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Mixed Dialkyltin(IV) Trifluoroacetates

Anju Midha[a], **Rajender D. Verma**[a, *], **K. Brown**[b],
and **R. V. Parish**[b]

[a] Department of Chemistry, Panjab University, Chandigarh-160014, India
[b] Department of Chemistry, UMIST, Manchester M60 IQD, United Kingdom

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Mixed dialkytin(IV) trifluoroacetates, $MeEtSn(O_2CCF_3)_2$, $EtPr^nSn(O_2CCF_3)_2$ and $Pr^nBu^nSn(O_2CCF_3)_2$ have been prepared by metathetical reactions of the corresponding dialkyltin(IV) chlorides with silver trifluoroacetate in CH_2Cl_2. They are monomeric in benzene and nonconducting in $MeNO_2$ and $MeCN$. Bidentate trifluoroacetate groups are indicated by their IR spectra. *Mössbauer* spectra confirm *trans*-arrangement of the R—Sn—R' moiety. ^1H, ^{19}F NMR and mass spectra are also discussed.

(Keywords: IR; Mass spectra; Mössbauer spectra; NMR, ^{19}F*)*

Gemischte Dialkylzinn(IV)-trifluoracetate

Die gemischten Dialkylzinn(IV)-trifluoroacetate $MeEtSn(O_2CCF_3)_2$, $EtPr^nSn(O_2CCF_3)_2$ und $Pr^nBu^nSn(O_2CCF_3)_2$ wurden über Metathese-Reaktionen der entsprechenden Dialkylzinn(IV)-chloride mit Silbertrifluoracetat in CH_2Cl_2 dargestellt. Sie sind monomer in Benzol und nichtleitend in $MeNO_2$ und $MeCN$. Die IR-Spektren zeigen zweizähnige Trifluoracetat-Gruppen an. Die *Mössbauer*-Spektren bestätigen die *trans*-Anordnung der R—Sn—R'-Einheit. Die ^1H-, ^{19}F-NMR und die Massenspektren werden ebenfalls diskutiert.

Introduction

Various organotin(IV) trifluoroacetates are known[1,2]. Few mixed alkyltin(IV) trifluoroacetates are reported[2–4]. This communication deals with the preparation and characterization of hitherto unknown mixed dialkyltin(IV) trifluoroacetates.

Experimental

$RR'SnCl_2$, $R = Me$, $R' = Et$, $R = Et$, $R' = Pr^n$, $R = Pr^n$, $R' = Bu^n$ and silver trifluoroacetate were prepared by literature methods[5–8]. In a typical prepara-

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Table 1. *Analytical data, m.p., molar conductance and molecular weights*

	Analyses (%)[a, b]					Molar Cond. (Ohm^{-1} cm^2 mol^{-1})		Mol. Wts	
Compound	Sn	F	C	H	m. p. (°C)	*Me*NO_2	*Me*CN	Calc.	Found
Me Et $Sn(O_2CCF_3)_2$	30.32	29.28	21.48	2.02	47-49	2.15	3.69	389	401
	(30.59)	(29.30)	(21.59)	(2.06)					
Et Pr^n $Sn(O_2CCF_3)_2$	28.28	27.30	25.69	2.79	50-52	4.41	8.70	417	425
	(28.54)	(27.34)	(25.90)	(2.88)					
Pr^n *Bu*^{n} $Sn(O_2CCF_3)_2$	26.22	25.10	29.10	3.54	55-57	3.09	6.46	445	470
	(26.74)	(25.62)	(29.66)	(3.59)					

[a] Calc. values are in parenthesis.

[b] Sn as SnO_2, F (Ref.[9]), C and H microanalytically.

Table 2. *Infrared spectral data* (cm^{-1})

$MeEtSn(O_2CCF_3)_2$		$EtPr^nSn(O_2CCF_3)_2$		$Pr^nBu^nSn(O_2CCF_3)_2$		
Solid	CCl_4	Solid	CCl_4	Solid	CCl_4	Assignments
2 945 m	2 945 m	2 945 m	2 945 m	2 945 m	2 945 m	ν_{as}CH
2 920 m	2 920 m	2 920 m	2 915 m	2 915 m	2 920 w	ν_{as}CH
2 860 w	2 860 w	2 860 m	2 860 m	2 860 m	2 860 m	ν_sCH
1 662 s	1 662 s	1 658 s	1 660 s	1 660 s	1 660 s	$\nu_{as}CO_2$
1 458 m	1 458 m	1 460 w	1 460 w	1 460 s	1 460 s	—
1 420 w	1 419 w	1 422 m	1 425 m	1 425 m	1 422 m	—
1 380 w	1 382 w	1 375 s	1 378 m	1 378 m	1 375 m	—
1 210 w	—	1 220 w	—	1 210 w	—	νCF_3
1 185 sb	—	1 190 sb	1 185 sb	1 190 s	1 185 sb	νCF_3
1 150 s	—	1 150-1 160 sb	—	1 150 s	—	νCF_3
1 015 s	—	1 020 m	—	1 022 w	—	$\rho_t CH_2$
960 s	—	980 s	—	960 s	—	$\rho_r CH_3$
850 s	850 s	850 s	850 s	850 s	845 s	νC—C
799 s	—	799 s	—	795 s	—	δOCO
728 s	—	728 s	—	725 s	—	CCO_2 (in-plane bend)
685 s	685 s	685 s	690 s	682 s	682 s	CF_3 bend
590 m	585 m	585 m	590 w	590 m	592 m	CF_3 sym. bend
570 w	570 w	545 w	—	550 w	545 w	ν_{as}Sn—C
515 w	512 m	512 m	510 s	510 s	530 s	CF_3 asy. bend
490 m	490 m	480 m	482 m	482 m	470 m	ν Sn—C
430 w	430 m	440 w	430 m	430 m	—	CCO γ-bend
345 s	—	340 s	—	382 m	380 m	CCO δ-bend
292 m	290 m	295 m,	—	295 m	295 m	ν Sn—O

tion of mixed dialkyltin(IV) trifluoroacetate stoichiometric amounts of the corresponding dialkyltin(IV) chloride and silver trifluoroacetate were stirred in dry CH_2Cl_2 for 2-3 h at room temperature. AgCl precipitated was filtered off in N_2 atmosphere. The filtrate was evaporated *in vacuo* to get a solid compound.

Results and Discussion

The preparation of **A**: $MeEtSn(O_2CCF_3)_2$, **B**: $EtPr^nSn(O_2CCF_3)_2$, and **C**: $Pr^nBu^nSn(O_2CCF_3)_2$ may be represented as:

$$RR'SnCl_2 + 2\,AgO_2CCF_3 \rightarrow RR'Sn(O_2CCF_3)_2 + 2\,AgCl$$

The compounds are colourless, hygroscopic solids, soluble in polar and non-polar organic solvents (Table 1).

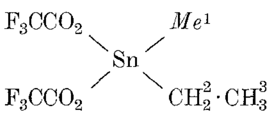
Table 3. *Mössbauer-*, H^1- *and* F^{19}-*NMR data*

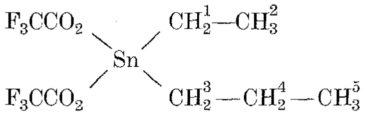
Compound	$\delta^{a,b}$ ($mm\,S^{-1}$)	Δ^{a} ($mm\,S^{-1}$)	$\delta(H)^{c}$ H_1	H_2	H_3	H_4	H_5	$\delta(F)$
MeEt$Sn(O_2CCF_3)_2$	1.68	4.31	1.27	1.80	1.45	—	—	74.98
EtPr^n $Sn(O_2CCF_3)_2$	1.69	4.52	1.79	1.49	1.87	1.56	1.16	74.99
Pr^n *Bu*^{n} $Sn(O_2CCF_3)_2$	1.69	4.55	multiplets			1.75-2.20 1.15-1.50		75.4

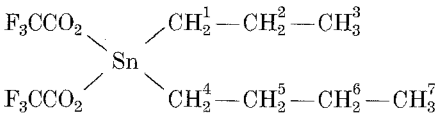
[a] $\pm$ 0.05 $mm\,S^{-1}$.

[b] Relative to SnO_2 at 80 K.

[c] The protons have been numbered as:







Infrared Spectra

The IR frequencies (4 000-200 cm^{-1}) of **A**-**C** (in KBr/nujol and 0.2 *M* solution in CCl_4) are recorded in Table 2 with tentative assignments. Solid and solution IR absorptions show essentially no change. Molecular weights in benzene indicate them to be monomeric in solution. The non-conducting nature of **A**-**C** in *Me*NO_2 and *Me*CN (Table 1) rule out their ionic nature. The positions of $\nu_{as}CO_2$ have been used in deciding the bonding mode in trifluoroacetates[1]. $\nu_{as}CO_2$ around 1 660 cm^{-1} in **A**-**C** (Table 2) are consistent with bidentate coordination of trifluoroacetate groups[1].

Mössbauer Spectra

Quadrupole splitting values of hexa-coordinated octahedral organotin(IV) compounds play an important role in deciding the relative positions of alkyl/aryl groups, particularly in dialkyl/aryltin(IV) compounds. It has been concluded that for *trans*-arrangement ($\sim$ 4 $mm\,S^{-1}$) of *R*-Sn-*R* is twice that for *cis*-arrangement. The values for **A**-**C** (Table 3) are in good agreement for the *trans*-arrangement of the alkyl groups. Almost similar isomer shifts of **A**-**C** may be due to same s-electron density around tin because of similar nature of the substituents.

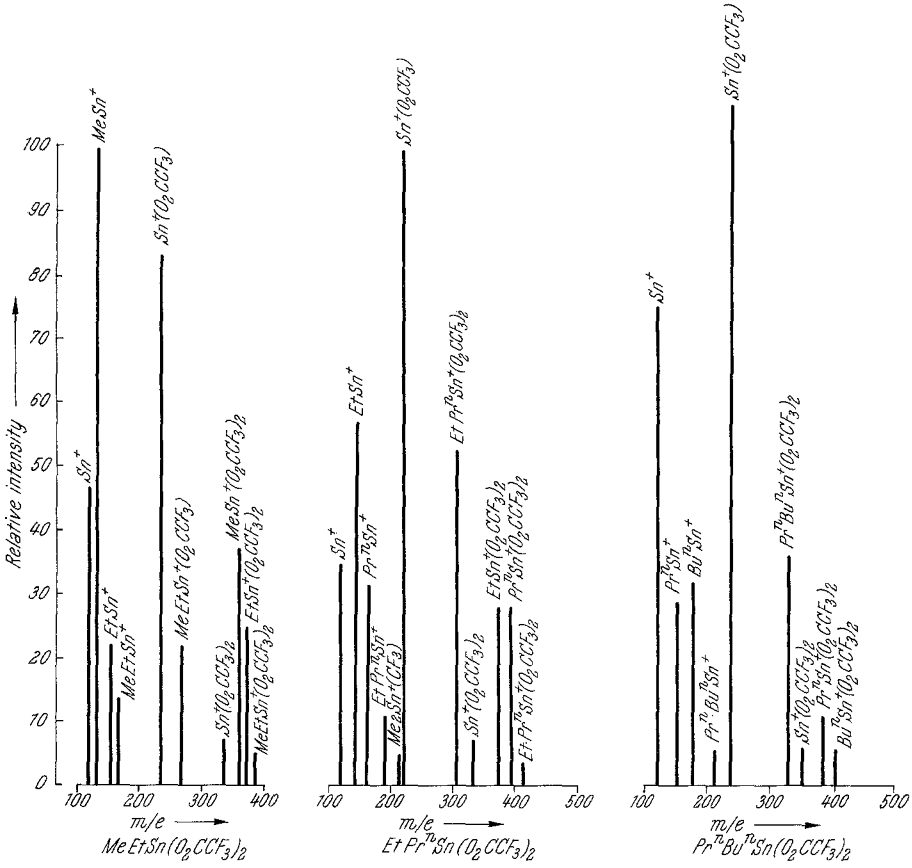


Fig. 1. Mass spectra of $RR'\mathrm{Sn(O_2CCF_3)_2}$

^{1}H *and* ^{19}F *NMR*

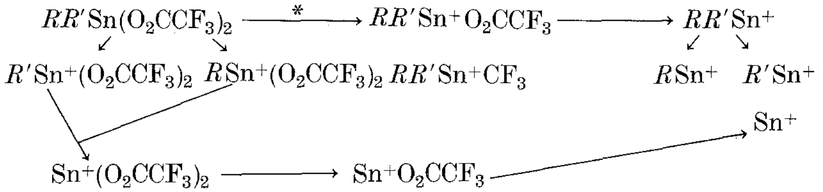
In view of the complex nature of the proton spectra of **A**-**C** (CCl_4 solution, Varian EM-390) it is difficult to assign it exhaustively. However, some assignments have been made (Table 3). The chemical shifts for methyl and ethyl protons in **A** are close to that of methyl protons in $Me_2\mathrm{SnCl_2}$[11] and methyl protons of the ethyl group (1.42 ppm) of $Et_2\mathrm{Sn(O_2CCF_3)_2}$[12]. In **B**, the chemical shifts lie close to those of the corresponding protons in diethyl (1.68, 1.42) and di-*n*-propyltin(IV) (1.50, 1.08) trifluoroacetates respectively. In **C**, the chemical shifts in the regions 1.75-2.20 may be assigned to H_1, H_2, H_4 and H_5 and 1.15-1.50 to H_3, H_6 and H_7 protons. These protons have been numbered as shown in Table 3.

The room temperature ^{19}F NMR spectra of CCl_4 and CH_2Cl_2 solutions of **A**–**C** exhibit a single peak around 75 ppm upfield[1,2] with respect to CCl_3F. The chemical shifts are independent of the solvent used. A small spread of chemical shifts in trifluoroacetates limits the utility of ^{19}F NMR data for interpretation of the nature of coordination of trifluoroacetate groups. The presence of only one peak indicates essentially free rotation of the CF_3 moiety about the C—C bond.

Mass Spectra

The assignments of the mass spectral peaks (^{120}Sn only) are given in Fig. 1. The common features of the spectra are the high stability of SnR_3^+ ions and the low abundance of the parent ions. The base peak in all these compounds is a mono-substituted tin fragment. The fragmentation pattern conforms to the hypothesis of preferred Sn^{IV} and Sn^{II} valence states in the tin containing fragments[13].

The probable fragmentation for $RR'Sn(O_2CCF_3)_2$ may be:



(* metastable peak observed)

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