

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 03-09-2003		2. REPORT TYPE Technical Viewgraph Presentation		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Methyl tin (IV) derivatives of HOTeF ₅ and HN (SO ₂ CF ₃) ₂				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
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				5e. TASK NUMBER A205	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-PR-ED-VG-2003-219	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-VG-2003-219	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES For presentation at the National ACS Meeting (Ionic Liquids Symposium) in New York, NY, taking place 7-11 September 2003. Also being used as a journal article for "Inorganic Chemistry."					
14. ABSTRACT					
20030929 083					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	A	18	Leilani Richardson
					19b. TELEPHONE NUMBER (include area code) (661) 275-5015

Methyl tin(IV) derivatives of



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Air Force Research Laboratory

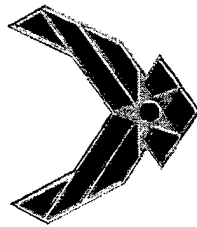
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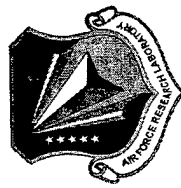
(661) 275-6278

Main Group Chemistry Symposium-226th National ACS Meeting, New York

September 11, 2003



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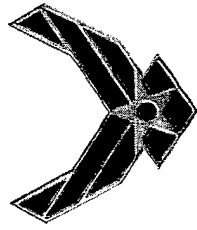
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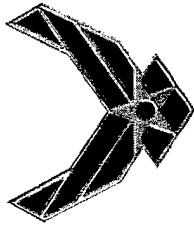
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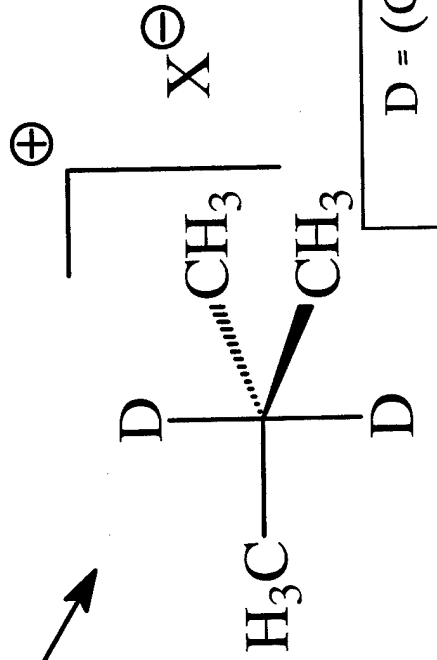
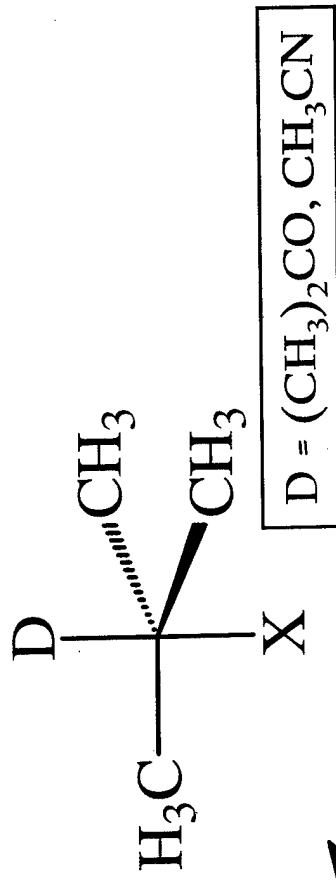
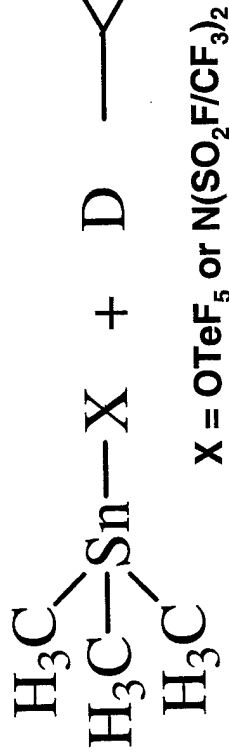
Synthesis of trimethyltin(IV) derivatives by acid solvolysis of $(\text{CH}_3)_4\text{Sn}$



- ✓ 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.

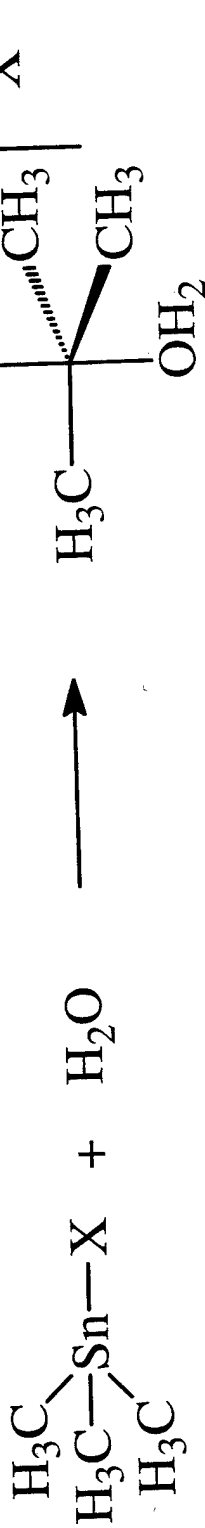
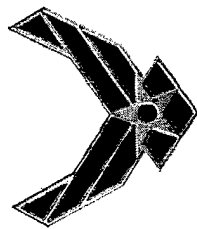


Coordination complex formation with donor solvents





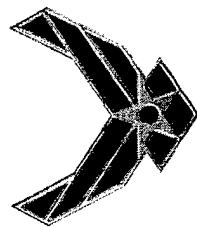
Formation of the hydrated trimethylstannyl cation



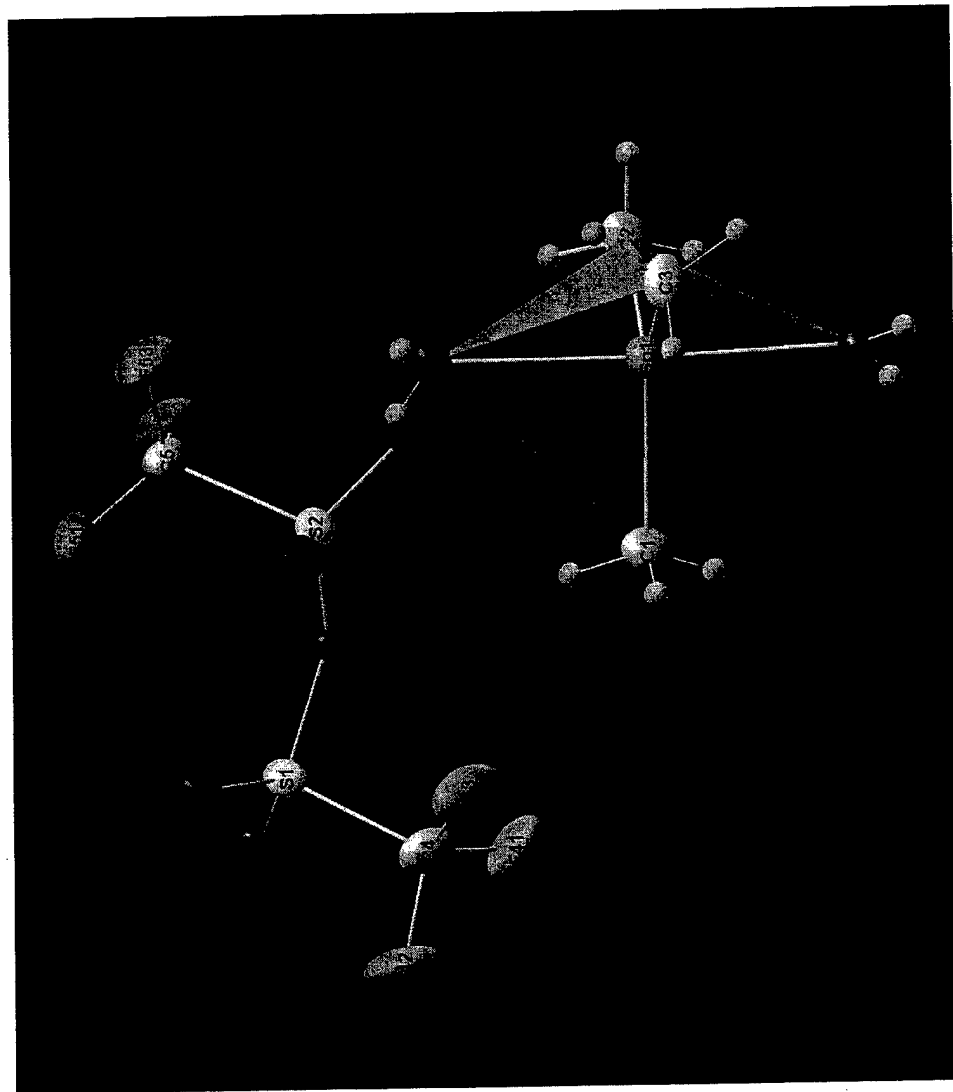
The hydrated salt can be isolated with $\text{N}(\text{SO}_2\text{CF}_3)_2$ anion but NOT for OTeF_5 anion.
The compound isolated is $[\text{Me}_3\text{Sn}(\text{OH}_2)_2]_2\text{SiF}_6$

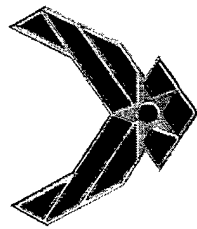


The hydrolysis of trimethyltin teflate results in the decomposition of the OTeF_5 group

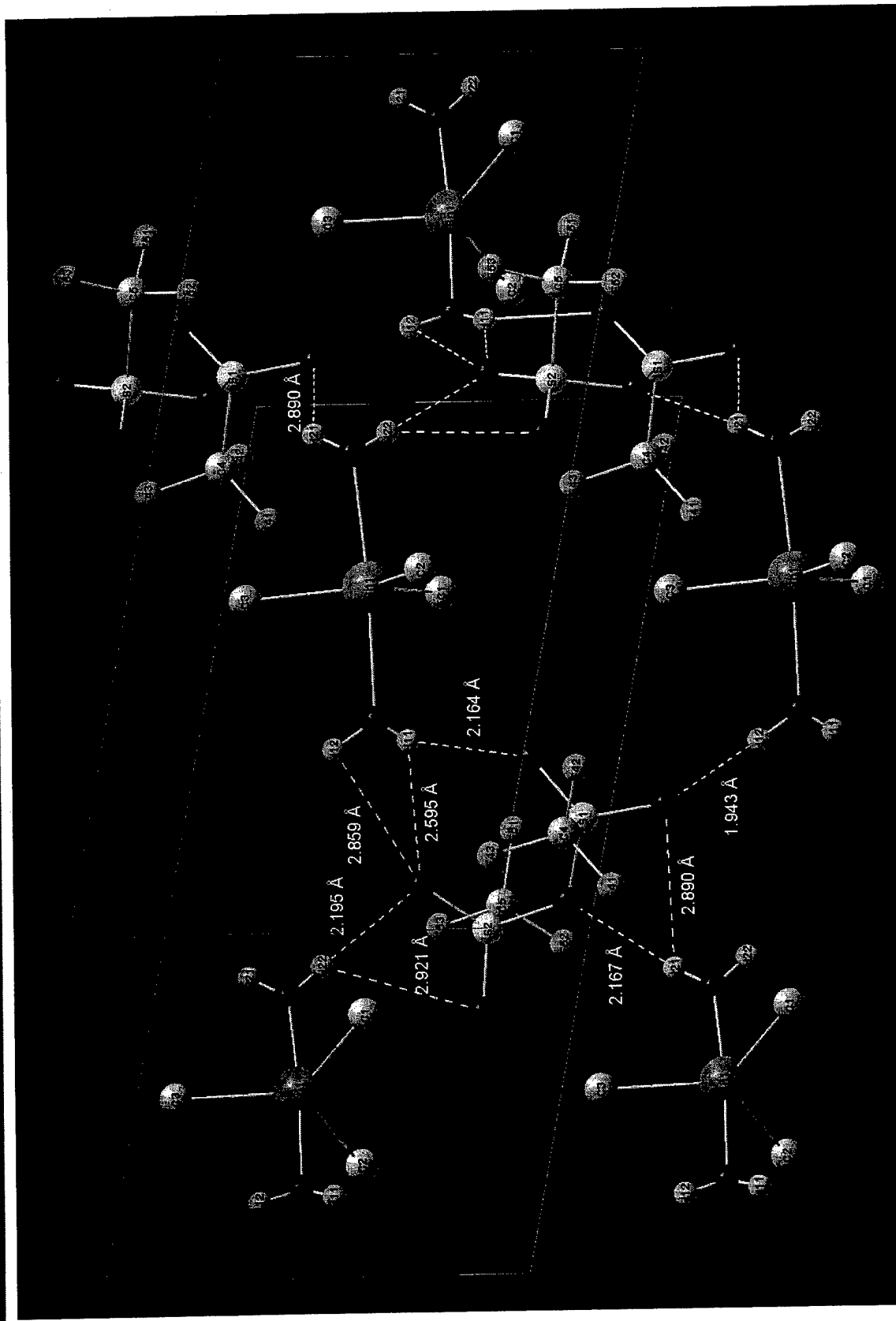
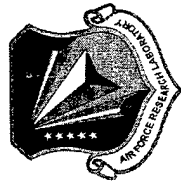


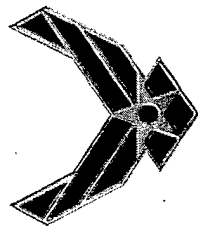
Hydrated trimethyltin(IV) cation





Hydrogen bonding





Multinuclear NMR Parameters



Table 1. ^1H , ^{13}C NMR Spectroscopic Data^a and calculated^{b,c} C-Sn-C angles for $(\text{CH}_3)_3\text{SnX}$ [X = OTeF_5 and $\text{N}(\text{SO}_2\text{F}/\text{CF}_3)_2$]

Solute	Solvent ^d	$\delta(^1\text{H})$ ppm	$2J(^{19}\text{Sn}-^1\text{H})$ Hz	$\theta(\text{C}-\text{Sn}-\text{C})^b$ ($^\circ$)	$\delta(^{13}\text{C})$ ppm	$1J(^{119}\text{Sn}-^{13}\text{C})$ Hz	$\theta(\text{C}-\text{Sn}-\text{C})^c$ ($^\circ$)
$(\text{CH}_3)_3\text{SnOTeF}_5$	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
$(\text{CH}_3)_3\text{SnOTeF}_5$	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
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$	neat	0.91	63.8(61.6)	114.7	1.6	416.8(400.3)	113.3
	CH_2Cl_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
	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
$[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$	DMSO	0.48	69.0(67.4)	119.0	0.7	512.2(499.0)	121.6
	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

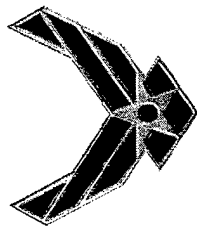
^a NMR spectroscopic data were recorded at 300 K.

^b Calc from relation: $\theta = 0.0161 [2J(^{19}\text{Sn}-^1\text{H})]^2 - 1.32 [2J(^{19}\text{Sn}-^1\text{H})] + 133.4$.

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

^d Acetone = $(\text{CD}_3)_2\text{CO}$, DMSO = $(\text{CD}_3)_2\text{SO}$.

^e Calculated from center of unresolved ^{119}Sn , ^{117}Sn satellites ($J_{\text{obs}} \times 1.023$)



NMR parameters ... continued



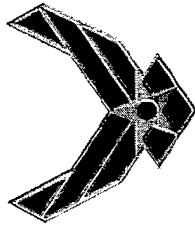
Table 2. ^{19}F , ^{119}Sn and ^{125}Te NMR Spectroscopic Data^a of $(\text{CH}_3)_3\text{SnX}$ [$\text{X} = \text{OTeF}_5$ and $\text{N}(\text{SO}_2\text{F}/\text{CF}_3)_2$]

Solute	Solvent ^b	$\delta(^{19}\text{F})$, 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	$J(^{125}\text{Te}-^{19}\text{F})$, Hz		$J(^{13}\text{C}-^{19}\text{F})$ Hz
		F_{ax}	F_{eq}					F_{ax}	F_{eq}	
$(\text{CH}_3)_3\text{SnOTeF}_5$	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	
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$	neat			55.5	242.5					
	CH_2Cl_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
	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
$[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$	CH_3CN			-79.0	59.0					
	DMSO			-79.1	42.8					

^a NMR spectroscopic data were recorded at 300 K

^b Acetone = $(\text{CD}_3)_2\text{CO}$, DMSO = $(\text{CD}_3)_2\text{SO}$

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



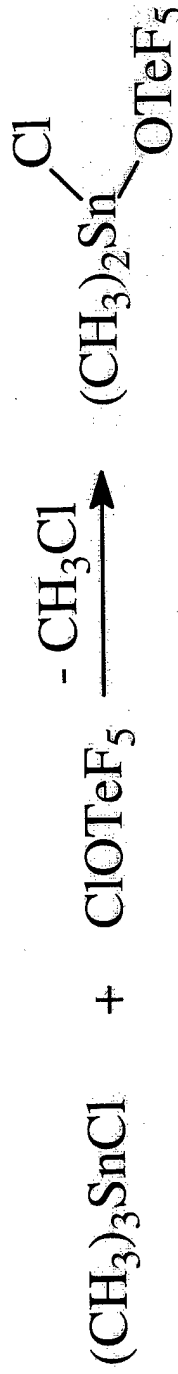
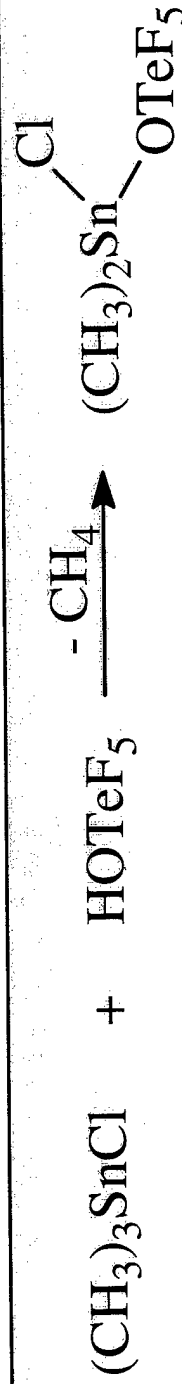
Sn-C versus Sn-Cl bond cleavage

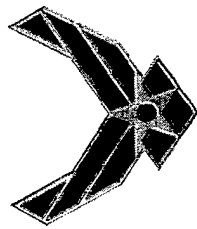


$\text{XN}(\text{SO}_2\text{CF}_3)_2$ (X = H, Cl) shows a preferential Sn-Cl bond cleavage

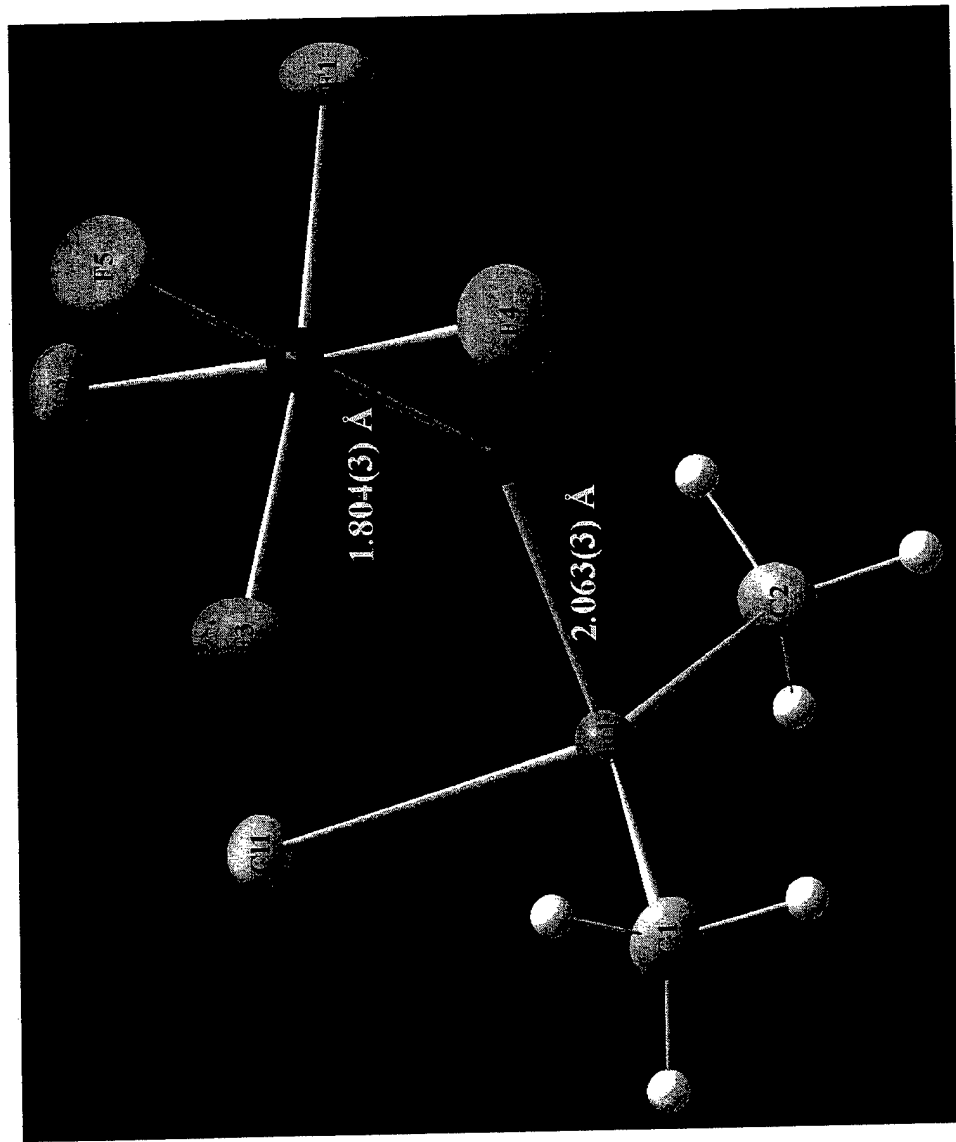
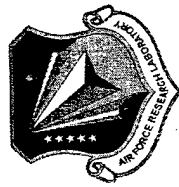


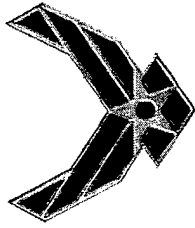
XOTeF_5 (X = H, Cl) shows a preferential Sn-C bond cleavage





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

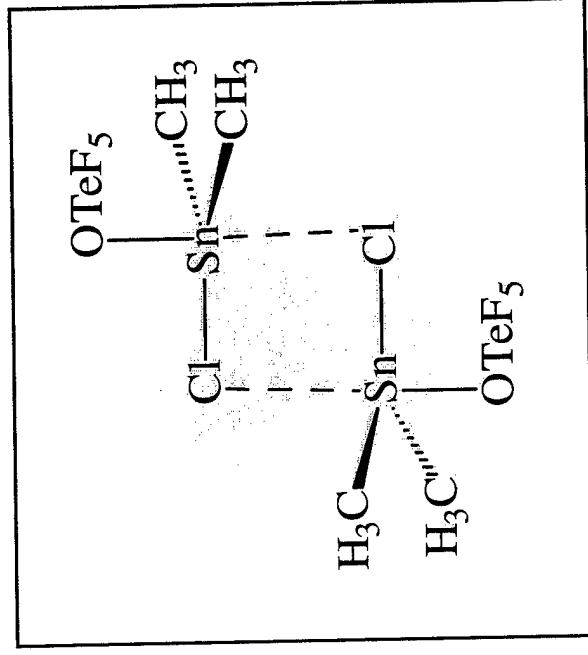


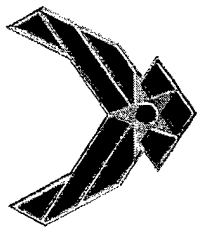


Tetra- or pentacoordinated tin???

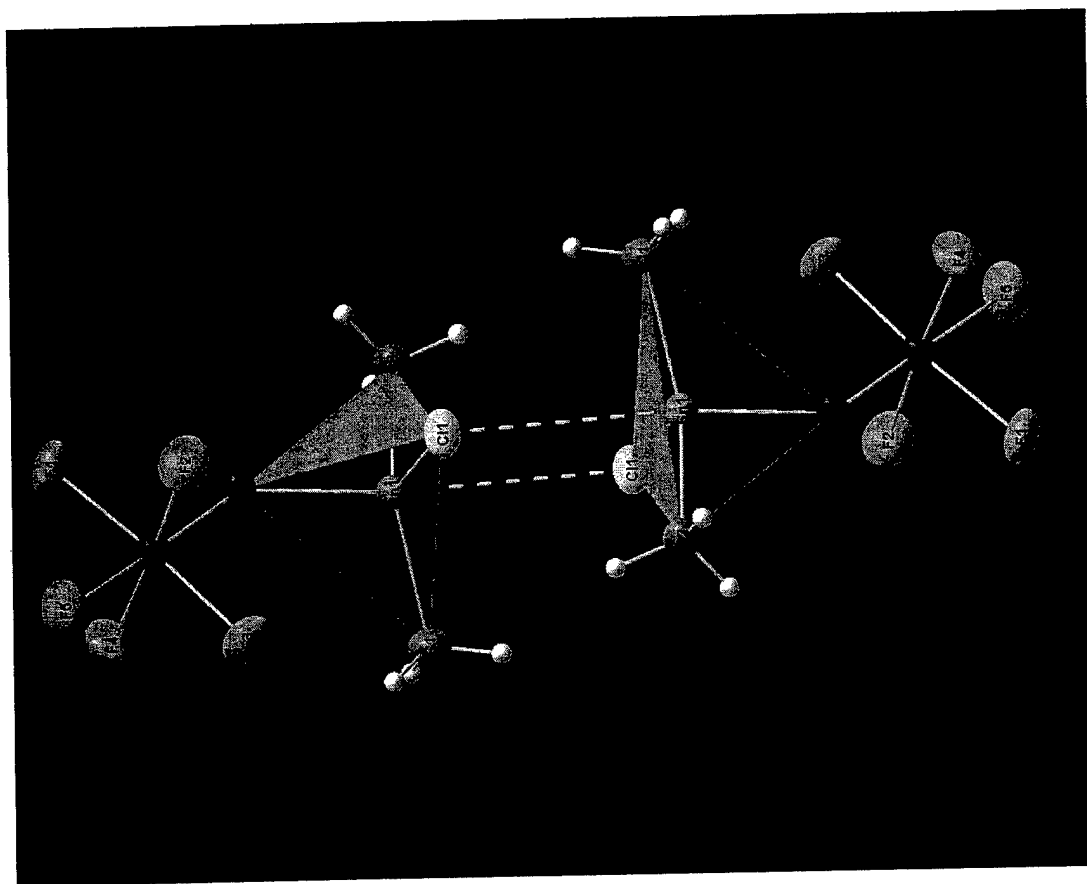


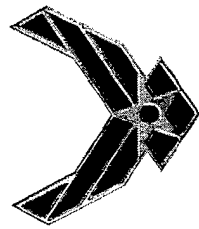
The C-Sn-C angle calculated using $^2J(^{119}\text{Sn}-^1\text{H})$ and $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants for $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ dissolved in CD_2Cl_2 is approximately -118° . The $\delta(^{119}\text{Sn})$ value of -120 ppm indicates that tin is present in a five-coordinate environment. The fifth coordination site is most likely occupied by a bridging chlorine ligand from a second $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$ molecule



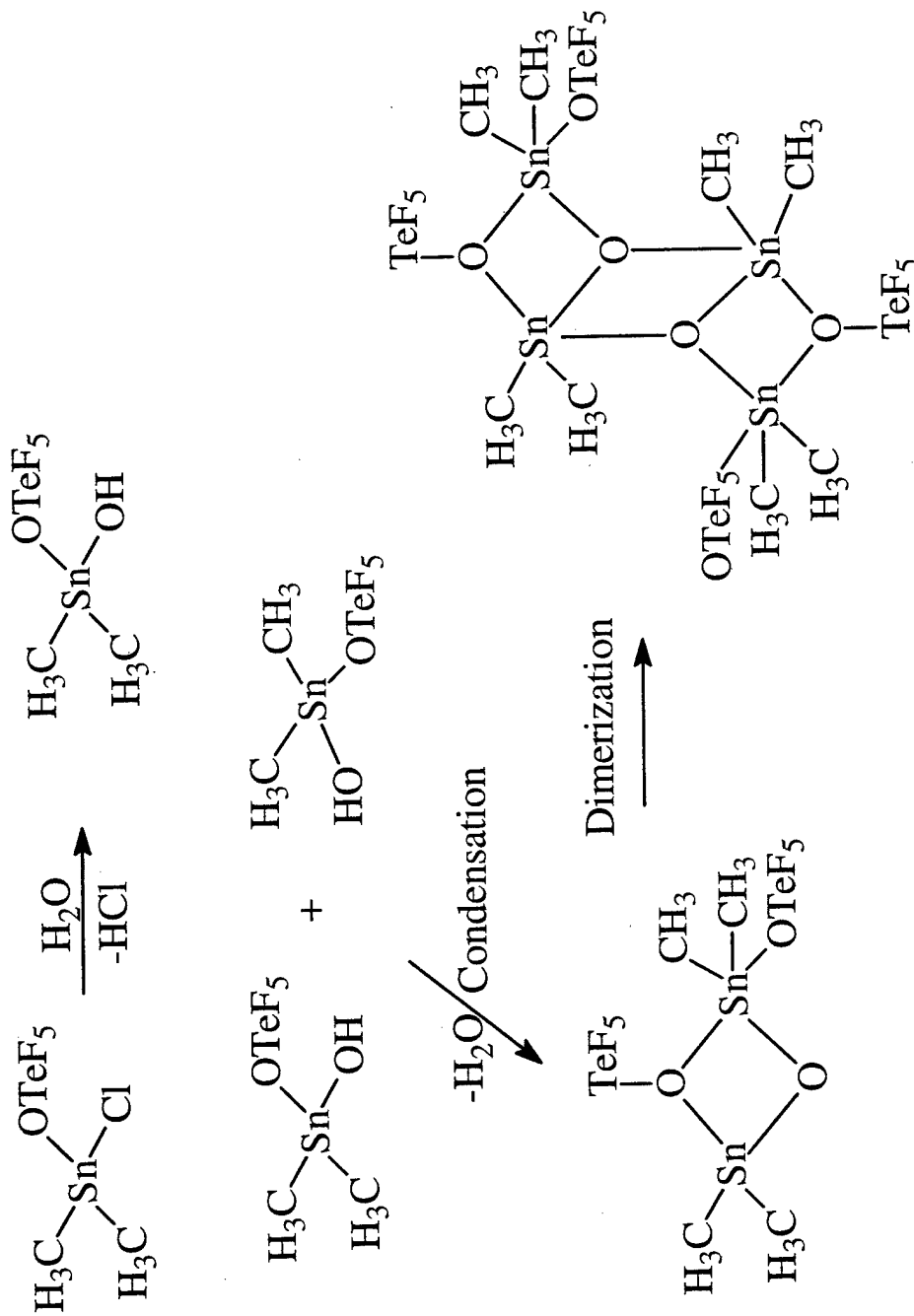


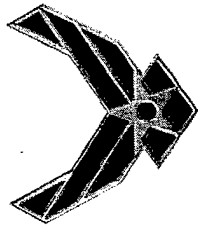
Dimerization via Sn...Cl contacts



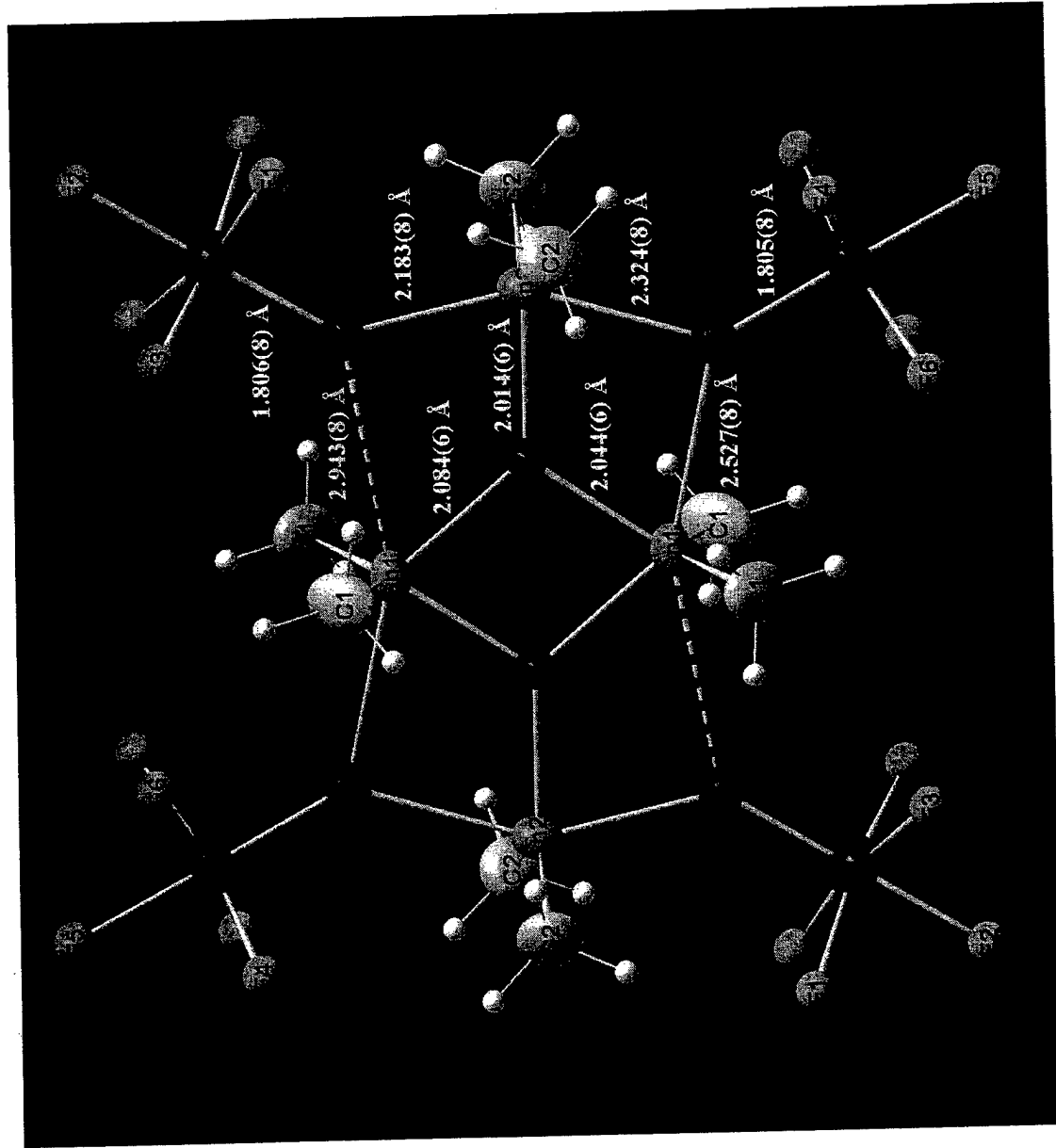


Hydrolysis of the Sn-Cl bond in $(CH_3)_2Sn(Cl)OTeF_5$



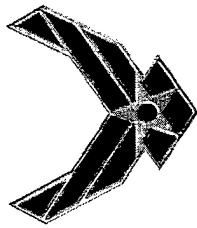


Structure of the dimethyloxotin(IV) teflate

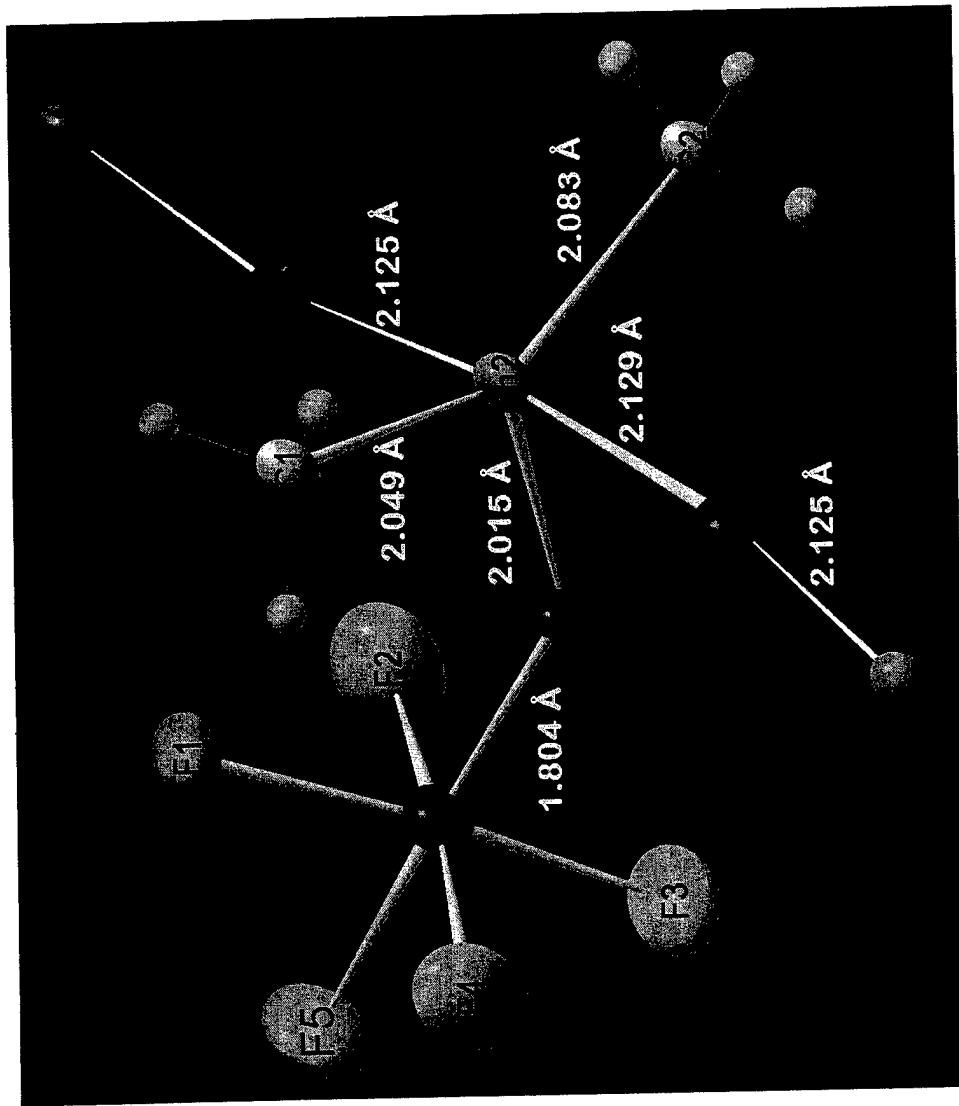


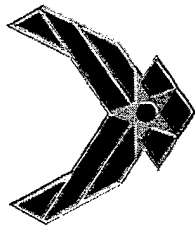
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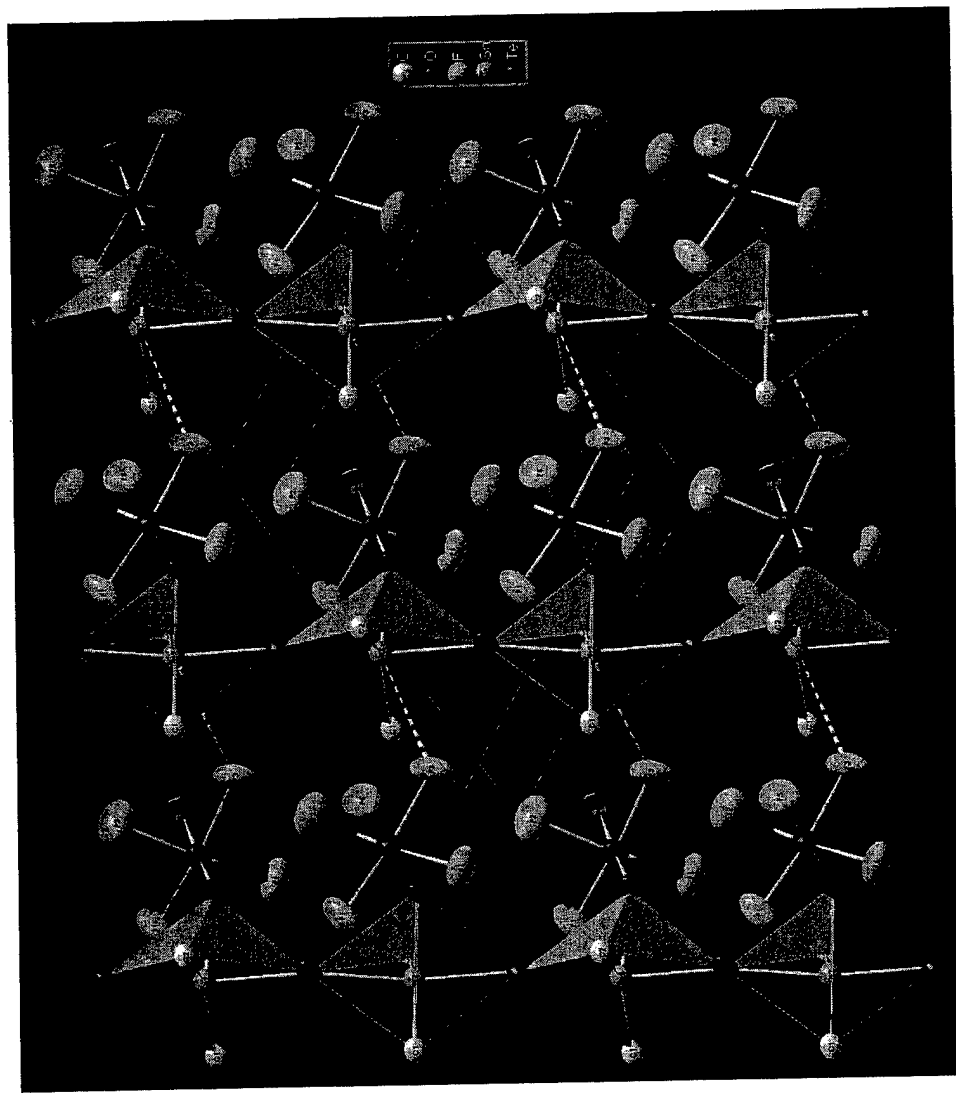


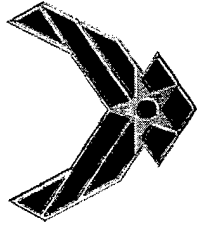
Structure of dimethyltinooxteflate





Crystal packing showing tin and tellurium polyhedra





Conclusions



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