# Solid State Structural Studies of Some New Derivatives of $HN(SO_2CF_3)_2$ and $HOTeF_5$

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14. ABSTRACT

**The šcisoidŠ form is less common. In the CCDC, only 6 structures show this conformation whereas the štransiodŠ form occurs in 15 remaining structures The šcisoidŠ conformation results from stronger cation-anion interaction šCisoidŠ observed exclusively when anion is chelated to the metal center The štransoidŠ form dominates in structures containing a šfreeŠ anion NO structure known containing both šcisoidŠ AND štransoidŠ geometry**

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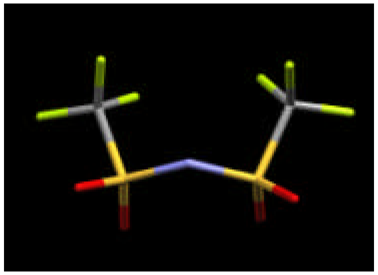
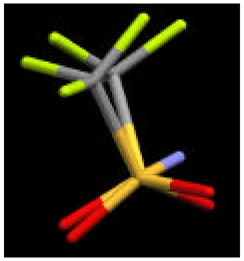
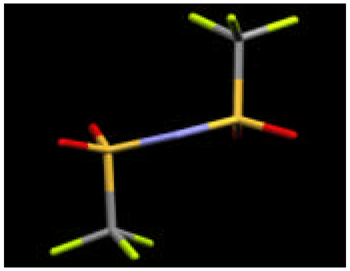
# *Coordination & isomerism in $N(SO_2CF_3)_2$ (NTf)*



**“Cisoid”**



**C-S--S-C “torsion”**



**“Transoid”**

- ✓ **The “cisoid” form is less common. In the CCDC, only 6 structures show this conformation whereas the “transiod” 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**

**DesMarteau, Pennington *et al.*, Soild State Sciences, 2002, *4*, 1535-1545**

# *Synthesis of metal(I) derivatives*

$$HN(SO_2CF_3)_2 \quad + \quad M_2CO_3 \xrightarrow{H_2O} 2\,MN(SO_2CF_3)_2 \quad + \quad CO_2 \quad + \quad H_2O$$

$$HX \quad + \quad Ag_2O \xrightarrow{C_6H_6} 2\,AgX\cdot C_6H_6$$

**X = $OTeF_5$ or NTf**

**These salts are colorless crystalline materials.  Some turn amorphous with time**

**nTe-O ($cm^{-1}$): IR (Ra) at ~865 (860)**

**$n_{as}$SO2 ($cm^{-1}$): IR (Ra) at ~1320(~1328)**

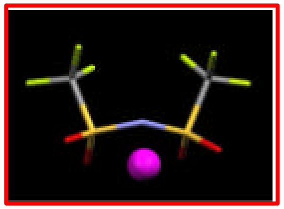
**$^1H$ NMR: $C_6H_6$ peak at 7.6-7.7 ppm**

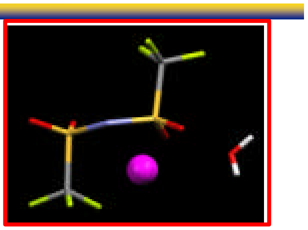
**Uncoordinated benzene: 7.3**

**$^{19}F$ NMR: ~-78 ppm ($CF_3$)**

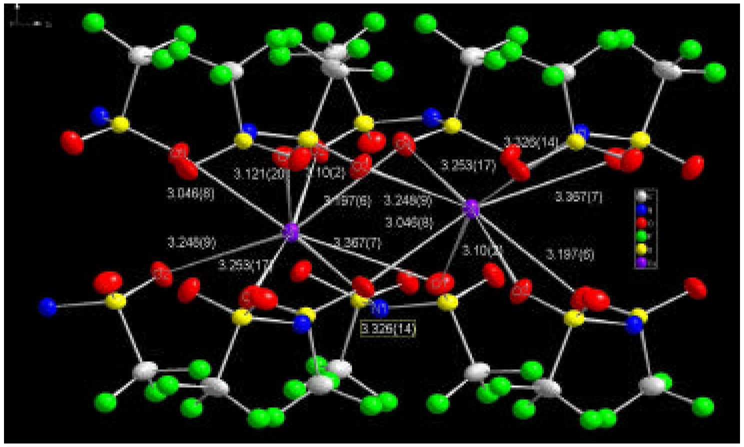
- ✓ **These salts are colorless and crystalline.**
- ✓ **Recrystallization from iso-propylalcohol gave anhydrous salts.**
- ✓ **Some of these salts turn amorphous with time**

# Structure of $CsN(SO_2CF_3)_2$ salts



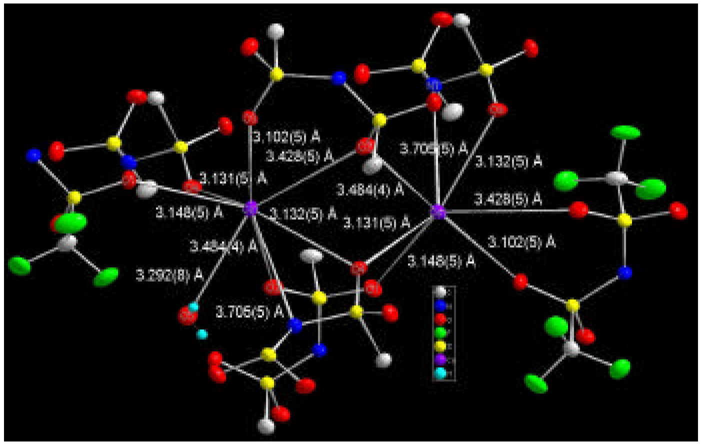


**$CsN(SO_2CF_3)_2$**



● C
● N
● O
● F
● S
● Cs
● H

**$CsN(SO_2CF_3)_2 \bullet H_2O$**



**Monoclinic *C*2/*c* [*ß* = 91.92(1)°]**

***a*** **=22.509(12), b = 7.029(4), c = 13.519(7) [Å]**

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

***R*1 = 0.0399, *S* = 1.024**

**Tetragonal *I*-4**

***a*** **=16.903(1), c = 7.8933(6) [Å]**

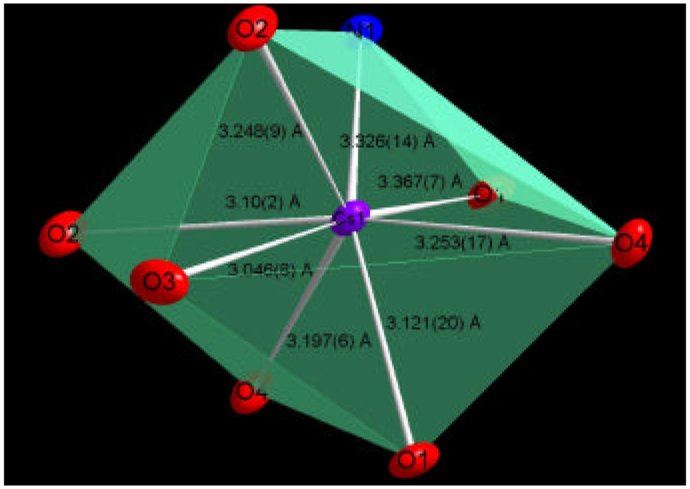
**Volume (Å$^3$) = 2255.2(3), Z = 6, *T* = *298 K***

***R*1 = 0.0307, *S* = 1.20**

# Coordination environment of Cs in $CsN(SO_2CF_3)_2$ salts

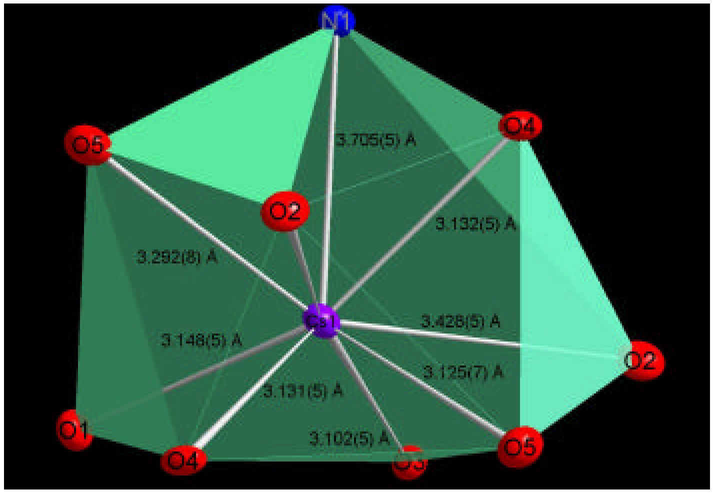
**$CsN(SO_2CF_3)_2$**

**Octa-coordinated with a short Cs-N bond**



**$CsN(SO_2CF_3)_2•H_2O$**

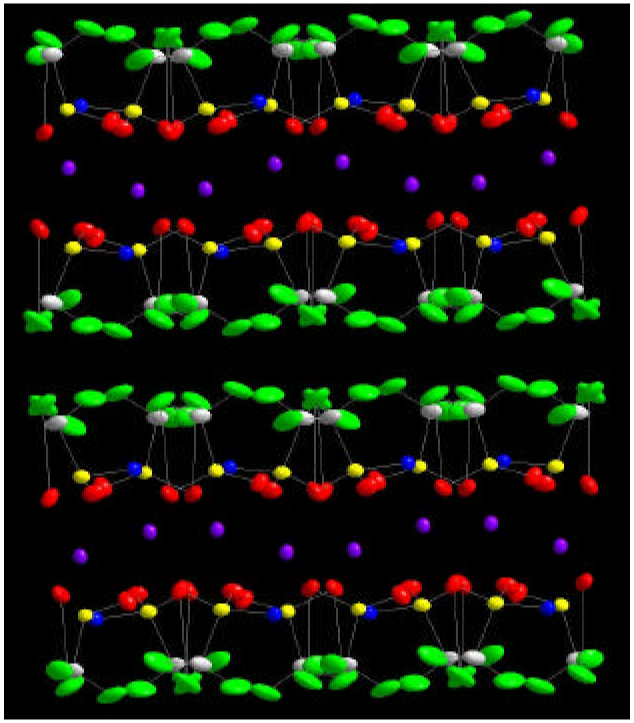
**Nona-coordinated with a long Cs-N bond**



# *Crystal packing in $CsN(SO_2CF_3)_2$ salts*

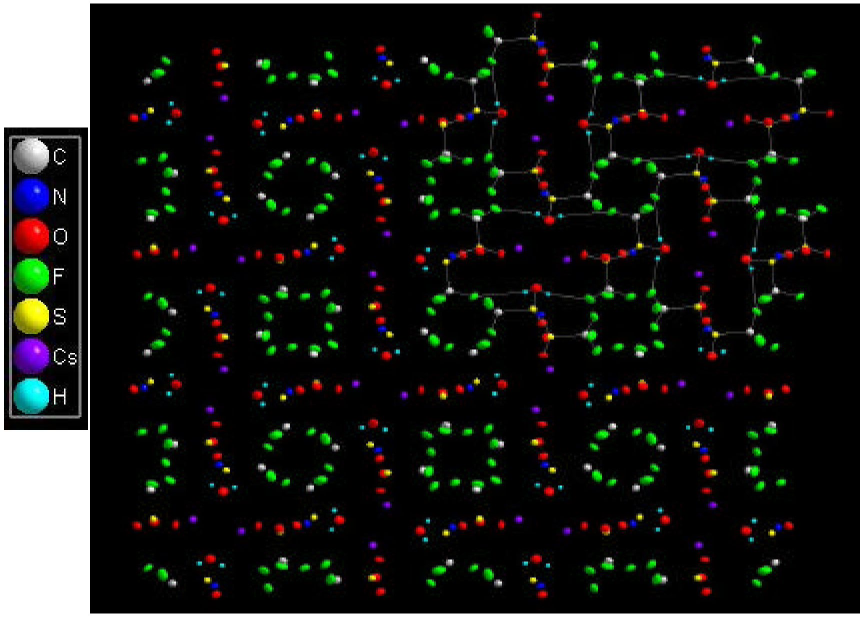
**$CsN(SO_2CF_3)_2$**

**Hydrophobic and hydrophillic Layering**

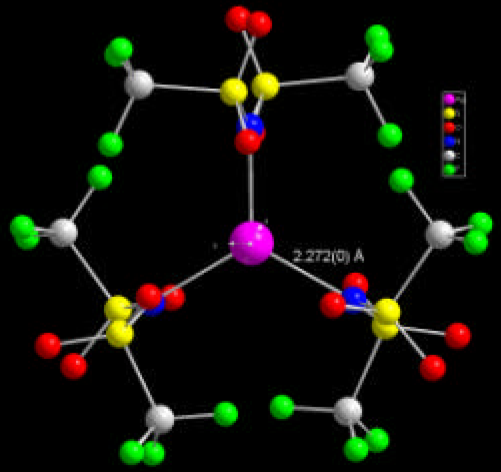


**$CsN(SO_2CF_3)_2{\bullet}H_2O$**

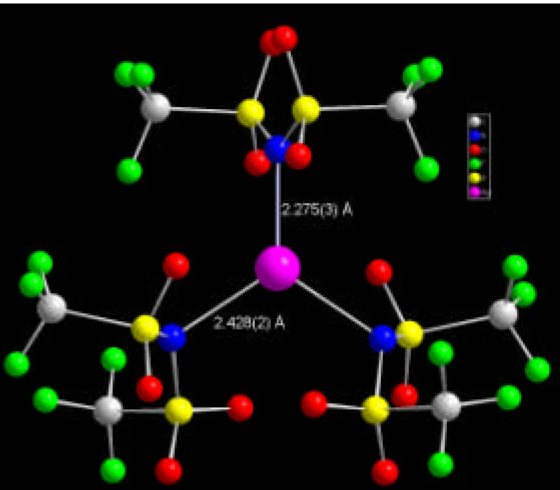
**“Swiss cheese” Tunnel/channel structure**



# Polymorphism in silver bis(trifluoromethylsulfonyl)imide



**Similar trans Ag-N distances, angles = 120°**



**Cis (long), trans (short) Ag-N distances, angles NOT 120º**

**Trigonal *P-3*$_1$c**

***a*** **=7.510(6) Å, c = 8.119(7) Å**

**Z = 6, *T = 298 K***

**Orthorhombic *P*bca**

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

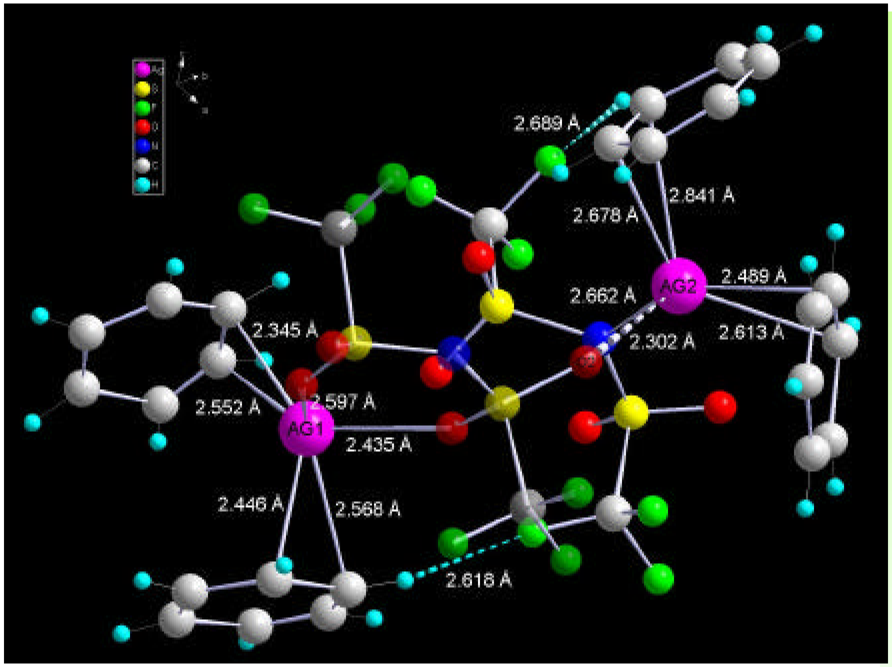
**Z = 4, *T = 298 K***

**Steric control of tricoordination around Ag is known in $[Ag(CpPh_2P)_3]^+ [BF_4]^-$**

**However, binary tricoordinated silver salts are unknown**

Baiada, A; Jardine, F. H.; Willett, R.D. Inorg. Chem. **1990**, *29*, 4805

# Structure of [AgN(SO$_2$CF$_3$)$_2$(C$_6$H$_6$)$_2$]



**Triclinic *P*-1**

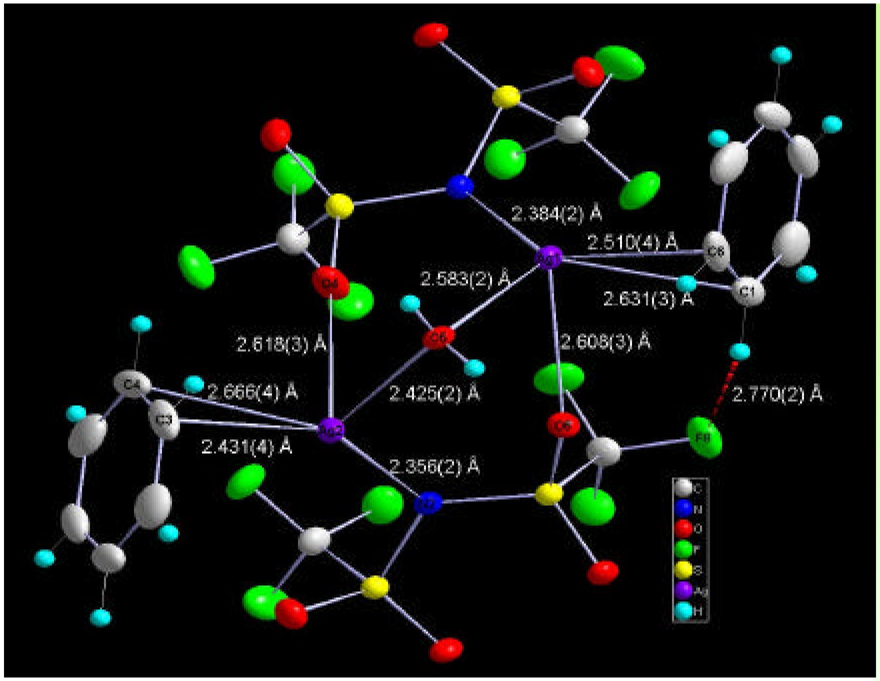
***a*** **= 7.6704(13)Å, b = 8.4295(14)Å, c = 8.8631(15)Å,**

a **= 111.673(3)°,** b **= 108.479(3)°,** g **= 97.798(3)°**

**V (Å$^3$) = 483.89(14), Z = 2, *T = 298(2) K* ; *R*1= 0.0432, *S* = 1.114**

- ✓ **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**

# Structure of $[AgN(SO_2CF_3)_2(C_6H_6)]_2{\cdot}H_2O$



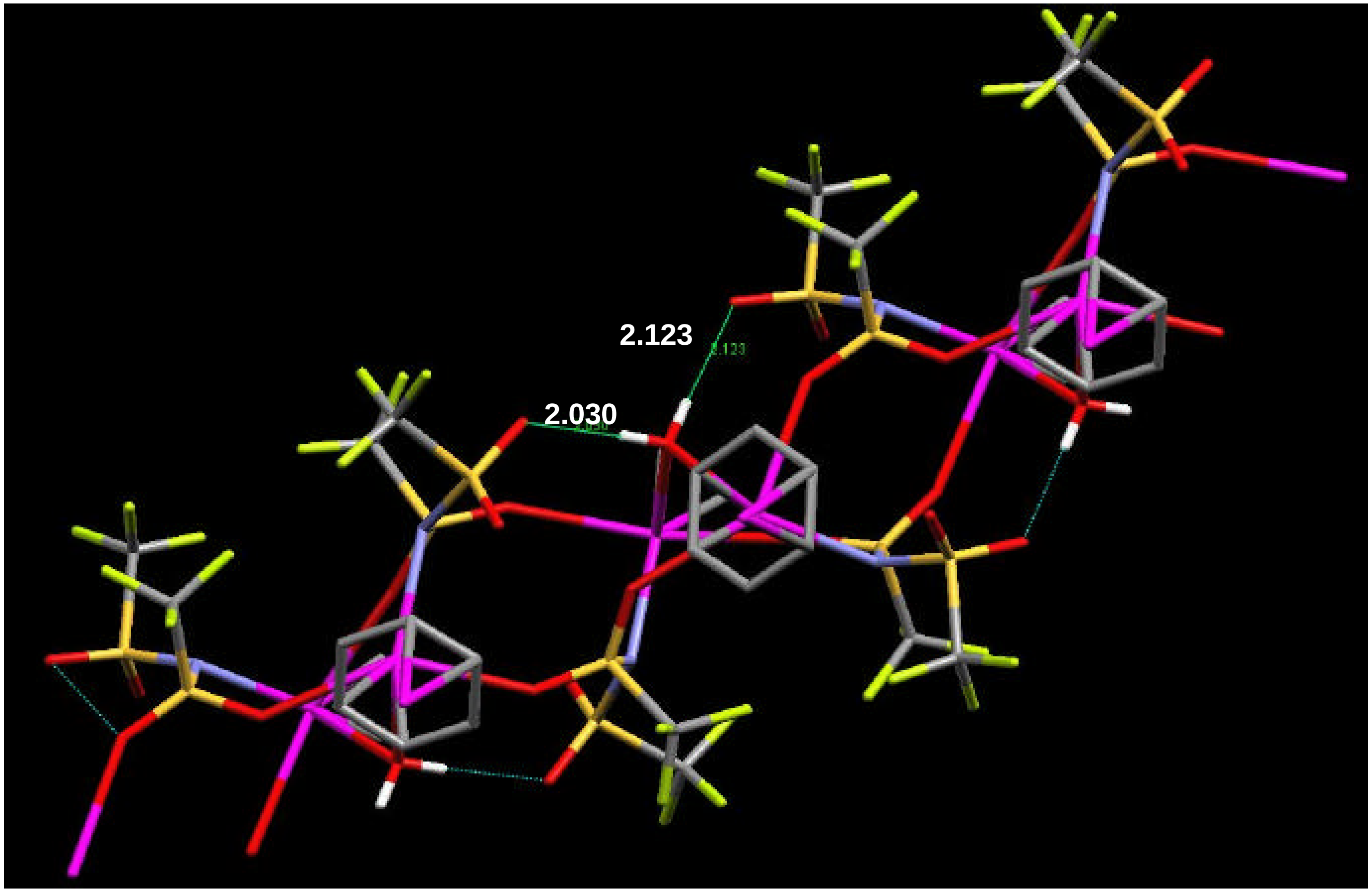
**Monoclinic $P2_1/n$**

**$a$ = 10.372(1)Å, $b$ = 19.823(2)Å, $c$ = 12.406(1)Å, $b$ = 108.536(3)°,**

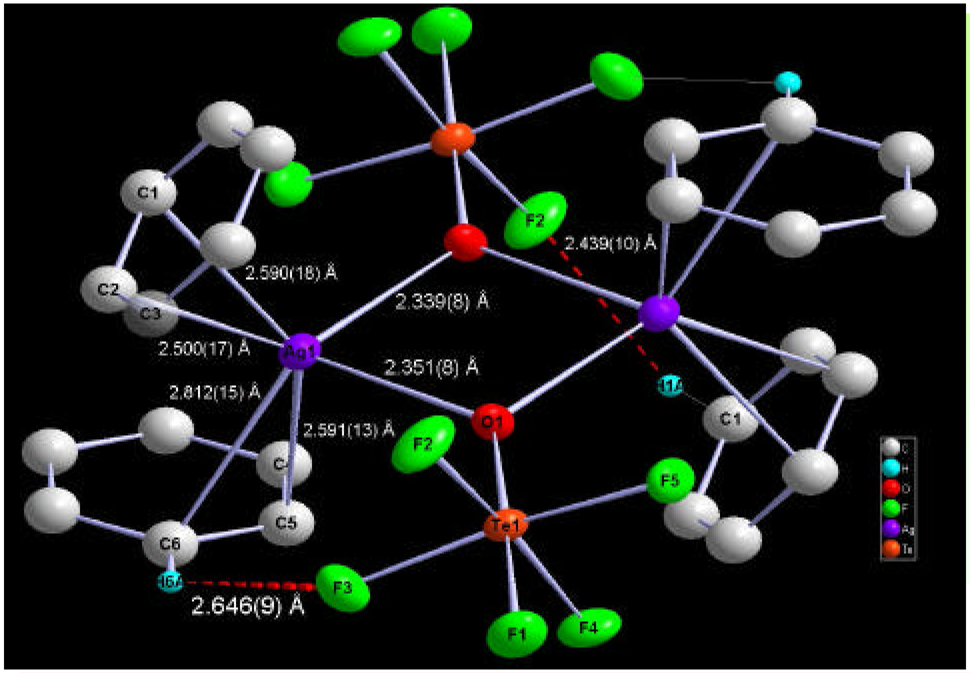
**V (Å$^3$) = 2148.5(5), Z = 8, $T$ = 173(1) K ; $R$1= 0.0224, $S$ = 1.04**

- ✓ **$N(SO_2CF_3)_2$ group is both N- as well as O-bonded to silver**
- ✓ **Water bridges the eigth-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)**
- ✓ **$N(SO_2CF_3)_2$ group is "*cisoid*"**
- ✓ **H…F bond distances observed close to sum of van der Waal distance**

# Crystal packing in $[AgN(SO_2CF_3)_2(C_6H_6)]_2 \cdot H_2O$



# Structure of $[AgOTeF_5(C_6H_6)_2]_2$



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

**Triclinic *P*-1**

***a* = 7.6704(13)Å, b = 8.4295(14)Å, c = 8.8631(15)Å,**

a **= 111.673(3)°,** b **= 108.479(3)°,** g **= 97.798(3)°**

**V (Å$^3$) = 483.89(14), Z = 2, *T = 298(2) K* ; *R*1= 0.0432, *S* = 1.114**

# *Synthesis of trimethyltin(IV) derivatives: Silver salt metathesis or acidolysis*

$$(CH_3)_3SnCl \quad + \quad AgX\text{-}C_6H_6 \xrightarrow{-\ AgCl} (CH_3)_3SnX \quad + \quad C_6H_6$$

$$X = OTeF_5 \text{ or } N(SO_2CF_3)_2$$

**MS shows $[M\text{-}CH_3]^+$ peak**

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

**nTe-O ($cm^{-1}$): IR (Ra) at 860 (856)**

**nSn-C ($cm^{-1}$) IR (Ra): asym: 552 (554); sym 518 (518)**

**$n_{as}SO_2$ ($cm^{-1}$): IR (Ra) at 1342(1327)**

**nSn-C ($cm^{-1}$) IR (Ra): asym: 558 (556); sym 520 (513)**

**nTe-O (cm-1) $F_5TeOCl$: IR (Ra) at 551 (554); nTe-O (cm-1) $F_5TeOTBA$: IR (Ra) at 867 (866);**

$$(CH_3)_4Sn \quad + \quad HX \xrightarrow{-\ CH_4} (CH_3)_3SnX$$

$$X = OTeF_5 \text{ or } N(SO_2CF_3)_2$$

# *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 ($^{119}$Sn Chemical shift +162 ppm from TMT)**

# Correlating spectroscopy and crystallography

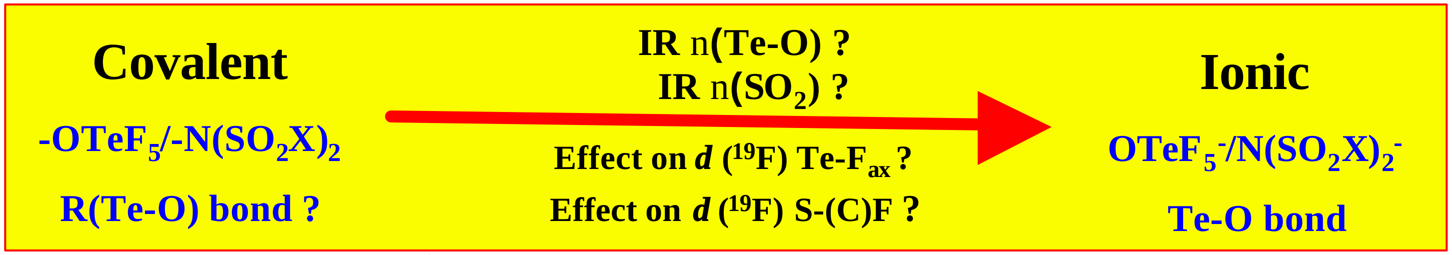
**Correlation of $^{2}J(^{119}Sn\text{-}^{1}H)$ and C-Sn-C angle (determined from x-ray crystallography) gives the following non-linear relationship:**

Lockhart, T. P.; Manders, W. F. *Inorg. Chem.* 1985, *25*, 892
Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* 1985, *107*, 4546

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

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

$$11.4T - 875 = |^{1}J(^{119}\text{Sn-}^{13}\text{C})|$$



**Covalent**

**$-OTeF_5/-N(SO_2X)_2$**

**R(Te-O) bond ?**

**IR n(Te-O) ?**
**IR n($SO_2$) ?**

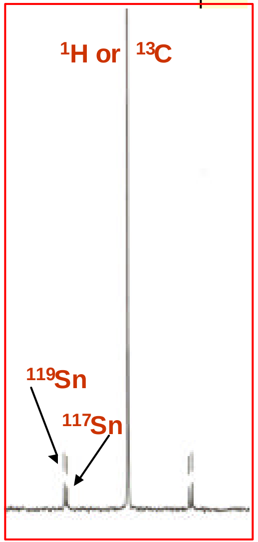
**Effect on *d* ($^{19}$F) Te-$F_{ax}$ ?**
**Effect on *d* ($^{19}$F) S-(C)F ?**

**Ionic**

**$OTeF_5^{-}/N(SO_2X)_2^{-}$**

**Te-O bond**

# Multinuclear NMR Parameters



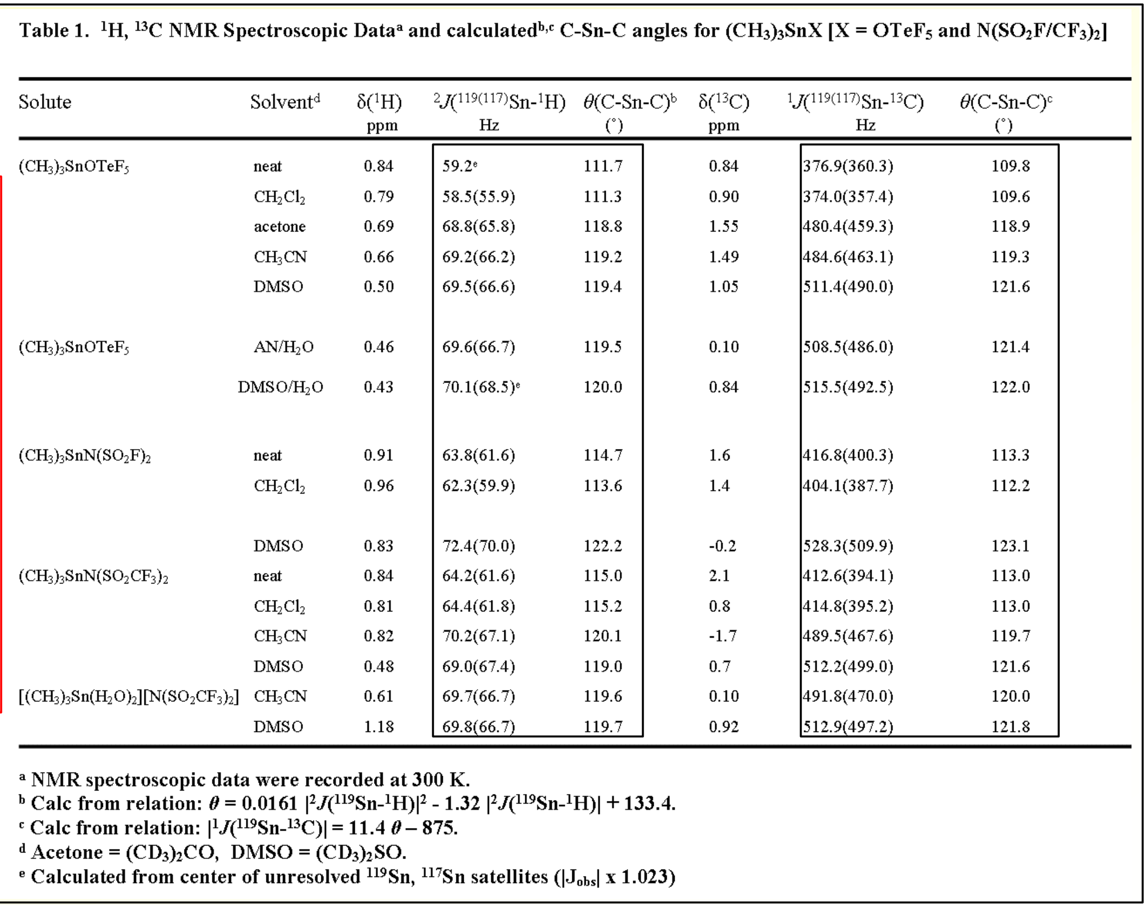


Table 1. $^{1}$H, $^{13}$C NMR Spectroscopic Data[a] and calculated[b,c] C-Sn-C angles for $(CH_3)_3SnX$ [X = $OTeF_5$ and $N(SO_2F/CF_3)_2$]

| Solute | Solvent[d] | $\delta(^{1}H)$ ppm | $^{2}J(^{119(117)}Sn\text{-}^{1}H)$ Hz | $\theta$(C-Sn-C)[b] (°) | $\delta(^{13}C)$ ppm | $^{1}J(^{119(117)}Sn\text{-}^{13}C)$ Hz | $\theta$(C-Sn-C)[c] (°) |
|---|---|---|---|---|---|---|---|
| $(CH_3)_3SnOTeF_5$ | neat | 0.84 | 59.2[e] | 111.7 | 0.84 | 376.9(360.3) | 109.8 |
| | $CH_2Cl_2$ | 0.79 | 58.5(55.9) | 111.3 | 0.90 | 374.0(357.4) | 109.6 |
| | acetone | 0.69 | 68.8(65.8) | 118.8 | 1.55 | 480.4(459.3) | 118.9 |
| | $CH_3CN$ | 0.66 | 69.2(66.2) | 119.2 | 1.49 | 484.6(463.1) | 119.3 |
| | DMSO | 0.50 | 69.5(66.6) | 119.4 | 1.05 | 511.4(490.0) | 121.6 |
| $(CH_3)_3SnOTeF_5$ | AN/$H_2O$ | 0.46 | 69.6(66.7) | 119.5 | 0.10 | 508.5(486.0) | 121.4 |
| | DMSO/$H_2O$ | 0.43 | 70.1(68.5)[e] | 120.0 | 0.84 | 515.5(492.5) | 122.0 |
| $(CH_3)_3SnN(SO_2F)_2$ | neat | 0.91 | 63.8(61.6) | 114.7 | 1.6 | 416.8(400.3) | 113.3 |
| | $CH_2Cl_2$ | 0.96 | 62.3(59.9) | 113.6 | 1.4 | 404.1(387.7) | 112.2 |
| | DMSO | 0.83 | 72.4(70.0) | 122.2 | -0.2 | 528.3(509.9) | 123.1 |
| $(CH_3)_3SnN(SO_2CF_3)_2$ | neat | 0.84 | 64.2(61.6) | 115.0 | 2.1 | 412.6(394.1) | 113.0 |
| | $CH_2Cl_2$ | 0.81 | 64.4(61.8) | 115.2 | 0.8 | 414.8(395.2) | 113.0 |
| | $CH_3CN$ | 0.82 | 70.2(67.1) | 120.1 | -1.7 | 489.5(467.6) | 119.7 |
| | DMSO | 0.48 | 69.0(67.4) | 119.0 | 0.7 | 512.2(499.0) | 121.6 |
| $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ | $CH_3CN$ | 0.61 | 69.7(66.7) | 119.6 | 0.10 | 491.8(470.0) | 120.0 |
| | DMSO | 1.18 | 69.8(66.7) | 119.7 | 0.92 | 512.9(497.2) | 121.8 |

[a] **NMR spectroscopic data were recorded at 300 K.**

[b] **Calc from relation: $\theta = 0.0161\,|^{2}J(^{119}Sn\text{-}^{1}H)|^2 - 1.32\,|^{2}J(^{119}Sn\text{-}^{1}H)| + 133.4$.**

[c] **Calc from relation: $|^{1}J(^{119}Sn\text{-}^{13}C)| = 11.4\,\theta - 875$.**

[d] **Acetone = $(CD_3)_2CO$, DMSO = $(CD_3)_2SO$.**

[e] **Calculated from center of unresolved $^{119}$Sn, $^{117}$Sn satellites ($|J_{obs}|$ x 1.023)**

# Multinuclear NMR parameters …continued

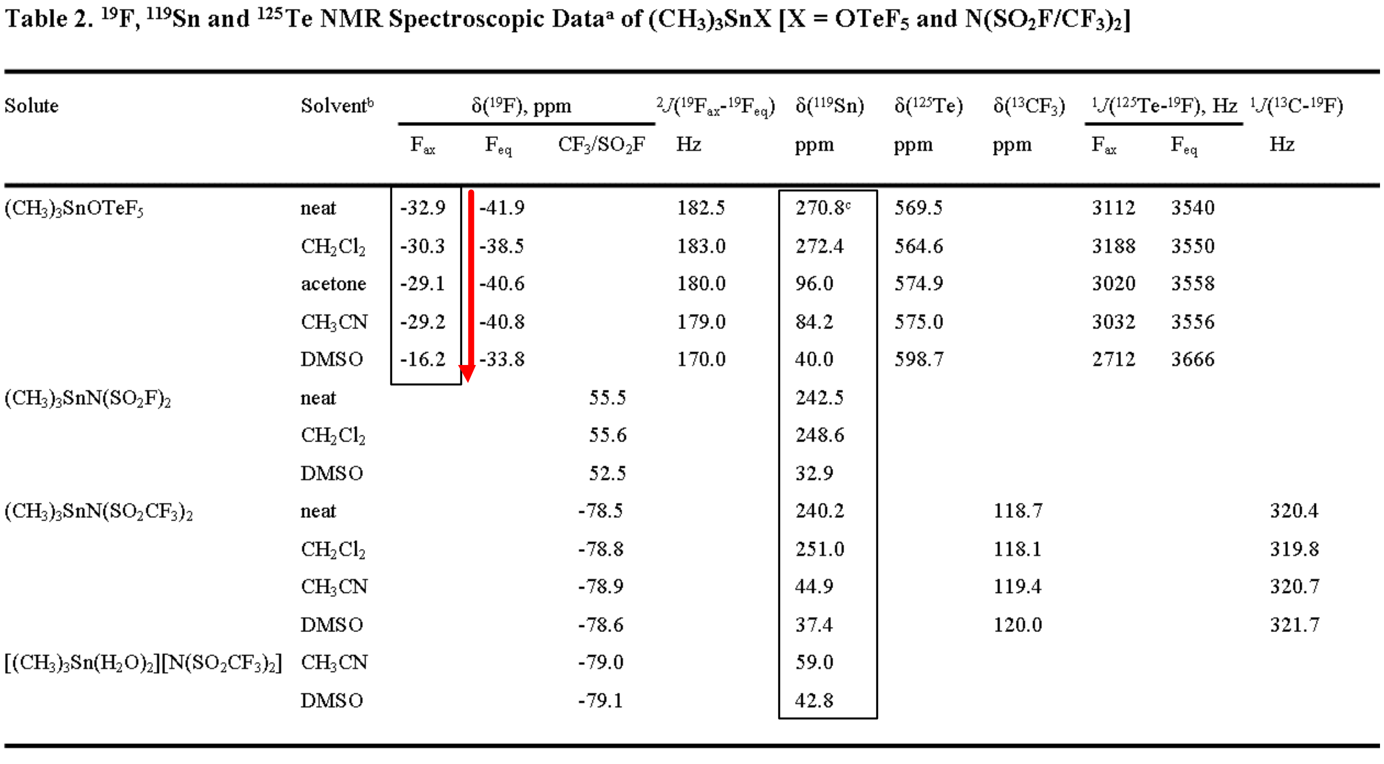


Table 2. $^{19}F$, $^{119}Sn$ and $^{125}Te$ NMR Spectroscopic Data[a] of $(CH_3)_3SnX$ [X = $OTeF_5$ and $N(SO_2F/CF_3)_2$]

| Solute | Solvent[b] | δ($^{19}F$), ppm |  |  | $^2J(^{19}F_{ax}-^{19}F_{eq})$ | δ($^{119}Sn$) | δ($^{125}Te$) | δ($^{13}CF_3$) | $^1J(^{125}Te-^{19}F)$, Hz |  | $^1J(^{13}C-^{19}F)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | $F_{ax}$ | $F_{eq}$ | $CF_3/SO_2F$ | Hz | ppm | ppm | ppm | $F_{ax}$ | $F_{eq}$ | Hz |
| $(CH_3)_3SnOTeF_5$ | neat | -32.9 | -41.9 |  | 182.5 | 270.8[c] | 569.5 |  | 3112 | 3540 |  |
|  | $CH_2Cl_2$ | -30.3 | -38.5 |  | 183.0 | 272.4 | 564.6 |  | 3188 | 3550 |  |
|  | acetone | -29.1 | -40.6 |  | 180.0 | 96.0 | 574.9 |  | 3020 | 3558 |  |
|  | $CH_3CN$ | -29.2 | -40.8 |  | 179.0 | 84.2 | 575.0 |  | 3032 | 3556 |  |
|  | DMSO | -16.2 | -33.8 |  | 170.0 | 40.0 | 598.7 |  | 2712 | 3666 |  |
| $(CH_3)_3SnN(SO_2F)_2$ | neat |  |  | 55.5 |  | 242.5 |  |  |  |  |  |
|  | $CH_2Cl_2$ |  |  | 55.6 |  | 248.6 |  |  |  |  |  |
|  | DMSO |  |  | 52.5 |  | 32.9 |  |  |  |  |  |
| $(CH_3)_3SnN(SO_2CF_3)_2$ | neat |  |  | -78.5 |  | 240.2 |  | 118.7 |  |  | 320.4 |
|  | $CH_2Cl_2$ |  |  | -78.8 |  | 251.0 |  | 118.1 |  |  | 319.8 |
|  | $CH_3CN$ |  |  | -78.9 |  | 44.9 |  | 119.4 |  |  | 320.7 |
|  | DMSO |  |  | -78.6 |  | 37.4 |  | 120.0 |  |  | 321.7 |
| $[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$ | $CH_3CN$ |  |  | -79.0 |  | 59.0 |  |  |  |  |  |
|  | DMSO |  |  | -79.1 |  | 42.8 |  |  |  |  |  |

[a] NMR spectroscopic data were recorded at 300 K

[b] Acetone = $(CD_3)_2CO$, DMSO = $(CD_3)_2SO$

[c] $^{119}Sn$ NMR shows a peak at 300.7 ppm in $HOTeF_5$

**$^{19}F_{ax}$ NMR for $TEAOTeF_5$ = -25.4 ppm**

**$B(OTeF_5)_3$ = -46.2 (Strauss et al., 1986)**

# $^{119}$Sn chemical shifts and anion basicity

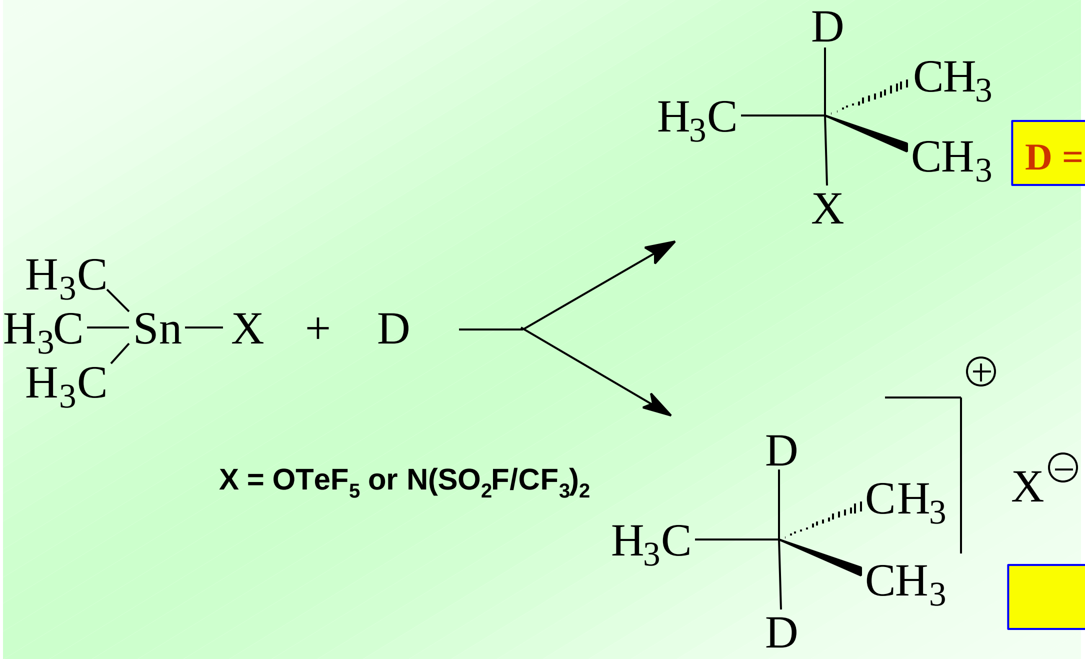
- *d* ($^{119}$Sn) values lower (more downfield) than +200 ppm show a highly deshielded tin nuclei. Sometimes stronger acids results in relatively higher (upfield) chemical shifts due to close contacts even in solution state:

| Compound ($Me_3SnX$) | *d* ($^{119}$Sn) |
|---|---|
| X = $ClO_4$ (unidentate) | 245 |
| X = $SO_3CF_3$ (bidentate) | 162 |

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

**$OTeF_5 < N(SO_2F)_2 \sim N(SO_2CF_3)_2 < ClO_4 < SO_2CF_3$**

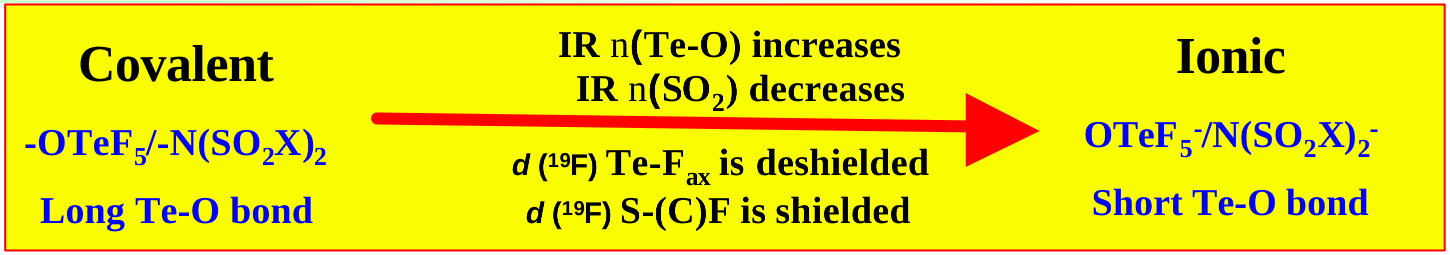
# Coordination complex formation with donor solvents



X = $OTeF_5$ or $N(SO_2F/CF_3)_2$

**D = $(CH_3)_2CO$, $CH_3CN$**

**D = $(CH_3)_2SO$**



**Covalent**

**$-OTeF_5/-N(SO_2X)_2$**

**Long Te-O bond**

**IR n(Te-O) increases**
**IR n($SO_2$) decreases**

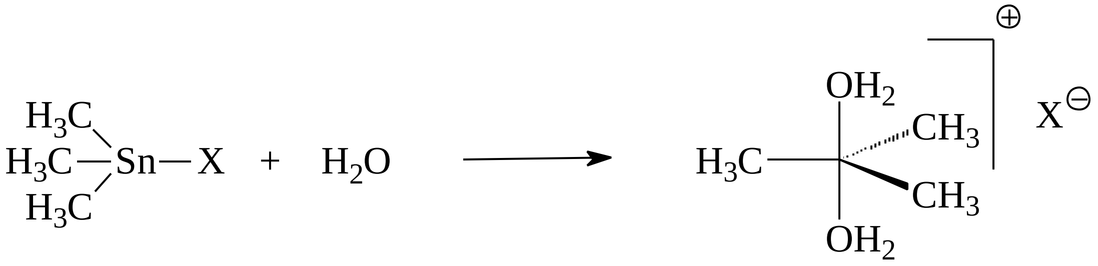
**d ($^{19}$F) Te-$F_{ax}$ is deshielded**
**d ($^{19}$F) S-(C)F is shielded**

**Ionic**

**$OTeF_5^-/N(SO_2X)_2^-$**

**Short Te-O bond**

# Formation of the hydrated trimethylstannyl cation



**The hydrated salt can be isolated with $N(SO_2CF_3)_2$ anion but NOT for $OTeF_5$ anion. The compound isolated after hydrolysis is $[Me_3Sn(OH_2)_2]_2SiF_6$**

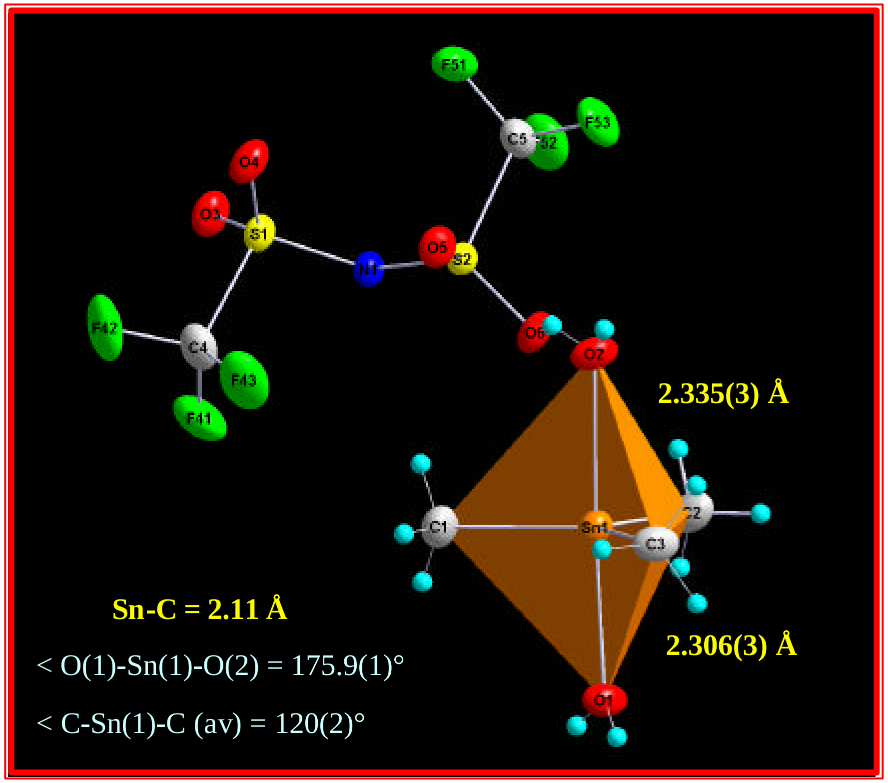
$$OTeF_5^- + 5H_2O \longrightarrow 5HF + OTe(OH)_5^-$$

$$4\,HF + SiO_2 \longrightarrow 2\,H_2O + SiF_4$$

$$2F^- + SiF_4 \longrightarrow SiF_6^{2-}$$

**The hydrolysis of trimethyltin teflate results in the decomposition of the $OTeF_5$ group**

# Hydrated trimethyltin(IV) cation



2.335(3) Å

2.306(3) Å

**Sn-C = 2.11 Å**

< O(1)-Sn(1)-O(2) = 175.9(1)°

< C-Sn(1)-C (av) = 120(2)°

**<u>Unit cell dimensions (Å)</u>**

**Monoclinic ($P2_1/c$)**

**$a$ =7.3072(1), b = 13.4649(2),**

**c = 16.821(2)**

**ß = 98.705(1) °**

**Volume (Å$^3$) = 1636.0(3) ,**

**Z = 4**

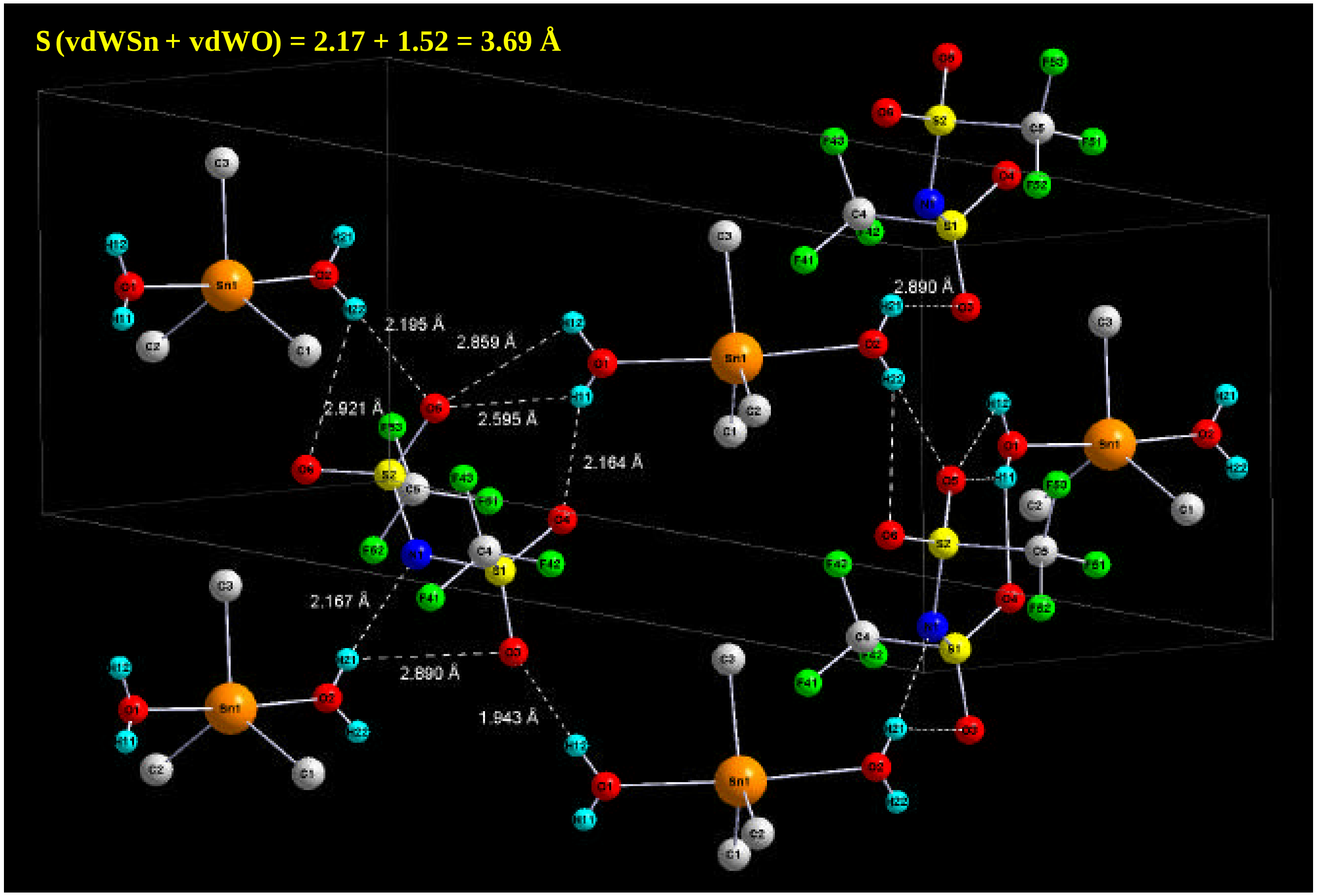
**T = 213(2)**

**$R1$ = 0.0367**

**$wR2$ = 0.0736**

**$S$ = 1.233**

# *Hydrogen bonding in hydrated trimethyltin(IV) cations*


S (vdWSn + vdWO) = 2.17 + 1.52 = 3.69 Å

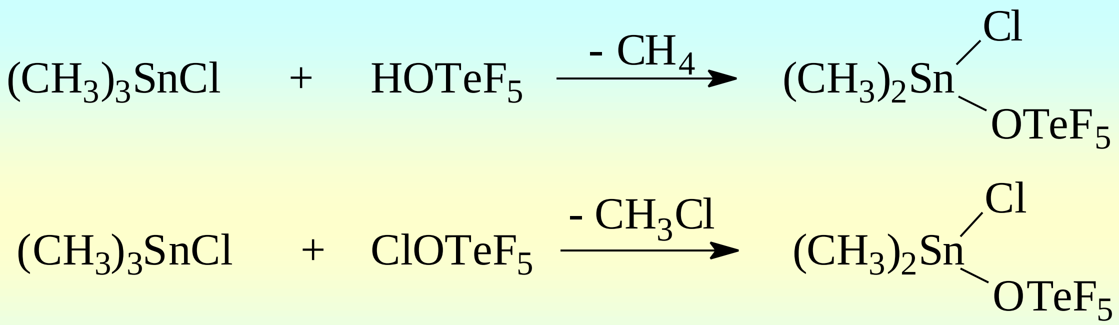
# *Sn-C versus Sn-Cl bond cleavage*

## $XN(SO_2CF_3)_2$ (X = H, Cl) shows a preferential Sn-Cl bond cleavage

$$(CH_3)_3SnCl + HN(SO_2CF_3)_2 \xrightarrow{-\ HCl} (CH_3)_3SnN(SO_2CF_3)_2$$

$$(CH_3)_3SnCl + ClN(SO_2CF_3)_2 \xrightarrow{-\ Cl_2} (CH_3)_3SnN(SO_2CF_3)_2$$

## $XOTeF_5$ (X = H, Cl) shows a preferential Sn-C bond cleavage

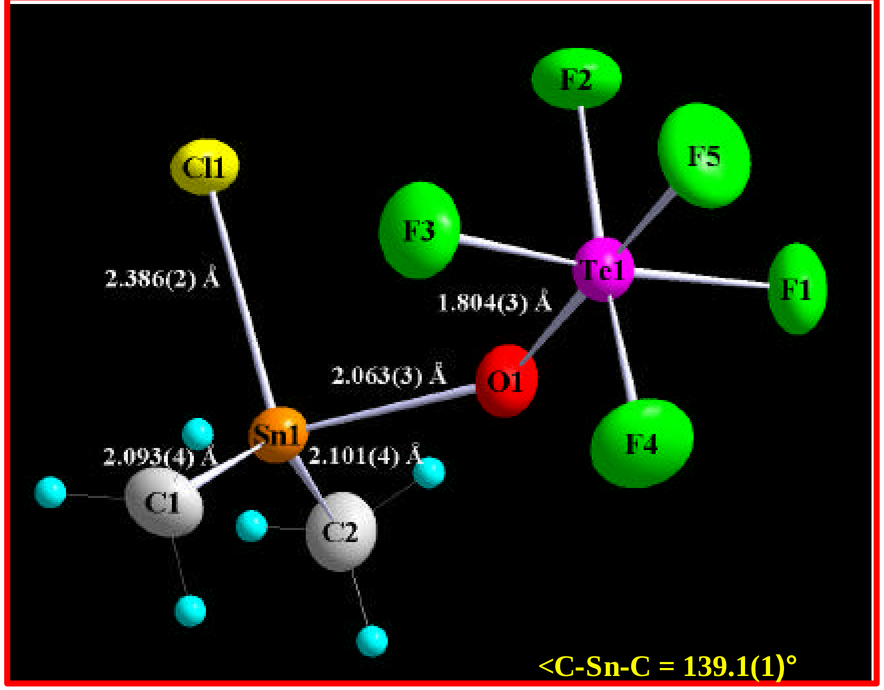


$$(CH_3)_3SnCl + HOTeF_5 \xrightarrow{-\ CH_4} (CH_3)_2Sn(Cl)(OTeF_5)$$

$$(CH_3)_3SnCl + ClOTeF_5 \xrightarrow{-\ CH_3Cl} (CH_3)_2Sn(Cl)(OTeF_5)$$

**According to Sladky and Kropshofer (*JCS Chem. Commun.*, 1973, 600), reaction of $(CH_3)_3SnCl$ with $HOTeF_5$ gives trimethyltin(IV) teflate exclusively!**

# Structure of $(CH_3)_2Sn(Cl)OTeF_5$



**Unit cell dimensions (Å)**

**Monoclinic $P2_1/n$**

**$a$ =5.8204(8), b = 10.782(1),**

**c = 15.493(2)**

**ß = 99.59(1) °**

**Volume ($Å^3$) = 971.7(2)**

**Z = 4**

***T = 218(2) K***

**$R1$ = 0.0282**

**$wR2$ = 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)**

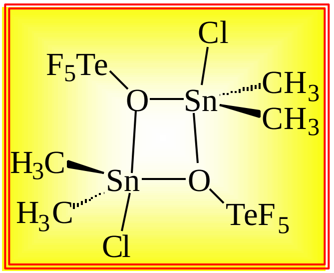
**Strauss et al., *Inorg. Chem*., 1986, *25*,** 2806 ***and references therein***

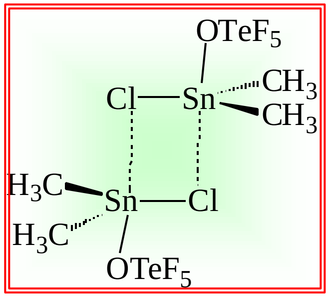
**n(TeO) = 856 $cm^{-1}$ in IR and Ra; n(SnO) = 427 (IR)/424 (Ra) $cm^{-1}$; n(SnCl) = 313 (Ra) $cm^{-1}$**

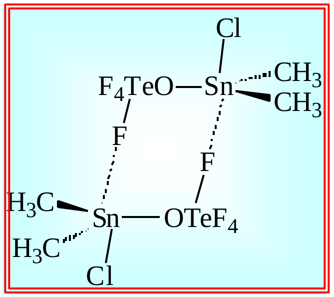
# *Tetra- or pentacoordinated tin???*

**The C-Sn-C angle calculated using $^{2}J(^{119}Sn-^{1}H)$ (67.9 Hz) and $^{1}J(^{119}Sn-^{13}C)$ (472 Hz) coupling constants for $(CH_3)_2SnCl(OTeF_5)$ dissolved in $CD_2Cl_2$ is approximately ~118º. The $d(^{119}Sn)$ 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 $Me_2SnCl(OTeF_5)$ molecule .**

**$^{119}Sn$ 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.**

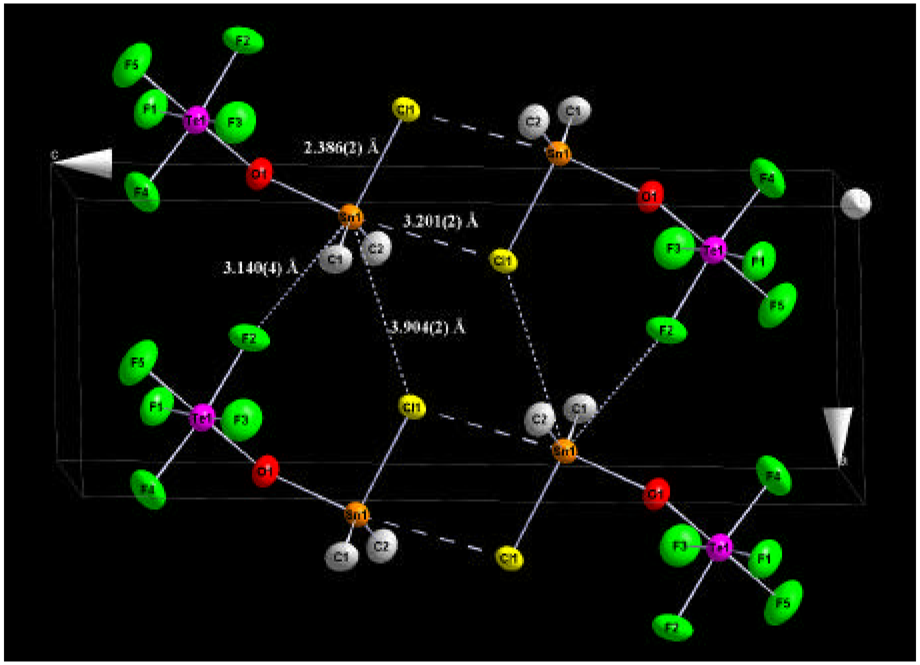


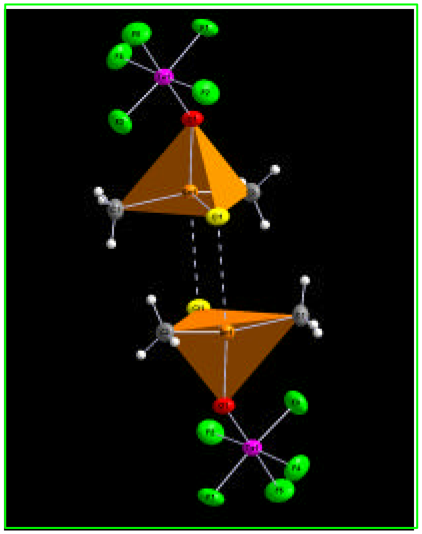




# Coordination environment around tin

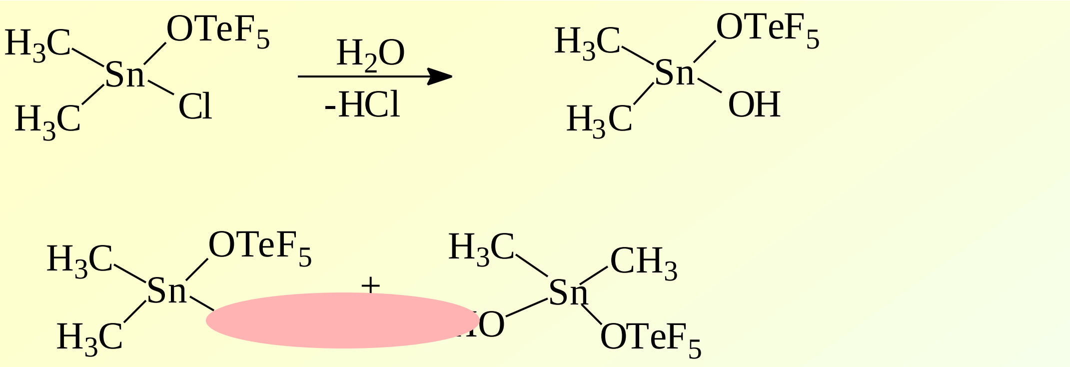
**Sn-Cl contact = 3.201(1) Å**
**Much shorter than the sum of van der Waal radii of tin and chlorine.**
**A longer Sn-Cl contact is also present at 3.904(2) Å.**
**S(vdWSn + vdWCl) = 2.17 + 1.75 = 3.92 Å**

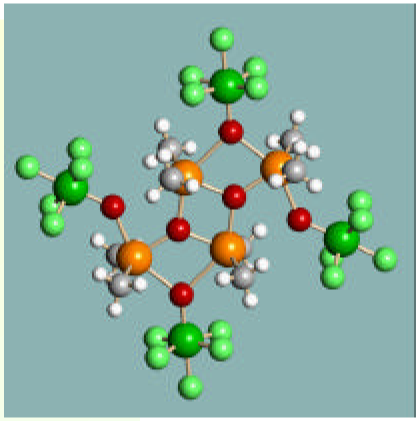


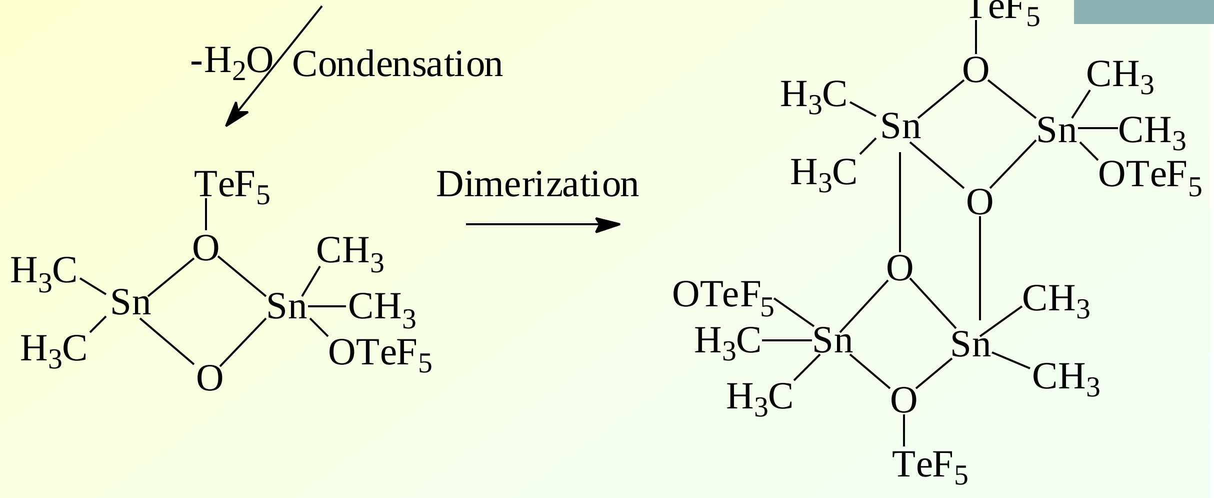


**One Sn-F contact is also found in the crystal lattice 3.140(4) Å, which is much shorter than the sum of van der Waal radii of tin and fluorine.**
**S(vdWSn + vdWF)**
**= 2.17 + 1.47 = 3.64 Å**

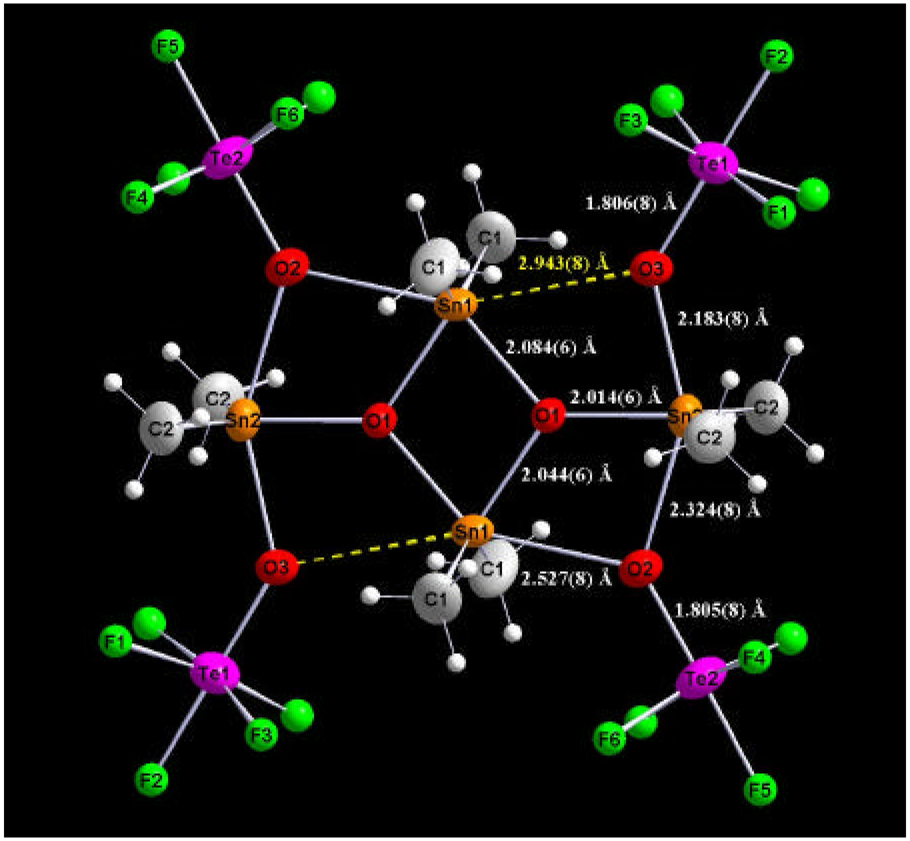
# Hydrolysis of the Sn-Cl bond in $(CH_3)_2Sn(Cl)OTeF_5$







# *Structure of the dimethyloxotin(IV) teflate*



**Unit cell dimensions (Å)**

**Orthorhombic**

**Space Group: *Pnnm***

**$a$ =12.574(6), b = 12.667(6),**

**c = 11.682(5)**

**Volume (Å$^3$) = 1860.6(1)**

**Z = 2**

***T* = 243 K**

***R*1 = 0.0376**

***wR*2 = 0.1021**

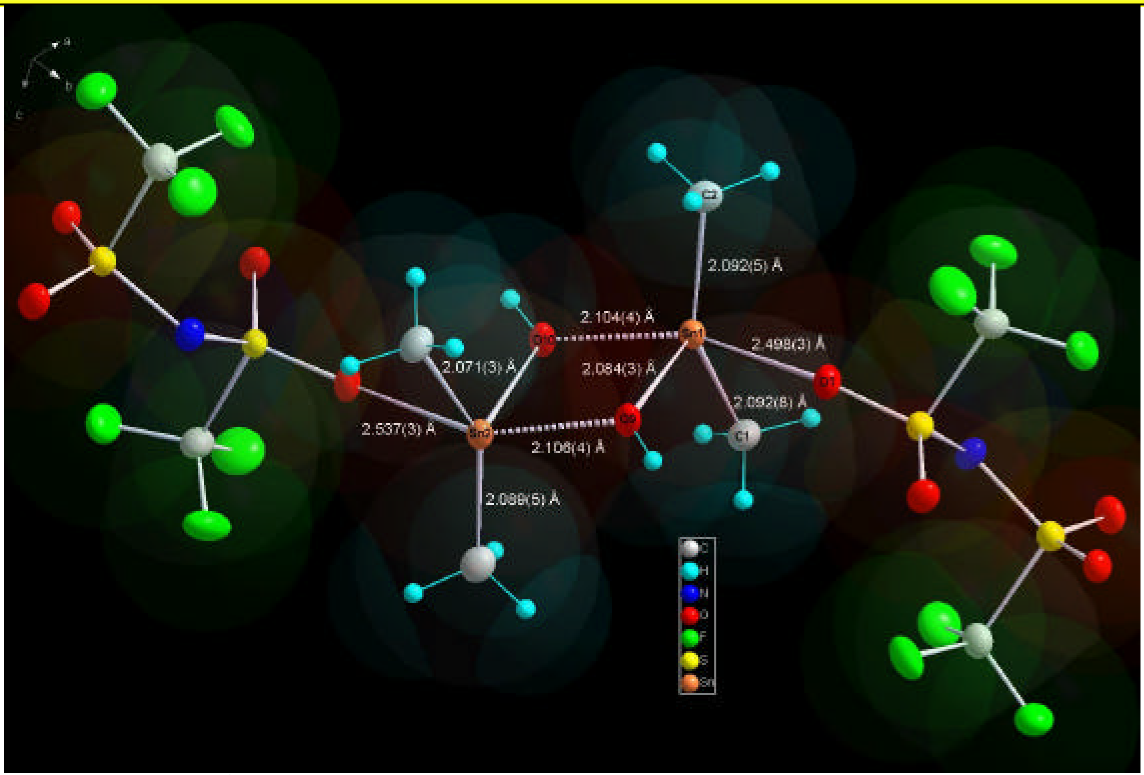
***S* = 1.04**

**S (vdWSn + vdWO) = 2.17 + 1.52**

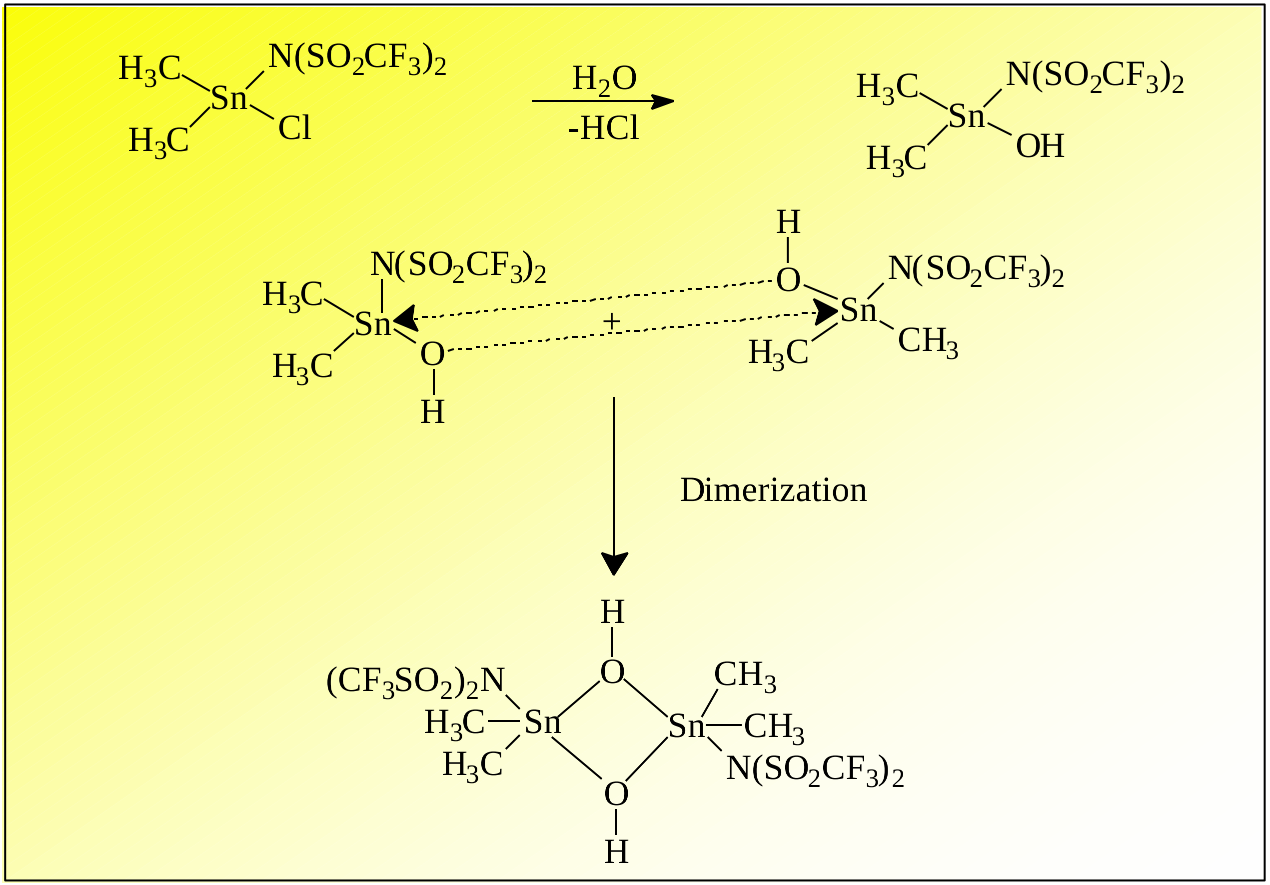
**= 3.69 Å**

# Reaction of the hydrated silver salt with $(CH_3)_2SnCl_2$

$$(CH_3)_2SnCl_2 + AgN(SO_2CF_3)_2.C_6H_6.H_2O \longrightarrow (CH_3)_2Sn(Cl)N(SO_2CF_3)_2 + C_6H_6 + H_2O$$



# Formation of $Me_2Sn(OH)N(SO_2CF_3)_2$



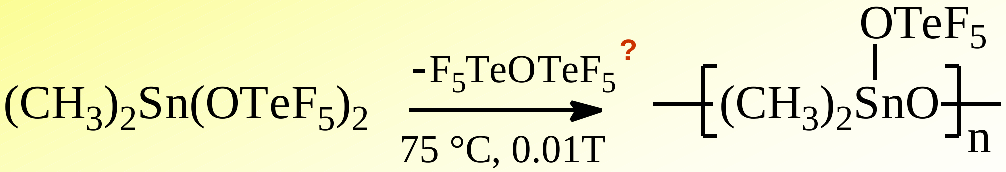
# *Solvolysis of $Me_4Sn$ in excess acid: Synthesis of dimethyltin(IV) teflate*

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

$$(CH_3)_4Sn \;+\; \text{xs } HOTeF_5 \xrightarrow[60\ °C,\ 40h]{-\ 2\ CH_4} (CH_3)_2Sn(OTeF_5)_2$$

**MS shows $[M\text{-}CH_3]^+$ peak**

✓ **Upon sublimation ~75 °C/0.01T a polymeric species is formed, probably due to the loss of $O(TeF_5)_2$**



$$(CH_3)_2Sn(OTeF_5)_2 \xrightarrow[75\ °C,\ 0.01T]{-F_5TeOTeF_5\ ?} \left[ (CH_3)_2\overset{\overset{\displaystyle OTeF_5}{|}}{Sn}O \right]_n$$

n(TeO) = **877 $cm^{-1}$** ; n(SnO) = **434 (IR) $cm^{-1}$**; $n_{as}$ **(SnC) = 591 $cm^{-1}$**, $n_s$ **(SnC) = 531 $cm^{-1}$**

# *Structure of dimethyltinooxteflate*

**Unit cell dimensions (Å)**

**Monoclinic $P2_1/n$**

***Rotational TWIN***

**$a$ =7.510(6), b = 15.729(12),**

**c = 8.119(7)**

**ß = 115.1(1) °**

**Volume (Å$^3$) = 876.7(12)**

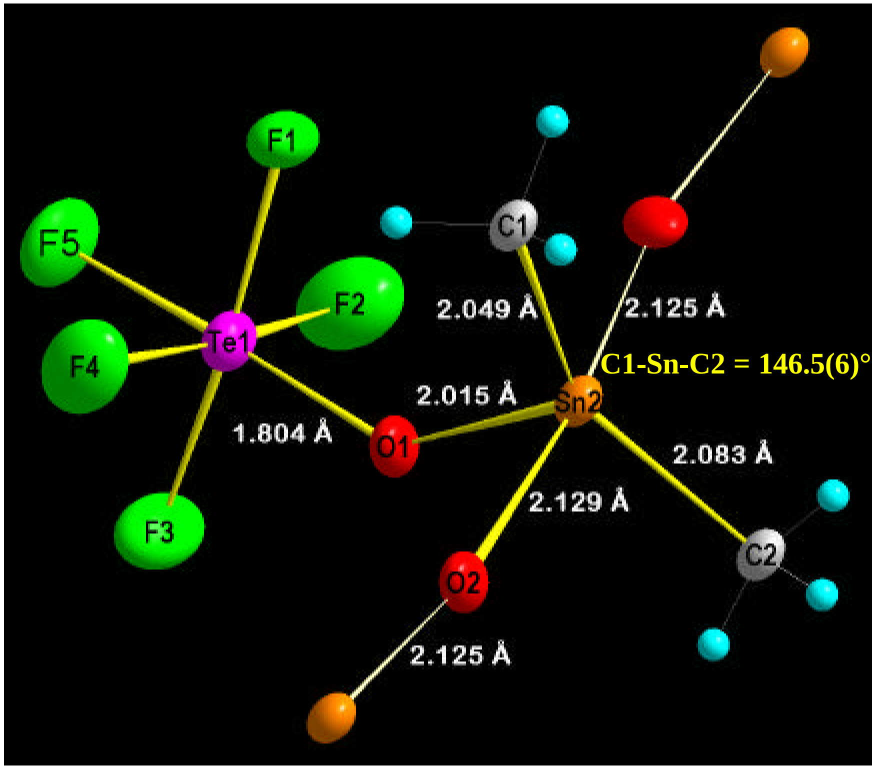
**Z = 4**

***T = 233(2) K***

**$R1$ = 0.1028**

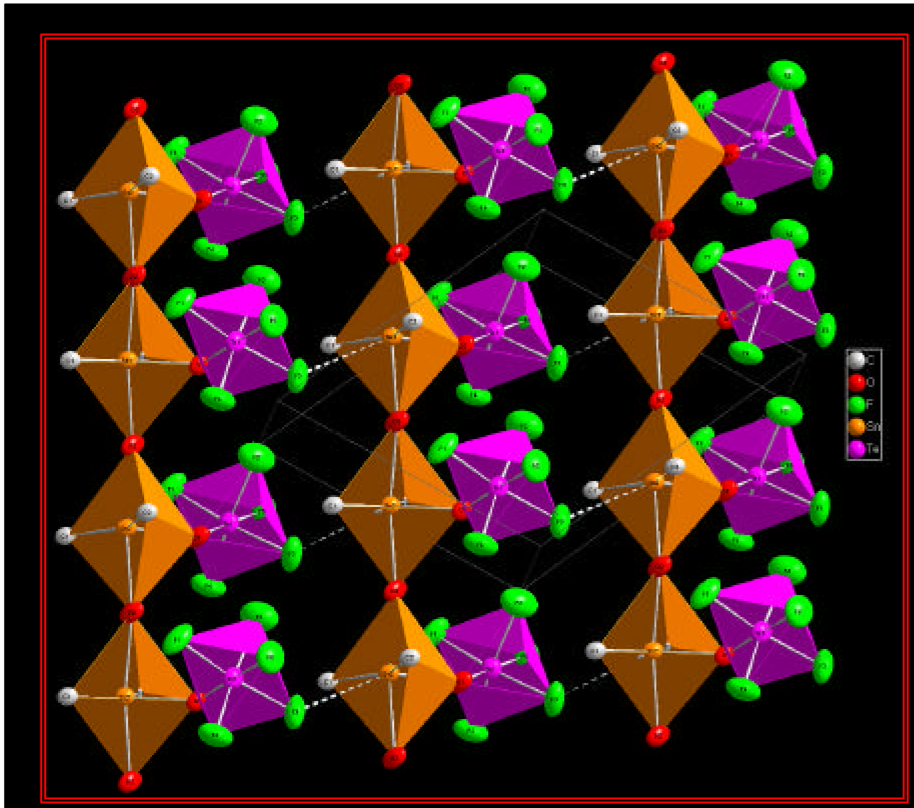
**$S$ = 1.84**

**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 Å**

**Sn-F distance in the crystal packing = 3.107(16) Å**

**The structure shows polymeric Sn-O chains bridged by a fluorine atom of the $OTeF_5$ group.**

**<Sn-O2-Sn* = 167.2°**

**(Sn* = ½ +x, ½ -y, ½ + 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 $Me_3Sn$ (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 $HOTeF_5$, 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.

# *Acknowledgments*

Dr. Karl Christe (AFRL/USC)

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Dr. Ronald Channell (AFRL)

Mr. Michael Huggins (AFRL)

FUNDING

AFOSR AFRL

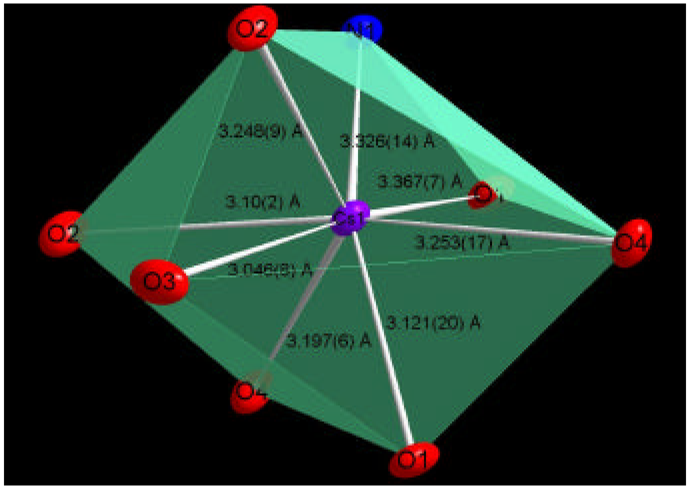
# BACKUP/SUPPL. SLIDES

# BACKUP

# Coordination environment of Cs in $CsN(SO_2CF_3)_2$ salts

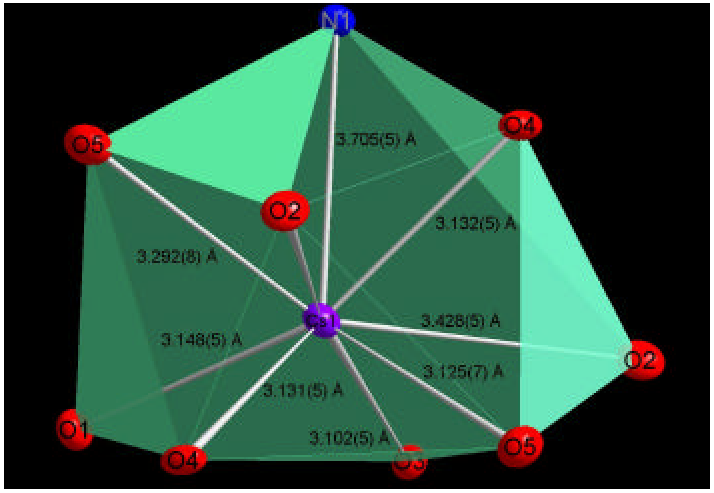
## $CsN(SO_2CF_3)_2$

**Octa-coordinated with a short Cs-N bond**



## $CsN(SO_2CF_3)_2$•$H_2O$

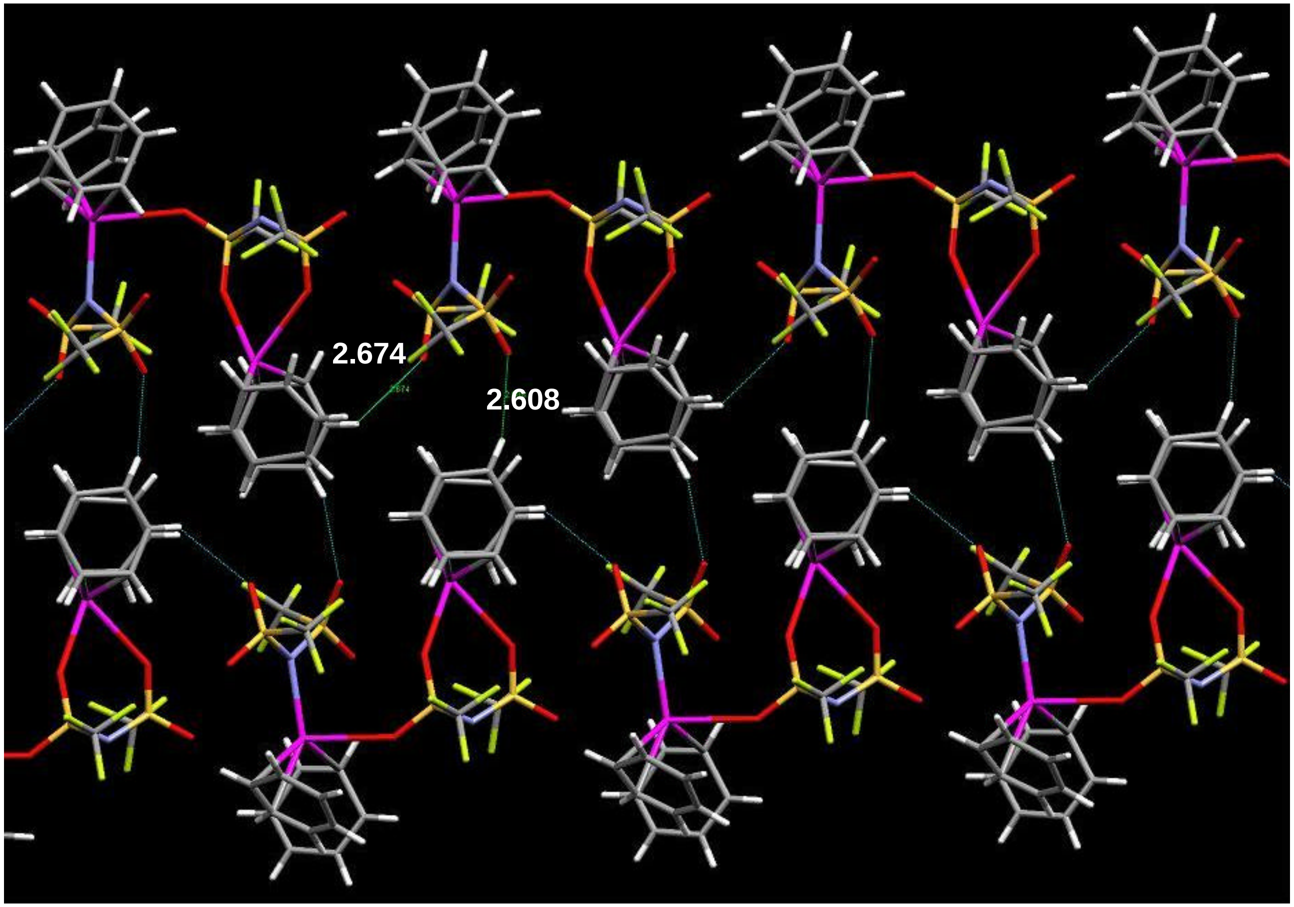
**Nona-coordinated with a long Cs-N bond**



**$CsN(SO_2CF_3)_2$ is reported to be ten-coordinated**

**DesMarteau, Pennington *et al*., Soild State Sciences, 2002, *4*, 1535-1545**

# Crystal packing in $[AgN(SO_2CF_3)_2(C_6H_6)_2]$



# Bond distances and angles $Me_2SnClOTeF_5$

| | |
|---|---|
| Sn(1)-C(2) | 2.104(4) |
| Sn(1)-C(1) | 2.115(4) |
| Sn(1)-C(3) | 2.120(4) |
| Sn(1)-O(1) | 2.306(3) |
| Sn(1)-O(2) | 2.335(3) |
| S(1)-O(3) | 1.427(2) |
| S(1)-O(4) | 1.428(3) |
| S(1)-N(1) | 1.573(3) |
| S(1)-C(4) | 1.825(5) |
| S(2)-O(6) | 1.421(3) |
| S(2)-O(5) | 1.433(3) |
| S(2)-N(1) | 1.589(3) |
| S(2)-C(5) | 1.844(4) |

| | |
|---|---|
| C(2)-Sn(1)-C(1) | 117.8(2) |
| C(2)-Sn(1)-C(3) | 120.1(2) |
| C(1)-Sn(1)-C(3) | 122.1(2) |
| C(2)-Sn(1)-O(1) | 89.83(15) |
| C(1)-Sn(1)-O(1) | 92.3(2) |
| C(3)-Sn(1)-O(1) | 87.19(13) |
| C(2)-Sn(1)-O(2) | 91.04(15) |
| C(1)-Sn(1)-O(2) | 90.8(2) |
| C(3)-Sn(1)-O(2) | 88.95(13) |
| O(1)-Sn(1)-O(2) | 175.94(11) |
| O(3)-S(1)-O(4) | 118.5(2) |
| O(3)-S(1)-N(1) | 107.6(2) |
| O(4)-S(1)-N(1) | 116.1(2) |
| O(3)-S(1)-C(4) | 104.0(2) |
| O(4)-S(1)-C(4) | 105.4(2) |
| O(6)-S(2)-O(5) | 118.2(2) |
| O(6)-S(2)-N(1) | 109.0(2) |
| O(5)-S(2)-N(1) | 115.3(2) |
| O(6)-S(2)-C(5) | 104.7(2) |
| O(5)-S(2)-C(5) | 105.0(2) |
| S(1)-N(1)-S(2) | 125.3(2) |