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THE PREPARATION AND TIN-119 MÖSSBAUER SPECTRA OF ANIONIC ORGANOPENTAHALOGENO- AND TETRAHALOGENO-STANNATE(IV) COMPLEXES

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Summary

A series of anionic monoorgano-pentahalogenostannate(IV) complexes, $M_2^+[RSnX_5]^{2-}$, where M = K^+, Me_4N^+, Et_4N^+ or $MePPh_3^+$; X = F, Cl or Br; R = Bu, Ph or $R'OCOCH_2CH_2$ (R' = Me or Et), has been prepared and these compounds have been studied by ^{119m}Sn Mössbauer spectroscopy. The novel monoorgano-tetrachlorostannate salts, $Me_4N^+[R'OCOCH_2CH_2SnCl_4]^-$, where R' = Et, Pr, i-Pr or Bu, have been synthesised and their infrared spectra indicate that the carbonyl group is coordinated to tin, thereby completing an octahedral configuration about the metal. When R' = Et, the pentachlorostannate salt, $(Me_4N)_2^+$-$[EtOCOCH_2CH_2SnCl_5]^{2-}$, containing a free carbonyl group, could also be isolated, whilst with the weaker electron donating methyl group, only the pentachlorostannate complex was formed.

Introduction

As part of a continuing investigation into the chemistry [1,2] and industrial applications [3] of monoorganotin(IV) derivatives, we have recently synthesised a range of salts containing $[RSnX_5]^{2-}$ and $[RSnX_4]^-$ anions and have studied the effect of varying R, X and the cation, M, on the stability of the complexes. The R groups chosen were those of importance industrially, i.e. R = Bu, Ph or $R'OCOCH_2CH_2$ [4].

There have been no systematic structural investigations into anionic monoorganotin salts of this type and the only X-ray study is on the methyltin complex, $Ph_4As[MeSnCl_4]$, in which the tin atom is occupying a trigonal bipyramidal geometry, with the alkyl group in an equatorial site [5]. Devaud [6] and Kazimir [7] have reported the syntheses of salts containing the monoorganopentafluorostannate ion, $[RSnF_5]^{2-}$, where R = Et, n-Bu or Ph, and found that a potassium cation was necessary to precipitate the complex fluoro-anion. In contrast, however, the organopentachlorostannate ion, $[RSnCl_5]^{2-}$, where R = Me, Et, Bu or Ph, is associated with rather larger cations, such as Me_4N^+ [8,9], Et_4N^+ [1,10,11], PyH^+ [9,10,12] or Ph_4As^+ [10], as is the $[RSnCl_4]^-$ ion, where R = Me, Et, Bu or Ph [5,9,10,13]. The only study of bromo- and iodostannate complexes appears to be that by Seyferth [8], who synthesised $(Me_4N)_2[PhSnBr_5]$, $Et_4N[EtSnBr_4]$ and $(Me_3NH)_2[MeSnI_5]$ *.

In this paper, we report the results of a synthetic and structural investigation on a wide range of monoorgano-halogenostannate salts, certain of which have subsequently been found to impart significant flame retardancy to woollen fabrics [3]. Further interest in these complexes arises from their possible involvement as intermediates in the direct reaction of stannous salts with alkyl halides (to produce the monoalkyltin trihalides: $RX + SnX_2 \rightarrow RSnX_3$), which are known [14,15] to be catalysed by the quaternary halides of the Group V elements.

Experimental

Complexes containing fluorostannate ions, $[RSnF_5]^{2-}$, $[RSnF_4Cl]^{2-}$ and $[RSnCl_3F_2]^{2-}$

The pentafluorostannate salts, $K_2[RSnF_5]$, where R = Bu, Ph or $BuOCOCH_2CH_2$, were prepared by Devaud's method [6], in which the appropriate organotin trichloride (1 mol) was added as a neat liquid, or, when R = $BuOCOCH_2CH_2$, in methanol solution, to aqueous potassium fluoride (5 mol). The products were precipitated immediately as dense white solids, which were washed with water and dried in vacuo, giving yields typically of 60—70%. Potassium monophenylpentafluorostannate [6] was recrystallised from a 1/1 v/v methanol/water mixture.

Potassium monobutyltetrafluoro-chlorostannate, $K_2[BuSnF_4Cl]$, was synthesised by the addition of bis(tetraethylammonium)butylpentachlorostannate, $(Et_4N)_2[BuSnCl_5]$ (1 mol) in acetone to a solution of potassium fluoride (4 mol) in 1/1 v/v acetone/water. The product was precipitated immediately as a dense white solid (46% yield), which was washed with water and dried in vacuo.

$(Me_4N)_2[BuOCOCH_2CH_2SnCl_3F_2] \cdot H_2O$ was prepared by the addition of a methanolic solution of 2-butoxycarbonylethyltin trichloride [16] (1 mol) to a solution of tetramethylammonium fluoride pentahydrate (2 mol) in methanol. The product was obtained as a hygroscopic white solid in 11% yield by evaporation of the solvent, followed by washing with ice cold methanol and drying in vacuo.

Complexes containing chlorostannate ions, $[RSnCl_5]^{2-}$ and $[RSnCl_4]^-$

The pentachlorostannate salts, $(Me_4N)_2[RSnCl_5]$, where R = Bu, Ph or $EtOCOCH_2CH_2$ were precipitated immediately when methanolic solutions of the appropriate organotin trichloride (1 mol) and tetramethylammonium chloride (2 mol) were mixed at room temperature. The products were separated by filtration, washed with methanol and dried in vacuo, to give stable white powders in yields of 70—90%. In the case of 2-ethoxycarbonylethyltin trichloride [16], a slight excess (2.25—2.50 mol) of tetramethylammonium chloride was used, to prevent contamination of the product with the tetrachlorostannate salt,

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* The salts $M_2[MeSnX_5]$, where $M^+ = PyH^+$ or $QuinH^+$ and X = Cl or Br, have also been reported [25].

$Me_4N[EtOCOCH_2CH_2SnCl_4]$. This latter salt was obtained as a white crystalline solid in 73% yield when dichloromethane solutions of tetramethylammonium chloride (1 mol) and 2-ethoxycarbonylethyltin trichloride (1 mol) were mixed at room temperature, followed by concentration of the solution and trituration with 60—80°C b.p. petroleum ether.

The pentachlorostannate complex, $(Me_4N)_2[MeOCOCH_2CH_2SnCl_5]$, was prepared by the autocatalysed methanolysis [17] of the analogous 2-ethoxycarbonylethyltin salt in excess refluxing methanol for 4 h. The product was obtained as a white powder after removal of the solvent. Although bis(tetraethylammonium)phenylpentachlorostannate, $(Et_4N)_2[PhSnCl_5]$, has been reported previously [10], our attempts to prepare this by mixing stoichiometric amounts of tetraethylammonium chloride and phenyltin trichloride yielded products which were consistently analytically impure. Bis(tetraethylammonium)-butylpentachlorostannate, $(Et_4N)_2[BuSnCl_5]$, was prepared according to previously reported methods and the melting point was in good agreement with earlier data [1].

$Me_4N[BuOCOCH_2CH_2SnCl_4]$ was precipitated as a white solid in 76% yield when methanolic solutions of tetramethylammonium chloride (1 mol) and 2-butoxycarbonylethyltin trichloride (1 mol) were mixed at room temperature. $Me_4N[PrOCOCH_2CH_2SnCl_4]$ was prepared by the addition of an n-propanol solution of 2-(n-propoxycarbonyl)ethyltin trichloride (1 mol) (prepared in situ by the autocatalysed transesterification [17] of $BuOCOCH_2CH_2SnCl_3$ with excess refluxing n-propanol for 4 h) to tetramethylammonium chloride (1 mol) in methanol. The product was precipitated immediately as a white powder in 97% yield. $Me_4N[i\text{-}PrOCOCH_2CH_2SnCl_4]$ was synthesised in a similar manner from $BuOCOCH_2CH_2SnCl_3$, using isopropanol as the transesterifying solvent. The yield was 57%.

Complexes containing bromostannate ions, $[RSnBr_5]^{2-}$, $[RSnBr_3Cl_2]^{2-}$, $[RSnBr_2Cl_3]^{2-}$, $[RSnBrCl_4]^{2-}$ and $[R'SnBrCl_3]^-$

The above mixed tetraethylammonium bromochlorostannate complexes ($R = Bu$; $R' = BuOCH_2CH_2$) were prepared by the addition of a methanolic solution of butyltin tribromide (from $BuSnCl_3$ (1 mol) and NaBr (3 mol) in refluxing acetone (4 h), b.p. 77—79°/0.2 mmHg. Lit. [18] 128—129°C/12 mmHg), butyltin trichloride or 2-butoxycarbonylethyltin trichloride (1 mol) to a solution of the appropriate tetraethylammonium halide (1 or 2 mol) in methanol, e.g. $BuSnCl_3 + Et_4NBr + Et_4NCl \rightarrow (Et_4N)_2[BuSnCl_4Br]$. The products crystallised out immediately, or on cooling to 0°C, in yields of 70—90%. Bis(tetraethylammonium)butyltrichlorodibromostannate, $(Et_4N)_2[BuSnCl_3Br_2]$, has been reported previously [1] and the melting point was in good agreement with earlier data. The monobutylpentabromostannate salts, $M_2[BuSnBr_5]$ ($M = MePPh_3^+$ or Et_4N^+), were prepared by the addition of a methanolic solution of butyltin tribromide (1 mol) to tetraethylammonium bromide (2 mol) or methyltriphenylphosphonium bromide (2 mol) in methanol. Evaporation of the solvent to a small volume, followed by cooling, gave lemon-yellow crystals of $(Et_4N)_2[BuSnBr_5]$ (85% yield). In the case of $(MePPh_3)_2[BuSnBr_5]$, it was necessary to evaporate the methanol to dryness and pump the residue at 0.4 mmHg to give the product as a pale yellow solid, which was washed with ice

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

Complex	Analysis Found (calcd.) (%)				M.p. (°C)
	C	H	N	Cl	
K_2BuSnF_5 [a]	13.84 (13.77)	2.33 (2.60)	—	—	>300
K_2BuSnF_4Cl	12.41 (13.15)	2.27 (2.48)	—	8.86 (9.70)	>300
$K_2[BuOCOCH_2CH_2SnF_5]$	19.61 (19.97)	2.89 (3.11)	—	—	>300
$(Me_4N)_2[BuOCOCH_2CH_2SnCl_3F_2] \cdot H_2O$	31.05 (32.25)	6.71 (7.04)	5.42 (5.02)	19.16 (19.04) [b]	>300
$(Me_4N)_2[BuSnCl_5]$	28.71 (28.74)	6.65 (6.65)	5.59 (5.59)	35.40 (35.35)	>300 (>305) [c]
$(Me_4N)_2[PhSnCl_5]$	32.16 (32.21)	5.57 (5.56)	5.32 (5.37)	33.91 (34.03)	>300 (>305) [c]
$(Me_4N)_2[MeOCOCH_2CH_2SnCl_5]$	27.40 (27.09)	5.98 (5.83)	5.08 (5.26)	33.08 (33.40)	>300
$(Me_4N)_2[EtOCOCH_2CH_2SnCl_5]$	28.59 (27.81)	6.04 (6.14)	5.13 (5.13)	32.53 (33.43)	>300
$Me_4N[EtOCOCH_2CH_2SnCl_4]$	24.83 (24.81)	3.93 (4.86)	3.51 (3.22)	32.80 (32.54)	>240 (dec.)
$Me_4N[PrOCOCH_2CH_2SnCl_4]$	26.70 (26.70)	5.33 (5.16)	3.18 (3.12)	31.00 (31.53)	>300
$Me_4N[i\text{-}PrOCOCH_2CH_2SnCl_4]$	26.12 (26.70)	5.21 (5.16)	3.21 (3.12)	31.80 (31.53)	>300
$Me_4N[BuOCOCH_2CH_2SnCl_4]$	28.34 (28.48)	5.50 (5.43)	3.13 (3.02)	31.02 (30.57)	>300
$Et_4N[BuOCOCH_2CH_2SnCl_3Br]$	31.83 (31.92)	5.85 (5.89)	2.46 (2.48)	18.45 (18.84) [d]	104—106
$(Et_4N)_2[BuSnCl_4Br]$	36.52 (36.51)	7.15 (7.51)	4.28 (4.26)	21.76 (21.55) [e]	169—171
$(Et_4N)_2[BuSnBr_5]$	27.95 (28.73)	5.71 (5.87)	3.62 (3.35)	[f]	>280 (dec.)
$(MePPh_3)_2[BuSnBr_5]$	43.48 (44.64)	3.83 (4.02)	—	[g]	116—119
$(Et_4N)_2[BuSnBr_3Cl_2]$	32.31 (32.14)	6.70 (6.56)	3.58 (3.75)	9.86 (9.51) [h]	148—149

[a] Reported in ref. 7, but no analytical data given. [b] Sn, 21.33 (21.25). [c] Reported in ref. 8, but no analytical data given. [d] Br, 14.22 (14.16). [e] Br, 12.20 (12.14). [f] Sn, 14.00 (14.24). [g] P, 4.99 (5.48). [h] Br, 31.92,(32.00).

cold isopropanol and dried. The yield was 96%.

The melting points and analytical data for the complexes are summarised in Table 1.

Attempts to prepare complexes containing iodostannate ions, $[RSnI_5]^{2-}$ or $[RSnI_4]^-$

Attempts to prepare the iodostannate salts, $M_2[RSnI_5]$ and $M[RSnI_4]$ or the mixed complexes, $M_2[RSnI_nX_{5-n}]$ and $M[RSnI_nX_{4-n}]$, from the appropriate butyl- or phenyl-tin trihalide and the tetraalkylammonium iodides, R_4NI (R = Et or Bu), benzyltriphenylphosphonium iodide or methyltriphenylarsonium iodide, were unsuccessful.

The reaction of tetraethylammonium iodide (2 mol) with butyltin tribromide (1 mol) in methanol gave dark brown needles of Et_4NI_3, m.p. 136—137°C, which crystallised out on standing (Found: C, 18.80; H, 3.95; N, 2.74; I, 74.51%. $C_8H_{20}I_3N$ calcd.: C, 18.91; H, 4.00; N, 2.72; I, 74.62%). Similarly, the only isolable product from the reaction between phenyltin triiodide (1 mol) and methyltriphenylphosphonium bromide (2 mol) in methanol was $MePPh_3I_3$, m.p. 88—91°C (Found: C, 34.65; H, 2.88%. $C_{19}H_{18}I_3P$ calcd.: C, 34.68; H, 2.76%).

Mössbauer spectra

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd., Oxford) with a 512-channel data store. A 15 mCi $Ba^{119m}SnO_3$ source was used at room temperature and samples were packed in perspex discs and cooled to 80 K, using a liquid nitrogen cryostat. The experimental error in the measured values of isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters is ± 0.05 mm s^{-1}.

Infrared spectra

Infrared spectra were recorded on a Grubb—Parsons Spectromaster Mark I instrument using potassium bromide discs or Nujol mulls.

Results and discussion

Monobutyl- and monophenyl-tin complexes

It is apparent from Table 1 that smaller cations are favoured by those mono-organotin anions which contain the smaller halogens. For example, although it was possible to obtain the potassium salts, $K_2[BuSnF_5]$, $K_2[BuSnF_4Cl]$ and

TABLE 2

^{119m}Sn MÖSSBAUER DATA FOR MONOBUTYL- AND MONOPHENYL-TIN SALTS

Complex	δ (mm s^{-1})	ΔE_Q (mm s^{-1})
$K_2[BuSnF_5]$	0.27	1.75
$K_2[BuSnF_5]$	0.54 [a]	1.54 [a]
$K_2[BuSnF_4Cl]$	0.47	2.00
$K_2[PhSnF_5]$	0.13	1.62
$K_2[PhSnF_5]$	0.07 [a]	1.45 [a]
$(Me_4N)_2[BuSnCl_5]$	1.10	2.10
$(Me_4N)_2[PhSnCl_5]$	0.84	1.72
$(Et_4N)_2[PhSnCl_5]$	0.90 [b]	1.65 [b]
$(Et_4N)_2[BuSnCl_5]$	1.03	1.93
$(Et_4N)_2[BuSnCl_5]$	1.12 [c]	1.86 [c]
$(Et_4N)_2[BuSnCl_4Br]$	1.08	1.95
$(Et_4N)_2[BuSnCl_3Br_2]$	1.15	1.90
$(Et_4N)_2[BuSnCl_3Br_2]$	1.20 [c]	1.85 [c]
$(Et_4N)_2[BuSnBr_3Cl_2]$	1.20	1.85
$(Et_4N)_2[BuSnBr_5]$	1.38	1.80
$(MePPh_3)_2[BuSnBr_5]$	1.38	1.90

[a] Ref. 7. [b] Ref. 10. [c] Ref. 1.

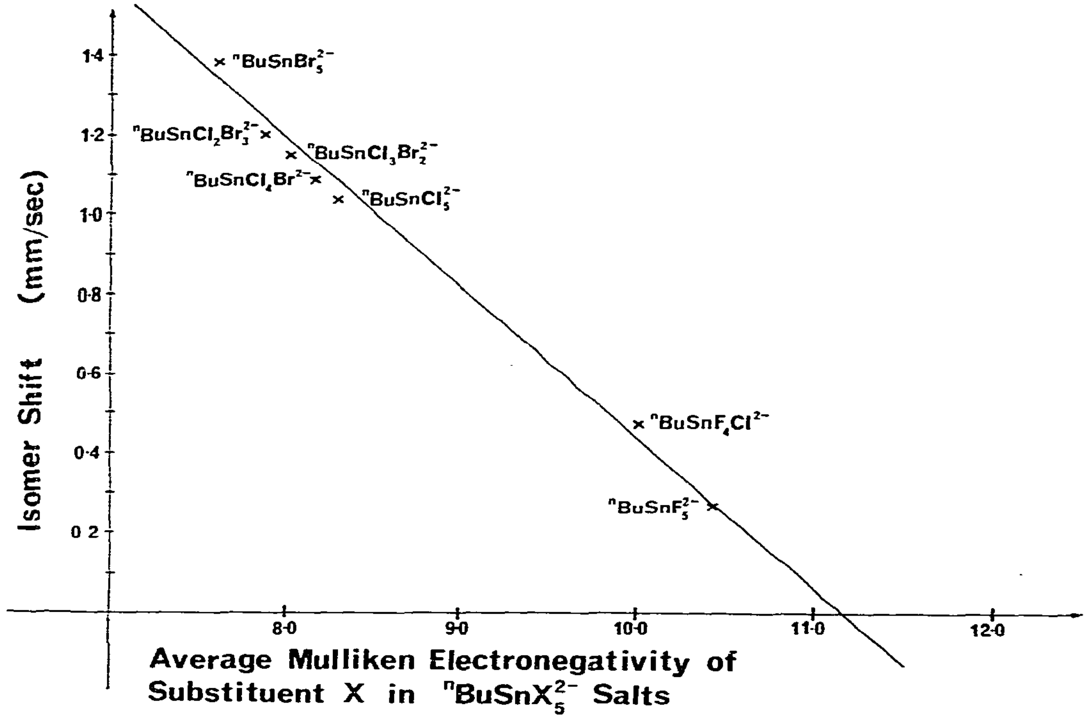

Fig. 1. Plot of isomer shift against average Mulliken electronegativity sum of the halogens for monobutylpentahalogenostannate complexes.

$K_2[PhSnF_5]$, the analogous chloro complexes required larger cations, e.g. $(Et_4N)_2[BuSnCl_5]$. Devaud has noted [6] a similar cation effect with $[EtSnF_5]^{2-}$ and $[EtSnCl_5]^{2-}$. Attempts to prepare monobutyl-, monophenyl- (and also monomethyl-) pentaiodostannate or tetraiodostannate salts were, however, unsuccessful, even with larger cations, such as $MeAsPh_3^+$. An interesting parallel may be drawn here with the monophenyllead complexes, where Lindemann and Huber [19] were able to synthesise salts containing the anions, $[PhPbX_5]^{2-}$ and $[PhPbX_4]^-$, when X = Cl or Br, but not when X = I.

The ^{119m}Sn Mössbauer spectra of the complexes are well-resolved quadrupole split doublets and the data are listed in Table 2.

Barbieri and his co-workers have shown [20] that the isomer shift values of monoorganotin compounds with the same coordination number show an approximate decrease with increasing average electronegativity of the groups bound to tin. The present series of potassium and tetraethylammonium monobutyl-pentahalogenostannates are ideally suited to test this observation further and, in Fig. 1, the average of the sum of the Mulliken electronegativities [21] of the halogens in these complexes is plotted against the isomer shift values.

It may be seen from Fig. 1 that an excellent linear relationship results, and by extrapolation, an isomer shift value of 1.67 mm sec^{-1} may be predicted for the $[BuSnI_5]^{2-}$ anion. The cation size does not significantly affect the value of δ, cf. $M_2[BuSnBr_5]$, where M = Et_4N or $MePPh_3$ (Table 2). A similar isomer shift/electronegativity relationship has been observed previously [1,21,22] for the inorganic hexahalogenostannate salts $[SnX_6]^{2-}$ and $[SnX_4Y_2]^{2-}$.

The quadrupole splitting values for the monobutyl- and monophenyl-pentahalogenostannates (Table 2) are typical of octahedral organotin complexes which contain one Sn—C bond [20].

2-Alkoxycarbonylethyltin complexes

The 2-alkoxycarbonylethyltin trichlorides, $ROCOCH_2CH_2SnCl_3$ [16], where R = Me, Et, Pr, i-Pr or Bu, were found to form complexes containing either a monoorganopentahalogenostannate dianion or a monoorganotetrahalogenostannate monoanion (Table 1). The Mössbauer data and antisymmetric carbonyl stretching frequencies for these novel salts are recorded in Table 3.

It is evident from the $\nu_{as}(CO)$ values that the monoorganopentahalogenostannate complexes contain a free carbonyl group, whereas the reduced $\nu_{as}(CO)$ frequencies in the mono-organotetrahalogenostannates are indicative [16,23,24] of a coordinated carbonyl group, which completes an octahedral coordination about tin (Fig. 2). A number of related mono-organotetrachlorostannate adducts, $Et_4N[RSnCl_4L]$, where R = Bu or Ph and L = monodentate N- or O-donor ligand, have recently been reported [10] by Cunningham et al.

It may be seen from Table 3 that, as the electron-donating ability of the RO group increases, the formation of the tetrachlorostannate salts is favoured, i.e. the electron density at, and, therefore, the coordinating power of, the carbonyl oxygen is increased. In the case of 2-ethoxycarbonylethyltin trichloride, both the tetrachlorostannate and the pentachlorostannate salts may be isolated, the formation of the former being favoured in dichloromethane solution, cf. ref. 10. The weakly nucleophilic bromide ion does not disrupt the intramolecular $C{=}O{\rightarrow}Sn$ coordination which exists in 2-butoxycarbonylethyltin trichloride [16,23], since this reacts with tetraethylammonium bromide to form the mixed tetrahalogenostannate complex (Table 3). However, with potassium fluoride and tetramethylammonium fluoride, 2-butoxycarbonylethyltin trichloride gives the pentahalogenostannate salts, containing a free carbonyl group. It is interesting to note that, as with the monobutyl- and monophenyl-tin complexes, the smaller anions are found in combination with smaller cations, e.g. $K_2[BuOCOCH_2CH_2SnF_5]$.

TABLE 3

^{119m}Sn MÖSSBAUER DATA AND ANTISYMMETRIC CARBONYL STRETCHING FREQUENCIES FOR 2-ALKOXYCARBONYL-ETHYLTIN SALTS

Complex	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\nu_{as}(CO)$ (cm^{-1})
$(Me_4N)_2[MeOCOCH_2CH_2SnCl_5]$	0.96	1.88	1724
$(Me_4N)_2[EtOCOCH_2CH_2SnCl_5]$	0.84	1.93	1724
$Me_4N[EtOCOCH_2CH_2SnCl_4]$	0.90	1.95	1640
$Me_4N[PrOCOCH_2CH_2SnCl_4]$	1.00	2.00	1640
$Me_4N[i\text{-}PrOCOCH_2CH_2SnCl_4]$	0.95	2.00	1640
$Me_4N[BuOCOCH_2CH_2SnCl_4]$	1.03	2.00	1640
$Et_4N[BuOCOCH_2CH_2SnCl_3Br]$	1.07	2.03	1640
$(Me_4N)_2[BuOCOCH_2CH_2SnCl_3F_2] \cdot H_2O$	0.74	2.08	1724
$K_2[BuOCOCH_2CH_2SnF_5]$	0.17	1.65	1724

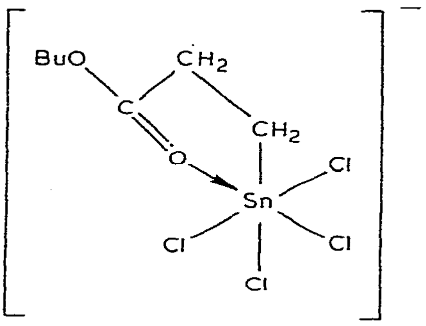

Fig. 2. Proposed structure of the anion in $Me_4N[BuOCOCH_2CH_2SnCl_4]$.

The Mössbauer isomer shifts of the complexes, as with the monobutyl- and monophenyl-tin analogues, decrease with increasing electronegativity of the halogen from 1.07 mm s^{-1} for $[BuOCOCH_2CH_2SnCl_3Br]^-$ to 0.17 mm s^{-1} for $[BuOCOCH_2CH_2SnF_5]^{2-}$. In the series of tetrachlorostannate salts, there is an approximate increase in δ with increasing electron-donating power of the OR group, reflecting the greater *s*-electron density at the tin nucleus. This effect is not observed in the two pentachlorostannates, where the carbonyl group is not involved in bonding to the tin. The six-coordinate pentachlorostannate dianion, $[EtOCOCH_2CH_2SnCl_5]^{2-}$ shows a lower δ value than the hexacoordinate monoanion, $[EtOCOCH_2CH_2SnCl_4]^-$, due to the reduced *s*-electron density at the tin nucleus in the former.

The quadrupole splitting values displayed by the tetrachlorostannate complexes (1.95—2.00 mm s^{-1}) are slightly larger than those of the pentachlorostannates and probably reflect the greater asymmetry at the tin nucleus in the tetrachlorostannate salts.

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References

1 A.G. Davies, L. Smith and P.J. Smith, J. Organometal. Chem., 23 (1970) 135.
2 A.G. Davies, L. Smith and P.J. Smith, J. Organometal. Chem., 39 (1972) 279.
3 P.A. Cusack, L.A. Hobbs, P.J. Smith and J.S. Brooks, J. Text. Inst., 71 (1980) 138.
4 A.G. Davies and P.J. Smith, Advan. Inorg. Chem. Radiochem., 23 (1980) 1.
5 M. Webster, K.R. Mudd and D.J. Taylor, Inorg. Chim. Acta, 20 (1976) 231.
6 M. Devaud, Rev. Chim. Mineral., 4 (1967) 921.
7 E.O. Kazimir, Ph. D. Thesis, Fordham University, 1969.
8 D. Seyferth, U.S. Pat., 3,070,615, 1969.
9 R.V. Parish and R.H. Platt, Inorg. Chim. Acta, 4 (1970) 65.
10 D. Cunningham, M. Little and K. McLoughlin, J. Organometal. Chem., 165 (1979) 287.

11 N.W.G. Debye, E. Rosenberg and J.J. Zuckerman, J. Amer. Chem. Soc., 90 (1968) 3234.
12 B.W. Fitzsimmonds, N.J. Seely and A.W. Smith, J. Chem. Soc. A, (1969) 143.
13 G. Tagliavini and P. Zanella, J. Organometal. Chem., 5 (1966) 299.
14 E.J. Bulten, J. Organometal. Chem., 97 (1975) 167.
15 J. Murphey and R.C. Poller, J. Organometal. Chem. Library, 9 (1980) 189.
16 R.E. Hutton, J.W. Burley and V. Oakes, J. Organometal. Chem., 156 (1978) 369.
17 L.A. Hobbs and P.J. Smith, Unpublished results.
18 C. Dörfelt, Ger. Pat., 1,152,693 (1961).
19 H. Lindemann and F. Huber, Z. Anorg. Allg. Chem., 394 (1972) 101.
20 R. Barbieri, L. Pellerito, N. Bertazzi and G.C. Stocco, Inorg. Chim. Acta, 11 (1974) 173.
21 C.A. Clausen and M.L. Good, Inorg. Chem., 9 (1970) 817.
22 R.H. Herber and H.-S. Cheng, Inorg. Chem., 8 (1969) 2145.
23 R.M. Haigh, A.G. Davies and M.-W. Tse, J. Organometal. Chem., 174 (1979) 163.
24 P.G. Harrison, T.J. King and M.A. Healy, J. Organometal. Chem., 182 (1979) 17.
25 P. Pfeiffer, B. Friedmann and H. Rekate, Ann., 376 (1910) 310.