$ ligand. The solution of $(CH_3)_3SnOTeF_5$ in DMSO-d_6, however, exhibits significantly different shifts and coupling constants. The $^{19}F_{ax}$ chemical shift appears at a higher value (−16.2 ppm), and the $^{1}J(^{125}Te-^{19}F_{ax})$ coupling constant is smaller. These are consistent with values found for $[N(n\text{-}Bu)_4][OTeF_5]$.[33] This suggests the presence of an $OTeF_5^-$ anion in solution as a consequence of the dissociation of $(CH_3)_3SnOTeF_5$ upon adduct formation with two strong donor molecules of DMSO (see eq 4). The donor-solvent assisted ionization of the trialkyl tin(IV) derivatives R_3SnX, yielding $[R_3Sn(Dn)_2][X]$, has previously been shown for $[Bu_3Sn(HMPA)_2][ClO_4]$,[39]

(35) Nádvornik, M.; Holeček, J.; Handliř, K.; Lyčka, A. *J. Organomet. Chem.* **1984**, *275*, 43.
(36) Holeček, J.; Nádvornik, M.; Handliř, K.; Lyčka, A. *J. Organomet. Chem.* **1986**, *315*, 299.
(37) Lockhart, T. P.; Manders, W. F. *Inorg. Chem.* **1986**, *25*, 892.
(38) Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1985**, *107*, 4546.

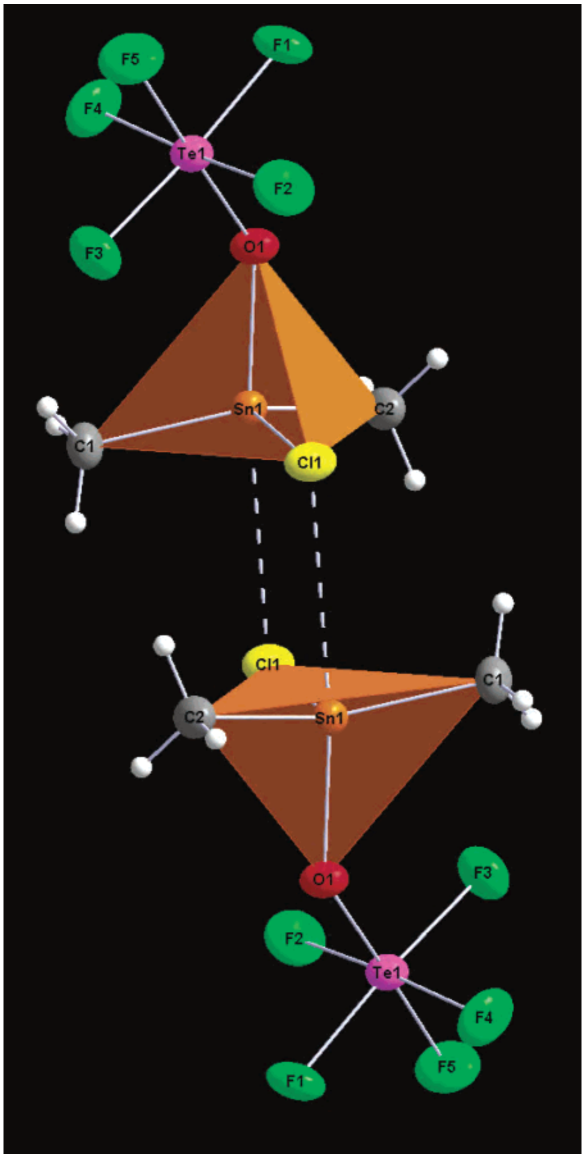


Figure 1. DIAMOND plot of $(CH_3)_2SnCl(OTeF_5)$ showing the dimer formation via Sn···Cl contacts. The thermal ellipsoids are at the 30% probability level.

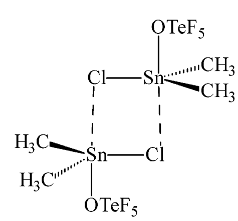
$[Ph_3Sn(HMPA)_2][ClO_4]$,[39] $[(CH_3)_3Sn(O{=}S(CH_3)_2][N(SO_2F)_2]$,[17] and $[(CH_3)_3Sn(py)_2][N(SO_2F)_2]$[17] in solution. This result was found in the present work for $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ in the solid state by X-ray crystallography (see Crystal Structures (b)).

(b) $(CH_3)_2SnCl(OTeF_5)$. Nuclear magnetic resonance spectroscopic data for $(CH_3)_2SnCl(OTeF_5)$ in CH_2Cl_2 and $(CD_3)_2CO$ solvents are listed in the Experimental Section. In both solvents, two sets of signals were observed. At room temperature, the tin signals are broadened to ~300 and ~3300 Hz in CD_2Cl_2 and $(CD_3)_2CO$ solutions, respectively. At 223 K, the line widths for the ^{119}Sn resonances in CD_2Cl_2 decrease somewhat and their relative intensities change compared to those recorded at room temperature, indicating that an equilibrium is operational, whose nature is presently not understood. In CD_2Cl_2 solvent, the ^{119}Sn resonances appear at 127 and 143 ppm which is in the chemical shift range for tetra- or pentacoordinate dimethyltin. In a separate ^{119}Sn NMR VT-experiment, using toluene-d_8 as a solvent, a similar effect was observed at 233 K. From this experiment, it was also noted that lowering the temperature from 298 to 213 K resulted in the shift of the peaks at ~144.4 and 128.0 ppm to 137.9 and ~104 ppm, respectively. The magnitude of the shift is ~6 ppm for the downfield peak, whereas the upfield peak is shifted ~24 ppm. Further, lowering of the temperature to 213 K resulted in immense broadening of the peak at ~104 ppm, which completely disappeared at 193 K. This complex behavior is not understood at this point and is beyond the scope of the current work.

As observed for $(CH_3)_3SnOTeF_5$ (vide supra), dissolution in donor solvents such as $(CD_3)_2CO$ results in an increase in ^{119}Sn shieldings to 33 and −79 ppm, which is consistent with pentacoordinate tin. In CD_2Cl_2 solution, two separate sets of ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR signals could be distinguished. At low temperature, a second set of ^{125}Te NMR signals was resolved. Small deviations in chemical shifts and coupling constants between the two sets indicate similar geometries of the two species present in solution. In $(CD_3)_2CO$, two very broad ^{119}Sn resonances could be distinguished. The NMR spectroscopic parameters of $OTeF_5$ in both solvents are similar to those for neat $(CH_3)_3SnOTeF_5$ (vide supra), indicating that the Sn−O bond has not been cleaved in those solutions.

The C−Sn−C angles for $(CH_3)_2SnCl(OTeF_5)$ in various solvents can be calculated from the $^2J(^{119}Sn-^1H)$ coupling constants using eq 9, as recommended by Lockhart[37] for dimethyl tin compounds with highly electronegative substituents. The C−Sn−C angle calculated using the $^2J(^{119}Sn-^1H)$ and $^1J(^{119}Sn-^{13}C)$ coupling constants for $(CH_3)_2SnCl(OTeF_5)$ dissolved in CH_2Cl_2 is ~118°. The $\delta(^{119}Sn)$ value of ~120 ppm indicates that tin is present in a five-coordinate environment. The fifth coordination site is most likely occupied by a bridging chlorine ligand from a second $Me_2SnCl(OTeF_5)$ molecule, as shown below:

$$\theta = 0.0105|^2J(^{119}Sn-^1H)|^2 - 0.799|^2J(^{119}Sn-^1H)| + 122.4 \quad (9)$$



Such a distorted trigonal bipyramidal structure could account for the increase of the C−Sn−C angle from a tetrahedral value of 109.5° to ~120°. The proposed structure is similar to the one found in the solid-state structure of $Me_2SnCl(OTeF_5)$, as shown in Figure 1.

In acetone-d_6, an increase in the $^2J(^{119}Sn-^1H)$ and $^1J(^{119}Sn-^{13}C)$ coupling constant values by ~21 and ~220 Hz, respectively, results in the increase in the calculated C−Sn−C

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Table 3. Crystal Data and Structure Refinement for $(CH_3)_2SnCl(OTeF_5)$ and $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$

empirical formula	$C_2H_6ClF_5OSnTe$	$C_5H_{13}F_6NO_6S_2Sn$
fw	422.81	479.97
T (K)	218(2)	213(2)
space group	$P2_1/n$	$P2_1/c$
unit cell dimensions		
a (Å)	5.8204(8)	7.3072(1)
b (Å)	10.782(1)	13.4649(2)
c (Å)	15.493(2)	16.821(2)
β (deg)	91.958(2)	98.705(1)
volume (Å^3)	971.7(2)	1636.00(3)
Z	4	4
D_{calcd} (g cm^{-3})	2.890	1.949
abs coeff (mm^{-1})	5.872	1.898
θ for data (deg)	2.30−29.30	1.95−28.27
GOF on F	1.088	1.233
R1, wR2 [$I > 2\sigma(I)$]^a	0.0282, 0.0712	0.0367, 0.0736
R1, wR2 (all data)^a	0.0333, 0.0743	0.0410, 0.0759

^{a} $R1 = (\Sigma(F_o - F_c)/F_o)$; $wR2 = [\Sigma(w(F_o - F_c)^2)/wF_o^2)]^{1/2}$.

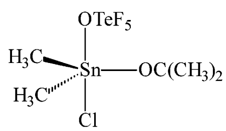
Table 4. Bond Lengths (Å) and Angles (deg) for $(CH_3)_2SnCl(OTeF_5)$

Bond Lengths and Contacts			
Sn(1)−O(1)	2.065(3)	Te(1)−F(5)	1.815(3)
Sn(1)−C(2)	2.094(4)	Te(1)−F(4)	1.819(3)
Sn(1)−C(1)	2.094(4)	Te(1)−F(1)	1.831(3)
Sn(1)−Cl(1)	2.3858(11)	Te(1)−F(3)	1.843(3)
O(1)−Te(1)	1.803(3)	Te(1)−F(2)	1.849(3)
Bond Angles			
O(1)−Sn(1)−C(2)	105.04(15)	F(5)−Te(1)−F(1)	86.50(14)
O(1)−Sn(1)−C(1)	95.44(14)	F(4)−Te(1)−F(1)	90.65(16)
C(2)−Sn(1)−C(1)	139.05(17)	O(1)−Te(1)−F(3)	94.68(13)
O(1)−Sn(1)−Cl(1)	94.64(9)	F(5)−Te(1)−F(3)	86.48(14)
C(2)−Sn(1)−Cl(1)	106.63(13)	F(4)−Te(1)−F(3)	90.54(17)
C(1)−Sn(1)−Cl(1)	106.58(13)	F(1)−Te(1)−F(3)	172.81(12)
Te(1)−O(1)−Sn(1)	137.59(17)	O(1)−Te(1)−F(2)	93.38(14)
O(1)−Te(1)−F(5)	178.67(15)	F(5)−Te(1)−F(2)	85.99(16)
O(1)−Te(1)−F(4)	93.57(15)	F(4)−Te(1)−F(2)	173.05(14)
F(5)−Te(1)−F(4)	87.06(16)	F(1)−Te(1)−F(2)	88.89(14)
O(1)−Te(1)−F(1)	92.33(12)	F(3)−Te(1)−F(2)	89.06(16)

Table 5. Bond Lengths (Å) and Angles (deg) for $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$

Bond Lengths and Contacts			
Sn(1)−C(2)	2.104(4)	S(1)−N(1)	1.573(3)
Sn(1)−C(1)	2.115(4)	S(1)−C(4)	1.825(5)
Sn(1)−C(3)	2.120(4)	S(2)−O(6)	1.421(3)
Sn(1)−O(1)	2.306(3)	S(2)−O(5)	1.433(3)
Sn(1)−O(2)	2.335(3)	S(2)−N(1)	1.589(3)
S(1)−O(3)	1.427(2)	S(2)−C(5)	1.844(4)
S(1)−O(4)	1.428(3)		
Bond Angles			
C(2)−Sn(1)−C(1)	117.8(2)	O(3)−S(1)−N(1)	107.6(2)
C(2)−Sn(1)−C(3)	120.1(2)	O(4)−S(1)−N(1)	116.1(2)
C(1)−Sn(1)−C(3)	122.1(2)	O(3)−S(1)−C(4)	104.0(2)
C(2)−Sn(1)−O(1)	89.83(15)	O(4)−S(1)−C(4)	105.4(2)
C(1)−Sn(1)−O(1)	92.3(2)	O(6)−S(2)−O(5)	118.2(2)
C(3)−Sn(1)−O(1)	87.19(13)	O(6)−S(2)−N(1)	109.0(2)
C(2)−Sn(1)−O(2)	91.04(15)	O(5)−S(2)−N(1)	115.3(2)
C(1)−Sn(1)−O(2)	90.8(2)	O(6)−S(2)−C(5)	104.7(2)
C(3)−Sn(1)−O(2)	88.95(13)	O(5)−S(2)−C(5)	105.0(2)
O(1)−Sn(1)−O(2)	175.94(11)	S(1)−N(1)−S(2)	125.3(2)
O(3)−S(1)−O(4)	118.5(2)		

angle to 137°. This increase, when compared to the values found in CD_2Cl_2 solution, indicates the formation of a distorted trigonal bipyramidal adduct:



(c)[(CH$_3$)$_3$Sn(H$_2$O)$_2$][N(SO$_2$CF$_3$)$_2$]. For the $N(SO_2F)_2$ ligand, the fluorine chemical shifts provide a means to distinguish ionic and covalent $N(SO_2F)_2$ moieties. Typical $\delta(^{19}F)$ values for covalent derivatives lie around 55.5 ppm, and for ionic derivatives, the resonance is more shielded by ∼3−52.5 ppm.[17] However, in the case of the $N(SO_2CF_3)_2$ group, the fluorine atoms are isolated by greater bond separation and, therefore, do not show any significant chemical shift difference between ionic and covalent derivatives.[18]

The ^{119}Sn chemical shifts for $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ in CD_3CN and DMSO-d_6 are 59.0 and 42.8 ppm, which are more shielded by ∼200 ppm compared to that of neat $(CH_3)_3SnN(SO_2CF_3)_2$.[18] This upfield shift confirms the presence of a pentacoordinate tin species which is either the $(CH_3)_3Sn(H_2O)_2^+$ cation that was found in the solid state or a cationic species with partially or completely displaced water molecules, that is, $(CH_3)_3Sn(H_2O)(Dn)^+$ or $(CH_3)_3Sn(Dn)_2^+$, with Dn = CH_3CN and DMSO.

Crystal Structures. Details of the data collection and other crystallographic information for $(CH_3)_2SnCl(OTeF_5)$ and $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ are given in Table 3. Bond lengths and bond angles for $(CH_3)_2SnCl(OTeF_5)$ and $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ are given in Tables 4 and 5, respectively.

(a) (CH$_3$)$_2$SnCl(OTeF$_5$). The crystal structure of $(CH_3)_2SnCl(OTeF_5)$, which crystallizes in the monoclinic system, contains $(CH_3)_2SnCl(OTeF_5)$ molecules with a distorted tetrahedral coordination around tin and a Sn−Cl distance of 2.386(1) Å. This is the same as the distance of 2.388(4) Å found in the crystal structures of $(C_2H_5)_2SnCl(OOCH_3)$.[15] The $OTeF_5$ group is tilted toward one methyl group (C(2)), resulting in a widening of the O(1)−Sn(1)−C(2) angle (105.04(15)°) compared to the O(1)−Sn(1)−C(1) (95.44(14)°) and O(1)−Sn(1)−Cl(1) (94.64(17)°) angles.

The coordination sphere around tin is extended to a trigonal bipyramidal structure by the formation of a Sn···Cl contact (Figure 1). The chlorine atom of one $(CH_3)_2SnCl(OTeF_5)$ molecule coordinates through the tetrahedral face formed by the chlorine and two carbon atoms, located at its vertexes, of a second molecule, and vice versa, resulting in dimer formation (Figure 1). These symmetry related contacts of 3.201(1) Å [Sn···Cl(1B) (2 − x, 1 − y, −z)] are significantly smaller than the sum of the van der Waals radii (3.91 Å)[40] (Table 3). The Sn···Cl contacts in $(CH_3)_2SnCl(OTeF_5)$ are similar to those in the chlorine-bridged methyltin(IV) derivatives ($((CH_3)_2SnCl)_2$ (3.240(3) and 3.292(3) Å)[41a] and $(CH_3)_3SnCl$ (3.269(2) Å).[7] However, they are significantly shorter than those in $(C_2H_5)_2SnCl(OOCCH_3)$ (3.875 Å),[15] bis(μ^2-chloro)chlorodimethyltin(diphenylcyclopropenone-O)tin(IV) (3.561 Å),[41b] and $(C_6H_5)_2SnCl_2$ (3.872 Å).[41c] In addition to the Sn···Cl contacts, one fluorine atom

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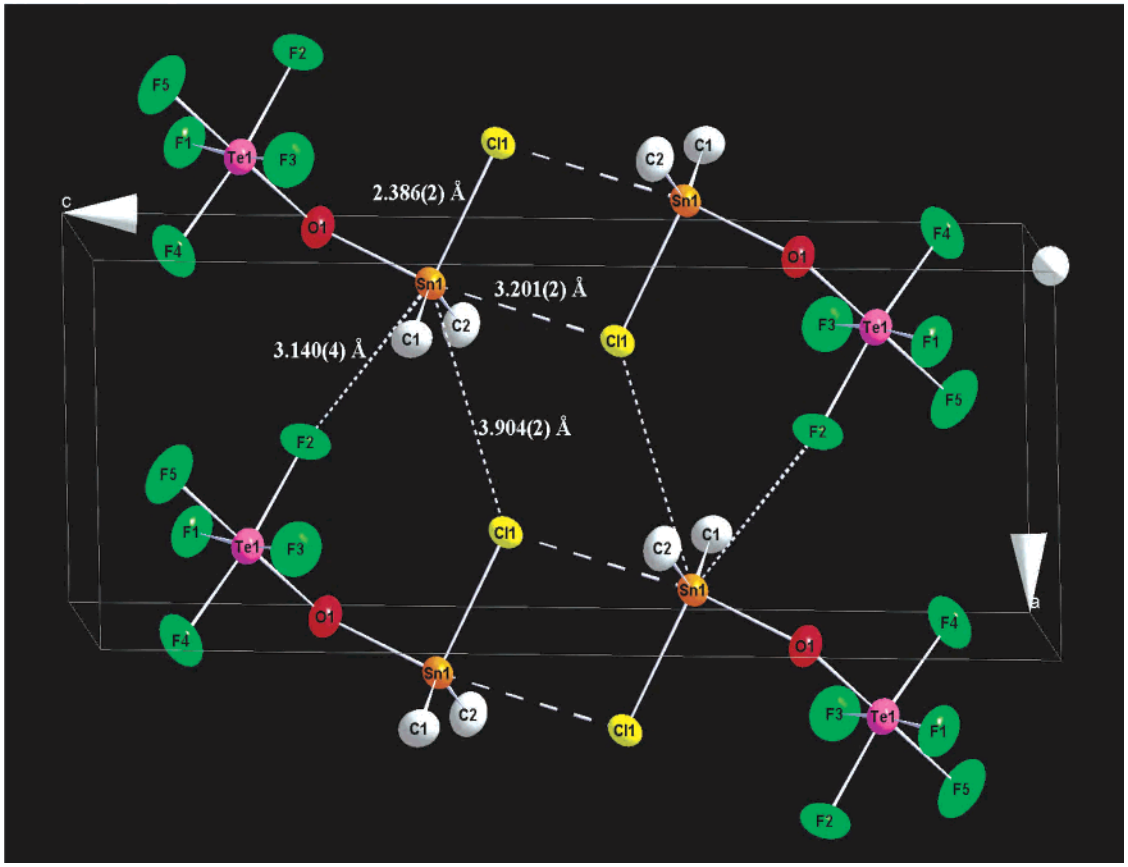
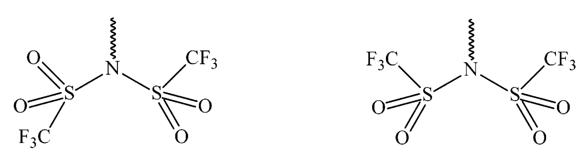


Figure 2. The unit cell along the *b*-axis of $(CH_3)_2SnCl(OTeF_5)$ showing extended Sn···halogen contacts.

of an OTeF$_5$ group exhibits a Sn···F(2) $(1 + x, y, z)$ contact of 3.141(3) Å (Σr_{VdW}(Sn−F) = 3.64 Å),[40] occupying the fourth corner of the square plane around tin, the other three being occupied by O(1), Cl(1), and Cl(1B) $(2 - x, 1 - y, -z)$ and extending the coordination number of tin to six. No long-range contacts are observed from the oxygen atom of the OTeF$_5$ group, implying that this anion shows no bridging via the oxygen atom. The crystal packing can be seen as a sheetlike polymeric structure containing chains with the Sn···F(2) contacts bridging the dimeric units (Figure 2).

The formation of fluorine contacts from F−Te−O containing anions with electrophilic metal centers, as well as cationic species, shows a large diversity.[42] The shortest reported contact,[43a] 2.197, is due to an H···F contact between methyl protons of the tetramethylammonium cation and a fluorine atom of the hexafluoromethoxytelluride anion. These contacts are shorter than the shortest contacts found in pentafluorooxotellurate derivatives; that is, X···F contacts of <2.35 Å can be found in $[(CH_3)_4N][ReO_2(OTeF_5)_4]$,[43b] $[(CH_3)_4N][Sb(OTeF_5)_6]$,[43c] $Zn(OTeF_5)_2{\cdot}3C_6H_5NO_2$,[43d] and Pd[$Ag(CH_2Cl_2)_2(OTeF_5)_2$]$_2$.[43e] Longer M···F interactions, close to the van der Waal limit, can be found in $Mn(CO)_5(OTeF_5)$ (3.52 Å)[43f] and $[(CH_3)_4N][Te(OTeF_5)_5]$ (3.506 Å).[43g]

(b) $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$. The crystal structure of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ contains separated $(CH_3)_3Sn(H_2O)_2^+$ cations and $N(SO_2CF_3)_2^-$ anions, which are shown in Figure 3. This structure is similar to that observed for $[(CH_3)_3Sn(H_2O)_2][N(SO_2CH_3)_2]$.[44] The tin atom is present in a trigonal bipyramidal structure with the three methyl groups in the equatorial position and the axial positions being occupied by the two water molecules with Sn−O distances of 2.306(3) and 2.335(3) Å. The trifluoromethyl groups on the $N(SO_2CF_3)_2$ anion can be present in the cis- or trans-conformation:



In the case of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$, the trifluromethyl groups are oriented in a trans-manner with respect to each other. This orientation is most favored and

(42) *Conquest 1.6, Cambridge Crystal Structure Database*; Cambridge University: Cambridge, U.K. (Jan 2004).

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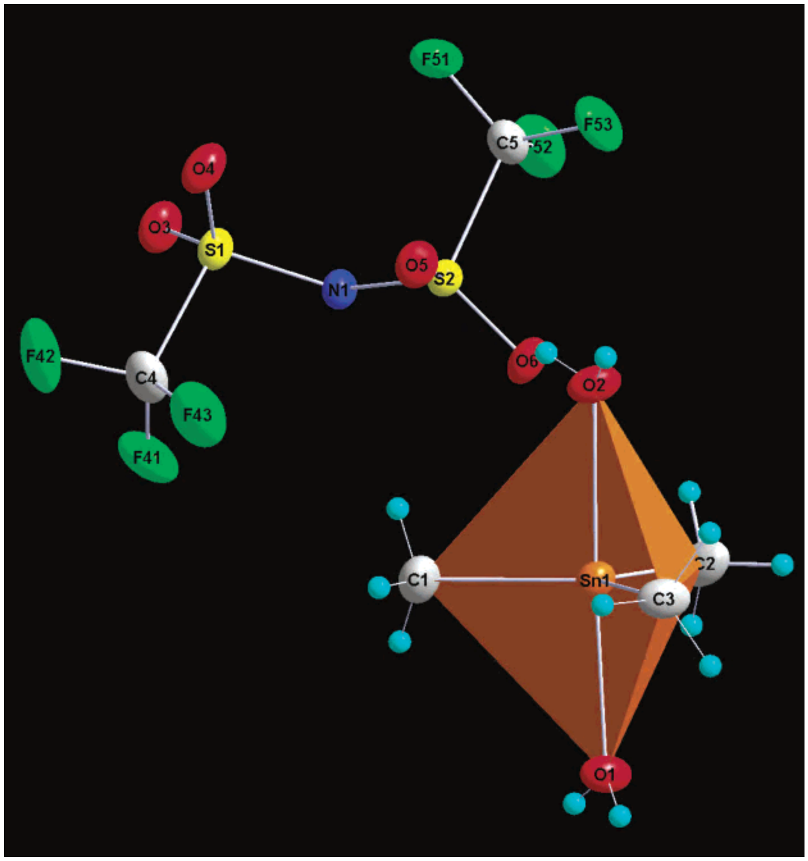

Figure 3. DIAMOND plot showing the trigonal bipyramidal geometry of the $(CH_3)_3Sn(H_2O)_2^+$ cation and the trans-conformation of the $N(SO_2CF_3)_2^-$ anion with thermal ellipsoids at the 50% probability level.

is found in the structures of $HN(SO_2CF_3)_2$,[45,46] $[Mg(H_2O)_6][N(SO_2CF_3)_2]$,[45] $[Cu(CO)_2][N(SO_2CF_3)_2]$,[47]and 1-ethyl-2-methyl-3-benzylimidazolium bis(trifluoromethylsulfonyl)imide.[48] However, the cis-conformation has been observed in $KN(SO_2CF_3)_2$.[46] The S−N distances of 1.589(3) and 1.573(3) Å are relatively short when compared to those reported for $HN(SO_2CF_3)_2$ (1.644(1)[45] and 1.647 Å[46]). The S−N−S angle is compressed from 128.4(2)°[45] in $HN(SO_2CF_3)_2$ to 125.3(2)° in the present compound. However, the latter value is significantly greater than the corresponding S−N−S angle of 121.5(2)° in the case of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CH_3)_2]$.[44] The crystal-packing diagram along the *c*-axis (Figure 4) shows a three-dimensional hydrogen-bonding network in the *ab*-plane. The O···H (x, $^1/_2 - y$, $^1/_2 + z$) contacts range from 1.95 to 2.60 Å, showing a tightly packed crystal lattice due to hydrogen bonding. A bifurcated hydrogen bond is formed from O(1)−H(11)···O(4) and O(1)−H(11)···O(5) at 2.16(5) and 2.60(5) Å (x, $^1/_2 - y$, $^1/_2 + z$), respectively. There is also a short contact resulting from one of the hydrogen atoms from a water molecule, O(2)−H(21), and the nitrogen atom of the $N(SO_2CF_3)_2$ group, that is, N(1)···H(21) ($-1 + x$, y, z), at 2.17(6) Å.

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Conclusions

In the present study, $(CH_3)_2SnCl(OTeF_5)$ was prepared by reacting $(CH_3)_3SnCl$ with $HOTeF_5$ or $ClOTeF_5$, where the Sn−C bond is cleaved. This represents the first structurally characterized methyl tin(IV) pentafluorooxotellurate. Multinuclear NMR spectroscopy of $(CH_3)_3Sn(OTeF_5)$ in various solvents revealed the strong dependence of the coordination environment of the tin(IV) species in solution on the donor strength of the solvent. In DMSO, the strongest donor solvent studied, the dissociation of the Sn−OTe bond was facilitated with the formantion of $[(CH_3)_3Sn(O{=}S(CH_3)_2)_2][OTeF_5]$. The crystal structure of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ unambiguously proves the existence of such solvated salts in the solid state and represents only the second crystal structure of such a solvated tin(IV) salt.

Experimental Section

Materials and Apparatus. Reactions were carried out in Teflon FEP or PFA ampules that contained Teflon coated magnetic stirring bars and were closed by stainless steel valves. Volatile materials were handled either on a stainless steel/Teflon-FEP vacuum line[49a] or on a Pyrex glass vacuum line equipped with grease-free Kontes glass-Teflon valves. Nonvolatile solids were handled in the dry nitrogen atmosphere of a glovebox.

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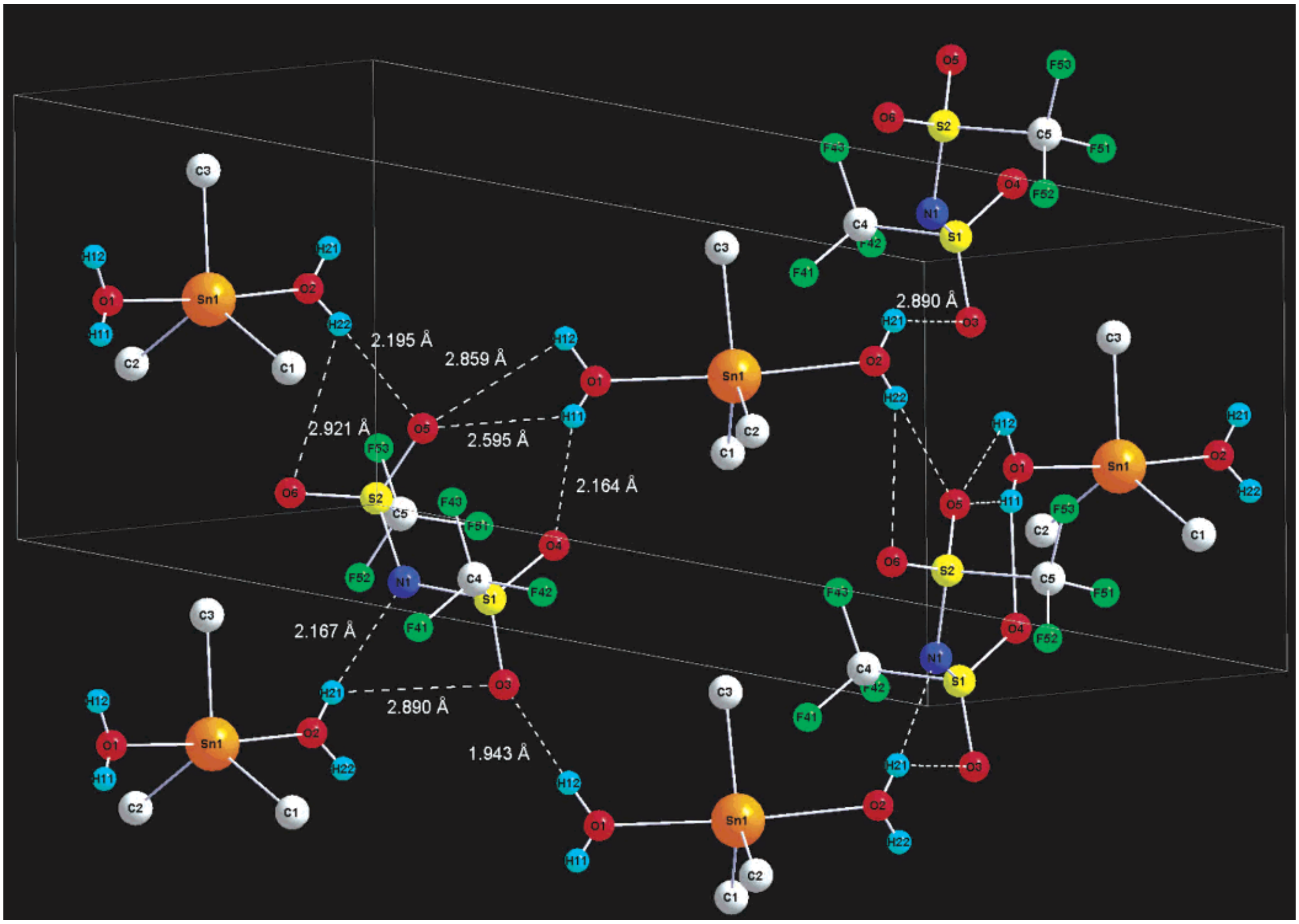

Figure 4. Crystal packing diagram of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ showing the hydrogen-bonding network.

Caution: *ClF is a strong oxidizer and requires careful handling in the absence of any organic material. Organotin(IV) compounds are very toxic by inhalation and should be handled using gloves in a fume hood.*[49b]

$(CH_3)_3SnCl$ and $Sn(CH_3)_4$ (Aldrich Chemical Co.) were used as received. $HOTeF_5$ was prepared from either $CsOTeF_5$ (Rocketdyne) or $pyHOTeF_5$ (kindly supplied by Prof. Steve Strauss, Colorado State University) after its reaction with concentrated H_2SO_4 and purified by fractional condensation at −78 °C over −45 °C. $ClOTeF_5$ was generated by the reaction of $HOTeF_5$ with an excess of ClF, followed by purification via fractional condensation as described earlier.[49c] $(CH_3)_3SnN(SO_2CF_3)_2$ was prepared as described earlier,[18] and $CFCl_3$ (Matheson) was dried by storage over P_4O_{10} before use.

Infrared and Raman Spectroscopy. Infrared spectra were recorded on a Mattson Galaxy 5030 FT-IR spectrometer using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on either a Bruker Equinox 55 FT-RA spectrometer using a Nd:YAG laser at 1064 nm and Pyrex melting point capillaries as sample containers or a Cary model 83 spectrometer using the 488 nm exciting line of an Ar ion laser.

NMR Spectroscopy. The NMR spectra were recorded at 500.13 MHz (^{1}H), 470.51 MHz (^{19}F), 125.76 MHz (^{13}C), 186.50 MHz (^{119}Sn), and 158.03 MHz (^{125}Te) on a Bruker AMX 500 spectrometer or at 400.13 MHz (^{1}H), 376.54 MHz (^{19}F), 100.62 MHz (^{13}C), 149.22 MHz (^{119}Sn), and 126.45 MHz (^{125}Te) on a Bruker Avance 400 NMR spectrometer using neat liquid/solutions in a sealed standard glass tube. The following external references were used: ^{1}H and ^{13}C, neat TMS (0 ppm); ^{19}F, neat $CFCl_3$ (0 ppm); ^{119}Sn, neat $Sn(CH_3)_4$ (0 ppm); ^{125}Te, a saturated aqueous $Te(OH)_6$ solution (710.9 ppm).[50] The AB_4 spin patterns in the ^{19}F NMR spectra were simulated using the program gNMR.[51]

Mass Spectrometry. The mass spectrometric data were collected on a JEOL JMS AX505HA or a HP Agilent 6890 GC mass spectrometer using the EI (electron ionization) method. The isotopic pattern were simulated using shareware software.[52]

X-ray Crystallography. The single crystal X-ray diffraction data were collected on a Bruker three-circle platform diffractometer equipped with a SMART CCD (charge-coupled device) detector with the *c*-axis fixed at 54.74° and by using Mo Kα radiation (λ = 0.710 73 Å) from a fine-focus tube. This diffractometer was equipped with an LT-3 apparatus for low temperature data collection using controlled liquid nitrogen boil off. The goniometer head, equipped with a Nylon Cryoloop with a magnetic base, was then used to mount the crystals using PFPE (perfluoropolyether) oil and mounted on the magnetic goniometer. Cell constants were determined from 90 30-s frames at ~215 K (see Table 3). A complete hemisphere of data was scanned on omega (0.3°) with a run time of 30 s/frame at a detector resolution of 512 × 512 pixels using the SMART software.[53] A total of 1271 frames were collected in

(50) Collins, M. J.; Schrobilgen, G. J. *Inorg. Chem*. **1985**, *24*, 2608.
(51) Budzelaar, P. H. M. *gNMR V4.1.0*; Cherwell Scientific Publishing: 1998.
(52) For simulations of isotopic distribution patterns, see: http://www.sisweb.com/cgi-bin/mass10.pl.

three sets, and final sets of 50 frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed on a PC running Windows NT using the SAINT software[54] to give the *hkl* file corrected for Lp/decay. The absorption correction was performed using the SADABS[55] program. The structures were solved by the direct method using the SHELX-90[56] program and refined by the least-squares method on F^2 using SHELXL-97[57] incorporated in SHELXTL Suite 5.10 for Windows NT.[58] All non-hydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The methyl hydrogen atoms in $(CH_3)_2SnCl(OTeF_5)$ and $[Me_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ were added at calculated positions while hydrogen atoms of the water molecules were located and refined isotropically from electron density maps.

Preparation of $(CH_3)_2SnCl(OTeF_5)$. Inside a drybox, $(CH_3)_3SnCl$ (1.3740 g, 6.8952 mmol) was loaded into a Teflon ampule, followed by the addition of $HOTeF_5$ (1.8057 g, 7.5363 mmol) in vacuo at −196 °C. The reactants were allowed to warm to room temperature for 12 h. When the volatile components were removed from the ampule and collected at −196 °C, the only volatile byproduct identified by infrared spectroscopy was CH_4 (in addition to some unreacted $HOTeF_5$). Further reaction for 3 h at 60 °C, followed by removal of all volatiles and subsequent sublimation, yielded a white solid in 73.2% yield that was identified by vibrational and multi-NMR spectroscopy and X-ray crystallography as $(CH_3)_2SnCl(OTeF_5)$.

Alternatively, a Teflon FEP ampule was loaded with $ClOTeF_5$ (0.6702 g, 2.445 mmol) in vacuo at −196 °C, followed by condensation of $CFCl_3$ solvent (3.1645 g) onto $ClOTeF_5$. Inside the drybox, $(CH_3)_3SnCl$ (0.4883 mg, 2.450 mmol) was then added at −196 °C to the frozen solution. After the ampule was evacuated at −196 °C, it was warmed to room temperature for 1.5 h. The volatile components were removed under dynamic vacuum at room temperature, and CH_3Cl was identified as the only volatile component besides $CFCl_3$ solvent via infrared spectroscopy. A white solid (0.7552 g) was isolated after removal of all volatile material in 72.7% crude yield. This solid was further purified by sublimation at ∼50 °C/0.001 Torr and identified as $(CH_3)_2SnCl(OTeF_5)$ by vibrational spectroscopy. Spectroscopic data obtained are as follows. **IR (AgCl), cm^{-1}:** 3041 w ($\nu_{as}CH_3$), 2941 w (ν_sCH_3), 1406 mw, 1314 w, 1284 w, 1210 mw, 1019 m, 860 vs (νTeO), 811 vs (ρCH_3), 693 vs (νTeF_{eq}), 617 ms (νTeF_{ax}), 580 mw (ν_{as}Sn−C), 524 m (ν_sSn−C), 426 ms. **Raman, cm^{-1} (relative (rel) intensity (int)):** 3024 (8); 2941 sh; 2925 (47); 1208 (18); 1186 (2); 857 (3); 702 (7); 686 (5); 629 (8); 616 (4); 581 (5); 568 (10); 518 (100); 423 (3); 313 (53); 229 (5); 179 (30); 143 (24); 119 (23). **Mass Spectrometry (MS) (EI) major ^{120}Sn fragments (pattern matches simulated spectra):** 409 $[M - CH_3]^+$ 85, 389 $[(CH_3)_2SnOTeF_5]^+$ 61, 169 $[(CH_3)_2SnF]^+$ 100. **NMR spectroscopic data; acetone-d_6 solvent at 300 K:** $\delta(^1H)$ = 1.73 ppm, s, $^1J(^{13}C-^1H)$ = 136.7 Hz, $^2J(^{117/119}Sn-^1H)$ = 87.4/91.3 Hz, $\Delta\nu_{1/2}$ = 1.5 Hz; $\delta(^{13}C)$ = 12.46 ppm, s, $^1J(^{117/119}Sn-^{13}C)$ = 659.5/695.1 Hz, $\Delta\nu_{1/2}$ = 17.8 Hz; $\delta(^{119}Sn)$ = −79.3 ppm, $\Delta\nu_{1/2}$ = 3220 Hz; $\delta(^{119}Sn)$ = 33.2 ppm, $\Delta\nu_{1/2}$ = 3350 Hz; $\delta(^{125}Te)$ = 572.56 ppm, d of quint, $^1J(^{125}Te-^{19}F_{eq})$ = 3553.4 Hz, $^1J(^{125}Te-^{19}F_{ax})$ = 3088.4 Hz, $\Delta\nu_{1/2}$ = 53.3 Hz. **CD_2Cl_2 solvent at 300 K:** $\delta(^1H)$ = 0.61 ppm, s, $^2J(Sn-^1H)$ = 67.9 Hz, $\Delta\nu_{1/2}$ = 23.7 Hz; $\delta(^{13}C)$ = 7.49 ppm, s, $^1J(Sn-^{13}C)$ = 472 Hz, $\Delta\nu_{1/2}$ = 50 Hz; $\delta(^{19}F_{ax})$ = −36.45 ppm, $^1J(^{125}Te-^{19}F_{ax})$ = 3325 Hz, $^2J(^{19}F_{ax}-^{19}F_{eq})$ = 182 Hz; $\delta(^{19}F_{eq})$ = −41.15 ppm, $^1J(^{125}Te-^{19}F_{eq})$ = 3551 Hz; $\delta(^{119}Sn)$ = 127.3 ppm, $\Delta\nu_{1/2}$ = 302 Hz; $\delta(^{125}Te)$ = 576.13 ppm, d of quint, $^1J(^{125}Te-^{19}F_{eq})$ = 3551 Hz, $^1J(^{125}Te-^{19}F_{ax})$ = 3325 Hz, $\Delta\nu_{1/2}$ = 271.8 Hz. Minor component: $\delta(^1H)$ = 0.47 ppm, s, $^2J(Sn-^1H)$ = 70 Hz, $\Delta\nu_{1/2}$ = 33.2 Hz; $\delta(^{13}C)$ = 6.48 ppm, s, $\Delta\nu_{1/2}$ = 66 Hz; $\delta(^{19}F_{ax})$ = −34.90 ppm, $^2J(^{19}F_{ax}-^{19}F_{eq})$ = 182 Hz; $\delta(^{19}F_{eq})$ = −40.17 ppm, $^1J(^{125}Te-^{19}F_{eq})$ = 3554 Hz; $\delta(^{119}Sn)$ = 142.7 ppm, $\Delta\nu_{1/2}$ = 313 Hz. The major component/minor component ratio is based on integrals of the ^{119}Sn resonances: 2.4/1.0. **$(CH_3)_2SnCl(OTeF_5)$ in CD_2Cl_2 solvent at 223 K:** $\delta(^1H)$ = 0.39 ppm, s, $^2J(Sn-^1H)$ = 68.4 Hz, $\Delta\nu_{1/2}$ = 12.8 Hz; $\delta(^{13}C)$ = 7.49 ppm, s, $^1J(Sn-^{13}C)$ = 474.3 Hz, $\Delta\nu_{1/2}$ = 12.1 Hz; $\delta(^{119}Sn)$ = 140.23 ppm, sept, $^2J(^{119}Sn-^1H)$ = 70.6 Hz, $\Delta\nu_{1/2}$ = 51 Hz; $\delta(^{125}Te)$ = 575.53 ppm, d of quint, $^1J(^{125}Te-^{19}F_{eq})$ = 3570.6 Hz, $^1J(^{125}Te-^{19}F_{ax})$ = 3276.8 Hz, $\Delta\nu_{1/2}$ = 112 Hz. Minor component: $\delta(^1H)$ = 0.25 ppm, s, $^2J(Sn-^1H)$ = 68.0 Hz, $\Delta\nu_{1/2}$ = 11.4 Hz; $\delta(^{13}C)$ = 8.76 ppm, s, $^1J(Sn-^{13}C)$ = 482.2 Hz, $\Delta\nu_{1/2}$ = 12.2 Hz; $\delta(^{119}Sn)$ = 114.7 ppm, $^2J(^{119}Sn-^1H) \gg$ 65 Hz, $\Delta\nu_{1/2}$ = 243 Hz; $\delta(^{125}Te)$ = 577.48 ppm, d of quint, $^1J(^{125}Te-^{19}F_{eq})$ = 3562.9 Hz, $^1J(^{125}Te-^{19}F_{ax})$ = 3306.7 Hz, $\Delta\nu_{1/2}$ = 97 Hz. The major component/minor component ratio is based on integrals of the ^{119}Sn resonances: 1.3/1.0.

Preparation of $(CH_3)_3Sn(OTeF_5)$. After condensation of $HOTeF_5$ (0.8428 g, 3.518 mmol) into a Teflon ampule via a stainless steel vacuum line at −196 °C, excess $Sn(CH_3)_4$ (3.1144 g, 17.429 mmol) was added on a glass vacuum line in vacuo at −196 °C. A brisk effervescence was observed upon slowly warming the reaction mixture to room temperature over a period of 45 min. The volatile components were then removed in vacuo at ∼20 °C, leaving behind a clear colorless liquid ($(CH_3)_3Sn(OTeF_5)$, 1.3819 g, 3.434 mmol). Inspection of the volatile material trapped at −196 °C by gas-phase infrared spectroscopy showed methane as the sole reaction byproduct. The colorless liquid, $(CH_3)_3Sn(OTeF_5)$, was characterized by vibrational spectroscopy and multi-NMR spectroscopy. Spectroscopic data obtained are as follows. **IR (AgCl), cm^{-1}:** 3009 w ($\nu_{as}CH_3$), 2929 w, (ν_sCH_3), 1402 w, 1296 w, 1202 mw, 860 s (νTeO), 789 s (ρCH_3), 688 vs (νTeF_{eq}), 613 mw (νTeF_{ax}), 552 ms (ν_{as}Sn−C), 518 m (ν_sSn−C), 429 ms. **Raman, cm^{-1} (rel int):** 3008 (7); 2930 (14); 1214 (6), 1204 sh; 856 (4), 781 (<1); 681 (72); 624 (4); 554 (16); 518 (100); 431 (4); 334 (5); 296 (4); 230 (4); 146 (22). **MS (EI) major ^{120}Sn fragments (pattern matches simulated spectra):** 389 $[(CH_3)_2SnOTeF_5]^+$ 46, 169 $[(CH_3)_2SnF]^+$ 100.

Preparation of $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$. A solution of $(CH_3)_3SnN(SO_2CF_3)_2$ in CH_2Cl_2 (0.25 g in 5 mL) was added to ∼10 mL of chloroform that was presaturated with water. The mixture was stirred for 30 min and then left undisturbed for ∼48 h inside a fume hood. During this time, colorless crystals had formed which were isolated, washed with cold CH_2Cl_2, and dried in vacuo. The vibrational data obtained are as follows. **IR (AgCl), cm^{-1}:** 3470 vs, br (νOH), 2996 sh ($\nu_{as}CH_3$), 2929 w, (ν_sCH_3), 1614 vs (δOH), 1346 vs, 1201 vs, 1133 vs, 1053 vs, 797 vs (ν_{as}SNS), 742 (ν_sSNS), 616 vs, 572 s, 514 s (ν_sSn−C). **Raman, cm^{-1} (rel int):** 2928 (32); 1242 (18); 1218 (11); 1132 (12); 746 (44); 560 (21); 523 (100); 401 (6); 342 (6); 316 (4); 277 (10); 157 (13); 140 (13), 119 sh.

NMR Studies in Donor Solvents. Approximately 100 mg of $(CH_3)_3SnOTeF_5$ was loaded into a 5-mm glass NMR tube inside a

(53) *SMART V 4.045*; software for the CCD detector system; Bruker AXS: Madison, WI, 1999.
(54) *SAINT V 4.035*; software for the CCD detector system; Bruker AXS: Madison, WI, 1999.
(55) *SADABS*, version 2.01; program for absorption correction for area detectors; Bruker AXS: Madison, WI, 2000.
(56) Sheldrick, G. M. *SHELXS-90*; program for the solution of crystal structure; University of Göttingen: Germany, 1990.
(57) Sheldrick, G. M. *SHELXL-97*; program for the refinement of crystal structure; University of Göttingen: Germany, 1997.
(58) *SHELXTL 5.10 for Windows NT*; program library for structure solution and molecular graphics; Bruker AXS: Madison, WI, 2000.

glovebox. The tube was sealed with a rubber septum, and ~0.5 mL of solvent was injected into the NMR tube via the septum prior to inserting the tube into the probe. When samples were prepared with aqueous AN/DMSO, white precipitates started forming within minutes, indicating the decomposition of the $OTeF_5$ group, as seen by the appearance of many complex signals in the ^{19}F and ^{125}Te NMR spectra. In the case of $(CH_3)_2SnCl(OTeF_5)$, NMR samples were prepared inside a drybox by loading ~50 mg of $(CH_3)_2SnCl(OTeF_5)$ into a 5-mm glass NMR tube connected to a Kontes valve via a Cajon Ultratorr union. Subsequently, ~0.5 mL of anhydrous solvent was vacuum distilled onto the solid, followed by flame sealing of the NMR tube. The samples were stored at −196 °C until their NMR spectroscopic characterization.

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Supporting Information Available: Tables of observed and calculated structure factors for Me_2SnOTF and SnH_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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