Solid State Structural Studies of Some New Derivatives of HN(SO$_2$CF$_3$)$_2$ and HOTeF$_5$

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The "cisoid" form is less common. In the CCDC, only 6 structures show this conformation whereas the "transoid" form occurs in 15 remaining structures. The "cisoid" conformation results from stronger cation-anion interaction observed exclusively when anion is chelated to the metal center. The "transoid" form dominates in structures containing a "free" anion. NO structure known containing both "cisoid" AND "transoid" geometry.
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Coordination & isomerism in \( N(SO_2CF_3)_2 \) (NTf)

The “cisoid” form is less common. In the CCDC, only 6 structures show this conformation whereas the “transoid” form occurs in 15 remaining structures.

- The “cisoid” conformation results from stronger cation-anion interaction.
- “Cisoid” observed exclusively when anion is chelated to the metal center.
- The “transoid” form dominates in structures containing a “free” anion.
- NO structure known containing both “cisoid” AND “transoid” geometry.

Synthesis of metal(I) derivatives

These salts are colorless and crystalline. Recrystallization from iso-propylalcohol gave anhydrous salts. Some of these salts turn amorphous with time.

\[
\begin{align*}
\text{HN(SO}_2\text{CF}_3)_2 & + \text{M}_2\text{CO}_3 \xrightarrow{\text{H}_2\text{O}} 2 \text{MN(SO}_2\text{CF}_3)_2 + \text{CO}_2 + \text{H}_2\text{O} \\
\text{HX} & + \text{Ag}_2\text{O} \xrightarrow{\text{C}_6\text{H}_6} 2 \text{AgX C}_6\text{H}_6 \\
\end{align*}
\]

\(X = \text{OTeF}_5\) or NTf

\(\nu\text{Te-O (cm}^{-1}\): IR (Ra) at \(~865\) (860)
\(\nu_{\text{as SO2 (cm}^{-1}\): IR (Ra) at \(~1320\)(~1328)

\(^1\text{H NMR}: \text{C}_6\text{H}_6\) peak at 7.6-7.7 ppm
Uncoordinated benzene: 7.3
\(^19\text{F NMR}: \sim78\) ppm (CF\(_3\))
Structure of CsN(SO$_2$CF$_3$)$_2$ salts

Monoclinic $C2/c$ [$\beta = 91.92(1)^\circ$]

\[ a = 22.509(12), \quad b = 7.029(4), \quad c = 13.519(7) \text{ [Å]} \]

Volume (Å$^3$) = 2137.5(19), \(Z = 8, \quad T = 298 K\)

\[ R1 = 0.0399, \quad S = 1.024 \]

Tetragonal $I-4$

\[ a = 16.903(1), \quad c = 7.8933(6) \text{ [Å]} \]

Volume (Å$^3$) = 2255.2(3), \(Z = 6, \quad T = 298 K\)

\[ R1 = 0.0307, \quad S = 1.20 \]
Coordination environment of Cs in CsN(SO$_2$CF$_3$)$_2$ salts

CsN(SO$_2$CF$_3$)$_2$  
Octa-coordinated with a short Cs-N bond

CsN(SO$_2$CF$_3$)$_2$•H$_2$O  
Nona-coordinated with a long Cs-N bond
Crystal packing in $\text{CsN(SO}_2\text{CF}_3)_2$ salts

$\text{CsN(SO}_2\text{CF}_3)_2$  
Hydrophobic and hydrophilic Layering

$\text{CsN(SO}_2\text{CF}_3)_2\cdot\text{H}_2\text{O}$  
“Swiss cheese” Tunnel/channel structure
Polymorphism in silver bis(trifluoromethylsulfonyl)imide

- **Trigonal** $P-3_1c$
  - $a = 7.510(6) \, \text{Å}$, $c = 8.119(7) \, \text{Å}$
  - $Z = 6$, $T = 298 \, \text{K}$

- **Orthorhombic** $Pbca$
  - $a = 7.510(6) \, \text{Å}$, $b = 15.729(12) \, \text{Å}$, $c = 8.119(7) \, \text{Å}$
  - $Z = 4$, $T = 298 \, \text{K}$

Steric control of tricoordination around Ag is known in $[\text{Ag(CpPh}_2\text{P)}_3]^+ \cdot [\text{BF}_4]^-$

However, binary tricoordinated silver salts are unknown.

Structure of $[\text{AgN}(\text{SO}_2\text{CF}_3)_2(\text{C}_6\text{H}_6)_2]$}

- Dimerization via S-O…Ag bonding (2.302 Å)
- Long range for unsymmetrical Ag-C bonds (2.345-2.841 Å)
- N(SO$_2$CF$_3$)$_2$ group is “transoid”
- H…F bond distances observed close to sum of van der Waal distance

Triclinic $P-1$

\[ a = 7.6704(13)\text{Å}, \quad b = 8.4295(14)\text{Å}, \quad c = 8.8631(15)\text{Å}, \]
\[ \alpha = 111.673(3)^\circ, \quad \beta = 108.479(3)^\circ, \quad \gamma = 97.798(3)^\circ \]
\[ V \ (\text{Å}^3) = 483.89(14), \quad Z = 2, \quad T = 298(2) \text{ K}; \quad R1= 0.0432, \quad S = 1.114 \]
Structure of 
\[ \text{[AgN(SO}_2\text{CF}_3)_2(\text{C}_6\text{H}_6)]_2\cdot\text{H}_2\text{O}} \]

✓ N(SO$_2$CF$_3$)$_2$ group is both N- as well as O-bonded to silver

✓ Water bridges the eighth-membered Ag-O-S-N-Ag-O-S-N ring forming two fused six-membered rings.

✓ Unsymmetrical Ag-C bonds (2.431-2.666 Å)

✓ N(SO$_2$CF$_3$)$_2$ group is "cisoid"

✓ H…F bond distances observed close to sum of van der Waal distance

Monoclinic $P2_1/n$

$a = 10.372(1)$ Å, $b = 19.823(2)$ Å, $c = 12.406(1)$ Å, $\beta = 108.536(3)^\circ$, $V (\text{Å}^3) = 2148.5(5)$, $Z = 8$, $T = 173(1)$ K; $R1 = 0.0224$, $S = 1.04$
Crystal packing in $[\text{AgN(SO}_2\text{CF}_3)_2(\text{C}_6\text{H}_6)]_2\cdot\text{H}_2\text{O}$
Structure of $[\text{AgOTeF}_5(\text{C}_6\text{H}_6)_2]_2$

- Dimeric structure
- Unsymmetrical Ag-C bonds
- Unsymmetrical and very long Te-O bonds
- H…F bonds observed

Triclinic $P-1$

\[ a = 7.6704(13)\text{Å}, \quad b = 8.4295(14)\text{Å}, \quad c = 8.8631(15)\text{Å}, \]
\[ \alpha = 111.673(3)^\circ, \quad \beta = 108.479(3)^\circ, \quad \gamma = 97.798(3)^\circ \]

\[ V = 483.89(14) \text{Å}^3, \quad Z = 2, \quad T = 298(2) \text{K}; \quad R1 = 0.0432, \quad S = 1.114 \]
Synthesis of trimethyltin(IV) derivatives: Silver salt metathesis or acidolysis

\[
(CH_3)_3SnCl + AgX-C_6H_6 \xrightarrow{-AgCl} (CH_3)_3SnX + C_6H_6
\]

\(X = OTeF_5\) or \(N(SO_2CF_3)_2\)

MS shows \([M-CH_3]^+\) peak

Trimethyltin(IV) teflate can be distilled at 50°C under vacuum (0.1 Torr)

\(\nu_{Te-O} (\text{cm}^{-1})\): IR (Ra) at 860 (856)

\(\nu_{Sn-C} (\text{cm}^{-1})\) IR (Ra): asym: 552 (554); sym 518 (518)

\(\nu_{as SO_2} (\text{cm}^{-1})\): IR (Ra) at 1342 (1327)

\(\nu_{Sn-C} (\text{cm}^{-1})\) IR (Ra): asym: 558 (556); sym 520 (513)

\(\nu_{Te-O} (\text{cm}^{-1})\) \(F_2TeOCl\): IR (Ra) at 551 (554); \(\nu_{Te-O} (\text{cm}^{-1})\) \(F_2TeOTBA\): IR (Ra) at 867 (866)

\[
(CH_3)_4Sn + HX \xrightarrow{-CH_4} (CH_3)_3SnX
\]

\(X = OTeF_5\) or \(N(SO_2CF_3)_2\)
Synthesis and properties of methyltin(IV) derivatives

- Tetramethyltin can be used in large excess to avoid disproportionation
- Reaction by-products can be easily removed under vacuum
- Trialkyltin(IV) derivatives are colorless viscous oils
- Highly sensitive to moisture
- Form complexes with donor solvents.
- Potentially stronger catalysts in organic synthesis compared to TMSOTf ($^{119}\text{Sn}$ Chemical shift +162 ppm from TMT)
Correlating spectroscopy and crystallography

Correlation of $^{2}J(^{119}\text{Sn}-^{1}\text{H})$ and C-Sn-C angle (determined from x-ray crystallography) gives the following non-linear relationship:

$$T \ (\text{C-Sn-C})^\circ = 0.0161 \ |^{2}J(^{119}\text{Sn}-^{1}\text{H})|^2 - 1.32 \ |^{2}J(^{119}\text{Sn}-^{1}\text{H})| + 133.4$$

Correlation of $^{1}J(^{119}\text{Sn}-^{13}\text{C})$ and C-Sn-C angle (determined from x-ray crystallography gives the following linear relation:

$$11.47T - 875 \ = \ |^{1}J(^{119}\text{Sn}-^{13}\text{C})|$$
<table>
<thead>
<tr>
<th>Solvent</th>
<th>δ(C) (ppm)</th>
<th>δ((^{119\text{Sn}})-C) (°)</th>
<th>δ((^{13\text{C}}) (°)</th>
<th>δ((^{119\text{Sn}})-Sn-(^{13\text{C}})) (°)</th>
<th>δ((^{119\text{Sn}})-Sn-(^{1\text{H}})) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_2)_2\text{SnOTeF}_5) neat</td>
<td>69.6 (66.7)</td>
<td>119.5</td>
<td>0.10</td>
<td>506.4 (486.0)</td>
<td>121.4</td>
</tr>
<tr>
<td>((\text{CH}_2)_2\text{SnOTeF}_5) acetone</td>
<td>69.5 (66.6)</td>
<td>119.4</td>
<td>1.05</td>
<td>511.6 (490.0)</td>
<td>121.6</td>
</tr>
<tr>
<td>((\text{CH}_2)_2\text{SnSO}_2\text{F}_3) neat</td>
<td>62.3 (59.9)</td>
<td>112.6</td>
<td>1.4</td>
<td>404.1 (287.7)</td>
<td>112.2</td>
</tr>
<tr>
<td>((\text{CH}_2)_2\text{SnSO}_2\text{CF}_3) neat</td>
<td>64.2 (61.6)</td>
<td>115.9</td>
<td>2.1</td>
<td>412.6 (394.1)</td>
<td>113.0</td>
</tr>
<tr>
<td>([(\text{CH}_2)_2\text{Sn(OH)}_2\text{][SO}_2\text{CF}_3\text{]}) CN</td>
<td>69.0 (67.4)</td>
<td>119.0</td>
<td>0.7</td>
<td>512.2 (499.0)</td>
<td>121.6</td>
</tr>
<tr>
<td>((\text{CH}_2)_2\text{Sn(OH)}_2\text{][SO}_2\text{CF}_3\text{]}) CN</td>
<td>69.7 (66.7)</td>
<td>119.6</td>
<td>0.10</td>
<td>491.8 (470.0)</td>
<td>120.0</td>
</tr>
<tr>
<td>((\text{CH}_2)_2\text{Sn(OH)}_2\text{][SO}_2\text{CF}_3\text{]}) DMSO</td>
<td>69.8 (66.7)</td>
<td>119.7</td>
<td>0.92</td>
<td>512.9 (497.2)</td>
<td>121.8</td>
</tr>
</tbody>
</table>

* NMR spectroscopic data were recorded at 300 K.
*\(^a\)\) Calc from relation: \(\theta = 0.0161 \left(\frac{1}{J(\^{119}\text{Sn}-\^{11\text{H}})}\right)^2 - 1.32 \left(\frac{1}{J(\^{119}\text{Sn}-\^{1\text{H}})}\right) + 133.4.
*\(^b\)\) Calc from relation: \(\left|\frac{1}{J(\^{119}\text{Sn}-\text{\^{13C}})}\right| = 11.4 \theta - 875.
*\(^c\) Acetone = (CD)_2CO, DMSO = (CD)_3SO.
*\(^d\) Calculated from center of unresolved \(^{119}\text{Sn}, \text{\^{117}\text{Sn}}\) satellites (\(\delta_{\text{iso}}\) x 1.023).
## Multinuclear NMR parameters
...continued

**Table 2. $^{19}$F, $^{119}$Sn and $^{125}$Te NMR Spectroscopic Data** of (CH$_3$)$_2$SnX [X = OTeF$_5$ and N(SO$_2$F/CF$_3$)$_2$]

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent$^b$</th>
<th>$\delta^{(19)}$(F), ppm</th>
<th>$\lambda^{(19)}$(F)$\leftrightarrow^{(19)}$Sn</th>
<th>$\delta^{(119)}$(Sn)</th>
<th>$\delta^{(125)}$(Te)</th>
<th>$\delta^{(13)}$(CF$_3$)</th>
<th>$\lambda^{(125)}$(Te)$\leftrightarrow^{(13)}$(F), Hz</th>
<th>$\lambda^{(13)}$(C)$\leftrightarrow^{(13)}$(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$)$_2$SnOTeF$_5$</td>
<td>neat</td>
<td>-32.9</td>
<td>-41.9</td>
<td>182.5</td>
<td>270.8</td>
<td>569.5</td>
<td>3112</td>
<td>3540</td>
</tr>
<tr>
<td></td>
<td>CH$_3$Cl$_2$</td>
<td>-30.3</td>
<td>-38.5</td>
<td>183.0</td>
<td>272.4</td>
<td>564.6</td>
<td>3188</td>
<td>3550</td>
</tr>
<tr>
<td></td>
<td>acetone</td>
<td>-29.1</td>
<td>-40.6</td>
<td>180.0</td>
<td>96.0</td>
<td>574.9</td>
<td>3020</td>
<td>3558</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td>-29.2</td>
<td>-40.8</td>
<td>179.0</td>
<td>84.2</td>
<td>575.0</td>
<td>3032</td>
<td>3556</td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>-16.2</td>
<td>-33.8</td>
<td>170.0</td>
<td>40.0</td>
<td>598.7</td>
<td>2712</td>
<td>3666</td>
</tr>
<tr>
<td>(CH$_3$)$_2$SnN(SO$_2$F)$_2$</td>
<td>neat</td>
<td>55.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_3$Cl$_2$</td>
<td>55.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>52.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$SnN(SO$_2$CF$_3$)$_2$</td>
<td>neat</td>
<td>-78.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_3$Cl$_2$</td>
<td>-78.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td>-78.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>-78.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(CH$_3$)$_2$Sn(H$_2$O)$_3$][N(SO$_2$CF$_3$)$_2$]</td>
<td>CH$_3$CN</td>
<td>-79.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>-79.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a NMR spectroscopic data were recorded at 300 K

b Acetone = (CD)$_3$CO, DMSO = (CD)$_3$SO

$^{119}$Sn NMR shows a peak at 300.7 ppm in HOTeF$_5$

$^{19}$F NMR for TEAOTeF$_5$ = -25.4 ppm

B(OTeF$_5$)$_3$ = -46.2 (Strauss et al., 1986)
$^{119}\text{Sn}$ chemical shifts and anion basicity

- $d\ (^{119}\text{Sn})$ values lower (more downfield) than +200 ppm show a highly deshielded tin nuclei. Sometimes stronger acids results in relatively higher (upfield) chemical shifts due to close contacts even in solution state:

<table>
<thead>
<tr>
<th>Compound (Me$_3$SnX)</th>
<th>$d\ (^{119}\text{Sn})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = ClO$_4$ (unidentate)</td>
<td>245</td>
</tr>
<tr>
<td>X = SO$_3$CF$_3$ (bidentate)</td>
<td>162</td>
</tr>
</tbody>
</table>

For trimethyltin(IV) derivates in dichloromethane solution the relative anion basicity can be ordered as:

OTeF$_5$ < N(SO$_2$F)$_2$ ~ N(SO$_2$CF$_3$)$_2$ < ClO$_4$ < SO$_2$CF$_3$
Coordination complex formation with donor solvents

\[ \text{H}_3\text{C}-\text{Sn}-\text{X} + \text{D} \]

\[ \text{D} = (\text{CH}_3)_2\text{CO}, \text{CH}_3\text{CN} \]

\[ \text{D} = (\text{CH}_3)_2\text{SO} \]

\[ \text{X} = \text{OTeF}_5 \text{ or } \text{N(SO}_2\text{X)}_2 \]

**Covalent**

- \( \text{OTeF}_5 / \text{N(SO}_2\text{X)}_2 \)
- Long Te-O bond

**IR** \( \nu(\text{Te-O}) \) increases
**IR** \( \nu(\text{SO}_2) \) decreases

\( d(19\text{F}) \text{ Te-F}_\text{ax} \) is deshielded
\( d(19\text{F}) \text{ S-(C)F} \) is shielded

**Ionic**

- \( \text{OTeF}_5^- / \text{N(SO}_2\text{X)}_2^- \)
- Short Te-O bond

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Formation of the hydrated trimethylstannyl cation

The hydrolysis of trimethyltin teflate results in the decomposition of the OTeF$_5$ group.

The hydrated salt can be isolated with N(SO$_2$CF$_3$)$_2$ anion but **NOT** for OTeF$_5$ anion.

The compound isolated after hydrolysis is [Me$_3$Sn(OH)$_2$]$_2$SiF$_6$.
Hydrated trimethyltin(IV) cation

Unit cell dimensions (Å)
Monoclinic (P2₁/c)

\[ \begin{align*}
    a &= 7.3072(1) \, \text{Å}, \\
    b &= 13.4649(2) \, \text{Å}, \\
    c &= 16.821(2) \, \text{Å}, \\
    \beta &= 98.705(1) \, ^\circ
\end{align*} \]

Volume (Å³) = 1636.0(3) Å³,

\[ Z = 4 \]

\[ T = 213(2) \]

\[ R_1 = 0.0367 \]

\[ wR_2 = 0.0736 \]

\[ S = 1.233 \]

Sn-C = 2.11 Å

< O(1)-Sn(1)-O(2) = 175.9(1)°

< C-Sn(1)-C (av) = 120(2)°

2.306(3) Å

2.335(3) Å
Hydrogen bonding in hydrated trimethyltin(IV) cations

\[ S(\text{vdWSn} + \text{vdWO}) = 2.17 + 1.52 = 3.69 \text{ Å} \]
Sn-C versus Sn-Cl bond cleavage

XN(SO$_2$CF$_3$)$_2$ (X = H, Cl) shows a preferential Sn-Cl bond cleavage

\[
\begin{align*}
(CH_3)_3SnCl + HN(SO_2CF_3)_2 & \rightarrow (CH_3)_3SnN(SO_2CF_3)_2 + HCl \\
(CH_3)_3SnCl + ClN(SO_2CF_3)_2 & \rightarrow (CH_3)_3SnN(SO_2CF_3)_2 + Cl_2
\end{align*}
\]

XOTeF$_5$ (X = H, Cl) shows a preferential Sn-C bond cleavage

\[
\begin{align*}
(CH_3)_3SnCl + HOTeF_5 & \rightarrow (CH_3)_2SnClOTeF_5 + CH_4 \\
(CH_3)_3SnCl + ClOTeF_5 & \rightarrow (CH_3)_2SnClOTeF_5 + CH_3Cl
\end{align*}
\]

According to Sladky and Kropshofer (JCS Chem. Commun., 1973, 600), reaction of (CH$_3$)$_3$SnCl with HOTeF$_5$ gives trimethyltin(IV) teflate exclusively!
Structure of $(\text{CH}_3)_2\text{Sn(Cl)}\text{OTeF}_5$

Unit cell dimensions (Å)
- Monoclinic $P2_1/n$
  - $a = 5.8204(8)$, $b = 10.782(1)$
  - $c = 15.493(2)$
  - $\beta = 99.59(1)^\circ$
- Volume $(\text{Å}^3) = 971.7(2)$
  - $Z = 4$
  - $T = 218(2) \text{ K}$
  - $R_1 = 0.0282$
  - $wR_2 = 0.0712$
  - $S = 1.088$

Te-O (Å) (X=OTeF$_5^-$) : B(X)$_3 = 1.874(6)$; [TBA][H(X)$_2$] = 1.800(4)av; [Au(X$_3$)]$_2$ = 1.91(2)


$\nu$(TeO) = 856 cm$^{-1}$ in IR and Ra; $\nu$(SnO) = 427 (IR)/424 (Ra) cm$^{-1}$; $\nu$(SnCl) = 313 (Ra) cm$^{-1}$
The C-Sn-C angle calculated using $^2J^{(119}\text{Sn}-^1\text{H})$ (67.9 Hz) and $^1J^{(119}\text{Sn}-^{13}\text{C})$ (472 Hz) coupling constants for $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ dissolved in CD$_2$Cl$_2$ is approximately ~118°. The $\delta^{(119}\text{Sn})$ value of ~142.7 ppm indicates that tin is present in a five-coordinate environment. The fifth coordination site can be occupied by a bridging chlorine, fluorine or oxygen from a neighboring Me$_2$SnCl(OTeF$_5$) molecule.

$^{119}\text{Sn}$ NMR show the presence of another broad peak at ~127 ppm, which is due to an equilibrium. In VT NMR studies using toluene-$d_8$ as a solvent, this peak disappears at -80 °C.
Coordination environment around tin

One Sn-F contact is also found in the crystal lattice 3.140(4) Å, which is much shorter than the sum of van der Waal radii of tin and fluorine.

\[ S(\text{vdWSn} + \text{vdWF}) = 2.17 + 1.47 = 3.64 \text{ Å} \]

Sn-Cl contact = 3.201(1) Å
Much shorter than the sum of van der Waal radii of tin and chlorine.
A longer Sn-Cl contact is also present at 3.904(2) Å.

\[ S(\text{vdWSn} + \text{vdWCl}) = 2.17 + 1.75 = 3.92 \text{ Å} \]
Hydrolysis of the Sn-Cl bond in \((\text{CH}_3)_2\text{Sn(Cl)OTeF}_5\)
Structure of the dimethyloxotin(IV) teflate

Unit cell dimensions (Å)

Orthorhombic
Space Group: \( Pnnm \)
\[
a = 12.574(6), \quad b = 12.667(6), \quad c = 11.682(5)
\]
Volume (Å\(^3\)) = 1860.6(1)
\[
Z = 2
\]
\[
T = 243 ~ K
\]
\[
R1 = 0.0376
\]
\[
wR2 = 0.1021
\]
\[
S = 1.04
\]
\[
S_{(vdWSn + vdWO)} = 2.17 + 1.52 = 3.69 \text{ Å}
\]
Reaction of the hydrated silver salt with \((\text{CH}_3)_2\text{SnCl}_2\)

\[
(\text{CH}_3)_2\text{SnCl}_2 + \text{AgN(SO}_2\text{CF}_3)_2\cdot\text{C}_6\text{H}_6\cdot\text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{Sn(Cl)N(SO}_2\text{CF}_3)_2 + \text{C}_6\text{H}_6 + \text{H}_2\text{O}
\]
Formation of $\text{Me}_2\text{Sn(OH)N(SO}_2\text{CF}_3)_2$
**Solvolysis of Me₄Sn in excess acid:**

**Synthesis of dimethyltin(IV) teflate**

**✓** Dimethyltin(IV) teflate is formed when tetramethyltin is reacted with excess teflic acid

\[
(\text{CH}_3)_4\text{Sn} + \text{xs HOTeF}_5 \xrightarrow{\text{60 } ^\circ\text{C, 40h}} (\text{CH}_3)_2\text{Sn(OTeF}_5)_2 - 2 \text{CH}_4
\]

MS shows [M-CH₃]⁺ peak

**✓** Upon sublimation ~75 °C/0.01T a polymeric species is formed, probably due to the loss of O(TeF₅)₂

\[
(\text{CH}_3)_2\text{Sn(OTeF}_5)_2 \xrightarrow{\text{75 } ^\circ\text{C, 0.01T}} (\text{CH}_3)_2\text{SnO} \quad \text{OTeF}_5 \quad \text{n}
\]

\[
\nu(\text{TeO}) = 877 \text{ cm}^{-1}; \nu(\text{SnO}) = 434 (\text{IR}) \text{ cm}^{-1}; \nu_{\text{as}} (\text{SnC}) = 591 \text{ cm}^{-1}, \nu_{\text{s}} (\text{SnC}) = 531 \text{ cm}^{-1}
\]
Structure of dimethylditinooxeteflate

Unit cell dimensions (Å)

Monoclinic $P2_1/n$

Rotational TWIN

$a = 7.510(6)$, $b = 15.729(12)$,
$c = 8.119(7)$

$\beta = 115.1(1) ^\circ$

Volume (Å³) = 876.7(12)

$Z = 4$

$T = 233(2)$ K

$R_1 = 0.1028$

$S = 1.84$

BASF = 0.256

C1-Sn-O1 = 110.2(5)°; C2-Sn-O1 = 103.3(6)°,
<equi. X-Sn-X (av)= 120°; O2-Sn-O2* = 169.9(5)°
Crystal packing showing tin and tellurium polyhedra

\[ S_{(vdwSn + vdwF)} = 2.17 + 1.47 = 3.64 \text{ Å} \]

Sn-F distance in the crystal packing

\[ = 3.107(16) \text{ Å} \]

The structure shows polymeric Sn-O chains bridged by a fluorine atom of the OTeF$_5$ group.

\[ <\text{Sn-O2-Sn*} = 167.2^\circ \]

\[ (\text{Sn*} = \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z) \]
Conclusions

- Silver salts containing the teflate and NTf form stable arene complexes. NTf conformation varies!

- $^{119}$Sn NMR chemical shifts can reflect the “electrophilic strength” and relative anion basicity for a Me$_3$Sn (IV) compound.

- During the solvolysis of trimethyltin chloride in HOTeF$_5$, there is a preferential cleavage of the Sn-C bond versus Sn-Cl bond

- Trimethyltin(IV) teflates/F-imides are highly electrophilic in nature and form 1:1 or 1:2 complexes with donor solvents

- Chlorodimethyltin(IV) teflate hydrolyzes to form a Sn-O ladder compound and sublimation of dimethyltin(II) bis(teflate) results in the formation of an oxo-bridged species.

- Use of hydrated silver salt to prepare methyltin derivatives results in the hydrolysis of trimethyltin derivative to form hydrated tin cation.

- Chlorodimethyltin NTf hydrolyzes to form the µ-(hydroxo) species, where NTf is in a trans orientation
Conclusions

- Trimethyltin(IV) derivates can easily be prepared by the reaction of acids with excess tetramethyltin.
- Trimethyltin(IV) derivatives are highly electrophilic and coordinate with solvents giving trigonal bipyramidal geometry.
- In case of water and DMSO, ionic salts are formed with two donor molecules occupying the axial position.
- During the solvolysis of trimethyltinchloride in HOTeF₅, there is a preferential cleavage of the Sn-C bond versus Sn-Cl bond.
- Chlorodimethyltin(IV) teflate hydrolysizes to form a Sn-O ladder compound.
- The sublimation of dimethyltin(II) bis(teflate) results in the formation of an oxo-bridged species.
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Coordination environment of Cs in CsN(SO$_2$CF$_3$)$_2$ salts

CsN(SO$_2$CF$_3$)$_2$

Octa-coordinated with a short Cs-N bond

CsN(SO$_2$CF$_3$)$_2$•H$_2$O

Nona-coordinated with a long Cs-N bond

CsN(SO$_2$CF$_3$)$_2$ is reported to be ten-coordinated

DesMarteau, Pennington et al., Solid State Sciences, 2002, 4, 1535-1545
Crystal packing in $[\text{AgN(SO}_2\text{CF}_3)_2\text{(C}_6\text{H}_6)_2]$
### Bond distances and angles

**Me$_2$SnClOTeF$_5$**

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<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
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<tr>
<td>Sn(1)-C(2)</td>
<td>2.104(4)</td>
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<tr>
<td>Sn(1)-C(1)</td>
<td>2.115(4)</td>
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<td>Sn(1)-C(3)</td>
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<td>S(1)-C(4)</td>
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