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THE SYNTHESIS AND TIN-119m MÖSSBAUER SPECTRA OF SOME TETRAALKYLAMMONIUM DI- AND TRI-ORGANOHALOGENOSTANNATE(IV) COMPLEXES

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Summary

Some new organohalogenostannate(IV) complexes of the type $M^+ \{R_2SnCl_2X\}^-$ ($M = Et_4N, Bu_4N$; $R = Me, Bu, Ph$; $X = Cl, Br, I$), $M_2^+ \{Ph_2SnCl_2X_2\}^{2-}$ ($M = Et_4N, Bu_4N$; $X = Cl, Br$) and $M^+ \{R_3SnClX\}^-$ ($M = Et_4N, Bu_4N$; $R = Bu, Ph$; $X = Cl, Br, I$) have been isolated and their Mössbauer spectra studied. Definite structural assignments have been made on the basis of the data thus obtained. The attempted synthesis of hexacoordinate triphenyltin complexes, $(Bu_4N)_2^+ \{Ph_3SnClX_2\}^{2-}$ was not successful, and the reasons for this are discussed.

Introduction

In this paper results are reported for a synthetic and structural study of a wide range of di- and tri-organohalogenostannate(IV) salts with tetraalkylammonium cations. Our original interest in these complexes was as possible intermediates in a direct synthesis of tetraalkyltins in which organic halide reacts with tin in the presence of tetraalkylammonium halide and zinc [1,2]. Subsequent results have, however, indicated that it is unlikely that these complexes are involved in this particular reaction in the way first envisaged [3].

There have been few reports of tetrabutylammonium organohalogenostannates [4,5,6,7] and no Mössbauer studies of such complexes. Only four penta-coordinate organohalogenostannate complexes containing this cation have previously been reported, $Bu_4N^+ \{Ph_2SnCl_3\}^-$ [4], $Bu_4N^+ \{Me_3SnI_2\}^-$ [5], $Bu_4N^+ \{Ph_3SnCl_2\}^-$ [7] and $Bu_4N^+ \{Ph_3SnClBr\}^-$ [7], and we have repeated the

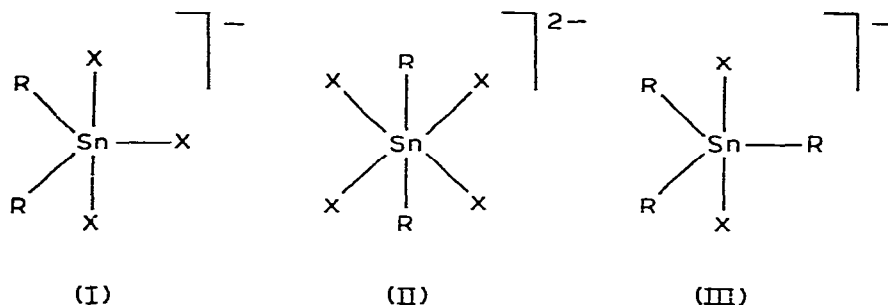


Fig. 1. Structures of organohalogenostannate complexes.

synthesis of three of these in order to record their Mössbauer spectra. We have succeeded in synthesising a further series of tetrabutylammonium organohalogenostannates with 5-coordinate anions, $\{R_3SnClX\}^-$, as well as two new bis-(tetrabutylammonium) diphenyltetrahalogenostannate complexes, $(Bu_4N)_2^+\{Ph_2SnCl_2X_2\}^{2-}$. We also report six new tetraethylammonium organohalogenostannates, five with pentacoordinate tin atoms in the complex anion, and one with hexacoordinate tin. All of these tetraethylammonium complexes are mixed bromo/chloro species, there being no previous reports of tetraethylammonium di- or tri-organohalogenostannates containing more than one kind of halogen.

Previous studies of related complexes have shown them to have the structures illustrated in Fig. 1, and similar structures are to be expected for each of the three structural types represented in this new series of complexes.

Diorganotrihalogenostannate anions which do not contain fluorine have been shown to have structure I (Fig. 1) by a variety of physical techniques, including infra-red spectroscopy [5], X-ray diffraction [8,9] and Mössbauer spectroscopy [10,11]. The X-ray diffraction studies [8,9] were of two different complexes containing the anion $\{Me_2SnCl_3\}^-$, which in both cases had the structure illustrated, with the axial sites occupied by chlorine atoms and the equatorial sites by two methyl groups and one chlorine atom. The Mössbauer spectra for this anion in other complexes [10,11] are consistent with this structure, as is the Mössbauer spectrum of $Et_4N^+\{Ph_2SnCl_3\}^-$ [10], though in this case there is no X-ray diffraction data to confirm the structure.

Structure II has been assigned to the anion of bis(pyridinium) diphenyltetra-chlorostannate by Mössbauer spectroscopy [10,12]. Point charge calculations [12,13] predict a value of ca. 4 mm sec^{-1} for the quadrupole splitting for a *trans*-octahedral structure, (II) and both reported values of ΔE_q are close to this. An X-ray diffraction study of the related dimethyltetrachlorostannate ion [14] confirmed that it has structure II and this had previously been predicted from its ΔE_q value of 4.32 mm sec^{-1} [10].

The anions of the complexes $Bu_4N^+\{Ph_3SnCl_2\}^-$ and $Bu_4N^+\{Ph_3SnClBr\}^-$ have been shown by NMR spectroscopy to have the trigonal bipyramidal structure, III, with equatorial phenyl groups [7]. An X-ray diffraction study of the related complex $Me_4N\{Ph_3SnCl_2\}$ reported in the same paper [7] confirms this structure for the triphenyldichlorostannate ion. Both the $\{Bu_3SnCl_2\}^-$ and the

$\{\text{Ph}_3\text{SnCl}_2\}^-$ ions were the subject of a combined X-ray diffraction—Mössbauer spectroscopic study [15], as the benzyltriphenylphosphonium and the phenylacetyltriphenylarsonium salts respectively, and this study confirmed that they have the structure illustrated.

Experimental

(i) Synthesis of dialkyltrihalogenostannate(IV) complexes

These complexes were prepared by adding a solution of tetraalkylammonium halide (0.01 mol) in either methanol or isopropanol to a solution of the dialkyltin dichloride (0.01 mol) in the same solvent and boiling for a few minutes. The crystals, which separated on standing in the refrigerator for 2–3 days, were filtered at the pump, and dried with filter paper. They were generally pure white or pale yellow (iodine-containing complexes were deep orange).

(ii) Synthesis of di- and tri-phenylhalogenostannate(IV) complexes

These complexes were prepared by mixing hot toluene solutions of either di- or tri-phenyltin chloride (0.005 mol) and tetraalkylammonium halide (0.005 mol or 0.01 mol) and allowing to cool to room temperature, whereupon white or pale yellow crystals separated out (iodine-containing complexes were deep orange). For the diphenyltin complexes, the ratio of tetraalkylammonium chloride or bromide to diphenyltin dichloride determined whether $\{\text{Ph}_2\text{SnCl}_2\text{X}\}^-$ or $\{\text{Ph}_2\text{SnCl}_2\text{X}_2\}^{2-}$ complexes were formed.

(iii) Synthesis of tributylhalogenostannate(IV) complexes

These complexes were prepared by adding tributyltin chloride (0.005 mol) dropwise to the tetraalkylammonium halide (0.005 mol), and dissolving this mixture in methanol, followed by boiling to low volume. Crystals separated following cooling and refrigeration for 2–3 days.

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

(iv) Mössbauer spectra

$^{119\text{m}}\text{Sn}$ Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd., Oxford) with a 512-channel data store. A 15 mCi $\text{Ba}^{119\text{m}}\text{SnO}_3$ 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 $\pm 0.05 \text{ mm sec}^{-1}$.

(v) Infra-red spectra

Infrared spectra were recorded on a Grubb-Parsons Spectrometer DM4 instrument, using Nujol mulls.

Results and discussion

The synthesis of 5-coordinate anionic complexes of tin was straightforward for simple alkyl- or aryl-tin compounds and analytical results and Mössbauer

TABLE 1
ANALYTICAL DATA FOR THE COMPLEXES

Complex	Found (calculated) (%)					Melting point
	C	H	N	Cl	X	
$\text{Bu}_4\text{N}^+\{\text{Me}_2\text{SnCl}_3\}^-$	42.61 (43.44)	8.32 (8.44)	2.75 (2.81)	21.43 (21.41)	—	117–119
$\text{Bu}_4\text{N}^+\{\text{Me}_2\text{SnCl}_2\text{Br}\}^-$	39.69 (39.15)	7.82 (7.61)	2.66 (2.53)	13.04 (12.87)	14.64 (14.50)	122
$\text{Bu}_4\text{N}^+\{\text{Me}_2\text{SnCl}_2\text{I}\}^-$	36.68 (36.69)	7.07 (7.13)	2.39 (2.38)	12.31 (12.06)	21.12 (21.57)	90–91
$\text{Et}_4\text{N}^+\{\text{Me}_2\text{SnCl}_2\text{Br}\}^-$	27.74 (27.92)	6.11 (6.05)	3.24 (3.25)	16.88 (16.52)	17.71 (18.61)	134
$\text{Bu}_4\text{N}^+\{\text{Bu}_2\text{SnCl}_3\}^-$	47.70 (49.55)	9.01 (9.29)	2.12 (2.41)	18.17 (18.32)	—	81
$\text{Bu}_4\text{N}^+\{\text{Bu}_2\text{SnCl}_2\text{Br}\}^-$	46.38 (46.03)	8.92 (8.64)	2.46 (2.23)	11.20 (11.34)	11.52 (12.78)	104–105
$\text{Bu}_4\text{N}^+\{\text{Bu}_2\text{SnCl}_2\text{I}\}^-$	42.81 (43.62)	7.78 (8.03)	1.87 (2.08)	9.82 (10.55)	18.18 (18.87)	53–54
$\text{Et}_4\text{N}^+\{\text{Bu}_2\text{SnCl}_2\text{Br}\}^-$	37.68 (37.37)	7.81 (7.39)	2.85 (2.72)	13.93 (13.82)	13.95 (15.57)	59–61
$\text{Bu}_4\text{N}^+\{\text{Ph}_2\text{SnCl}_3\}^-$	53.17 (54.04)	7.32 (7.40)	2.35 (2.25)	16.96 (17.14)	—	91–92 ^a
$\text{Bu}_4\text{N}^+\{\text{Ph}_2\text{SnCl}_2\text{Br}\}^-$	50.75 (50.47)	7.11 (6.91)	2.30 (2.10)	10.63 (10.66)	^d (12.01)	99–101
$\text{Bu}_4\text{N}^+\{\text{Ph}_2\text{SnCl}_2\text{I}\}^-$	47.29 (27.24)	6.49 (6.45)	2.14 (1.96)	9.95 (9.96)	15.39 (17.82)	92–93
$\text{Et}_4\text{N}^+\{\text{Ph}_2\text{SnCl}_2\text{Br}\}^-$	42.51 (43.34)	5.59 (5.42)	2.62 (2.53)	12.28 (12.82)	15.07 (14.44)	124–125
$\text{Bu}_4\text{N}^+\{\text{Bu}_3\text{SnCl}_2\}^-$	54.25 (55.74)	10.34 (10.45)	2.10 (2.32)	11.38 (11.78)	—	93–95
$\text{Bu}_4\text{N}^+\{\text{Bu}_3\text{SnClBr}\}^-$	50.70 (51.12)	9.47 (9.58)	1.99 (2.13)	4.59 (5.40)	12.79 (12.27)	59–60
$\text{Et}_4\text{N}^+\{\text{Bu}_3\text{SnClBr}\}^-$	44.99 (44.84)	8.66 (8.78)	3.12 (2.61)	6.31 (6.63)	16.48 (14.94)	64–67
$\text{Bu}_4\text{N}^+\{\text{Ph}_3\text{SnCl}_2\}^-$	60.35 (61.56)	7.28 (7.69)	1.81 (2.11)	10.39 (10.71)	—	89–93 ^b (decomp.)
$\text{Bu}_4\text{N}^+\{\text{Ph}_3\text{SnClBr}\}^-$	57.66 (56.88)	7.30 (7.11)	1.95 (1.95)	5.49 (4.94)	10.15 (11.15)	114–116 ^c
$\text{Bu}_4\text{N}^+\{\text{Ph}_3\text{SnClI}\}^-$	53.80 (54.09)	6.81 (6.76)	1.85 (1.85)	4.70 (4.30)	16.75 (16.83)	92–94
$\text{Et}_4\text{N}^+\{\text{Ph}_3\text{SnClBr}\}^-$	51.81 (52.41)	5.96 (5.88)	2.39 (2.35)	5.80 (5.96)	13.59 (13.44)	128–129
$(\text{Bu}_4\text{N})_2^+\{\text{Ph}_2\text{SnCl}_4\}^{2-}$	56.62 (58.75)	8.77 (9.12)	2.92 (3.11)	15.61 (15.30)	—	119–122
$(\text{Bu}_4\text{N})_2^+\{\text{Ph}_2\text{SnCl}_2\text{Br}_2\}^{2-}$	53.70 (53.46)	8.35 (8.30)	2.80 (2.83)	7.03 (7.18)	16.81 (16.19)	121
$(\text{Et}_4\text{N})_2^+\{\text{Ph}_2\text{SnCl}_2\text{Br}_2\}^{2-}$	43.34 (43.99)	6.72 (6.54)	3.97 (3.67)	8.85 (9.29)	21.08 (20.95)	161–165

^a Given in ref. 4 as 101°C. ^b Given in ref. 7 as 115–118°C (decomp). ^c Given in ref. 7 as 123–124°C.

^d Not determined.

TABLE 2
 ^{119}mSn MÖSSBAUER DATA FOR THE COMPLEXES

Complex	δ (mm sec $^{-1}$)	ΔE_{q} (mm sec $^{-1}$)
$\text{Bu}_4\text{N}^+\{\text{Me}_2\text{SnCl}_3\}^-$	1.39	3.40
$\text{Bu}_4\text{N}^+\{\text{Me}_2\text{SnCl}_2\text{Br}\}^-$	1.36	3.27
$\text{Bu}_4\text{N}^+\{\text{Me}_2\text{SnCl}_2\text{I}\}^-$	1.41	3.27
$\text{Et}_4\text{N}^+\{\text{Me}_2\text{SnCl}_2\text{Br}\}^-$	1.43	3.52
$\text{Bu}_4\text{N}^+\{\text{Bu}_2\text{SnCl}_3\}^-$	1.56	3.52
$\text{Bu}_4\text{N}^+\{\text{Bu}_2\text{SnCl}_2\text{Br}\}^-$	1.55	3.30
$\text{Bu}_4\text{N}^+\{\text{Bu}_2\text{SnCl}_2\text{I}\}^-$	1.58	3.37
$\text{Et}_4\text{N}^+\{\text{Bu}_2\text{SnCl}_2\text{Br}\}^-$	1.51	3.37
$\text{Bu}_4\text{N}^+\{\text{Ph}_2\text{SnCl}_3\}^-$	1.20	2.56
$\text{Bu}_4\text{N}^+\{\text{Ph}_2\text{SnCl}_2\text{Br}\}^-$	1.28	2.66
$\text{Bu}_4\text{N}^+\{\text{Ph}_2\text{SnCl}_2\text{I}\}^-$	1.32	2.69
$\text{Et}_4\text{N}^+\{\text{Ph}_2\text{SnCl}_2\text{Br}\}^-$	1.36	3.27
$\text{Bu}_4\text{N}^+\{\text{Bu}_3\text{SnCl}_2\}^-$	1.52	3.55
$\text{Bu}_4\text{N}^+\{\text{Bu}_3\text{SnClBr}\}^-$	1.46	3.47
$\text{Et}_4\text{N}^+\{\text{Bu}_3\text{SnClBr}\}^-$	1.48	3.63
$\text{Bu}_4\text{N}^+\{\text{Ph}_3\text{SnCl}_2\}^-$	1.31	2.86
$\text{Bu}_4\text{N}^+\{\text{Ph}_3\text{SnClBr}\}^-$	1.28	2.86
$\text{Bu}_4\text{N}^+\{\text{Ph}_3\text{SnClI}\}^-$	1.37	3.04
$\text{Et}_4\text{N}^+\{\text{Ph}_3\text{SnClBr}\}^-$	1.34	3.14
$(\text{Bu}_4\text{N})_2^+\{\text{Ph}_2\text{SnCl}_4\}^{2-}$	1.33	3.42
$(\text{Bu}_4\text{N})_2^+\{\text{Ph}_2\text{SnCl}_2\text{Br}_2\}^{2-}$	1.39	3.65
$(\text{Et}_4\text{N})_2^+\{\text{Ph}_2\text{SnCl}_2\text{Br}_2\}^{2-}$	1.39	3.60

data for all the complexes prepared appear in Tables 1 and 2. One pentacoordinate complex which could not be synthesised was $\text{Bu}_4\text{N}^+\{\text{Bu}_3\text{SnClI}\}^-$, as previously noted [16], and presumably this is because the combined steric hindrance of the iodide ion and the low acceptor strength of the parent organotin compound prevented the ion from forming. Similarly, the synthesis of the six-coordinate anionic complexes from diphenyltin dichloride and tetraalkylammonium chloride or bromide was straightforward. An attempt to make the complex $(\text{Bu}_4\text{N})_2^+\{\text{Ph}_2\text{SnCl}_2\text{I}_2\}^{2-}$ did not, however, succeed this time, presumably because of the steric problem of attempting to accommodate two bulky iodide atoms in the hexacoordinate structure II.

The Mössbauer parameters we have obtained for these new complexes are in good agreement with those previously reported for similar complexes, and it is possible to make definite structural assignments on the basis of this data. Dialkyltrihalogenostannate salts, including those of the $\{\text{Me}_2\text{SnCl}_3\}^-$ ion, whose structure has been definitely assigned [8,9], have been shown to have ΔE_{q} values in the region 3.25–3.75 mm sec $^{-1}$ [11,13,17], and this is taken to indicate a trigonal bipyramidal structure with two axial halogens and one equatorial halogen and two equatorial alkyl groups (I). Our dialkyltrihalogenostannate salts also have ΔE_{q} values within this range, and are thus presumed to have the

same structure, although it is not possible to assign the positions of the different halogen atoms in the mixed chloro/bromo or chloro/iodo species. The increase in δ from approximately 1.40 mm sec^{-1} in the dimethyltin complexes to about 1.55 mm sec^{-1} in the dibutyltin complexes indicates an increase in the *s*-electron density at the tin nucleus in the latter, and is a phenomenon which has been observed in related dimethyltin and dibutyltin complexes [18]. The diphenyltrihalogenostannates were found to have ΔE_q values in the region $2.56\text{--}3.27 \text{ mm sec}^{-1}$, and this may be taken to indicate that they, too, have the structure illustrated as I and previously reported [10].

The tributyl-dihalogenostannate complexes have ΔE_q values of around 3.50 mm sec^{-1} , and can thus be assigned the trigonal bipyramidal structure shown as III in Fig. 1. The values of ΔE_q are similar to those reported for $\{R_3\text{SnX}_2\}^-$ ions ($R = \text{alkyl}$) [13,15,19], and the values of δ are close to those of similar tributyltin species [15], including $\text{Ph}_3(\text{PhCH}_2)\text{P}\{\text{Bu}_3\text{SnCl}_2\}$, the structure of which has been determined by X-ray diffraction [15]. The triphenyltin complexes have lower ΔE_q values, at around 3.00 mm sec^{-1} , which are in the same region as values reported for similar ions which have been shown to have structure III [13,15,19]. We thus conclude that these new triphenyltin complexes also have this structure, thereby confirming the previous structural assignments made from NMR spectroscopy [7].

Finally, the Mössbauer data for the new diphenyltetrahalogenostannate complexes indicate that these ions have the *trans*-octahedral structure shown as II in Fig. 1. The ΔE_q values of about 3.50 mm sec^{-1} may be taken to signify a distortion from a regular *trans*-octahedral structure, for which point-change calculations predict a value of 4.00 mm sec^{-1} [12,13]. The values obtained are close to those found previously for the $\{\text{Ph}_2\text{SnCl}_4\}^{2-}$ ion [10,12].

It did not prove possible to form organohalogenostannates from the functionally substituted dialkyltin compound $(\text{MeOCOCH}_2\text{CH}_2)_2\text{SnCl}_2$. Reaction mixtures returned mainly unchanged starting materials, plus some products resulting from halogen exchange with the tetraalkylammonium halide, i.e. $(\text{MeOCOCH}_2\text{CH}_2)_2\text{SnClX}$. This failure to complex with halide ions indicates that the intramolecular donor-acceptor bond between the tin atom and the carbonyl oxygen atom is stronger in this compound than in the similar monoorganotin compound. Such monoorganotin compounds have been found to form hexacoordinate complexes, such as $(\text{Me}_4\text{N})_2\{\text{MeOCOCH}_2\text{CH}_2\text{SnCl}_5\}$, which has been shown by infrared spectroscopy to contain an uncoordinated carbonyl group [20].

Unsuccessful attempts were made to produce hexacoordinate complexes of the type $M_2\{R_2\text{SnCl}_2X_2\}$ ($M = \text{Et}_4\text{N}, \text{Bu}_4\text{N}$; $R = \text{Me}, \text{Bu}$; $X = \text{Cl}, \text{Br}, \text{I}$) and $M_2\{R_3\text{SnClX}_2\}$ ($M = \text{Et}_4\text{N}, \text{Bu}_4\text{N}$; $R = \text{Bu}, \text{Ph}$; $X = \text{Cl}, \text{Br}, \text{I}$) using methods similar to those described for the synthesis of the pentacoordinate complexes from the same reagents. In a number of cases, the products were the pentacoordinate complexes, corresponding to 1 : 1 adducts of the organotin compound, and the tetraalkylammonium halide. In other cases, elemental analysis gave results indicating intermediate compositions between 1 : 1 and 1 : 2, whilst for triphenyltin chloride a series of products was isolated having satisfactory elemental analyses for formulation as 1 : 2 adducts, and being apparently hexacoordinate (see Table 3).

TABLE 3
ANALYTICAL AND MÖSSBAUER DATA FOR APPARENTLY 6-COORDINATE TRIPHENYLHALOGENOSTANNATES

Apparent complex	Found (calculated) (%)				Mössbauer parameters			Mössbauer parameters of related 5-coordinate complexes	
	C	H	N	Cl	X	δ (mm sec ⁻¹)	ΔE_Q (mm sec ⁻¹)	δ (mm sec ⁻¹)	ΔE_Q (mm sec ⁻¹)
(Bu ₄ N) ⁺ ₂ {Ph ₃ SnCl ₃ } ²⁻	60.98 (63.81)	8.44 (9.25)	2.42 (2.97)	10.96 (11.32)	—	1.29	2.89	1.31	2.86
(Bu ₄ N) ⁺ ₂ {Ph ₃ SnClBr ₂ } ²⁻	57.73 (57.18)	8.13 (8.29)	2.46 (2.66)	3.87 (3.88)	14.22 (15.24)	1.32	2.99	1.28	2.86
(Bu ₄ N) ⁺ ₂ {Ph ₃ SnClI ₂ } ²⁻	53.05 (53.41)	7.85 (7.74)	2.53 (2.49)	3.19 (3.15)	21.50 (22.50)	1.36	2.94	1.37	3.04

Examination of the Mössbauer spectra for these complexes showed them to be almost identical (within experimental error) to those for the related penta-coordinate complexes. Moreover, for one such complex, “(Bu₄N)₂{Ph₃SnCl₃}”, the low frequency infrared spectrum was identical with that of its 5-coordinate homologue, with the $\nu(\text{Sn}-\text{Cl})$ at 240 cm⁻¹, a frequency characteristic of the pentacoordinate ion, {Ph₃SnCl₂}⁻ [4]. Finally, our attention has been drawn to the recent work of Smith and Khoo [21] who report the complexes Ph₃SnCl·bipy and Ph₃SnCl·phen to be hexacoordinate on the basis of ΔE_q values in the region 3.25–3.35 mm sec⁻¹, which are significantly higher than the usual region for pentacoordinate triphenyltin species, around 3.00 mm sec⁻¹ [10,19,22]. On the basis of this evidence, we infer that the complexes reported in Table 3 are not hexacoordinate, but simply mixtures of highly compatible salts which are difficult to separate by fractional crystallisation. These results cast doubt on the early results by workers in this field [23], which appeared to indicate the satisfactory synthesis of a number of triphenyltrihalogenostannate salts on the basis of elemental analysis only. It is known, by contrast, that trimethyltrihalogenostannates can be made, since (Me₄N)₂{Me₃SnCl₃}²⁻ has been produced [24], and shown to give a ΔE_q value consistent with its formulation as a hexacoordinate species.

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