AMMONIUM DI(CARBOXYLATO)TRIPHENYLSTANNATES. CRYSTAL STRUCTURES OF DICYCLOHEXYLAMMONIUM BIS(TRIFLUORO-ACETATO) TRIPHENYLSTANNATE, DIISOPROPYLAMMONIUM BIS[BIS(*N*,*N*-DIMETHYLTHIO-CARBAMOYLTHIO)ACETATO]-TRIPHENYLSTANNATE AND 2,2'-IMINODIPYRIDINIUM BIS(TRIFLUOROACETATO)TRIPHENYLSTANNATE

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Abstract. The crystal structures of dicyclohexylammonium bis(trifluoroacetato)triphenylstannate (**1**), diisopropylammonium bis[(*N*,*N*-dimethylthiocarbamoylthio)acetato]triphenylstannate (**2**) and 2,2'-iminodipyridinium bis(chlorodifluoroacetato)triphenylstannate (**3**) consist of ammonium cations and stannate anions that are linked by $N\cdots O$ hydrogen bonds into linear chains [(**1**) 2.784(4) Å; (**2**) 2.780(5) Å, 2.950(6) Å; (**3**) 2.779(7) Å, 3.073(8) Å]. The tin atom in the five-coordinate stannates shows *trans*-C_3SnO_2 trigonal bipyramidal coordination [(**1**) $\Sigma_{C\text{-}Sn\text{-}C}$ 360.0(4)°, O-Sn-O 174.1(1)°, Sn-O 2.258(2) Å; (**2**) $\Sigma_{C\text{-}Sn\text{-}C}$ 359.9(6)°, O-Sn-O 178.8(1)°, Sn-O 2.213(3) Å , 2.227(3) Å; (**3**) $\Sigma_{C\text{-}Sn\text{-}C}$ 359.5(6)°, O-Sn-O 179.7(2)°; Sn-O 2.194(5), 2.310(5) Å]. The δ_{iso} chemical shifts in the solid-state ^{119}Sn MAS NMR spectra of (**1**), (**2**) and tetramethylammonium bis(trifluoroacetato)triphenylstannate are of the order of -300 ppm relative to tetramethyltin; the spectra yield axially-symmetric chemical shift tensors and -1 asymmetry parameters.

Introduction

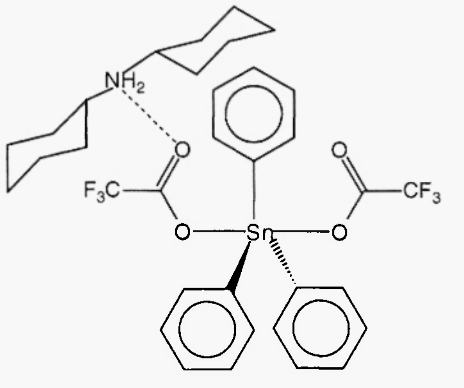
The bis(trifluoroacetato)triphenylstannate ion as its tetramethylammonium [1] and 2,2'-iminodipyridinium [2] salts represents an unusual example of a bis(carboxylato)triorganostannate, which is an organotin compound whose tin atom is linked covalently to two carboxylato anions. The tetramethylammonium salt exists as discrete ammonium and stannate ions; the ammonium and stannate ions are linked by hydrogen bonds in the 2,2'-iminodipyridinium salt. Such stannates differ from (dicarboxylato)triorganostannates, which possess one dianionic dicarboxylato group; the dianionic dicarboxylato group can behave either as a bridge to connect the triphenyltin cations into a polyanionic chain, as in dicyclohexylammonium succinatotriphenylstannate [3] and in trimethylsulfonium oxalatotriphenylstannate [4], or as a bidentate ligand that chelates the triphenyltin cation, as in dicyclohexylammonium oxalatotriphenylstannate [5]. A carboxylato group with strongly electron-withdrawing substituents such as the trifluoroacetato anion furnishes a bis(trifluoroacetato)triphenylstannate by analogy with the chloride anion, which yields the dichlorotriphenylstannate anion with triphenyltin chloride [6]. On the other hand, tetramethylammonium bis(coumarin-3-carboxylato)triphenylstannate [7] presents an anomaly as coumarin-3-carboxylic acid is not normally considered a strong organic acid. The synthesis of the di(carboxylato)triphenylstannates is now extended to dicyclohexylammonium bis-(trifluoroacetato)triphenylstannate (Scheme 1) and dicyclohexylammonium [bis(*N*,*N*-dimethyldithio-carbamoyl)acetato]triphenylstannate. The latter stannate did not furnish single crystals, and the stannate anion was instead isolated as the diisopropylammonium salt (Scheme 2). 2,2'-Iminodipyridinium bis(chlorodifluoroacetato)triphenylstannate (Scheme 3) has also been synthesized and its crystal structure determined.

Experimental

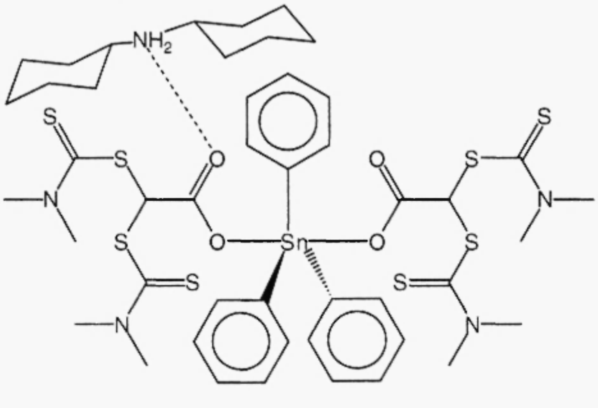
Synthesis and NMR spectroscopy

Solid-state ^{119}Sn and ^{13}C MAS NMR spectra were recorded on a Bruker MSL-300S instrument (^{119}Sn at 111.922 MHz and ^{13}C at 75.47 MHz) by using the procedure reported previously [8]. The ^{119}Sn NMR spectra were acquired at 5 - 7 KHz, and were analyzed by using the manufacturer's *WINFIT* program to derive the principal components of the chemical shift tensor. The components are defined ($\delta_{11} > \delta_{22} > \delta_{33}$) as: isotropic chemical shift, $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$; span, $W = |\delta_{11} - \delta_{33}|$; skew, $k = 3(\delta_{22} - \delta_{iso})/W$

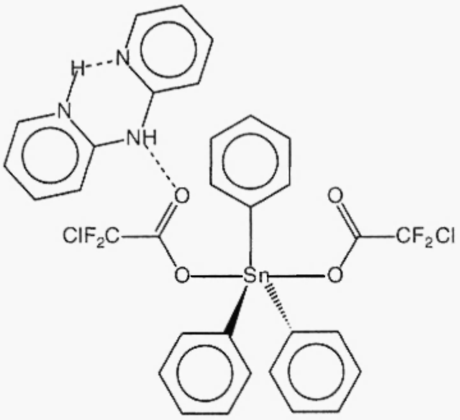
[9]. Solid-state ^{13}C spectra were acquired at 4 kHz with suppression of spinning side bands.



Scheme 1



Scheme 2



Scheme 3

Triphenyltin hydroxide (3.67 g, 10 mmol) was added to a mixture of dicyclohexylamine (1.81 g, 10 mol) and trifluoroacetic acid (2.28 g, 20 mmol) in 50 mL ethanol. The mixture was heated to dissolve the hydroxide; slow cooling of the filtered solution gave the ammonium stannate (**I**) as large crystals having a hexagonal cross section. Solid-state ^{119}Sn NMR: $\delta_{iso} = -268$, $\delta_{11} = 0$, $\delta_{22} = -403$, $\delta_{33} = -403$ ppm; W = 403, k = -1. Solid-state ^{13}C NMR: 160.0 (C=O); 160.0, 144.1, 139.4, 135.3, 128.3 (phenyl C); 53.5 (N-CH); 29.1, 24.1 (CH_2) ppm.

In the preparation of the [bis(*N*,*N*-dimethylthiocarbamoylthio)acetatotriphenylstannate] analog, bis(*N*,*N*-dimethylthiocarbamoylthio)acetic acid (2.98 g, 10 mmol) [10] was first treated with dicyclohexylamine in ethanol and the solution filtered; a filtered ethanol solution of triphenyltin hydroxide (1.84 g, 5 mmol) when added to this solution gave an immediate precipitate that was not soluble in a large excess of ethanol. Diisopropylamine, triphenyltin hydroxide and the carboxylic acid in ethanol gave diisopropylammonium bis[(*N*,*N*-dimethylthiocarbamoylthio)acetato]triphenylstannate (**2**), which separated as clear crystals on slow cooling of the solution. The ^{119}Sn NMR spectrum shows the presence of other tin sites (at –52 and -49 ppm) besides the main resonance: $\delta_{iso} = -326$, $\delta_{11} = -45$, $\delta_{22} = -467$, $\delta_{33} = -467$ ppm; W = 422, k = -1. The corresponding values for the other two signals are: $\delta_{iso} = -52$, $\delta_{11} = 32$, $\delta_{22} = -37$, $\delta_{33} = -150$ ppm; W = 182, k = 0.25; $\delta_{iso} = -49$, $\delta_{11} = 32$, $\delta_{22} = -77$, $\delta_{33} = -101$ ppm; W = 132, k = -0.64.

The reaction of di-2-pyridylamine, triphenyltin hydroxide and chlorodifluoroacetic acid under similar reaction conditions yielded 2,2'-iminodipyridinium bis(chlorodifluoroacetato)triphenylstannate (**3**).

The solid-state NMR parameters for tetramethylammonium bis(trifluoroacetato)triphenylstannate, which has already been authenticated crystallographically [1], are: ^{119}Sn NMR: $\delta_{iso} = -290$, $\delta_{11} = 32$, $\delta_{22} = -451$, $\delta_{33} = -451$ ppm; W = 483, k = -1. Solid-state ^{13}C NMR: 160.0 (C=O); 152.4, 151.1, 146.2, 145.6, 139.4, 135.3, 129.7, 127.7 (phenyl C); 118.5 ($-CF_3$); 52.9 (N-CH) ppm.

Crystallography

Room-temperature diffraction measurements were performed on a colorless specimen of (**1**) with an Enraf-Nonius *CAD*-4 diffractometer (graphite-monochromatized Mo-$K\alpha$ radiation, λ 0.71073 Å). Auto-indexing procedures gave a *C*-centered cell, and accurate cell dimensions were calculated from 25 reflections in the θ = 12.25 - 12.75° range [11]. The 4497 absorption-corrected [12] reflections (transmission factors = 0.384 - 0.415) were collected by ω-scans (collection range: $0 \leq h \leq 11$, $-9 \leq k \leq 25$, $-25 \leq l \leq 25$) up to 2θ = 55° ($h + k = 2n + 1$ reflections not collected); the raw data were reduced to F^2 and $\sigma(F^2)$ values. No decay in quality was evident from three reflections used to monitor the crystal for every hour of exposure to X-rays. The 4023 independent reflections were used for solution [13] and for refinement [14]. The trifluoromethyl group is disordered, and the six F atoms were given 0.5 site occupancies each; distance restraints (C-F = 1.33±0.01 Å, F F 2.17±0.02 Å) were imposed on each set of F atoms. The refinement on 237 parameters converged to R = 0.0275 for 3538 $I > 2\sigma(I)$ reflections. Hydrogen atoms were generated and allowed to ride on their parent atoms with U – $1.5U_{eq}$(C,N). The maximum shift/esd was less than 0.001 and final difference map was diffuse, with no peaks/holes larger than ±1 eÅ^{-3}. The absolute structure parameter [15] was -0.04(2). The structure is shown as an *ORTEP* [16] plot in Fig. 1*a* and the hydrogen bond interactions as a *PLUTON* [17] plot in Fig. 1*b*. Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.

Crystal data: $C_{34}H_{39}F_6NO_4Sn$, *FW* 758.35, orthorhombic, $C222_1$, a 9.0175(5) Å, b 20.159(1) Å, c 19.2934(9) Å, V 3507.1(3) Å^3, Z 4, $D_{X\text{-ray}}$ 1.436 g cm^{-3}, F(000) 1544, μ 0.797 mm^{-1}.

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Å^2) for dicyclohexylammonium bis(trifluoroacetato)triphenylstannate

Atom	x	y	z	U_{eq}
Sn1	0.0000	0.09539(1)	0.7500	0.0431(1)
F1 (50%)	0.145(1)	0.1081(6)	1.0234(4)	0.125(5)
F2 (50%)	0.314(1)	0.0650(6)	0.9619(7)	0.169(6)
F3 (50%)	0.265(1)	0.1652(5)	0.9519(5)	0.134(4)
F1' (50%)	0.163(1)	0.0750(5)	1.0181(3)	0.119(4)
F2' (50%)	0.340(1)	0.1010(9)	0.9543(4)	0.145(6)
F3' (50%)	0.162(2)	0.1705(3)	0.9752(5)	0.155(4)
O1	0.1510(2)	0.1012(1)	0.8432(1)	0.053(1)
O2	- 0.0125(4)	0.0551(1)	0.9158(1)	0.066(1)
N1	- 0.2314(4)	0.0000	1.0000	0.059(1)
C1	0.0000	- 0.0105(2)	0.7500	0.050(1)
C2	0.0958(4)	- 0.0459(2)	0.7921(2)	0.065(1)
C3	0.0953(5)	- 0.1150(1)	0.7923(2)	0.080(1)
C4	0.0000	- 0.1490(2)	0.7500	0.085(1)
C5	- 0.1647(3)	0.1505(1)	0.8047(1)	0.048(1)
C6	- 0.1233(4)	0.2012(2)	0.8483(2)	0.066(1)
C7	- 0.2277(5)	0.2352(2)	0.8878(2)	0.083(1)
C8	- 0.3740(5)	0.2173(2)	0.8840(2)	0.082(1)
C9	- 0.4182(4)	0.1676(2)	0.8405(2)	0.080(1)
C10	- 0.3133(4)	0.1341(2)	0.8011(2)	0.062(1)
C11	0.1010(3)	0.0848(2)	0.9020(1)	0.049(1)
C12	0.1997(4)	0.1076(2)	0.9618(2)	0.078(1)
C13	- 0.3197(4)	0.0514(2)	1.0387(2)	0.066(1)
C14	- 0.2256(6)	0.1100(2)	1.0565(3)	0.101(2)
C15	- 0.3152(7)	0.1619(2)	1.0961(3)	0.125(2)
C16	- 0.3913(6)	0.1338(3)	1.1587(3)	0.106(2)
C17	- 0.4802(7)	0.0741(3)	1.1407(2)	0.119(2)
C18	- 0.3879(5)	0.0218(3)	1.1030(2)	0.098(1)

U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor.

A quadrant of 9618 reflections ($0 \leq h \leq 14$, $0 \leq k \leq 22$, $-26 \leq l \leq 26$; $2\theta_{max}$ 50°) was collected for the faint tan-crystal of (**2**). The data were corrected for absorption (transmission factors = 0.397 - 0.591). The refinements on 523 parameters and 9155 independent reflections converged to R = 0.0456 for 6600 $I > 2\sigma(I)$ reflections. Atomic coordinates and isotropic temperature factors are listed in Table 2. The structure is shown in Fig. 2.

Table 2. Atomic coordinates and equivalent isotropic temperature factors (Å^{-}) for diisopropylammonium bis[bis(*N*,*N*-dimethylthiocarbamoylthio)acetato]triphenylstannate

Atom	*x*	*y*	*z*	U_{eq}
Sn1	0.40753(2)	0.23741(1)	0.65805(1)	0.0387(1)
S1	0.0270(1)	0.4378(1)	0.6014(1)	0.0585(3)
S2	0.2176(1)	0.4500(1)	0.5304(1)	0.0707(4)
S3	- 0.0065(1)	0.2946(1)	0.6304(1)	0.0558(3)
S4	- 0.0181(2)	0.2392(1)	0.5046(1)	0.0783(4)
S5	0.6815(1)	0.1551(1)	0.8355(1)	0.0509(3)
S6	0.9178(1)	0.1579(1)	0.8113(1)	0.1197(8)
S7	0.6935(1)	0.0174(1)	0.7856(1)	0.0565(3)
S8	0.6938(1)	0.0236(1)	0.6532(1)	0.0719(4)
O1	0.2528(2)	0.2903(1)	0.6170(1)	0.047(1)
O2	0.2362(2)	0.3815(2)	0.6765(1)	0.051(1)
O3	0.5615(2)	0.1821(1)	0.6990(1)	0.047(1)
O4	0.4754(3)	0.0918(2)	0.7347(1)	0.053(1)
N1	0.1101(4)	0.5552(2)	0.5704(2)	0.064(1)
N2	- 0.1101(5)	0.1836(3)	0.5912(2)	0.102(2)
N3	0.7308(4)	- 0.0895(2)	0.7195(2)	0.066(1)
N4	0.8492(4)	0.2003(2)	0.9104(2)	0.073(1)
N5	0.1885(4)	0.4795(2)	0.7595(2)	0.065(1)
C1	0.3593(4)	0.2479(2)	0.7440(2)	0.043(1)
C2	0.4356(4)	0.2720(3)	0.7915(2)	0.062(1)
C3	0.4064(6)	0.2813(3)	0.8474(2)	0.076(2)
C4	0.3017(6)	0.2664(3)	0.8576(3)	0.078(2)
C5	0.2231(5)	0.2418(3)	0.8119(3)	0.073(2)
C6	0.2524(4)	0.2333(2)	0.7549(2)	0.057(1)
C7	0.5094(4)	0.3137(2)	0.6241(2)	0.047(1)
C8	0.6046(4)	0.2939(3)	0.6007(2)	0.059(1)
C9	0.6674(5)	0.3423(3)	0.5746(2)	0.076(2)
C10	0.6358(5)	0.4101(3)	0.5713(3)	0.087(2)
C11	0.5430(5)	0.4313(3)	0.5936(3)	0.097(2)
C12	0.4802(5)	0.3823(3)	0.6193(3)	0.079(2)
C13	0.3609(4)	0.1587(2)	0.5932(2)	0.051(1)
C14	0.4435(6)	0.1241(3)	0.5682(3)	0.083(2)
C15	0.4168(10)	0.0797(4)	0.5195(4)	0.127(3)
C16	0.3080(12)	0.0672(4)	0.4976(3)	0.139(5)
C17	0.2261(8)	0.1001(3)	0.5211(3)	0.122(3)
C18	0.2514(6)	0.1462(3)	0.5688(3)	0.083(2)
C19	0.2028(3)	0.3428(2)	0.6348(2)	0.040(1)
C20	0.0862(3)	0.3515(2)	0.5981(2)	0.046(1)
C21	0.1225(4)	0.4869(2)	0.5653(2)	0.052(1)
C22	0.0232(5)	0.5874(3)	0.5996(3)	0.078(2)
C23	0.1835(5)	0.6026(3)	0.5444(3)	0.089(2)
C24	- 0.0490(4)	0.2336(3)	0.5731(2)	0.058(1)
C25	- 0.1299(8)	0.1772(4)	0.6539(3)	0.145(4)
C26	- 0.1583(9)	0.1287(5)	0.5505(4)	0.179(5)
C27	0.5577(3)	0.1266(2)	0.7296(2)	0.040(1)
C28	0.6730(3)	0.1083(2)	0.7654(2)	0.041(1)
C29	0.8260(4)	0.1729(3)	0.8562(2)	0.057(1)
C30	0.7657(6)	0.2140(3)	0.9491(2)	0.092(2)
C31	0.9648(6)	0.2192(5)	0.9353(3)	0.143(3)
C32	0.7092(4)	- 0.0214(2)	0.7164(2)	0.051(1)
C33	0.7412(6)	- 0.1291(3)	0.7756(3)	0.098(2)
C34	0.7431(6)	- 0.1286(3)	0.6658(3)	0.101(2)
C35	0.1686(6)	0.4294(3)	0.8079(2)	0.078(2)
C36	0.0588(5)	0.3943(3)	0.7877(3)	0.094(2)
C37	0.1732(9)	0.4674(4)	0.8673(3)	0.155(4)
C38	0.2958(5)	0.5206(3)	0.7659(3)	0.089(2)
C39	0.3974(6)	0.4742(4)	0.7831(4)	0.130(3)
C40	0.2987(6)	0.5571(4)	0.7067(4)	0.115(3)

U_{eq} is defined as one-third the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Crystal data: $C_{40}H_{57}N_5O_4S_8Sn$, *FW* 1047.08, monoclinic, $P2_1/n$, *a* 12.1290(8) Å, *b* 19.219(1) Å, *c* 22.600(1) Å, β 98.612(5)°, *V* 5208.8(5) Å^3, *Z* 4, $D_{X\text{-ray}}$ 1.335 g cm^{-3}, *F*(000) 2168, μ 0.852 mm^{-1}.

The set of 6112 reflections ($0 \le h \le 12$, $0 \le k \le 20$, $-21 \le l \le 21$; $2\theta_{max}$ 50°) was collected for the colorless crystal of (**3**). The data were corrected for absorption (transmission factors = 0.452 - 0.513). Phenyl groups were refined as rigid hexagons. One -$CClF_2$ is disordered over two sites; for both -$CClF_2$ groups, distance restraints (C-Cl 1.79±0.01Å, C-F 1.33+0.01Å, Cl···F 2.56±0.02 Å, F···F 2.17±0.02 Å) were imposed. For the disordered ClF_2C- group, EADP restraints in were applied to the Cl and F atoms and an *ISOR* restraint to the F1 atom. The refinement on 382 parameters and 5657 independent reflections converged to $R = 0.0581$ for 3778 $I > 2\sigma(I)$ reflections. Atomic coordinates and isotropic temperature factors are listed in Table 3. The structure is shown in Fig. 3.

Table 3. Atomic coordinates and equivalent isotropic temperature factors (Å^2) for 2,2'-iminodipyridinium bis(chlorodifluoroacetato)triphenylstannate

Atom	*x*	*y*	*z*	U_{ec}
Sn1	0.28830(4)	0.21882(3)	0.03497(2)	0.0535(2)
Cl1 (50%)	- 0.024(3)	0.367(2)	- 0.137(1)	0.153(6)
Cl1' (50%)	0.010(3)	0.367(2)	- 0.159(1)	0.153(6)
Cl2	0.4850(3)	0.0055(2)	0.1981(1)	0.116(1)
F1 (50%)	0.044(3)	0.461(1)	- 0.045(1)	0.205(8)
F2 (50%)	0.157(2)	0.4697(6)	- 0.139(1)	0.078(3)
F1' (50%)	0.020(3)	0.423(1)	- 0.040(1)	0.205(8)
F2' (50%)	0.118(2)	0.4922(5)	- 0.117(1)	0.078(3)
F3	0.5115(7)	- 0.0247(4)	0.0687(3)	0.159(3)
F4	0.3481(7)	- 0.0795(3)	0.1180(4)	0.140(3)
O1	0.1865(5)	0.3304(3)	- 0.0036(3)	0.064(1)
O2	0.2957(6)	0.3437(4)	- 0.1041(3)	0.089(2)
O3	0.3858(5)	0.1132(3)	0.0719(3)	0.068(1)
O4	0.2070(6)	0.0419(4)	0.0833(4)	0.099(2)
N1	0.4369(4)	0.4144(2)	- 0.2099(2)	0.072(2)
N2	0.4574(4)	0.4387(2)	- 0.3325(2)	0.075(2)
N3	0.6142(4)	0.4922(2)	- 0.2244(2)	0.072(2)
C1	0.1927(4)	0.2352(3)	0.1337(2)	0.056(2)
C2	0.0724(5)	0.2722(3)	0.1344(2)	0.075(2)
C3	0.0143(5)	0.2845(3)	0.1999(3)	0.099(3)
C4	0.0765(7)	0.2598(4)	0.2646(2)	0.101(3)
C5	0.1969(6)	0.2227(4)	0.2638(2)	0.095(3)
C6	0.2550(5)	0.2104(3)	0.1984(3)	0.079(2)
C7	0.1927(5)	0.1719(3)	- 0.0600(2)	0.062(2)
C8	0.2641(5)	0.1556(4)	- 0.1202(3)	0.109(4)
C9	0.1992(8)	0.1361(5)	- 0.1858(3)	0.149(5)
C10	0.0629(8)	0.1329(4)	- 0.1912(3)	0.117(4)
C11	- 0.0085(5)	0.1493(4)	- 0.1311(4)	0.125(4)
C12	0.0564(5)	0.1688(4)	- 0.0655(3)	0.096(3)
C13	0.4791(4)	0.2681(3)	0.0348(2)	0.054(2)
C14	0.5699(5)	0.2447(3)	- 0.0141(2)	0.072(2)
C15	0.6946(4)	0.2768(4)	- 0.0115(3)	0.086(3)
C16	0.7285(4)	0.3322(4)	0.0400(3)	0.089(3)
C17	0.6378(6)	0.3556(3)	0.0890(3)	0.094(3)
C18	0.5130(5)	0.3235(3)	0.0864(2)	0.075(2)
C19	0.2056(8)	0.3568(4)	- 0.0645(4)	0.063(2)
C20	0.1046(8)	0.4195(4)	- 0.0940(4)	0.120(4)
C21	0.3220(9)	0.0532(5)	0.0862(4)	0.068(2)
C22	0.4130(8)	- 0.0137(5)	0.1113(4)	0.092(3)
C23	0.3906(7)	0.4071(5)	- 0.2804(4)	0.066(2)
C24	0.4133(9)	0.4365(6)	- 0.4030(4)	0.092(3)
C25	0.3004(9)	0.4015(6)	- 0.4221(5)	0.092(3)
C26	0.2307(8)	0.3660(6)	- 0.3693(5)	0.085(3)
C27	0.2763(8)	0.3684(5)	- 0.2976(5)	0.075(2)
C28	0.5444(7)	0.4531(4)	- 0.1800(4)	0.062(2)
C29	0.7171(8)	0.5339(5)	- 0.1963(5)	0.079(2)
C30	0.7500(9)	0.5357(5)	- 0.1244(5)	0.085(3)
C31	0.6757(9)	0.4930(6)	- 0.0788(5)	0.095(3)
C32	0.5711(9)	0.4518(5)	- 0.1055(4)	0.078(2)

U_{eq} is defined as one-third the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Crystal data: $C_{32}H_{25}N_3O_4F_4Cl_2Sn$, *FW* 781.14, monoclinic, $P2_1/n$, *a* 10.2028(6) Å, *b* 7.533(1) Å, *c* 18.441(1) Å, β 93.133(5)°, *V* 3293.8(3) Å^3, *Z* 4, $D_{\text{X-ray}}$ 1.575 g cm^{-3}, *F*(000) 1560, μ 1.001 mm^{-1}.

Supplementary material: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC113874, CCDC113875 and CCDC113876. Copies of the available material can be obtained, free of charge, on application to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk). The F_o/F_c listings are available from the first author (e-mail: h1nswen@umcsd.um.edu.my) up to one year after this publication has appeared.

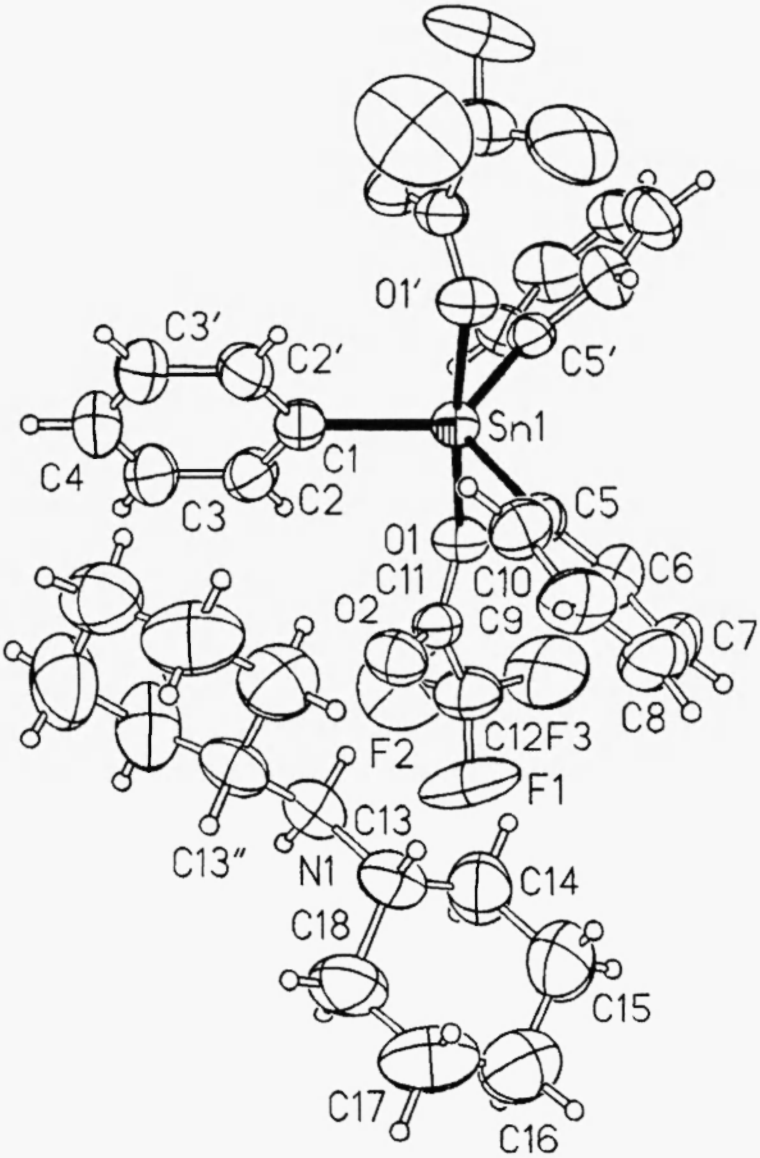


Fig.1*a*. *ORTEP* plot of dicyclohexylammonium bis(trifluoroacetato)triphenylstannate at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles: Sn1-C1 2.134(3) Å, Sn1-C5 2.133(3) Å, Sn1-C5^i 2.133(3) Å, Sn1-O1 2.258(2) Å, Sn1-O1^i 2.258(2) Å; C1-Sn1-C5 121.4(1)°, C1-Sn1-C5^i 121.4(1)°, C1-Sn1-O1 93.0(1)°, C1-Sn1-O1^i 93.0(1)°, C5-Sn1-C5^i 117.3(2)°, C5-Sn1-O1 90.0(1)°, C5-Sn1-O1^i 87.0(1)°, C5^i-Sn1-O1 87.0(1)°, C5^i-Sn1-O1^i 90.0(1)°, O1-Sn1-O1^i 174.1(1)°. Symmetry transformation: $i = -x, y, 1.5 - z$.

Results and discussion

The bis(trifluoroacetato)triphenylstannate anion as its dicyclohexylammonium (Fig. 1*a*) salt has the five-coordinate tin atom in a *trans*-C_3SnO_2 coordination environment, the tin atom being covalently bonded to three equatorially positioned phenyl groups and two axially positioned carboxylato anions. The tin atom lies on a two-fold axis, so that the two tin-oxygen distances are equal to each other [Sn-O 2.258(2) Å]. The tin-oxygen distance is similar to those [2.219(3) Å, 2.255(4) Å] in the tetramethylammonium as well as those [2.200(5) Å, 2.252(5) Å] in the 2,2'-iminodipyridinium salt, whose tin atoms lie in general positions in their crystal structures. The tin-oxygen bond distances in the three stannates are longer than the corresponding distances in four-coordinate triphenyltin carboxylates, but are shorter than the bridging distances in carboxylate-bridged triphenyltin carboxylates [18].

The stannate shows minor differences in other bond dimensions compared with the corresponding bond dimensions that are found in the tetramethylammonium [1] and 2,2'-iminodipyridinium [2] salts. The dicyclohexylammonium cation as counterion forces the anions and cations to be linked into a linear zig-zag chain by a hydrogen bond [N O 2.787(4) Å] (Fig. 1*b*) whereas the 2,2'-iminodipyridinium cation induces the hydrogen-bonded chain to adopt a helical conformation. If the regularity of the coordination polyhedron around the tin atom as defined by the percentage displacement along the Berry pseudorotation (trigonal bipyramid — square pyramid) pathway [19], the dicyclohexylammonium is most regular (97%) whereas the tetramethylammonium salt is the least (88%). Interestingly, the latter compound has several solvent-accessible voids in the crystal structure, although none is large enough to accommodate a water molecule.

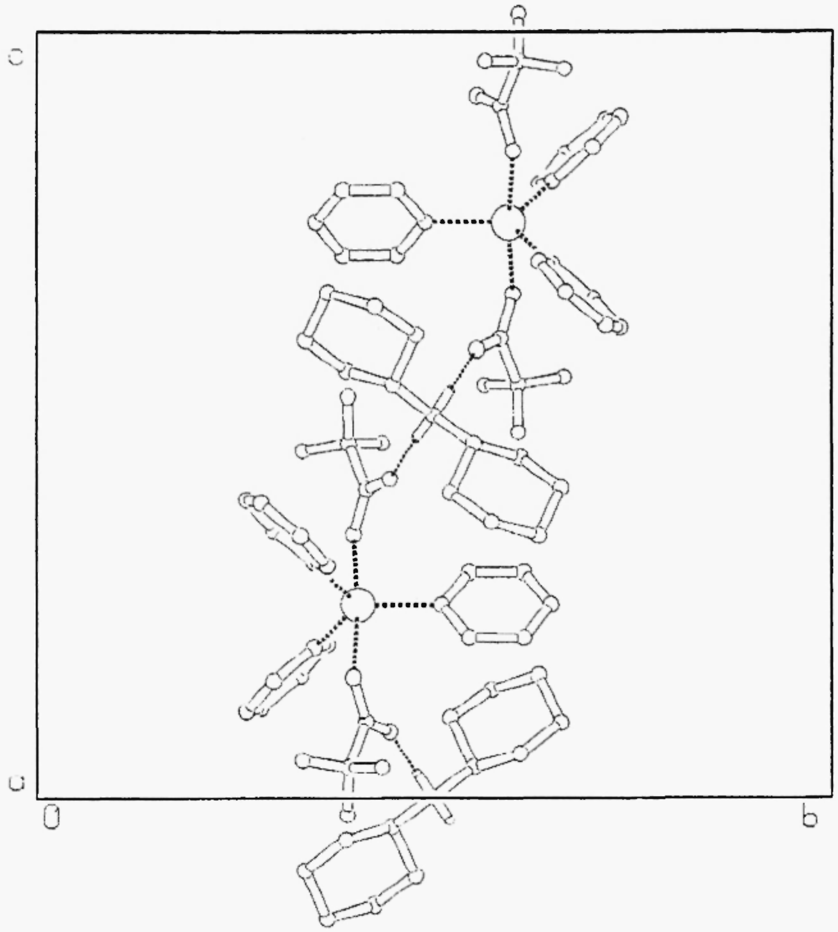


Fig.1*b*. *PLUTON* plot of the hydrogen-bonded polymeric chain of dicyclohexylammonium bis(trifluoroacetato)triphenylstannate projected along the *a*-axis of the unit cell. The Sn atom lies on the crystallographic two-fold axis. Hydrogen bonds: N1 O2 = N1 O2^i = 2.787(4) Å. Symmetry transformation *i* = -*x*, *y*, 1.5 - *z*.

Triphenyltin bis(*N*,*N*-dimethylthiocarbamoylthiol)]acetate displays Lewis acceptor properties similar to those of triphenyltin trifluoroacetate [20] in forming adducts with ethanol, quinoline *N*-oxide and water [21,22,23]. In the bis[bis(*N*,*N*-dimethylthiocarbamoylthio)acetato]triphenylstannate (Fig. 2*a*), the two tin-oxygen bond distances [Sn-O 2.213(3) Å, 2.227(3) Å] are of the same length; the distances exceed that [2.160(3) Å] found in triphenyltin bis(*N*,*N*-dimethylthiocarbamoylthio)acetate dihydrate [23] and that [Sn-O 2.147(4) Å] found in triphenyltin bis(*N*,*N*-dimethylthiocarbamoylthio)acetate quinoline *N*-oxide [22].

The stannate ions are linked by hydrogen bonds into a helical chain (Fig. 2*b*). The hydrogen bonding distances are somewhat longer than those [2.706(2) Å, 2.757(2) Å] found in the organic ammonium carboxylate, dicyclohexylammonium bis(*N*,*N*-dimethylthiocarbamoylthio)acetate [24], but are shorter than those [2.81(3) - 2.98(2) Å] found in bis(diisopropylammonium) tris(2,6-pyridinedicarboxylato)bis(dibutylstannate) trihydrate [25]. Bond dimensions involving the bis(*N*,*N*-dimethylthiolcarbamoylthiolyl)acetato anion do not differ significantly from those found in dicyclohexylammonium bis(*N*,*N*-dimethylthiocarbamoylthio)acetate [24] and tetramethylammonium bis(*N*,*N*-dimethylthiocarbamoylthio)acetate bis(*N*,*N*-dimethylthiocarbamoyl-thio)acetic acid [26].

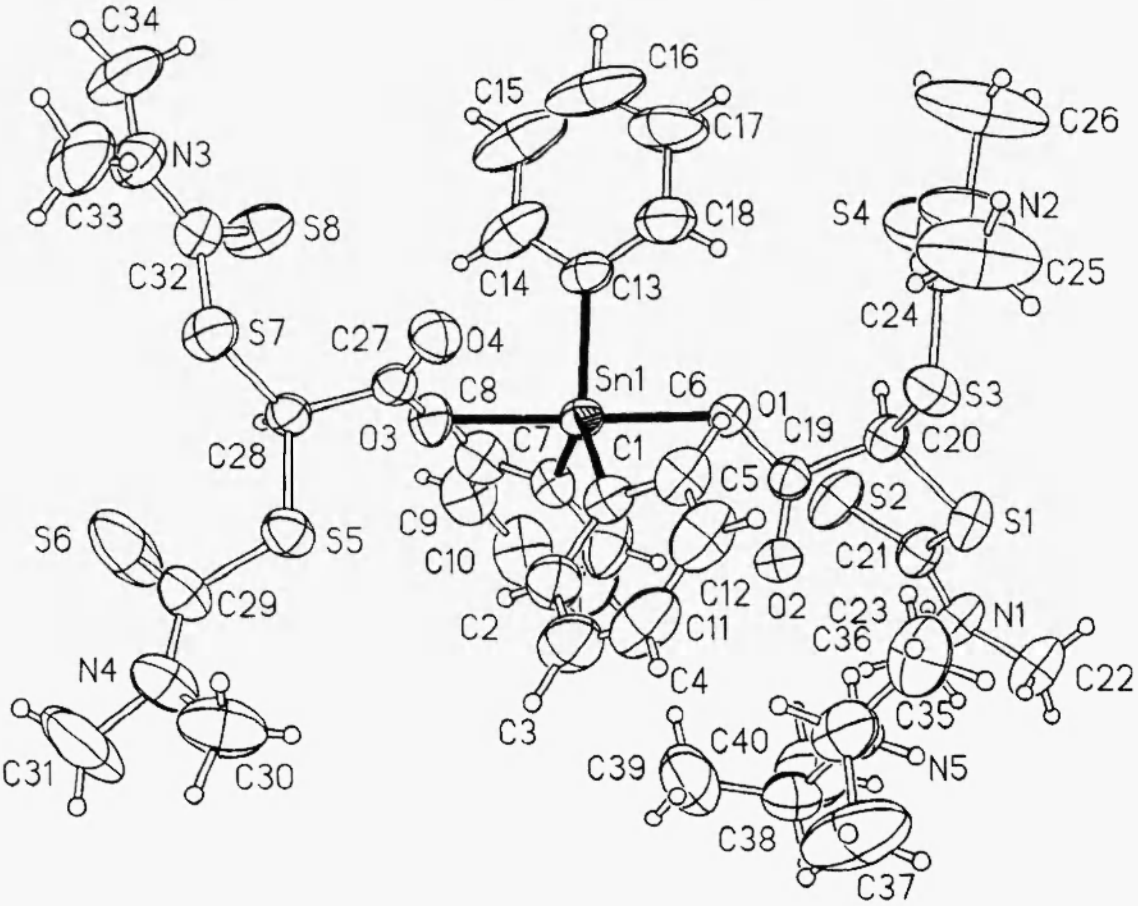


Fig.2*a*. *ORTEP* plot of diisopropylammonium bis[(*N*,*N*-dimethyldithiocarbamoyl)acetato]-triphenylstannate at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles: Sn1-C1 2.121(4) Å, Sn1-C7 2.132(4) Å, Sn1-C13 2.124(4) Å, Sn1-O1 2.213(3) Å, Sn1-O3 2.227(3) Å; C1-Sn1-C7 121.2(2)°, C1-Sn1-C13 128.2(2)°, C1-Sn1-O1 90.4(1)°, C1-Sn1-O3 89.7(1)°, C7-Sn1-C13 110.5(2)°, C7-Sn1-O1 92.0(1)°, C7-Sn1-O3 89.0(1)°, C13-Sn1-O1 85.2(1)°, C13-Sn1-O3 93.8(2)°, O1-Sn1-O3 178.8(1)°.

The 2,2'-iminodipyridinium series of stannate consists of the bis(chlorodifluoroacetato)triphenylstannate (Fig. 3), the bis(trifluoroacetato)triphenylstannate as well as 'mixed' (chlorodifluoroacetato)(trifluoroacetato)triphenylstannate [2]. The attempt to characterize the bis(trichloroacetato)triphenylstannate was unsuccessful as the compound precipitated from solution as a fine powder. The tin-oxygen distances in the present bis(chlorodifluoroacetato)stannate [2.194(5) Å, 2.310(5) Å] are similar to those [2.220(5) Å, 2.252(5) Å] found in the bis(difluoroacetato)triphenylstannate and those [2.206(4) Å, 2.294(4) Å] found in the (chlorodifluoroacetato)(trifluoroacetato)triphenylstannate [2]. The distances in (3) are longer than the covalent tin-oxygen distance [2.186(3) Å] found in bis(aquachlorodifluoroacetatotriphenyltin 1,10-phenanthroline) [27].

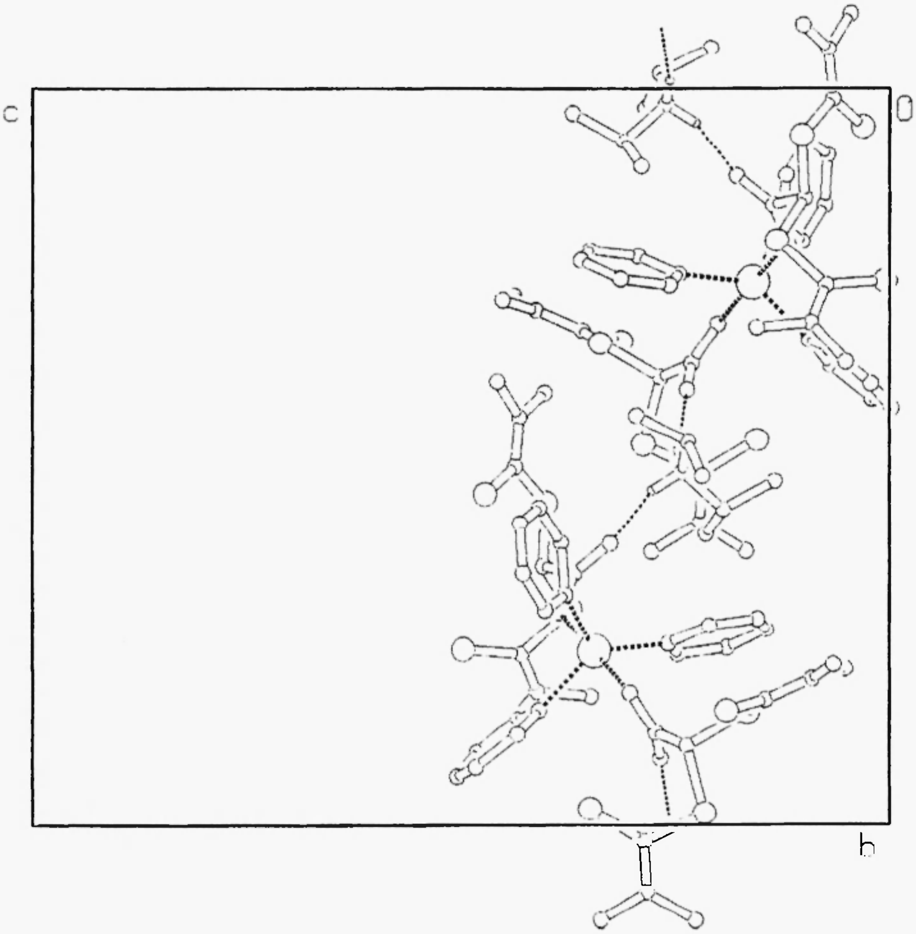


Fig.2*b*. *PLUTON* plot of the hydrogen-bonded polymeric chain of diisopropylammonium bis[(*N*,*N*-dimethyldithiocarbamoyl)acetato]triphenylstannate projected along the *a*-axis of the unit cell. Hydrogen bonds: N5 O2 = 2.780(5), N5 O4' 2.950(6) Å. Symmetry transformation *i* = 0.5 - *x*, 0.5 + *y*, 1.5 - *z*.

The ^{119}Sn NMR resonances of the dicyclohexylammonium bis(trifluoroacetato)triphenylstannate (**1**), tetramethylammonium bis(trifluoroacetato)triphenylstannate [1] and diisopropylammonium bis[(*N*,*N*-dimethyldithiocarbamoyl)acetato]triphenylstannate (**2**) appear at -300±40 ppm relative to tetramethyltin, in agreement with the *trans*-trigonal bipramidal geometries found from crystallographic analysis. The spectra also show chemical-shift tensors that are symmetric, i.e., the principal components decrease in the order $\delta_{11} > \delta_{22} > \delta_{33}$, as determined from simulation of the spinning side-band patterns. The asymmetry parameter or skew, κ, which is calculated from these principal components, is a numerical representation of the overall shape of the spinning side-band pattern. The skew ranges from +1 for a prolate pattern to -1 for an oblate pattern [9]. The solid-state spectra recorded in this work, as exemplified by the spectrum of tetramethylammonium bis(trifluoroacetato)triphenylstannate in Fig. 4, have an oblate pattern (k = -1). On the other hand, a prolate pattern (k = 0.63) is noted in the spectrum of *cis*-trigonal bipyramidal triphenyltin

N,N-diethyldithiocarbamate [8]. The k parameter appears to be a reliable indicator of the disposition of the non-organic group in five-coordinate trioganotin compounds: indeed, the use of the skew parameter can be complementary to the use of tin-119*m* Mössbauer quadrupole splittings ($QS_{trans} \sim 2QS_{cis}$ [28]) for distinguishing between the five-coordinate *cis*/*trans* geometries.

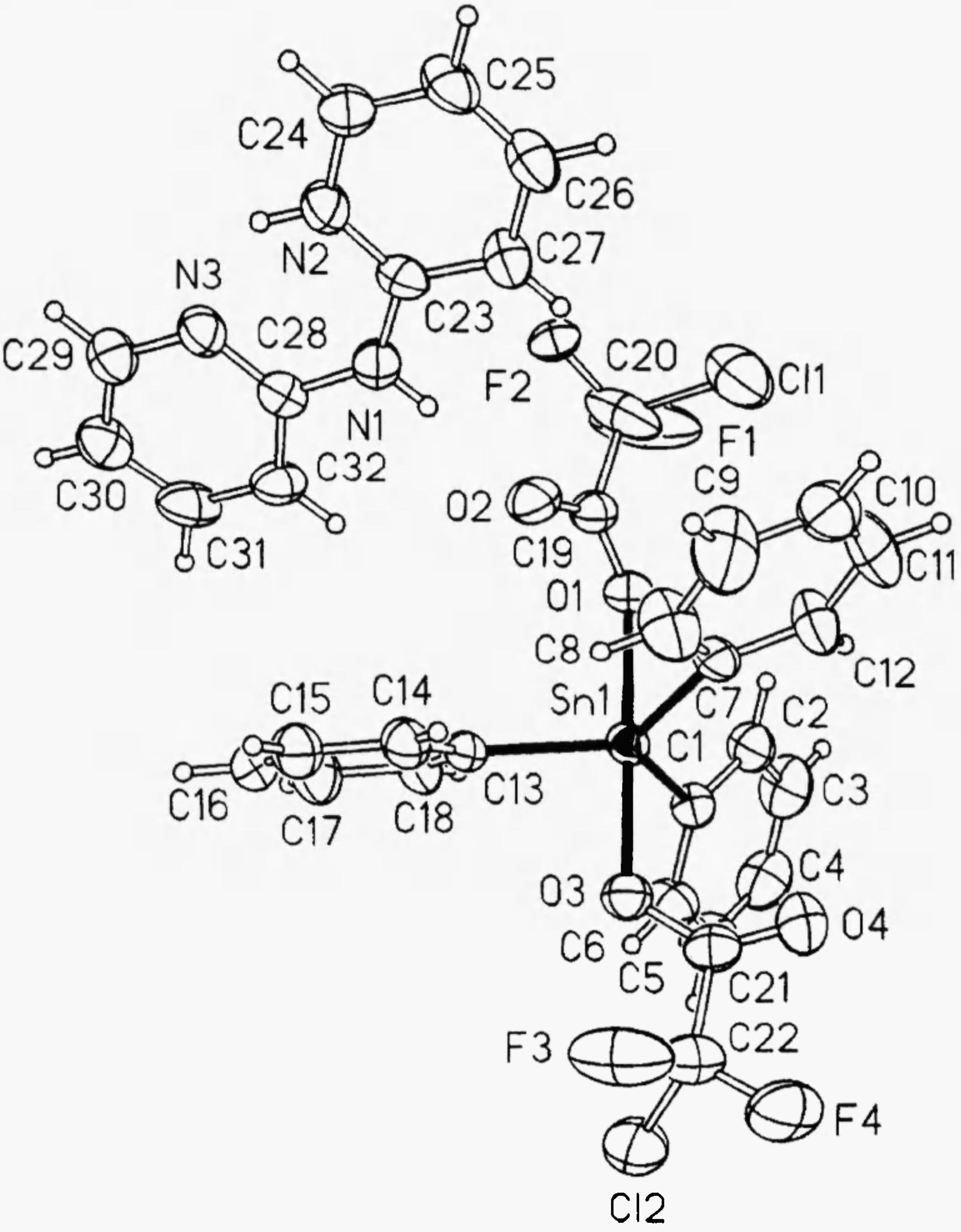


Fig.3. *ORTEP* plot of 2,2'-iminodipyridinium bis(chlorodifluoroacetato)triphenylstannate at the 30% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles: Sn1-C1 2.131(3) Å, Sn1-C7 2.123(4) Å, Sn1-C13 2.129(4) Å, Sn1-O1 2.310(5) Å, Sn1-O3 2.194(5) Å; C1-Sn7-C1123.1(2)°, C1-Sn1-C13 14.1(2)°, C1-Sn1-O1 86.0(2)°, C1-Sn1-O3 94.0(2)°, C7-Sn1-C13 122.3(2)°, C7-Sn1-O1 84.0(2)°, C7-Sn1-O3 96.3(2)°, C13-Sn1-O1 93.0(2)°, C13-Sn1-O3 86.8(2)°, O1-Sn1-O3 19.7(2)°.

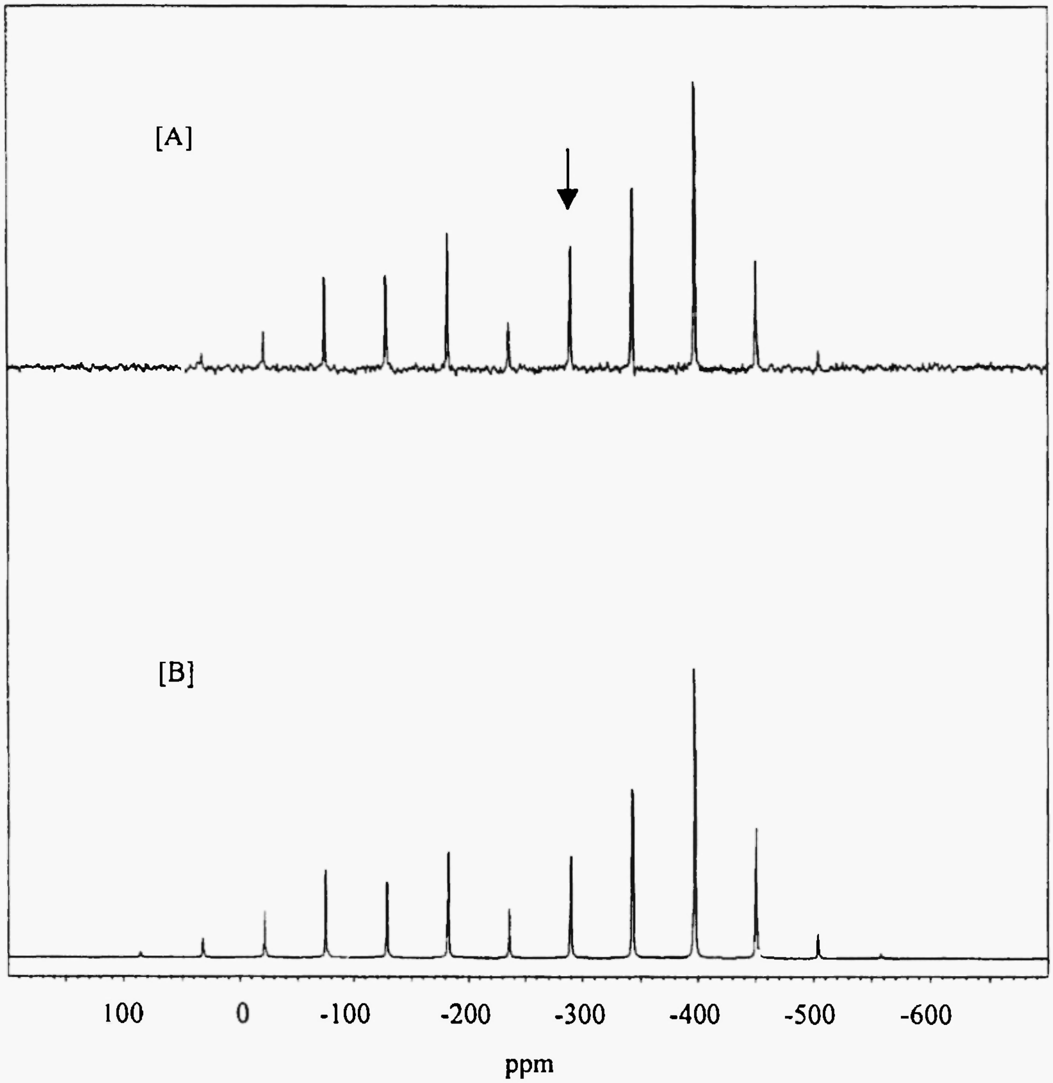


Fig.4. Solid-state ^{119}Sn MAS NMR spectrum of tetramethylammonium bis(trifluoroacetato)-triphenylstannate. [A]: Spectrum measured at 6 kHz with the isotropic peak at -290 ppm marked with an arrow. [B]: Simulated spectrum (see Experimental for details).

Acknowledgments
We thank the National Science Council for R & D, Malaysia (IRPA 09-02-03-004, 09-02-03-0371) for supporting this work.

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Received: January 14, 1999 - Accepted: January 21, 1999 - Accepted in revised camera-ready format: February 3, 1999