

**Effect of Ligand Coordination on Complex Formation:  
Synthesis & Structural Studies of metal(I) salts  
containing the  $\text{N}(\text{SO}_2\text{CF}_3)_2$  and  $\text{OTeF}_5$  groups**



**Ashwani Vij**  
**Air Force Research Laboratory**  
**PRSP**  
**ashwani.vij@edwards.af.mil**  
**(661) 275-6278**

**Award Symposium for Dr. Surya Prakash-227th National ACS Meeting, New York, March 29, 2004**

**Distribution Statement A: Approved for public release; distribution unlimited**

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>23 MAR 2004</b>	2. REPORT TYPE		3. DATES COVERED -		
4. TITLE AND SUBTITLE <b>Effect of Ligand Coordination on Complex Formation: Synthesis &amp; Structural Studies of metal(I) salts</b>			5a. CONTRACT NUMBER <b>F04611-99-C-0025</b>		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) <b>Ashwani Vij; Vandana Vij; William Wilson; Fook Tham</b>			5d. PROJECT NUMBER <b>2303</b>		
			5e. TASK NUMBER <b>M2C8</b>		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>ERC Incorporated,555 Sparkman Drive,Huntsville,AL,35816-0000</b>			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>The original document contains color images.</b>					
14. ABSTRACT <b>The šcisoidŠ form is less common. In the CCDC, only 6 structures show this conformation where as the štransiodŠ form occurs in 15 remaining structures The šcisoidŠ conformation results from stronger cation-anion interaction The šcisoidŠ exclusively when anion is chelated to the metal center The štransoidŠ form dominates in structures containing a šfreeŠ anion NO structure known with both šcisoidŠ AND štransoidŠ geometry</b>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES <b>39</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			



## *Coworkers & Collaborators*



### **Ms. Vandana Vij and Dr. William W. Wilson**

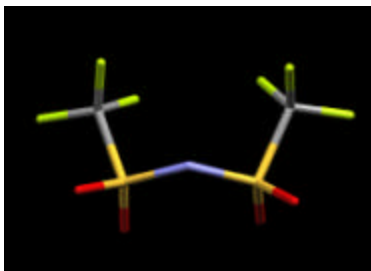
Air Force Research Laboratory, PRSP, Bldg 8451, 10 E. Saturn Blvd. Edwards Air Force Base,  
CA 93524

### **Dr. Fook S. Tham**

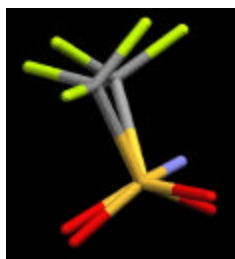
Department of Chemistry, University of California, Riverside CA 92521



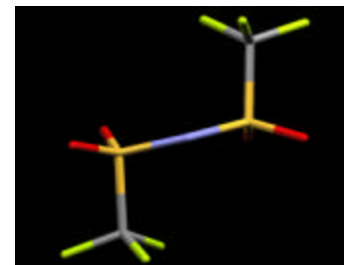
## Coordination & isomerism in $N(\text{SO}_2\text{CF}_3)_2$



**“Cisoid”**



**C-S--S-C  
“torsion”**



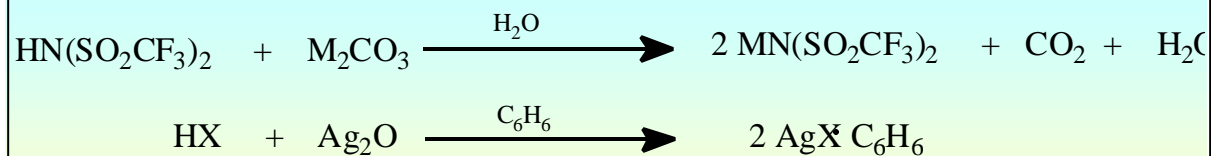
**“Transoid”**

- ✓ The “cisoid” form is less common. In the CCDC, only 6 structures show this conformation where as the “transoid” form occurs in 15 remaining structures
- ✓ The “cisoid” conformation results from stronger cation-anion interaction
- ✓ The “cisoid” exclusively when anion is chelated to the metal center
- ✓ The “transoid” form dominates in structures containing a “free” anion
- ✓ NO structure known with both “cisoid” AND “transoid” geometry

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



## Synthesis of metal(I) derivatives



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

$\nu_{\text{Te-O}}$  ( $\text{cm}^{-1}$ ): IR (Ra) at ~865 (860)

$\nu_{\text{as SO}_2}$  ( $\text{cm}^{-1}$ ): 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: ~-78 ppm ( $\text{CF}_3$ )

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

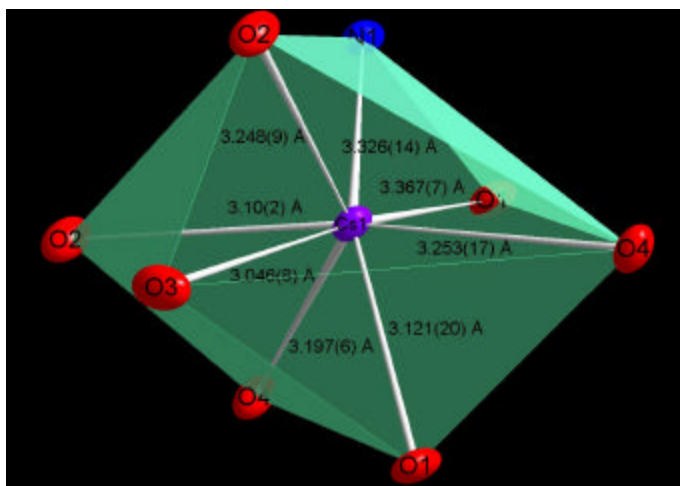




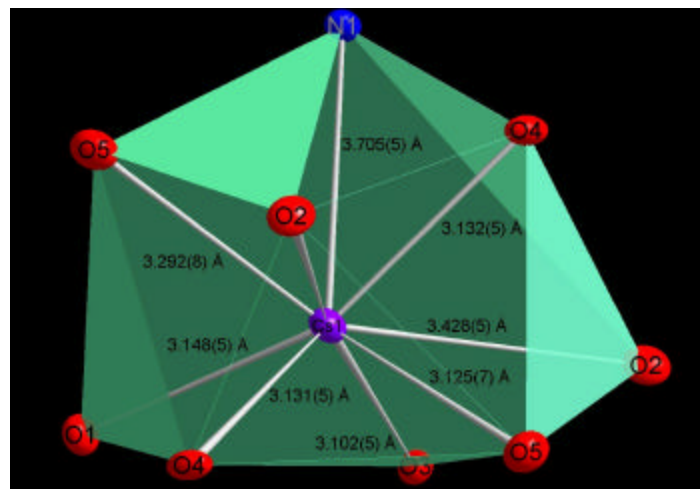
# Coordination environment of Cs in $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



Octa-coordinated with a short Cs-N bond



Nona-coordinated with a long Cs-N bond

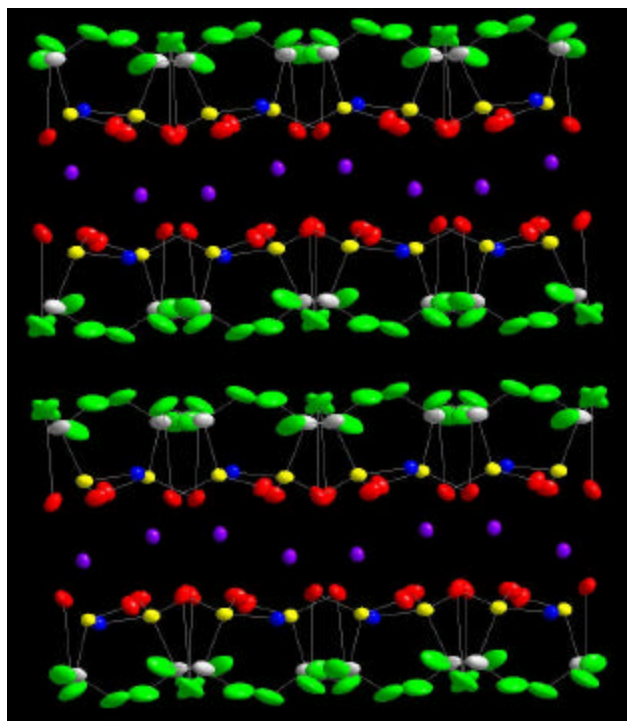




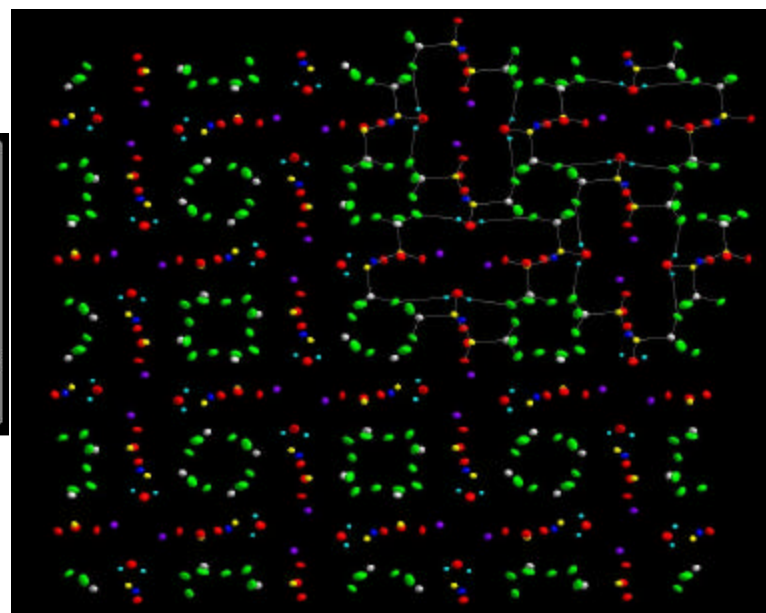
# Crystal packing in $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



Hydrophobic and hydrophilic Layering



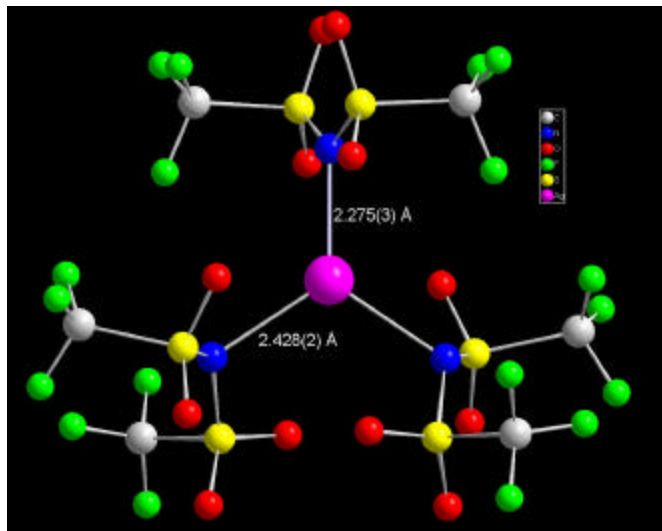
“Swiss cheese” Tunnel/channel structure







# Polymorphism in $\text{AgN}(\text{SO}_2\text{CF}_3)_2$



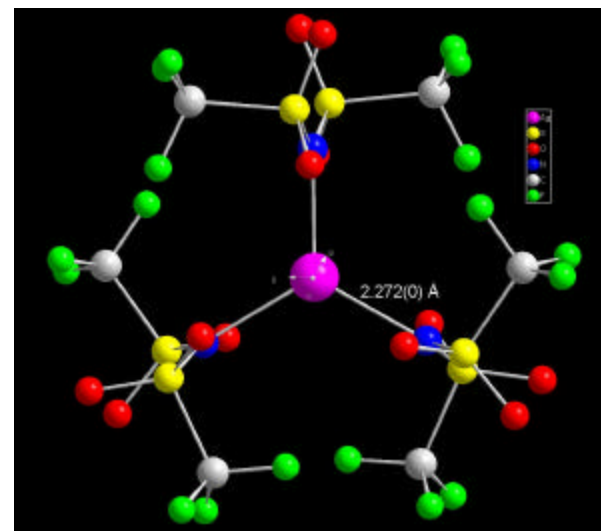
## Unit cell dimensions (Å)

Orthorhombic  $P2_1/n$

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

Volume (Å<sup>3</sup>) = 876.7(12),  $Z = 4$ ,  $T = 298\text{ K}$

$R1 = 0.1028$ ,  $S = 1.84$



## Unit cell dimensions (Å)

Trigonal  $P-3_1c$

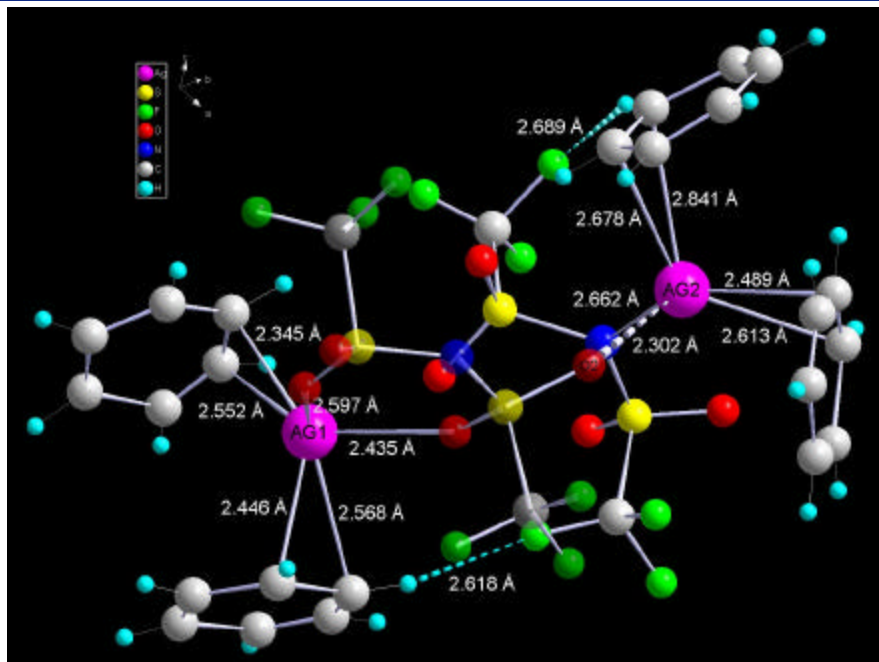
$a = 7.510(6)$ ,  $c = 8.119(7)$

Volume (Å<sup>3</sup>) = 876.7(12),  $Z = 6$ ,  $T = 298\text{ K}$

$R1 = 0.1028$ ,  $S = 1.84$



## Structure of $[AgN(SO_2CF_3)_2(C_6H_6)_2]$



### Triclinic $P-1$

$a = 7.6704(13) \text{ \AA}$ ,  $b = 8.4295(14) \text{ \AA}$ ,  $c = 8.8631(15) \text{ \AA}$ ,

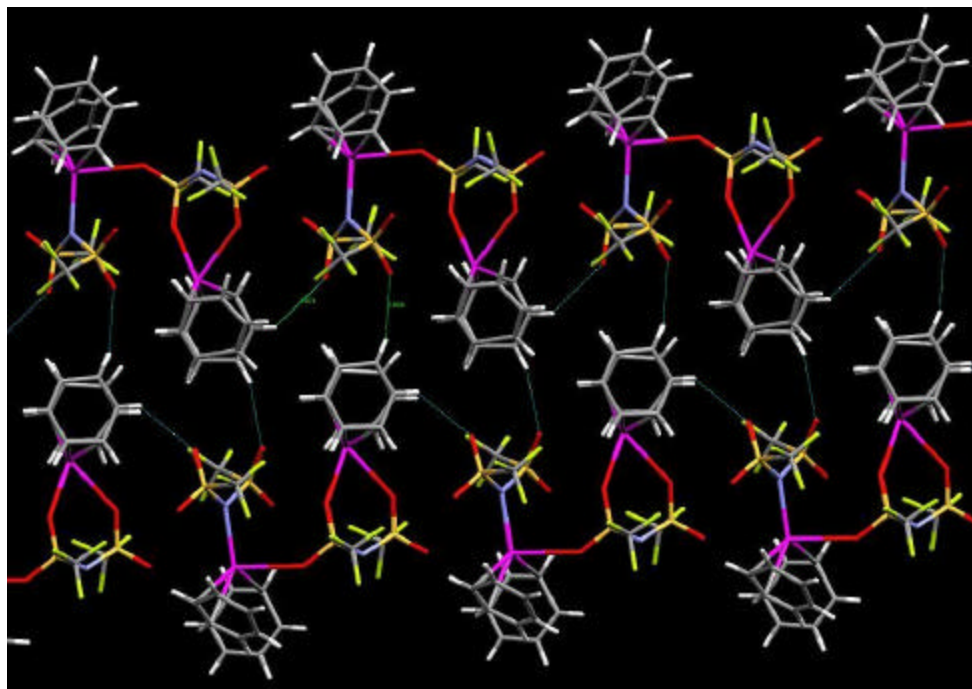
$\alpha = 111.673(3)^\circ$ ,  $\beta = 108.479(3)^\circ$ ,  $\gamma = 97.798(3)^\circ$

$V (\text{ \AA}^3) = 483.89(14)$ ,  $Z = 2$ ,  $T = 298(2) \text{ K}$ ;  $R1 = 0.0432$ ,  $S = 1.114$

- ✓ Dimerization via S-O...Ag bonding (2.302 Å)
- ✓ Long unsymmetrical Ag-C bonds
- ✓  $N(SO_2CF_3)_2$  group is “transoid”
- ✓ H...F bond distances observed close to sum of van der Waal distance

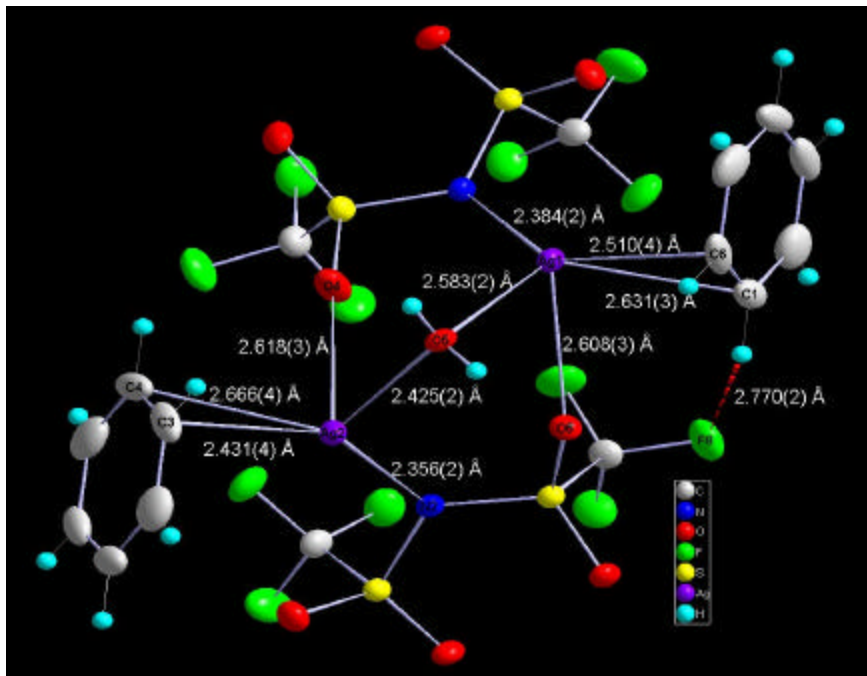


# Crystal packing in $[AgN(SO_2CF_3)_2(C_6H_6)_2]$





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



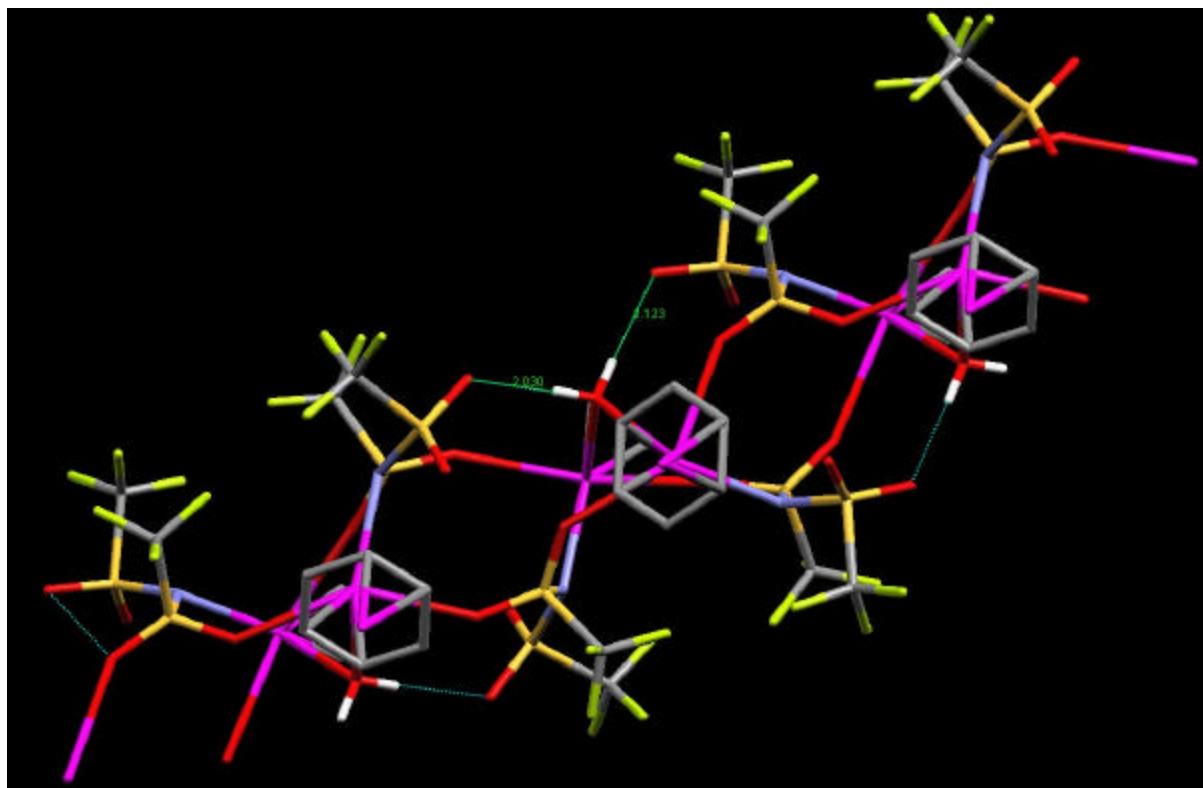
Monoclinic  $P2_1/n$

$a = 10.372(1) \text{ \AA}$ ,  $b = 19.823(2) \text{ \AA}$ ,  $c = 12.406(1) \text{ \AA}$ ,  $\beta = 108.536(3)^\circ$ ,  
 $V (\text{ \AA}^3) = 2148.5(5)$ ,  $Z = 8$ ,  $T = 173(1) \text{ K}$ ;  $R1 = 0.0224$ ,  $S = 1.04$

- ✓  $N(SO_2CF_3)_2$  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
- ✓  $N(SO_2CF_3)_2$  group is "cisoid"
- ✓ H...F bond distances observed close to sum of van der Waal distance



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



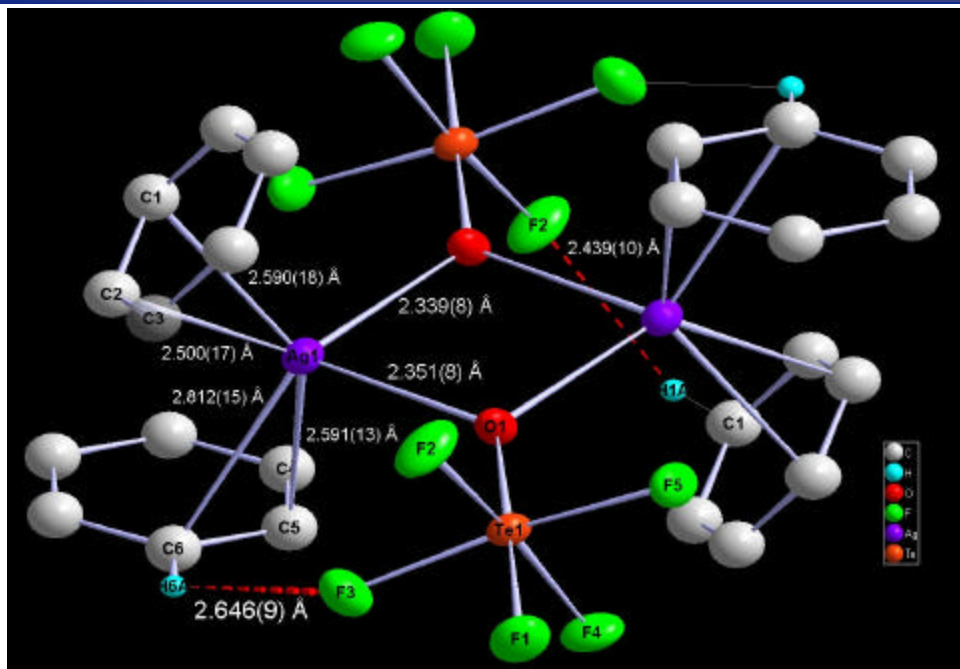
March 29, 2004

Award Symposium for Dr. Surya Prakash, 227<sup>th</sup> ACS National Meeting, Anaheim  
Distribution A: Approved for public release; distribution unlimited

12



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



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

### Triclinic $P-1$

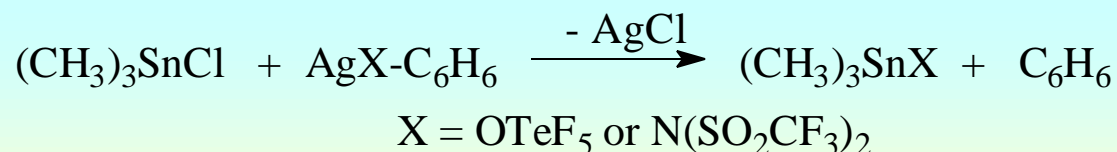
$a = 7.6704(13) \text{ \AA}$ ,  $b = 8.4295(14) \text{ \AA}$ ,  $c = 8.8631(15) \text{ \AA}$ ,

$\alpha = 111.673(3)^\circ$ ,  $\beta = 108.479(3)^\circ$ ,  $\gamma = 97.798(3)^\circ$

$V (\text{ \AA}^3) = 483.89(14)$ ,  $Z = 2$ ,  $T = 298(2) \text{ K}$ ;  $R1 = 0.0432$ ,  $S = 1.114$



## Reaction of silver salts: Synthesis of trimethyltin(IV) derivatives



MS shows [M-CH<sub>3</sub>]<sup>+</sup> peak

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

nTe-O (cm<sup>-1</sup>): IR (Ra) at 860 (856)

nSn-C (cm<sup>-1</sup>) IR (Ra): asym: 552 (554); sym 518 (518)

n<sub>as</sub>SO<sub>2</sub> (cm<sup>-1</sup>): IR (Ra) at 1342(1327)

nSn-C (cm<sup>-1</sup>) IR (Ra): asym: 558 (556); sym 520 (513)

nTe-O (cm<sup>-1</sup>) F<sub>5</sub>TeOCl: IR (Ra) at 551 (554); nTe-O (cm<sup>-1</sup>) F<sub>5</sub>TeOTBA: IR (Ra) at 867 (866);

- ✓ Trimethyltin(IV) derivatives are colorless viscous oils.
- ✓ Highly moisture sensitive
- ✓ Potentially stronger catalysts in organic synthesis compared to TMSOTf





## ***What is so interesting about $(\text{CH}_3)_3\text{Sn}$ derivatives of strong acids??***



- ✓ **The Sn-C bond cleavage can be selective i.e., there is a competition between Sn-C and Sn-Cl bond cleavage depending upon the acid used.**
  - ✓ **The trimethyltin(IV) derivatives of strong acids are extremely electrophilic reagents that have application in organic synthetic reactions.**
- 
- ✓ **The electrophilic nature of an organotin(IV) compound can be reflected by its  $^{119}\text{Sn}$  chemical shift i.e, deshielding.  $^{119}\text{Sn}$  has a spin of  $\frac{1}{2}$ , relative abundance of 8.58 % and has high relative sensitivity (30x  $^{13}\text{C}$ ).**
  - ✓ **Can  $^{119}\text{Sn}$  chemical shifts (in neat liquids or as a solution in “low-coordinating” solvents) be correlated to anion basicities in case of trimethyltin(IV) derivatives?**





## Correlating spectroscopy and crystallography



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

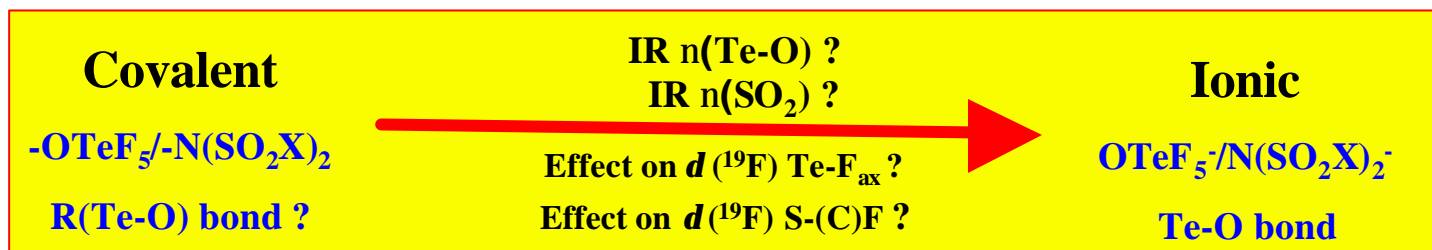
$$T(\text{C-Sn-C})^\circ = 0.0161 |^2J(^{119}\text{Sn}-^1\text{H})|^2 - 1.32 |^2J(^{119}\text{Sn}-^1\text{H})| + 133.4$$

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

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

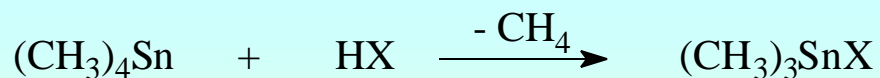
Lockhart, T. P.; Manders, W. F. *Inorg. Chem.* 1985, 25, 892

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





## Synthesis of trimethyltin(IV) derivatives



X = OTeF<sub>5</sub> or N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>

MS shows [M-CH<sub>3</sub>]<sup>+</sup> peak

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

nTe-O (cm<sup>-1</sup>): IR (Ra) at 860 (856)

nSn-C (cm<sup>-1</sup>) IR (Ra): asym: 552 (554); sym 518 (518)

n<sub>as</sub>SO<sub>2</sub> (cm<sup>-1</sup>): IR (Ra) at 1342(1327)

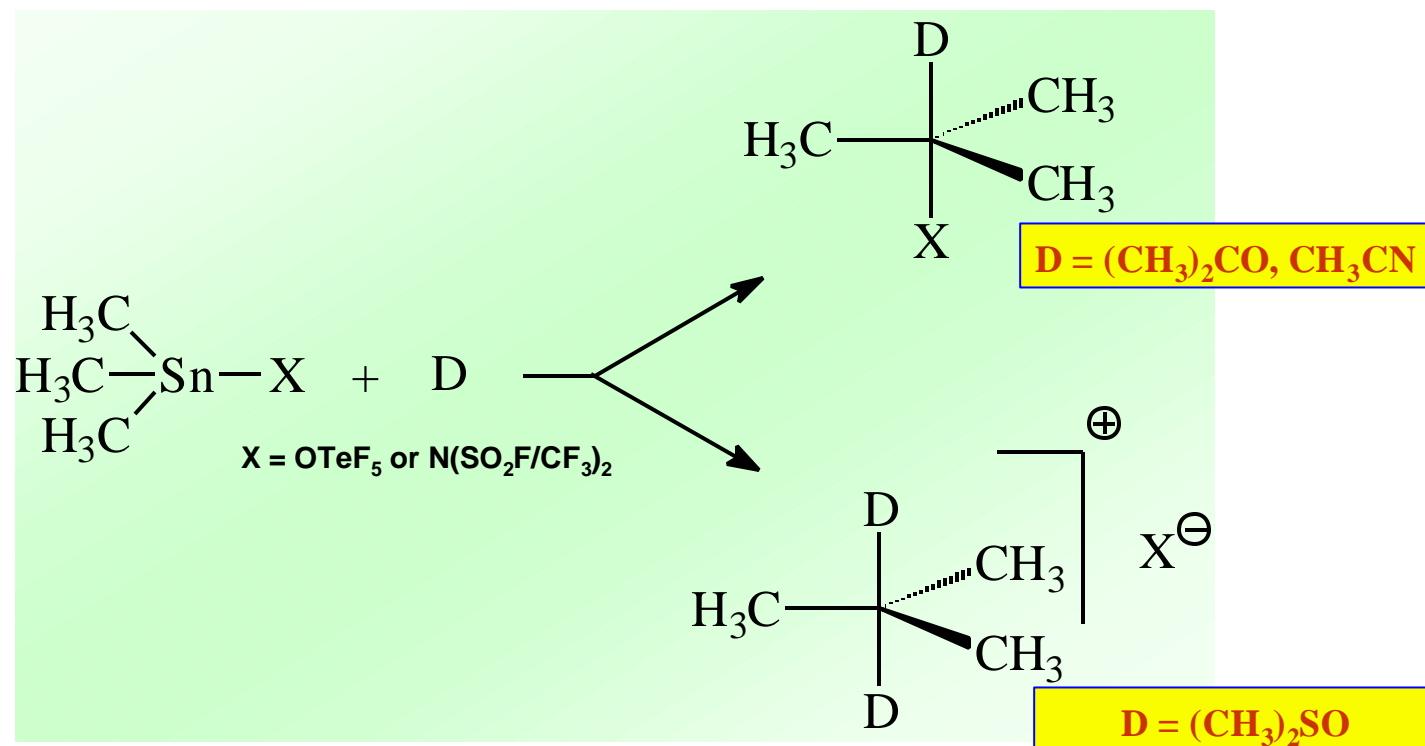
nSn-C (cm<sup>-1</sup>) IR (Ra): asym: 558 (556); sym 520 (513)

nTe-O (cm<sup>-1</sup>) F<sub>5</sub>TeOCl: IR (Ra) at 551 (554); nTe-O (cm<sup>-1</sup>) F<sub>5</sub>TeOTBA: IR (Ra) at 867 (866);

- ✓ Tetramethyltin is used in large excess
- ✓ Reaction by-products can be easily removed under vacuum
- ✓ Trialkyltin(IV) derivatives are colorless viscous oils that are highly sensitive to moisture and donor solvents.

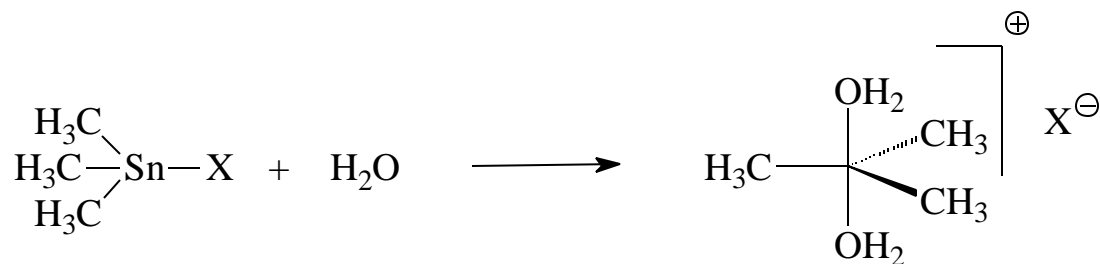


## Coordination complex formation with donor solvents

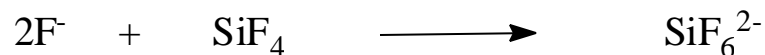
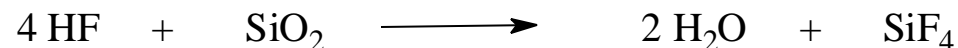
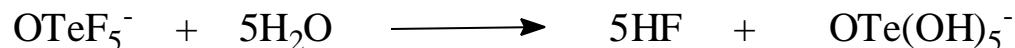




## Formation of the hydrated trimethylstannyl cation



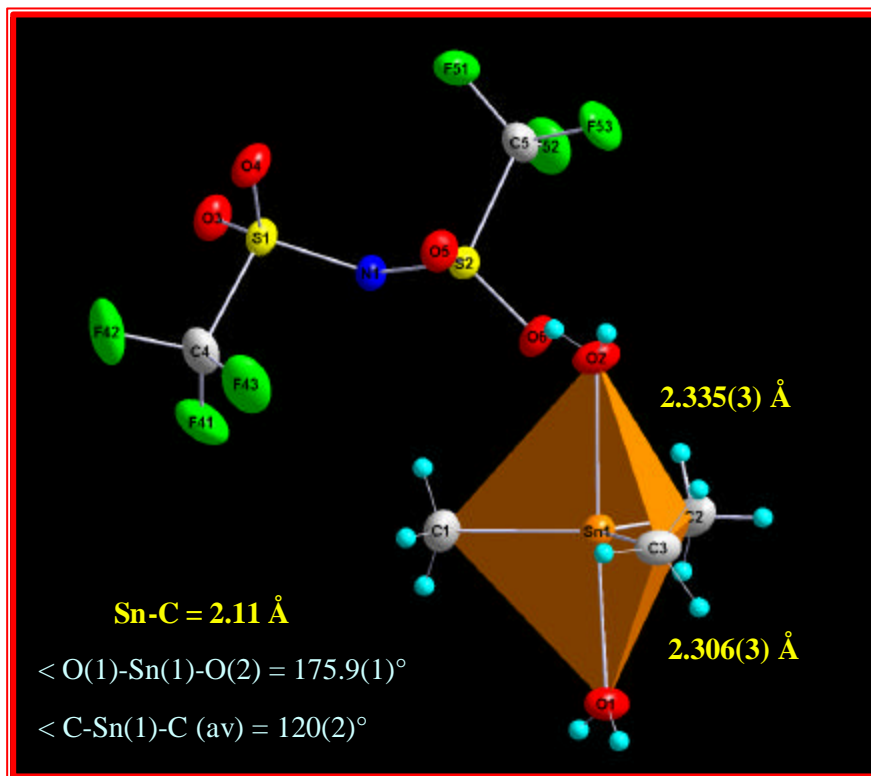
The hydrated salt can be isolated with  $\text{N}(\text{SO}_2\text{CF}_3)_2$  anion but **NOT** for  $\text{OTeF}_5$  anion.  
The compound isolated after hydrolysis is  $[\text{Me}_3\text{Sn}(\text{OH}_2)_2]_2\text{SiF}_6$



The hydrolysis of trimethyltin teflate results in the decomposition of the  $\text{OTeF}_5$  group



# Hydrated trimethyltin(IV) cation



## Unit cell dimensions (Å)

Monoclinic ( $P2_1/c$ )

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

$c = 16.821(2)$

$\beta = 98.705(1)^\circ$

Volume (Å<sup>3</sup>) = 1636.0(3) ,

$Z = 4$

$T = 213(2)$

$R1 = 0.0367$

$wR2 = 0.0736$

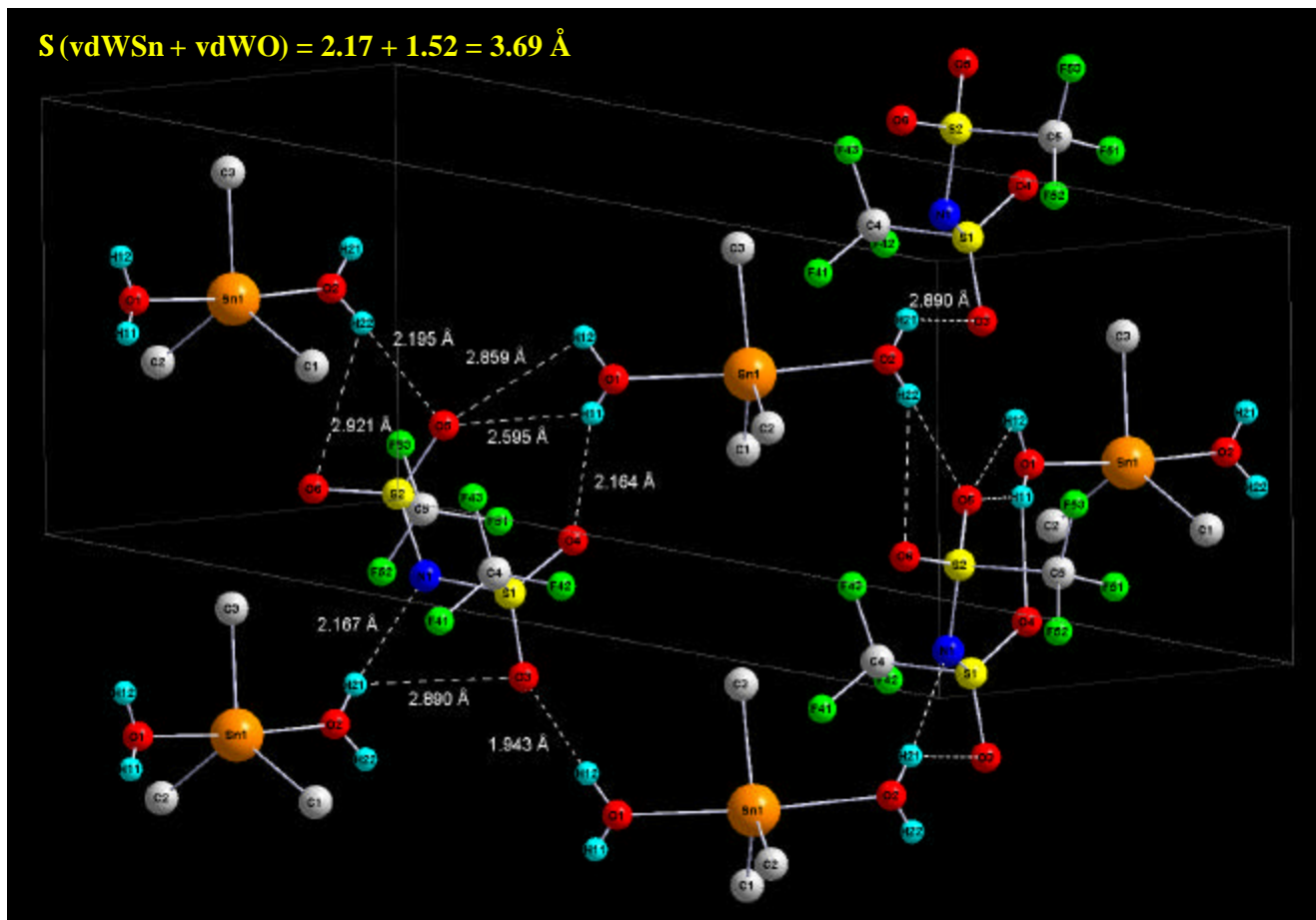
$S = 1.233$



## Hydrogen bonding in hydrated trimethyltin(IV) cations



$$S(\text{vdWSn} + \text{vdWO}) = 2.17 + 1.52 = 3.69 \text{ \AA}$$



March 29, 2004

Award Symposium for Dr. Surya Prakash, 227<sup>th</sup> ACS National Meeting, Anaheim  
Distribution A: Approved for public release; distribution unlimited

21



# Multinuclear NMR Parameters

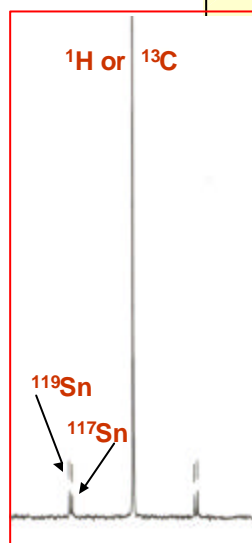


Table 1.  $^1\text{H}$ ,  $^{13}\text{C}$  NMR Spectroscopic Data<sup>a</sup> and calculated<sup>b,c</sup> C-Sn-C angles for  $(\text{CH}_3)_3\text{SnX}$  [X =  $\text{OTeF}_5$  and  $\text{N}(\text{SO}_2\text{F}/\text{CF}_3)_2$ ]

Solute	Solvent <sup>d</sup>	$\delta(^1\text{H})$ ppm	$^2J(^{119}(\text{Sn})-^1\text{H})$ Hz	$\theta(\text{C-Sn-C})^b$ ( $^\circ$ )	$\delta(^{13}\text{C})$ ppm	$^1J(^{119}(\text{Sn})-^{13}\text{C})$ Hz	$\theta(\text{C-Sn-C})^c$ ( $^\circ$ )
$(\text{CH}_3)_3\text{SnOTeF}_5$	neat	0.84	59.2 <sup>e</sup>	111.7	0.84	376.9(360.3)	109.8
	$\text{CH}_2\text{Cl}_2$	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
	$\text{CH}_3\text{CN}$	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
$(\text{CH}_3)_3\text{SnOTeF}_5$	AN/ $\text{H}_2\text{O}$	0.46	69.6(66.7)	119.5	0.10	508.5(486.0)	121.4
	DMSO/ $\text{H}_2\text{O}$	0.43	70.1(68.5) <sup>e</sup>	120.0	0.84	515.5(492.5)	122.0
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$	neat	0.91	63.8(61.6)	114.7	1.6	416.8(400.3)	113.3
	$\text{CH}_2\text{Cl}_2$	0.96	62.3(59.9)	113.6	1.4	404.1(387.7)	112.2
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$	DMSO	0.83	72.4(70.0)	122.2	-0.2	528.3(509.9)	123.1
	neat	0.84	64.2(61.6)	115.0	2.1	412.6(394.1)	113.0
	$\text{CH}_2\text{Cl}_2$	0.81	64.4(61.8)	115.2	0.8	414.8(395.2)	113.0
	$\text{CH}_3\text{CN}$	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
$[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$	$\text{CH}_3\text{CN}$	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

<sup>a</sup> NMR spectroscopic data were recorded at 300 K.

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

<sup>c</sup> Calc from relation:  $[^1J(^{119}\text{Sn}-^{13}\text{C})] = 11.4 \theta - 875$ .

<sup>d</sup> Acetone =  $(\text{CD}_3)_2\text{CO}$ , DMSO =  $(\text{CD}_3)_2\text{SO}$ .

<sup>e</sup> Calculated from center of unresolved  $^{119}\text{Sn}$ ,  $^{117}\text{Sn}$  satellites ( $[J_{\text{obs}}] \times 1.023$ )



# Multinuclear NMR parameters ...continued



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

Solute	Solvent <sup>b</sup>	$\delta(^{19}\text{F})$ , ppm			$^2J(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}})$ Hz	$\delta(^{119}\text{Sn})$ ppm	$\delta(^{125}\text{Te})$ ppm	$\delta(^{13}\text{CF}_3)$ ppm	$^1J(^{125}\text{Te}-^{19}\text{F})$ , Hz		
		$\text{F}_{\text{ax}}$	$\text{F}_{\text{eq}}$	$\text{CF}_2/\text{SO}_2\text{F}$					$\text{F}_{\text{ax}}$	$\text{F}_{\text{eq}}$	Hz
$(\text{CH}_3)_3\text{SnOTeF}_5$	neat	-32.9	-41.9		182.5	270.8 <sup>c</sup>	569.5		3112	3540	
	$\text{CH}_2\text{Cl}_2$	-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	
	$\text{CH}_3\text{CN}$	-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	
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$	neat			55.5	242.5						
	$\text{CH}_2\text{Cl}_2$			55.6	248.6						
	DMSO			52.5	32.9						
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$	neat			-78.5	240.2		118.7				320.4
	$\text{CH}_2\text{Cl}_2$			-78.8	251.0		118.1				319.8
	$\text{CH}_3\text{CN}$			-78.9	44.9		119.4				320.7
	DMSO			-78.6	37.4		120.0				321.7
$[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$	$\text{CH}_3\text{CN}$			-79.0	59.0						
	DMSO			-79.1	42.8						

<sup>a</sup> NMR spectroscopic data were recorded at 300 K

<sup>b</sup> Acetone =  $(\text{CD}_3)_2\text{CO}$ , DMSO =  $(\text{CD}_3)_2\text{SO}$

<sup>c</sup>  $^{119}\text{Sn}$  NMR shows a peak at 300.7 ppm in  $\text{HOTeF}_5$

$^{19}\text{F}_{\text{ax}}$  NMR for  $\text{TEAOTeF}_5$  = -25.4 ppm

$\text{B}(\text{OTeF}_5)_3$  = -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:

➤ <u>Compound (<math>\text{Me}_3\text{SnX}</math>)</u>	<u><math>d(^{119}\text{Sn})</math></u>
$\text{X} = \text{ClO}_4$ (unidentate)	245
$\text{X} = \text{SO}_3\text{CF}_3$ (bidentate)	162

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

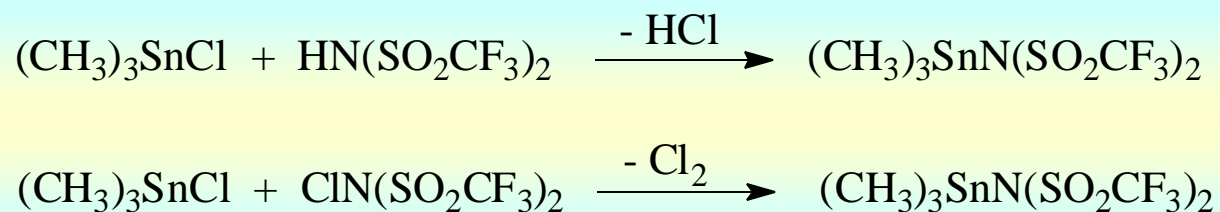




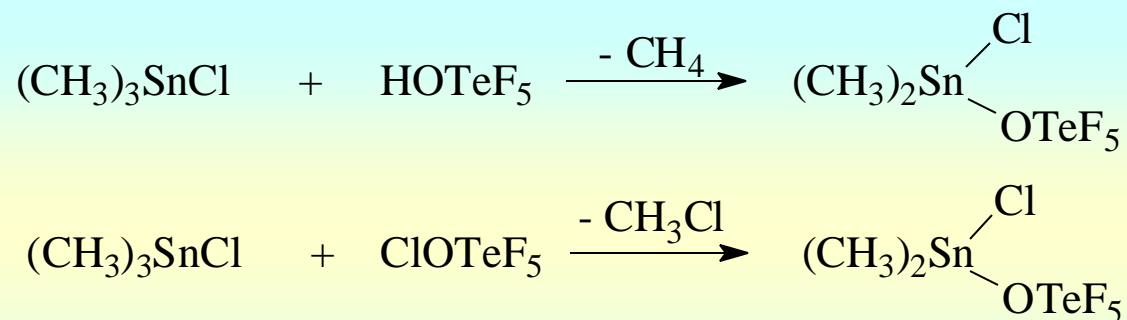
## ***Sn-C versus Sn-Cl bond cleavage***



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



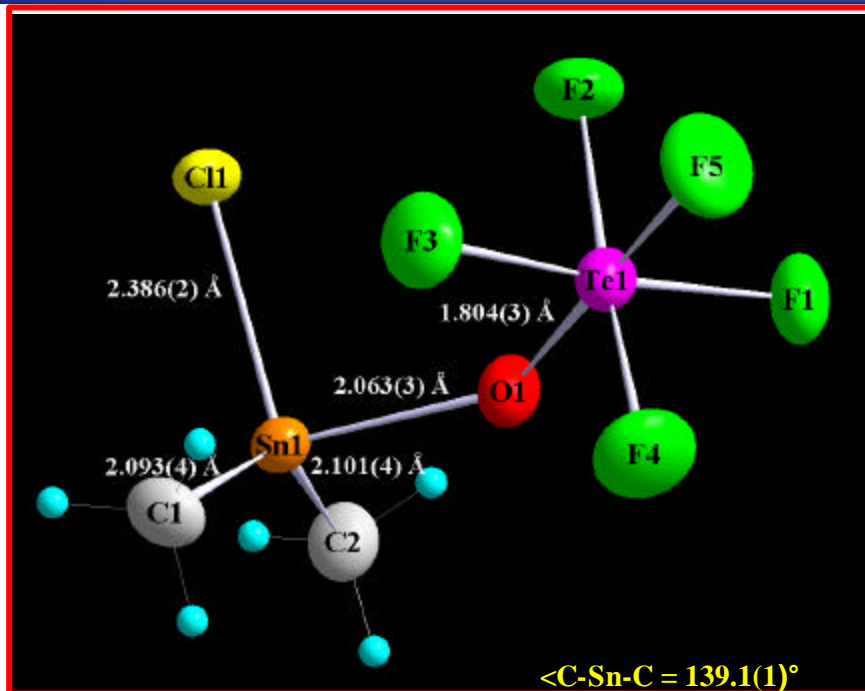
**$\text{XOTeF}_5$  (X = H, Cl) shows a preferential Sn-C bond cleavage**



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



## Structure of $(\text{CH}_3)_2\text{Sn}(\text{Cl})\text{OTeF}_5$



### Unit cell dimensions ( $\text{\AA}$ )

Monoclinic  $P2_1/n$

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

$c = 15.493(2)$

$\beta = 99.59(1)^\circ$

Volume ( $\text{\AA}^3$ ) = 971.7(2)

$Z = 4$

$T = 218(2) \text{ K}$

$R1 = 0.0282$

$wR2 = 0.0712$

$S = 1.088$

$\text{Te-O} (\text{\AA}) (\text{X}=\text{OTeF}_5) : \text{B}(\text{X})_3 = 1.874(6)$ ;  $[\text{TBA}][\text{H}(\text{X})_2] = 1.800(4)\text{av}$ ;  $[\text{Au}(\text{X}_3)]_2 = 1.91(2)$

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

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



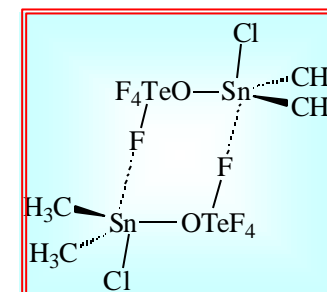
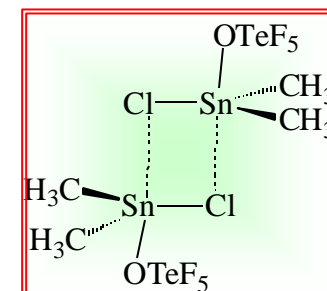
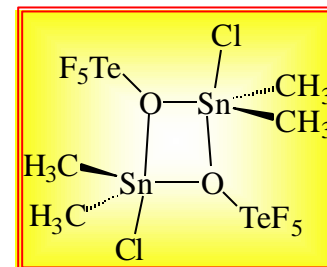
## Tetra- or pentacoordinated tin???



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  $\text{CD}_2\text{Cl}_2$  is approximately  $\sim 118^\circ$ . The  $d(^{119}\text{Sn})$  value of  $\sim 142.7$  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  $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$  molecule.

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

Mass spectrum shows  $[\text{M}-\text{CH}_3]^+$  peak as the highest peak indicating that the dimer is not stable in the gas phase

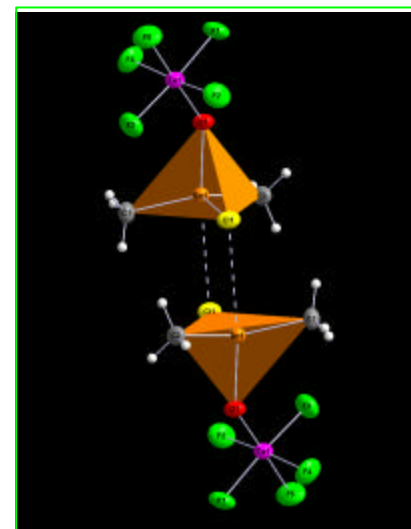
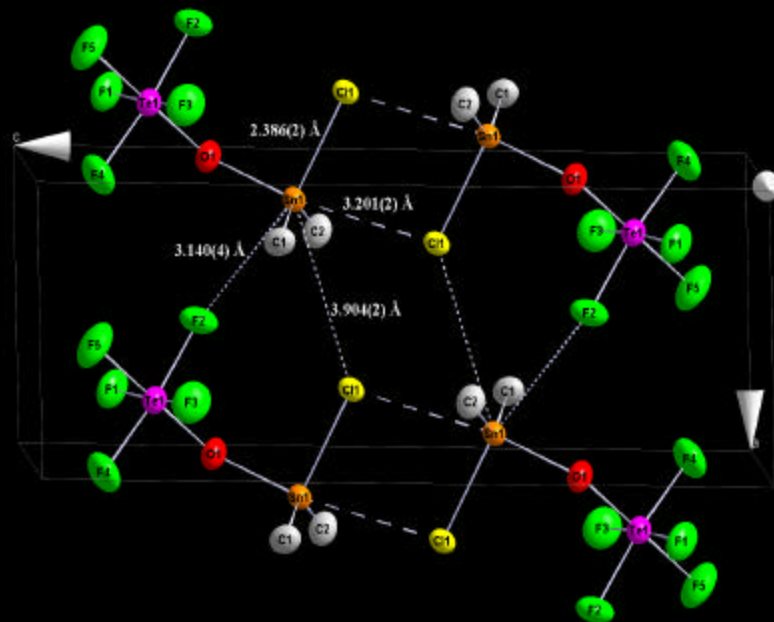




## Coordination environment around tin



Sn-Cl contact found in the crystal lattice is 3.201(1) Å, which is 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.  
 $S(\text{vdWSn} + \text{vdWCl}) = 2.17 + 1.75 = 3.92 \text{ Å}$

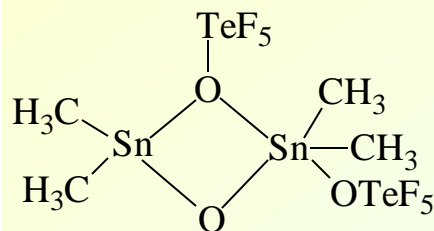
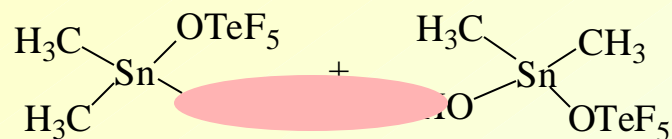
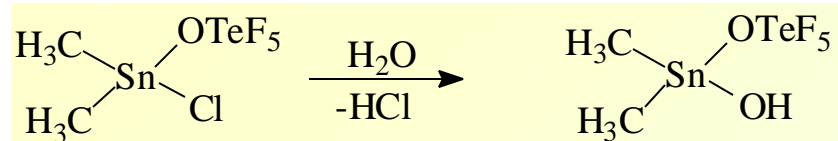


One Sn-F contact is also found in the crystal lattice 3.140(4) Å, which is much shorter than the sum of van der Waal radii of tin and fluorine.

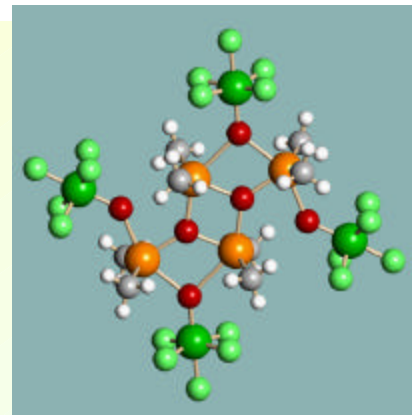
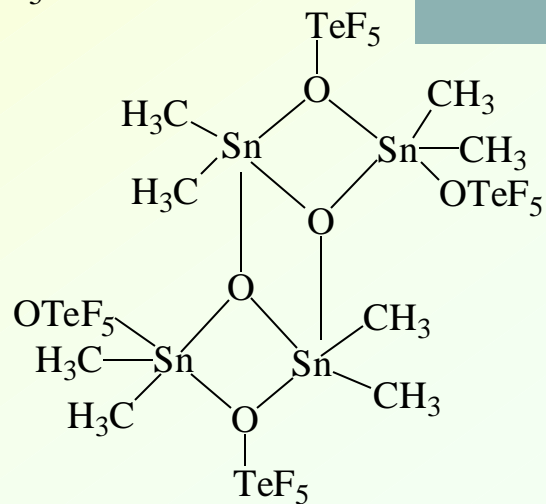
$$S(\text{vdWSn} + \text{vdWF}) = 2.17 + 1.47 = 3.64 \text{ Å}$$



## Hydrolysis of the Sn-Cl bond in $(\text{CH}_3)_2\text{Sn}(\text{Cl})\text{OTeF}_5$



Dimerization



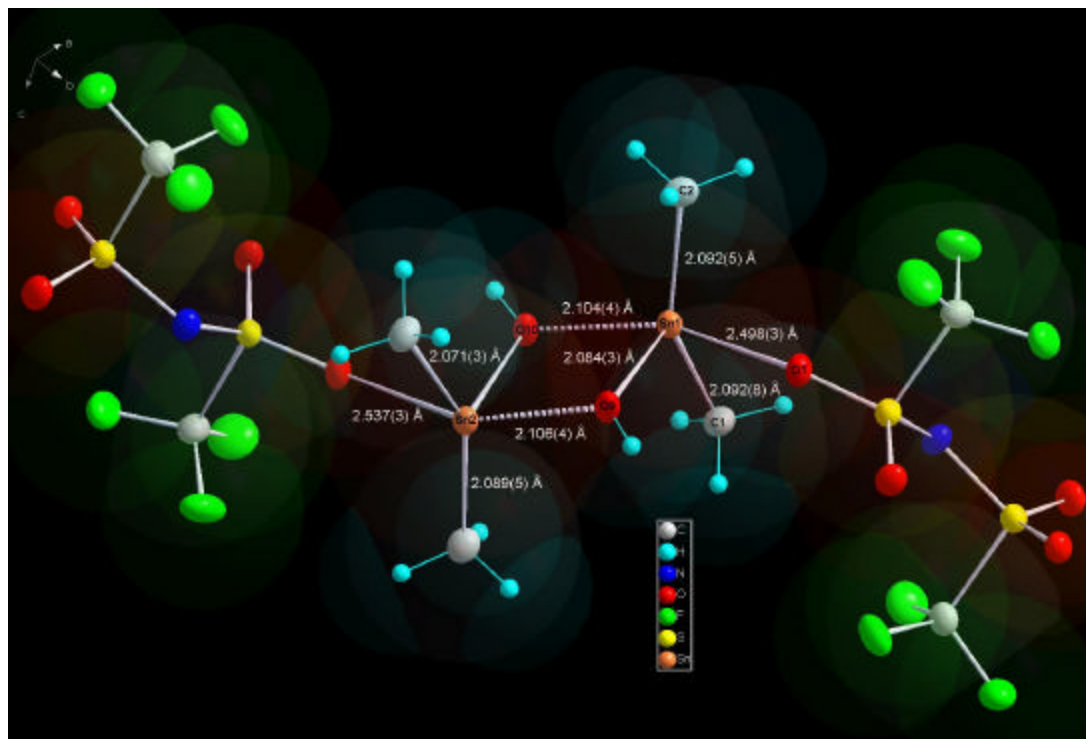








# Structure of $\text{Me}_2\text{Sn}(\text{OH})\text{N}(\text{SO}_2\text{CF}_3)_2$

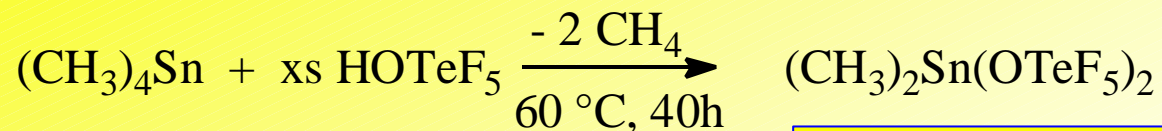




## Solvolysis of $\text{Me}_4\text{Sn}$ in excess acid: Synthesis of dimethyltin(IV) teflate

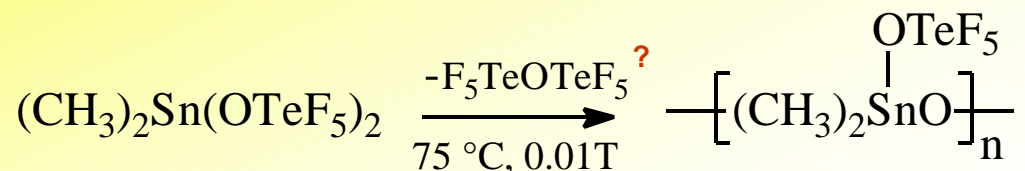


- ✓ Dimethyltin(IV) teflate is formed when tetramethyltin is reacted with excess teflic acid



MS shows  $[\text{M}-\text{CH}_3]^+$  peak

- ✓ Upon sublimation  $\sim 75\text{ }^\circ\text{C}/0.01\text{T}$  a polymeric species is formed, probably due to the loss of  $\text{O}(\text{TeF}_5)_2$



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



# Structure of dimethyltinooxteflate



## Unit cell dimensions ( $\text{\AA}$ )

Monoclinic  $P2_1/n$

Rotational TWIN

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

$c = 8.119(7)$

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

Volume ( $\text{\AA}^3$ ) = 876.7(12)

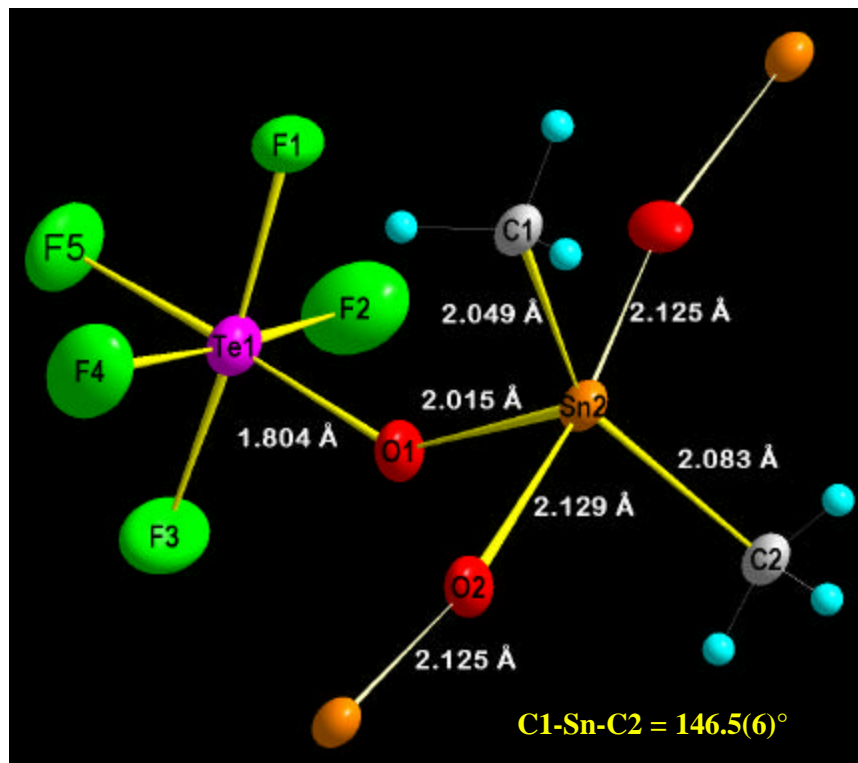
$Z = 4$

$T = 233(2) \text{ K}$

$R1 = 0.1028$

$S = 1.84$

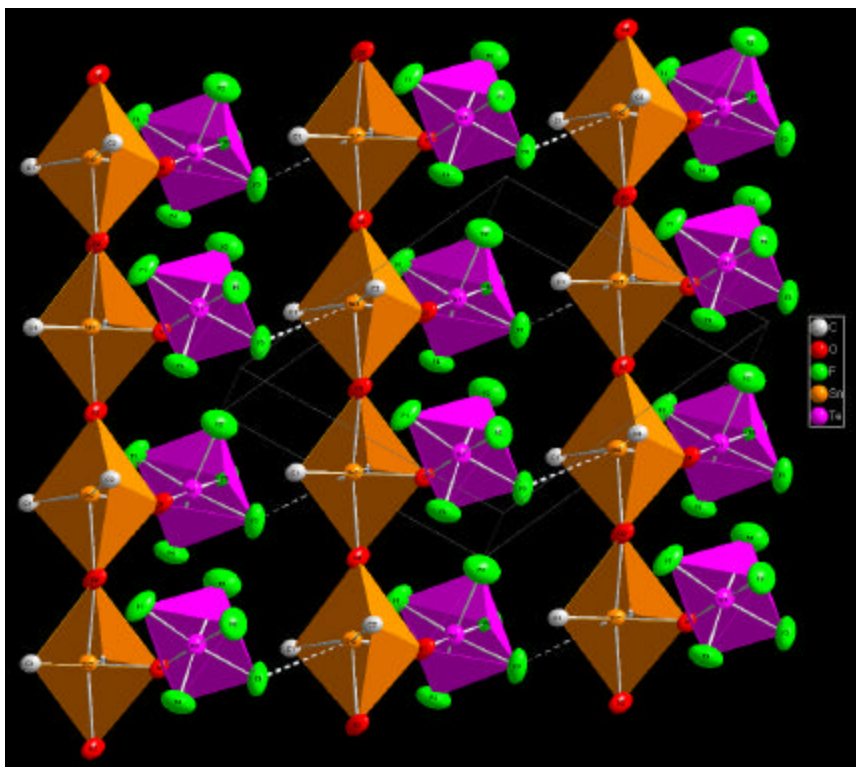
BASF = 0.256



$\text{C1-Sn-O1} = 110.2(5)^\circ$ ;  $\text{C2-Sn-O1} = 103.3(6)^\circ$ ,  
 $\langle \text{equi. X-Sn-X (av)} \rangle = 120^\circ$ ;  $\text{O2-Sn-O2}^* = 169.9(5)^\circ$



## Crystal packing showing tin and tellurium polyhedra



$$S_{(\text{vdwSn} + \text{vdwF})} = 2.17 + 1.47 \\ = 3.64 \text{ \AA}$$

$$\text{Sn-F distance in the crystal packing} \\ = 3.107(16) \text{ \AA}$$

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

$$\angle \text{Sn-O2-Sn}^* = 167.2^\circ$$

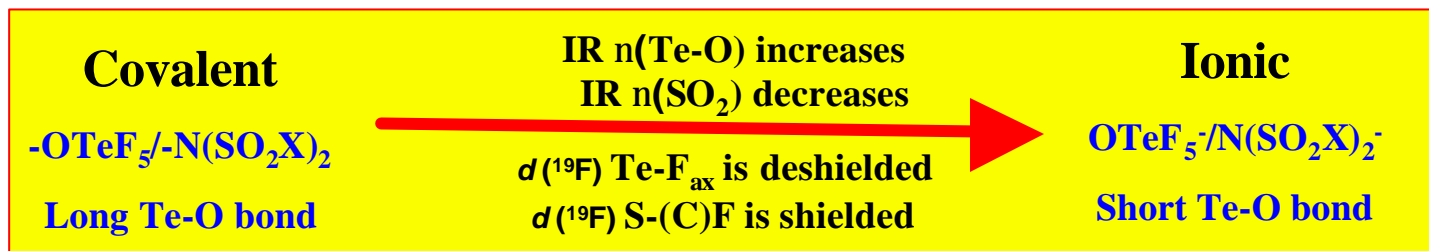
$$(\text{Sn}^* = \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$$



## Conclusions



- Trimethyltin(IV) teflates/F-imides are highly electrophilic in nature and form 1:1 or 1:2 complexes with donor solvents
- $^{119}\text{Sn}$  NMR chemical shifts can reflect the “electrophilic strength” and relative anion basicity for a  $\text{Me}_3\text{Sn}$  (IV) compound.
- During the solvolysis of trimethyltinchloride in  $\text{HOTeF}_5$ , there is a preferential cleavage of the Sn-C bond versus Sn-Cl bond
- 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.





# Acknowledgments



Dr. Karl Christe (AFRL/USC)

Dr. Michael Berman (AFOSR)

Dr. Don Woodbury (DARPA)

Dr. Ronald Channell (AFRL)

Mr. Michael Huggins (AFRL)

## FUNDING

DARPA, AFOSR

ERC Inc.



## BACKUP/SUPPL. SLIDES



# BACKUP



## Bond distances and angles $\text{Me}_2\text{SnClOTeF}_5$



• Sn(1)-C(2)	2.104(4)	C(2)-Sn(1)-C(1)	117.8(2)
• Sn(1)-C(1)	2.115(4)	C(2)-Sn(1)-C(3)	120.1(2)
• Sn(1)-C(3)	2.120(4)	C(1)-Sn(1)-C(3)	122.1(2)
• Sn(1)-O(1)	2.306(3)	C(2)-Sn(1)-O(1)	89.83(15)
• Sn(1)-O(2)	2.335(3)	C(1)-Sn(1)-O(1)	92.3(2)
• S(1)-O(3)	1.427(2)	C(3)-Sn(1)-O(1)	87.19(13)
• S(1)-O(4)	1.428(3)	C(2)-Sn(1)-O(2)	91.04(15)
• S(1)-N(1)	1.573(3)	C(1)-Sn(1)-O(2)	90.8(2)
• S(1)-C(4)	1.825(5)	C(3)-Sn(1)-O(2)	88.95(13)
• S(2)-O(6)	1.421(3)	O(1)-Sn(1)-O(2)	175.94(11)
• S(2)-O(5)	1.433(3)	O(3)-S(1)-O(4)	118.5(2)
• S(2)-N(1)	1.589(3)	O(3)-S(1)-N(1)	107.6(2)
• S(2)-C(5)	1.844(4)	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)