Journal of Organometallic Chemistry, 49 (1973) 417–424

ELECTRON IMPACT FRAGMENTATION OF DIMETHYLCHLOROTIN CARBOXYLATES, TETRAMETHYL-1,3-BIS(CARBOXY)DISTANNOXANES AND TETRAMETHYL-1-(CARBOXY)-3-HYDROXYDISTANNOXANES

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(Received July 5th, 1972)

SUMMARY

Mass spectral studies of dimethylchlorotin carboxylates and their hydrolyses products, tetramethyl-1,3-bis(carboxy)distannoxanes and tetramethyl-1-(carboxy)-3-hydroxydistannoxanes show that the former are polymeric solids with some polymeric character retained in the gas phase, while the latter are dimeric solids. Evidence is found for carboxylate bridging in all of the compounds. Spectra of halogen-containing molecules contain numerous, relatively intense peaks assigned to recombination species with Sn–X bonds.

INTRODUCTION

Recently we reported the preparation and spectral studies of several new dimethylchlorotin carboxylates[1,2], and their hydrolyses products, tetramethyl-1,3-bis(carboxy)distannoxanes and tetramethyl-1-(carboxy)-3-hydroxydistannoxanes[3]. Based on infrared, Mössbauer, and ^{1}H and ^{19}F NMR spectra, pentacoordinate tin is present in the solid carboxylates and in their methylene chloride or chloroform solutions. The solid carboxylates appear to be polymeric with bridging carboxylate units.

However, in solution, non-fluorinated carboxylate-containing compounds are very likely to be chelate monomers, while the polyfluorocarboxylates retain polymeric character. Similarly, based largely on infrared data, the distannoxanes are dimeric compounds with a central four-membered $(Sn-O)_2$ ring in which the tin atoms are pentacoordinate (or perhaps with both pentacoordinate and hexacoordinate tin atoms).

Results of mass spectral examination of these compounds support the above spectral data in the assignment of polymeric structures and bridging carboxylate groups for the carboxylates and dimeric entities for the distannoxanes. A large number of relatively intense recombination fragments which contain Sn–X bonds are observed for compounds which contain halogen. Only rarely is a molecule-ion obtained and then only of very low intensity.

Apparently because of the large number of tin isotopes, mass spectra have not been used extensively to study tin compounds. We have found this a valuable addition to our structural studies. We report our results below.

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* Alfred P. Sloan Foundation Fellow, 1970–1972.

EXPERIMENTAL

The syntheses of $RC(O)OSn(Cl)(CH_3)_2$[2], $RC(O)OSn(CH_3)_2OSn(CH_3)_2OC(O)R$[3], and $RC(O)OSn(CH_3)_2OSn(CH_3)_2OH$[3] have been described. Mass spectra were recorded with a Hitachi–Perkin Elmer RMU-6E mass spectrometer which operated at an ionization potential of 70 eV. A direct insertion probe was used for sample introduction. The respective insertion temperatures were as follows: $RC(O)OSn(Cl)(CH_3)_2$: R = CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3, CF_2Cl, 25°; C_2F_5, 260°; C_3F_7, 70°. $RC(O)OSn(CH_3)_2OSn(CH_3)_2OC(O)R$: R = CH_2Cl, 260°; CH_2Br, CH_2I, 270°; CCl_3, 285; C_2F_5, 240°. $RC(O)OSn(CH_3)_2OSn(CH_3)_2OH$: R = CF_3, 230°; C_3F_7, 260°; CF_2Cl, 260°, $(CH_3)_3SnCl$, 25°.

An ion acceleration voltage of 1800 V was used in cases where $m/e < 600$; 900 V was used for $m/e > 600$. An ionizing current of 80 μA was a constant throughout this series as was the ion source temperature at 200°.

The high resolution spectrum of $CF_3C(O)OSn(Cl)(CH_3)_2$ was determined using an Associated Electronics Industries MS-9 mass spectrometer operating at 70 eV. The exact masses of the species were determined with (perfluoro-tert-butyl)-amine as the internal standard.

RESULTS AND DISCUSSION

Tin isotope abundance patterns are observed for the organostannoxanes. Ions which contain 2, 3 or 4 tin atoms or tin atoms and halogens (Cl and/or Br) also show very characteristic patterns.

Mass spectra of $(CH_3)_2SnClOC(O)R$

All of the carboxylates, with the exception of R = C_3F_7, have mass spectral peaks for which the *m/e* values are higher than the molecular mass of the monomeric species. This indicates that polymeric structures persist in the vapor state. The fragments identified as $[RC(O)O]_2SnCl^+$, $[RC(O)O]_2SnCH_3^+$, and $RC(O)OSnClCH_3OC(O)^+$ provide evidence for the existence of bridging RC(O)O groups in this series of compounds which is supported by other spectral data enumerated elsewhere[2]. Because of the unfavorable oxidation state of tin, molecule-ions for organotin compounds are always of very low intensity[6,7]. However, when R = $CHCl_2$, a molecule-ion (0.77%) is observed. With the exception of dimethylchlorotin acetate which has a base peak at *m/e* 43, all the carboxylates studied exhibit a base peak at *m/e* 205. The species obtained from the parent ions by loss of a methyl group or chlorine atom occur in every case. Fragments at *m/e* 185, 155, 135 and 120 are relatively abundant and are assigned to $(CH_3)_2SnCl^+$ (loss of carboxylate group), $SnCl^+$, $SnCH_3^+$, and Sn^+. The main fragmentation ions observed are listed in Table 1 with the intensities given relative to the base peak. It is seen that the fragmentation patterns of all the compounds are quite similar. Although only the ^{120}Sn-containing fragments are listed, all the tin-containing ions show good agreement with natural isotopic abundances.

Because of the similarity of the mass spectra of these compounds, the spectrum of dimethylchlorotin trifluoroacetate is taken as a representative example and is shown in Fig. 1.

As has been pointed out for other organotin systems[7-9], the most stable and,

TABLE 1

MASS SPECTRA OF DIMETHYLCHLOROTIN CARBOXYLATES, $(CH_3)_2SnClOC(O)R$. COMPARISON OF SOME PERTINENT PEAKS (^{120}Sn)

Compound	*CF_3*	*C_2F_5*	*C_3F_7*	*$CClF_2$*	*CH_3*	*CH_2Cl*	*$CHCl_2$*	*CCl_3*
$RC(O)OSnClCH_3OC(O)^+$	Trace	Trace	Trace	Trace			0.3	Trace
$[RC(O)O]_2SnCl^+$					Trace	0.9		
$[RC(O)O]_2SnCH_3^+$						Trace	0.2	Trace
M^+							0.7	
$(M-CH_3)^+$	6.9	6.7	0.73	3.9	8.3	5.6	8.0	2.6
$(M-Cl)^+$	6.9	7.3	1.5	2.0	14[a]	5.5	4.7	1.6
205	100	100	100	100	20[b]	100	100	100
$R\overset{O}{\overset{\Vert}{C}}OSn^+$	5.6	2.0		1.1	6.6	3.6	7.3	0.3
$(CH_3)_2Sn^+Cl$ (185)	30	51	36	44	18	56	54	47
$SnCl^+$ (155)	53	67	73	67	18	70	52	56
$SnCH_3^+$ (135)	15	23	20	11	10	20	19	11
Sn^+ (120)	20	34	29	20	8.8	30	16	20
$RC(O)^+$	4.2	8.5	6.4		100	4.5		0.75
R^+	41	42	22	10	32[c]	33	20	16
Cl^+ (35)	2.8	3.6	3.6	6.7	<0.10	0.60	4.7	14
CH_3^+	7.0	29	20	20	32	45	3.9	6.0

[a] *m/e* 209 = $[(CH_3)_2{}^{120}SnOC(O)CH_3]^+ + CH_3{}^{120}Sn^{37}Cl_2^+ + CH_3{}^{122}Sn^{35}Cl^{37}Cl^+$. [b] *m/e* 205 = $CH_3{}^{120}Sn{}^{35}Cl_2^+ + CH_3C(O)O^{116}Sn(CH_3)_2^+$. [c] $R^+ = CH_3$.

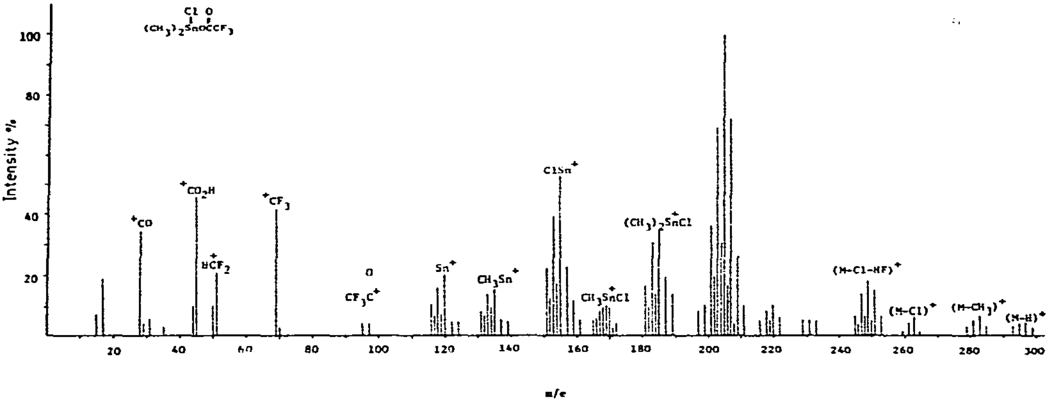


Fig. 1. Mass spectrum of dimethylchlorotin trifluoroacetate.

therefore, most abundant tin-containing fragments are the tri- and mono-substituted ions (Table 1) and these make a significant contribution to the overall spectrum whereas disubstituted tin-containing ions do not. The greater ease with which Sn–C bonds are cleaved compared with that of the Sn–Cl bond is evident from the relative intensities of the peaks resulting from such cleavages, *e.g.*, $Sn-Cl^+$ (*m/e* 155) is much more intense than $Sn-CH_3^+$ (*m/e* 135) even though two CH_3 groups are present in the molecule.

For the perfluorocarboxylates, the base peak at *m/e* 205 might be explained based on a rearrangement ion, CF_3OSn^+ but such an explanation is not possible for the acetates. Reexamination of this peak set was carried out with high resolution mass spectrometry by determining the exact mass of the fragment (*m/e* 201) which contains the ^{116}Sn ion. The possible ions with their exact (calculated) masses are listed in Table 2. The $\left[(CH_3)_2Sn\begin{smallmatrix}\diagup OH\\ \diagdown OH_2\end{smallmatrix}\right]^+$ ion was assigned to a peak at *m/e* 185 in the mass spectra of $(CH_3)_3SnO_2CCH_3$, $(CH_3)_3SnO_2CCD_3$ and $(CH_3)_3SnO_2SCH_3$[10]. The same species might well be formed in the fragmentation of the $(CH_3)_2SnClO_2CR$ compounds. However, comparison of the calculated and experimental numbers in Table 2 permits the assignment of this fragment to $(CH_3SnCl_2)^+$ unequivocally. The intensity ratio of the tin and chlorine isotopes was used to determine the elemental composition and showed that the peaks at *m/e* 201, 203, 205, 207 and 209 for these compounds contain two chlorine atoms.

It should be mentioned that the mass spectrum of $(CH_3)_3SnCl$ also shows very weak peaks at *m/e* 201, 203, 205, 207, 209 which could be attributed to a recombination species, such as $(CH_3SnCl_2)^+$. However, the base peak is $[(CH_3)_2SnCl]^+$ (*m/e* 185).

Species which result from the abstraction of halogens by tin-containing fragments are found not only at *m/e* 205 but also fragments obtained from the molecule-ion via loss of a methyl group and gain of one chlorine are found in the spectra of several compounds although their intensities are low. In fluorine substituted carboxylates the peaks at *m/e* 139, 154, 169, and 189 were assigned to SnF^+, CH_3SnF^+, $(CH_3)_2SnF^+$ and CH_3SnClF^+ (Table 3). Abstraction of halogens by Group IVB-containing species is observed frequently, *e.g.*, in the mass spectra of the series of compounds $(RC(O)O)_nSi(CH_3)_{4-n}$ ($R=CF_3$, C_2F_5, C_3F_7), the base peak[11] is $(CH_3)_2SiF^+$ when $n=1$ or 2 and is $(CH_3)SiF_2^+$ when $n=3$.

TABLE 2

POSSIBLE SPECIES AT *m/e* 201

Species	*Exact mass*[5]
$CH_3SnCl_2^+$	200.86292
$\left[CH_3ClSn\begin{smallmatrix}\diagup OH\\ \diagdown OH_2\end{smallmatrix}\right]^+$	200.90736
CF_3OSn^+	200.89187
Experimental value	200.86326

TABLE 3

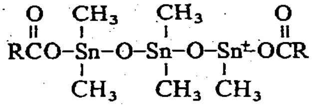
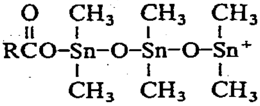
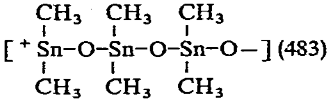
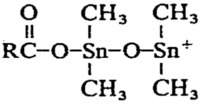
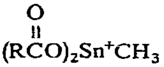
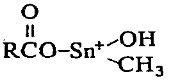
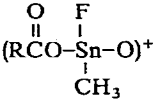
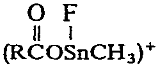
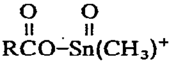
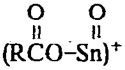
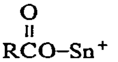
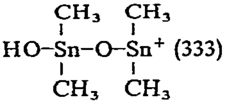
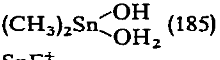
SOME SnF-CONTAINING PEAKS IN CARBOXYLATE SPECTRA

Species	*m/e*	CF_3	C_2F_5	C_3F_7	CF_2Cl
SnF^+	139	5.0	8.8	7.3	3.3
CH_3SnF^+	154	17.4[a]	23.0[a]	21.8[a]	18.9[a]
$(CH_3)_2SnF^+$	169	10.3	17.0	21.8	8.9
CH_3SnClF^+	189	13.9	16.7	10.9	12.2

[a] Includes contributions from $^{119}Sn^{35}Cl$ and $^{117}Sn^{35}Cl$, also.

TABLE 4

MASS SPECTRA OF $RCO_2Sn(CH_3)_2OSn(CH_3)_2OH$ AND $[C_2F_5C(O)OSn(CH_3)_2]_2O$

Compound	*CF_3*	*C_3F_7*	*CF_2Cl*	*$[C_2F_5C(O)OSn(CH_3)_2]_2O$*
 $R\overset{O}{\overset{\|}{C}}O-\underset{CH_3}{\overset{CH_3}{Sn}}-O-\underset{CH_3}{\overset{CH_3}{Sn}}-O-\underset{CH_3}{Sn^{+}}-O\overset{O}{\overset{\|}{C}}R$	[a]	1.2	1.7	9.9
 $R\overset{O}{\overset{\|}{C}}O-\underset{CH_3}{\overset{CH_3}{Sn}}-O-\underset{CH_3}{\overset{CH_3}{Sn}}-O-\underset{CH_3}{\overset{CH_3}{Sn^{+}}}$	2.3	0.8	1.1	7.9
 $[{}^{+}\underset{CH_3}{\overset{CH_3}{Sn}}-O-\underset{CH_3}{\overset{CH_3}{Sn}}-O-\underset{CH_3}{\overset{CH_3}{Sn}}-O-]$ (483)	1.9	2.9	2.9	8.5
 $R\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\overset{CH_3}{Sn}}-O-\underset{CH_3}{\overset{CH_3}{Sn^{+}}}$	4.0	1.8	1.9	22.2
 $(R\overset{O}{\overset{\|}{C}}O)_2Sn^{+}CH_3$				21.7
 $R\overset{O}{\overset{\|}{C}}O-Sn^{+}\left<\begin{matrix}OH\\CH_3\end{matrix}\right.$	29.7	15.4	8.0	
 $(R\overset{O}{\overset{\|}{C}}O-\underset{CH_3}{\overset{F}{Sn}}-O)^{+}$	10.3	2.6	12.7	19.7[b]
 $(R\overset{O}{\overset{\|}{C}}O\overset{F}{Sn}CH_3)^{+}$	36.7	21.1	5.7	37.1
 $R\overset{O}{\overset{\|}{C}}O-\overset{O}{\overset{\|}{Sn}}(CH_3)^{+}$	81.6	58.2	15.9	89.9
 $(R\overset{O}{\overset{\|}{C}}O-\overset{O}{\overset{\|}{Sn}})^{+}$	3.5		1.7	4.7
 $R\overset{O}{\overset{\|}{C}}O-Sn^{+}$	12.8	3.3	8.6	8.6
 $HO-\underset{CH_3}{\overset{CH_3}{Sn}}-O-\underset{CH_3}{\overset{CH_3}{Sn^{+}}}$ (333)	2.7	3.3	1.0	19.7[b]
$[(CH_3)_2Sn(O)F]^{+}$ or  $(CH_3)_2Sn\left<\begin{matrix}OH\\OH_2\end{matrix}\right.$ (185)	30.9	15.5	100.0[c]	28.5
SnF_3^{+}	2.6	2.5	2.9	2.9
$CH_3SnF_2^{+}$	24.5	27.0	7.4	28.0
$(CH_3)_2SnF^{+}$	100.0	100.0	39.0	100.0
$(F-Sn-O)^{+}$ (155)	15.8	7.3	49.0[d]	17.9
CH_3SnF^{+} (154)	8.4	5.6	10.2	6.9
SnF^{+} (139)	31.5	33.0	18.4	44.5
$Sn-CH_3^{+}$ (135)	45.9	31.3	36.7	49.6
Sn^{+} (120)	21.1	12.1	25.7	18.4
$RC(O)^{+}$	4.5	3.1	0.8	4.2
R^{+}	51.2	100.0[e]	11.9	16.4

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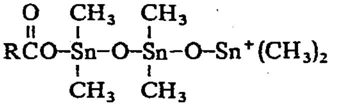
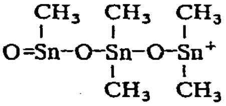
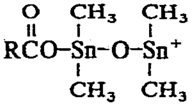
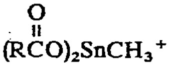
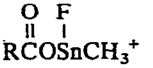
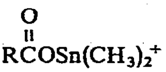
[a] No examination. [b] $m/e = 333$. [c] $m/e = 185$ $[(CH_3)_2SnCl]^{+}$. [d] $m/e = 155$ $(SnCl)^{+}$. [e] $m/e = 169$ are $(C_3F_7)^{+}$ and $(CH_3)_2SnF^{+}$.

Mass spectra of $RC(O)OSn(CH_3)_2OSn(CH_3)_2OC(O)R$ *and* $RC(O)OSn(CH_3)_2OSn(CH_3)_2OH$

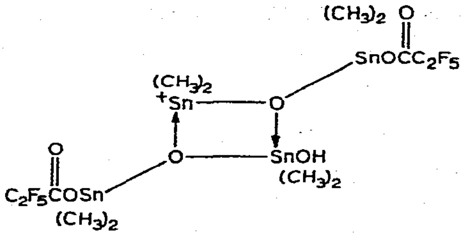
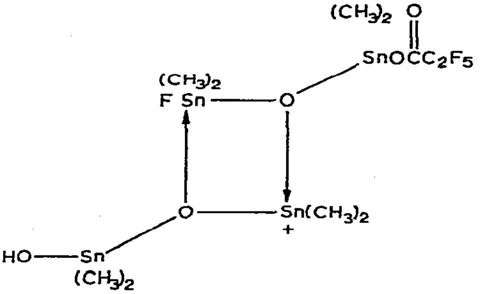
Infrared studies led us to suggest that both the bis(carboxy)distannoxanes and carboxyhydroxydistannoxanes were dimeric solids with a central ladder type structure[3]. These dimeric structures are strongly supported by the mass spectral data reported here (Tables 4 and 5). *E.g.*, in the spectrum of $C_2F_5C(O)OSn(CH_3)_2OSn(CH_3)_2OC(O)C_2F_5$, a fragment at *m/e* 1121 derived from the dimeric parent ion less $C_2F_5CO_2$ has a relative abundance of 1.2%. The observed and theoretical tin isotope distributions for this series of peaks are in agreement. Additional species of molecular

TABLE 5

MASS SPECTRA OF $RCO_2Sn(CH_3)_2OSn(CH_3)_2O_2CR$

	CH_2Cl	*CH_2Br*	*CH_2I*	*CCl_3*
 $R\overset{\overset{O}{\parallel}}{C}O{-}\underset{CH_3}{\overset{CH_3}{Sn}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Sn}}{-}O{-}Sn^+(CH_3)_2$	0.5			
 $O{=}\overset{CH_3}{Sn}{-}O{-}\underset{CH_3}{\overset{CH_3}{Sn}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Sn^+}}$	1.1			
 $R\overset{\overset{O}{\parallel}}{C}O{-}\underset{CH_3}{\overset{CH_3}{Sn}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Sn^+}}$	1.3			
 $(R\overset{\overset{O}{\parallel}}{C}O)_2SnCH_3^+$	14.8	5.4	1.4	
 $R\overset{\overset{O}{\parallel}}{C}O\overset{\overset{F}{\vert}}{Sn}CH_3^+$	37.0	11.7	2.5	0.3
 $R\overset{\overset{O}{\parallel}}{C}OSn(CH_3)_2^+$	75.0	52.4	66.1	0.2
 $R\overset{\overset{O}{\parallel}}{C}OSn^+$	10.6	7.9	5.9	Very weak
$CH_3SnX_2^+$	30.9	69.6	21.7	100.0
CH_3SnX^+	9.2	13.1	10.8	6.7
$(CH_3)_2SnX^+$	100.0	100.0	100.0	30.3
SnX^+	38.4	66.1	61.6	60.6
CH_3Sn^+ (135)	31.4	35.7	48.2	9.8
Sn^+	16.6	28.6	34.3	20.5
$RC(O)O^+$	9.1	11.9	21.2	0.4
R^+	40.8	32.7	31.8	6.4

weight in excess of that of the monomer are present, *e.g.*:

	m/e	(%)
	975	1.2
	831	0.3
$\overset{+}{Sn}(CH_3)_2OSn(CH_3)_2OSn(CH_3)_2OSn(CH_3)_2OC(O)C_2F_5$	811	0.6
$CF_3C(O)OSn(CH_3)_2OSn(CH_3)_2OSn(CH_3)_2O\overset{+}{Sn}(CH_3)_2$	761	0.8

These fragments occur via bond cleavages in the parent dimer accompanied in some cases by halogen or hydroxy recombination. The migrating species $[RC(O)O]_2SnCH_3^+$ are very intense in the spectra.

It should be noted that $(CH_3)_2SnX^+$ (X = F, Cl, Br or I) is the base peak when $R = CH_2Cl$, CH_2Br, CH_2I and C_2F_5, and $CH_3SnCl_2^+$ is the base peak when $R = CCl_3$. The abstraction of halogen by tin to form the strong tin–halogen bond is a dominant force in the system.

As is true for the bis(carboxy)distannoxane dimers, molecule-ions are not observed for the carboxyhydroxydistannoxane dimers, but the analogous $RC(O)OSn(CH_3)_2OSn(CH_3)_2OSn(CH_3)OC(O)R^+$, $RC(O)OSn(CH_3)_2OSn(CH_3)_2OSn(CH_3)_2^+$ and $RC(O)OSn(CH_3)_2OSn(CH_3)_2^+$ fragments do appear. The spectrum observed when $R = CF_2Cl$ is a typical one in which fragments from dimer less an carboxylate group or dimer less OH are present at low intensity (not listed in Table 5). High intensity peaks of fragments that result from recombination of OH or RC(O)O with other tin-containing species are observed invariably. Many species which arise from Sn–X bond formation are detected in the spectra and included in Tables 4 and 5.

CONCLUSION

These mass spectral studies have provided valuable additional structural information concerning dimethylchlorotin carboxylates and their hydrolysis products, tetramethyl-1,3-bis(carboxyloxy)distannoxanes and tetramethyl-1-(carboxyloxy)-3-hydroxydistannoxanes. Corroborating the conclusions based on infrared spectral data, the distannoxanes are dimeric solids. Fragments observed indicate that carboxylate bridging must occur in all of the compounds and that the solid dimethylchlorotin carboxylates are polymeric, an association which is maintained even in the vapor phase.

ACKNOWLEDGEMENTS

Fluorine research at the University of Idaho is supported by the Office of Naval Research and the National Science Foundation. We thank Dr. R. A. De Marco, Mr. G. B. Derr and Mr. D. J. McIntosh for mass spectra. Our special gratitude is due Mr. B. J. Nist of the University of Washington for the high resolution mass spectral data.

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