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RAM GOPAL GOEL

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INFRARED SPECTROSCOPIC STUDIES OF SOME ORGANOTIN(IV) AND ORGANOANTIMONY(V) DERIVATIVES

ABSTRACT

Triphenyl-, trimethyl- and dimethyltin(IV), and trimethylantimony (V) derivatives of a wide variety of acids, including those of very strong acids, as well as derivatives of a transition metal oxyanion, were synthesized. Their structural characteristics in the solid state, under strictly anhydrous conditions, were determined from their infrared spectra. These spectroscopic results can only be interpreted in terms of a very strong interaction between the organometal group and the corresponding anionic group, and provide strong evidence for coordination or partial covalent bonding between the organometal group and the anionic group. Contrary to earlier reports, no evidence is found for the existence of free R_3Sn^+ , R_2Sn^{2+} or R_3Sb^{2+} cations in the solid state.

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ORGANOTIN(IV) AND ORGANOANTIMONY(V) DERIVATIVES

by

RAM GOPAL GOEL

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DOCTOR OF PHILOSOPHY

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of

Chemistry

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ABSTRACT

Triphenyl-, trimethyl- and dimethyltin(IV), and trimethylantimony(V) derivatives of a wide variety of acids, including those of very strong acids, as well as derivatives of a transition metal oxyanion, were synthesized. Their structural characteristics in the solid state, under strictly anhydrous conditions, were determined from their infrared These spectroscopic results can only be interpreted spectra. in terms of a very strong interaction between the organometal group and the corresponding anionic group, and provide strong evidence for coordination or partial covalent bonding between the organometal group and the anionic group. Contrary to earlier reports, no evidence is found for the existence of free R_3Sn^+ , R_2Sn^{2+} or R_3Sb^{2+} cations in the solid state.

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CHAPTER 1

INTRODUCTION

Tin (symbol Sn) is an element of atomic number 50 and occurs in group IVb and the 5th period of the periodic table. Organotin compounds are substances in which at least one tincarbon bond is present. The first organotin compound was described in 1852 by Löwig, and many significant contributions were made in this field during the next few decades. Although research in organometallic chemistry shifted then to other areas, interest in organotin chemistry was revived in about 1940, and at the present time a vast amount of literature exists on the subject. Two excellent reviews (1, 2a) of organotin chemistry appeared in 1960 covering almost all the available literature on the subject to that time.¹ Up to 1960, research in organotin chemistry was largely confined to preparative reactions. However since 1960, significant contributions have been made towards the study of stereochemistry of organotin compounds. The aim of this discussion is to review briefly the stereochemistry of organotin(IV) acid derivatives.

A neutral tin atom has fourteen electrons outside the krypton core, its configuration being $[Kr] (4d)^{10} (5s)^2 (5p)^2$. The ground state for the tin atom is a ³P state, derived from the s^2p^2 configuration. The first excited state of the tin atom is

¹After the completion of this text, a brief review on "Coordination in Organotin Chemistry" by R. C. Poller, has appeared in J. Organometal. Chem., 3,321-329(1965).

a ${}^{5}S$ state arising from a sp 3 configuration. The known oxidation states of tin, i.e. Sn(II) and Sn(IV), are derived from the ground state and the first excited state of the tin atom respectively. Organotin compounds of both oxidation states are known, however, the Sn(IV) is more commonly encountered. The tetraalkyl- and tetraaryl-tins, R₄Sn, are typically covalent, monomeric, tetrahedral compounds. The lower molecular weight compounds are soluble in common organic solvents but the higher molecular weight substances are soluble only in more non-polar solvents such as benzene, pyridine or chloroform. If one (or more) R groups in an R₄Sn compound is replaced by a halogen or any other anionic group, then the resulting compound may be considered an organotin(IV) acid derivative e.g. R₃SnX, R₂SnX₂ etc.

The organotin halides with the exception of fluorides are either low-melting solids or liquids at room temperature. They are soluble in organic solvents and the lower members in a series are also soluble in polar solvents such as water and alcohol, and are volatile. In general, all the organotin fluorides are nonvolatile solids which are soluble only in water and usually melt or decompose above 200[°].

Organotin chlorides, bromides and iodides are usually considered to be covalent compounds derived from the sp^3 configuration of the tin atom. The electron diffraction studies (3) of $(CH_3)_3SnX$, $(CH_3)_2SnX_2$, and $(CH_3)SnX_3$ (where X = Cl, Br or I) have shown that, in the gaseous state, these compounds have a tetrahedral configuration. Raman and infrared studies of alkyl and aryltin halides (Cl, Br, I) (4-8) have demonstrated that the tetrahedral configuration of the tin atom is still maintained in

the liquid and solid state, as well as in solution in inert nonpolar solvents. In solid trimethyltin chloride and bromide however, halogen bridging has been invoked (7). The dipole moment studies on several organotin chlorides also indicate a tetrahedral configuration of the tin atom in these compounds (1).

The electron diffraction results (3) showed that the Sn-X (X=C1, Br, I) bond length increases in the series SnX_A , $(CH_3)SnX_3$, $(CH_3)_2SnX_2$ and $(CH_3)_3SnX$. A decrease in the Sn-X bond length with increasing X substitution may be considered to indicate an increase in the Sn-X bond order. The electron density on the tin atom may be anticipated to decrease with an increase in the number of electronegative substituents, and this may result in the back donation of the p electrons to the empty 5d tin From a recent infrared study of methyltin chlorides, orbitals. a distinct fall in the Sn-Cl stretching force constants through the series $SnCl_4$, (CH₃) $SnCl_3$, (CH₃) $_2SnCl_2$ and (CH₃) $_3SnCl$ has been reported (4). This sequence follows the increasing inductive effect of the methyl groups facilitating the ionization of the Sn-Cl bond. However, Lorberth and Nöth (9) have recently reported on the basis of dipole moment determinations of $R_{4-n}SnCl_n$ (where $R = CH_3$, C_2H_5 , C_4H_9 , or C_6H_5) an increase in polarity of the Sn-Cl bond with increasing value of n. The authors suggest that the fact that the Sn-Cl bond becomes more polar by increasing the number of chlorine atoms in spite of a decrease in Sn-Cl bond distance, apparently shows that $d\Pi - p \prod$ bonding is only weak and cannot compensate for the electron abstraction caused by the negative inductive effect of the chlorine atoms. Thus the net

effect on the Sn-Cl bond seems to be an increase in polarity of about 10 percent in going from trimethyltin chloride to methyltin chloride. However, the authors recognize that, considering the assumptions involved in the calculations of these results, the variation in the polarity of the Sn-Cl bond is not significant and that other interpretations for this variation are possible, e.g. change in atomic polarization, and change in the Sn-R bond moment due to a change in the Sn-C distance.

There are other divergent views as well on the existence of dT-pT bonding in organotin halides. From the measurements of nuclear quadrupole coupling constants of 35 Cl in mono- and di-n-butyltin chlorides and mono- and diphenyltin chlorides, it has been suggested (10) that the T bond character of the Sn-Cl bond increases with increase in substitution of the Cl atom by an organic group. The ultraviolet (11) and infrared (8) spectroscopic studies of the homologues $(C_{6}H_{5})_{n}SnCl_{4-n}$ have been reported to indicate that the Sn-C_{ar}(a_r = aryl) bond has some double bond character. The authors consider that the negative inductive effect of the chlorine atom results in the donation of the T electrons from the phenyl groups to the empty 5d orbitals of the tin atom.

The bonding in organotin halides has also been recently studied by means of proton n.m.r. and Mössbauer spectra. From a study of the variation of the 117 Sn-CH₃ and 119 Sn-CH₃ coupling constants in methyltin chlorides, Holmes and Kaesz (12) have estimated that the s orbital participation by the tin atom in the formation of the Sn-C bond decreases with the increase in

the number of methyl groups. By assuming 25 percent s-character in the tin orbitals in $(CH_3)_4$ Sn, the s- character in the tin orbitals involved in bonding with the methyl groups has been estimated to be 32 percent in dimethyltin dichloride and 48 percent in methyltin trichloride. From the Mössbauer spectral studies of organotin compounds, Herber and Stoeckler (13) have concluded that the difference in percentage ionic character between a tin - sp³ hybridized carbon atom, a tin - sp² hybridized atom and a tin - halogen atom bond in the triaryl or trialkyl cannot be greater than ~5 percent. From similar Mössbauer studies, Hayes (14) has reported that in organotin halides, the relative degrees of ionicity of the fluoride, chloride and bromide substituents are 1.0: 0.65: 0.65: (±0.05).

Conductivity measurements on various organotin halides (C1, Br, I) have conclusively shown that these compounds are not true electrolytes in the pure state (1, 2a). However, when dissolved in water, pyridine, or acetone, these compounds are relatively good conductors; but in benzene, ethyl ether, nitrobenzene or nitromethane they are poor conductors (1, 2a). The electrolytic behaviour of alkyltin halides in hydrolytic solvents or in Lewis bases is due to the formation of addition compounds. Aqueous solutions of organotin halides are slightly acidic due to hydrolysis (1, 2a). The equilibrium between, say, trimethyltin chloride and pyridine, alcohol, or water has been represented (2a) as shown below:

$(CH_3)_3SnC1 + C_5H_5N$	>	$(CH_3)_3 Sn.NC_5 H_5^+ + C1^-$
(CH ₃) ₃ SnCl + ROH	>	$(CH_3)_3Sn.OHR^+ + C1^-$
$(CH_3)_3SnC1 + H_20$	\longrightarrow	$(CH_3)_3Sn.0H_2^+ + C1^-$
$(CH_3)_3SnOH_5 + H_2O$	>	$(CH_{3})_{2}SnOH + H_{2}O^{+}$

Rochow and Seyferth (15), and Rochow, Seyferth, and Smith (16), have reported a complete dissociation of dimethyltin dichloride in water, according to the following equations:

$$(CH_{3})_{2}SnCl_{2} + n H_{2}0 \longrightarrow (CH_{3})_{2}Sn(H_{2}0)_{n}^{2+} + 2C1^{-}$$

$$(CH_{3})_{2}Sn(H_{2}0)_{n}^{2+} \longrightarrow (CH_{3})_{2}Sn(H_{2}0)_{n-1}OH^{+} + H_{3}O^{+}$$

These authors have further stated that in water, amines, or amides, the solvated dimethyltin cation probably remains tetrahedral.

Although there is clear evidence for the ionization of alkyltin halides (or other acid derivatives) in the presence of a suitable Lewis base or where the solvent is also a donor, recent accumulated evidence indicates that the tetrahedral configuration of the tin atom is no longer retained in the solvated R_3Sn^4 or $R_{2}Sn^{++}$ cations. The only experimental evidence for the tetrahedral configuration of the solvated R_3Sn^+ or R_2Sn^{2+} cations is the reported (17, 18) partial resolution of $(CH_3)(C_2H_5)(C_3H_9)SnI$ from aqueous solution by conversion into the camphor sulphonate, followed by reconversion into iodide. However, attempts to repeat this experiment in the intervening years have not been successful (19, 20, 21). The ¹¹⁷Sn-CH₃ and ¹¹⁹Sn-CH₃ coupling constant data, obtained from the proton n.m.r. spectra of trialkyltin chlorides in water (12) or Lewis bases such as tetramethylene sulphoxide, N,N- dimethylacetamide or N,N-dimethylformamide (22), indicate a trigonal bipyramidal configuration around the tin atom, and a planar trialkyltin group. As will be discussed later, five coordination of the tin atom has been shown in many other trialkyltin derivatives.

Similarly, from recent Raman and proton n.m.r. studies of aqueous solutions of dimethyltin perchlorate and nitrate, McGrady and Tobias (21) have concluded that aqueous solutions of dimethyltin(IV) compounds contain an aquocation with a linear C-Sn-C skeleton and that, in all probability, four water molecules are coordinated to the cation in the equatorial plane by highly polar bonds.

Organotin halides form complexes with halogen ions e.g.

$$R_2SnX_2 + 2X \longrightarrow R_2SnX_4^2$$

It has been reported (23) that the stability of six coordinate anions of tin falls as the number of electronegative halogen substituents decreases, giving the series $\operatorname{SnCl}_6^2 > \operatorname{RSnCl}_5 > \operatorname{R}_2 \operatorname{SnCl}_4 >$ $\operatorname{R}_3 \operatorname{SnCl}_3^2$. In addition, organotin chlorides, bromides and iodides react with certain electron-pair donors to form addition compounds. The majority of the adducts are of the type $\operatorname{R}_n \operatorname{SnX}_{4-n}.2L$ (where R = organic group, X = Cl, Br or I, and L = an electronpair donor)(1). The range and stability of the addition compounds formed appear to decrease as the number of organic groups increases and, for tetraorganotins, there is no evidence of Lewis acid behaviour. No addition compound of organotin fluorides has been reported either.

Although addition compounds of organotin halides have been known for a long time, little information was available until very recently on their stereochemistry and structure. Earlier workers (24) favoured an ionic formulation for compounds such as $(CH_3)_3SnCl.Py$ involving a tetrahedral cation i.e. $(CH_3)_3SnPy^+Cl^-$. However, the crystal structure determination of

this compound, by Beattie, McQuillan, and Hulme (25,26) has shown that (CH₃)₃SnCl.Py is a molecular compound of trigonal bipyramidal configuration in which the trimethyltin group is planar and the chlorine atom and the pyridine molecule occupy the axial posi-Later Clark and O'Brien (27) found that such trimethyltin tion. derivatives as perchlorate and nitrate form stable diammonia adducts which contain the five coordinate cation $(CH_3)_3 Sn(NH_3)_2^+$ in the solid state, as shown by their infrared studies. Clark. O'Brien, and Pickard (28) confirmed the earlier reports (24) that trimethyltinbromide and chloride form unstable diadducts with ammonia or pyridine which readily lose one mole of the base to give stable monoadducts. The infrared studies by these authors show that the diadducts can be formulated as $(CH_3)_3 SnL_2^{+} \tilde{X}$ (where L = Lewis base, X = halogen). Matwiyoff and Drago (22) have reported the formation of 1:1 addition compounds between trialkyltin chlorides and Lewis bases such as tetramethylene sulphoxide, N,N-dimethylacetamide, or N,N-dimethylformamide. The infrared spectroscopic and tin-hydrogen coupling constant data (22) of these compounds again indicate trigonal bipyramidal structures containing planar trimethyltin groups. The existence of a five coordinate tin atom has also been proposed (29) in compounds of the type $R_3 Sn \vec{R}$, where \vec{R} is an unsaturated organic radical containing two nitrogen atoms in the 1,3 position (e.g. imidazole).

Addition compounds of triphenyltin chloride and bromide with nitrogen bases have been described in the literature (1). However, Kupchik and Lanigan (30) recently reported the products of reaction between triphenyltin bromide and amonia to be

bis(triphenyltin) oxide and ammonium bromide. These workers concluded that the reaction proceeded via an intermediate containing a Sn-N bond which was of low hydrolytic stability. Unfortunately no other work appears to have been reported on the nitrogen base adducts of triphenyltin halides.

Dialkyl- and diphenyltin dihalides (C1, Br, I) form 1:1 addition compounds with chelate ligands such as 1,10 phenanthroline and 2,2 bipyridyl. With pyridine or its hydrochloride, 1:2 addition compounds are formed. Similar adducts are also formed with methyltin trihalides and tin tetrahalides. In contrast, trialkyltin halides do not form addition compounds with chelate ligands. These addition compounds are apparently six The compound $(CH_3)_2SnCl_2.2Py$ is a weak electrolyte coordinated. in acetonitrile (31); therefore an ionic formulation for such addition compounds is most unlikely. From a survey of the known stereochemistry of $MX_4.2L$ (where M = IVb group element, X =halogen) adducts, Beattie (32) has suggested that small ligands tend to give cis adducts, while ligands which are sterically hindered tend to give trans adducts. Beattie has further pointed out that by considering the possibility of $d\Pi - p\Pi$ bonding in the Sn-X bond, the cis adduct is favoured assuming that Π bonding from X to Sn is more important than T bonding involving L. A strongly coordinating ligand could also have the effect of reducing $d\Pi - p\Pi$ bonding between the halogen and the tin atoms, in which case one factor favouring a cis configuration is lost. The infrared spectroscopic studies of $(CH_3)_2 SnCl_2.2Py$ and other dimethyltin dichloride and methyltin trichloride addition compounds indicate (33) that these compounds are six coordinate, with trans methyl

groups in the case of coordinated $(CH_3)_2 SnCl_2$.

So far this discussion has been largely concerned with the stereochemistry of organotin(IV) chlorides, bromides and iodides and their addition compounds. As stated earlier in contrast to these halides, the organotin(IV) fluorides are high-melting, non-volatile solids and are insoluble in organic solvents. On the basis of these differences in physical properties, the fluorides have been considered to be ionic compounds. Other organotin acid derivatives, like nitrates and sulphates, have also been included in this category. Coates(2a) has stated, "Compounds in which the R_3Sn or R_2Sn group is combined with a highly electronegative group, such as fluoride, nitrate, sulphate, or sulphonate, have quite different physical properties. Their high melting points and low volatility indicate a salt-like constitution."

Rochow, Seyferth, and Smith (16) reported the preparation of a large number of dimethyltin(IV) acid derivatives, and, from a comparison of their solubilities with those of corresponding salts of bivalent tin and lead, these authors reported, "In dimethyltin dichloride it is probable that the $5s^2$ and $5p^2$ electrons are involved in sp hybrid orbitals leading to a symmetrical covalent molecule, but in the dimethyltin cation, the methyl groups probably occupy the $5s^2$ orbitals above, and the other electrons are given up to the anion. In water and amines or amides, the solvated cation probably remains tetrahedral, but we believe that in anhydrous salts the $(CH_3)_2Sn^{++}$ ion resembles $:Sn^{++}$ and should also resemble $:Pb^{++}$ and $:T1^+$ in structure." ionization of the $5p^2$ electrons is correct, the anhydrous $(CH_3)_2Sn^{++}$ ion should be linear. Afterwards Freeman (34) reported di-nbutyltin acetate to be an ionic compound on the basis of the low carbonyl frequency in the infrared absorption spectrum. Later, a systematic infrared spectroscopic study was made by Okawara, Webster, and Rochow (35) who proposed an ionic structure for diand trimethyltin carboxylates. The infrared spectra of these compounds showed only one Sn-C stretching frequency in each case and this was interpreted in terms of the presence of discrete planar $(CH_3)_3Sn^+$ and linear $(CH_3)_2Sn^{2+}$ cations. Furthermore, the spectra due to the carboxylate group in each compound were similar to the spectrum of the corresponding free carboxylate anion. This fact was considered as evidence for the existence of free carboxylate anions in these compounds.

However, as was pointed out by Beattie and Gilson (36), the effective symmetry of an ionic and of a bridging carboxylate group is the same, and the infrared spectroscopic results of dimethyltin carboxylates are also consistent with a coordinated structure involving bridging or chelating carboxylate groups and an octahedral configuration around the tin atom with a linear dimethyltin group. Similarly, the infrared spectrum of trimethyltin acetate can be explained in terms of planar trimethyltin groups linked by bridging acetate groups in which case the tin atom will have a trigonal bipyramidal configuration. Subsequently, Janssen, Luijten, and van der Kerk (37) showed by detailed infrared studies that trialkyltin acylates exist as linear polymers (in which each tin atom has a trigonal bipyramidal configuration) in the solid and molten states and in concentrated solutions in

non-polar solvents, but are monomeric tetrahedral compounds in dilute solutions. These conclusions were confirmed later by Okawara and Ohara (38).

Okawara, Webster, and Rochow (35) also proposed an ionic structure for trimethyltin fluoride on the basis of the appearance of only one Sn-C stretching frequency in the infrared spectrum of this compound. However, the crystal structure determination of this compound by Clark, O'Brien, and Trotter (39) has clearly shown that trimethyltin fluoride consists of trimethyltin groups and fluorine atoms arranged alternatively in a chain-like manner. The electron density distribution can only be interpreted in terms of five coordinate tin atoms and non-linear unsymmetrical Sn-F--Sn bridges consistent with a non-ionic type of compound. A similar polymeric structure involving five coordinate tin atoms and Sn-O-Sn bridges has been reported for trimethyltin hydroxide from infrared evidence (40,41) as well as a preliminary study on crystal structure determination (42).

In a systematic study of trimethyltin derivatives of strong acids such as trimethyltin nitrate, perchlorate, tetrafluoroborate, hexafluoroarsenate and hexafluoroantimonate, Clark and O'Brien (27,43) and Clark, O'Brien, and Pickard (28) found no evidence for the existence of $(CH_3)_3Sn^+$ cation in the solid state. Their results indicate a polymeric structure, (involving bridging anionic groups and planar trimethyltin groups) for these compounds in the solid state. Similar results have been reported by other workers for trimethyltin perchlorate (44), nitrate (45), and tetrafluoroborate (46). Most of the structural evidence for these compounds has been obtained by infrared spectroscopic results whereby "coordination" by, say, perchlorate to the trimethyltin group has been deduced from the observation that the perchlorate group has C_{2v} (or lower) symmetry in accord with behaviour as a bidentate or bridging group. Such a lowering of symmetry in the solid state could be attributed to coordination. Alternatively, crystal field effects might produce such spectroscopic effects. However, the following discussion shows that the reported spectroscopic effects are mainly due to coordination.

In discussing the symmetry of the ligand from the infrared spectrum obtained in the crystalline state, a knowledge of the site group or factor group analysis is desirable. However, a survey of the infrared spectra of a variety of ionic as well as coordination compounds in which the corresponding ionic groups act as coordinating ligands shows that, in general, the effects of coordination upon the vibrational modes of the ligands are more pronounced than the effects due to crystal field. Infrared spectra of ionic and coordination compounds have been reviewed by Nakamoto (47) and the specific examples will be discussed later in the text. If the symmetry of the anion is lowered upon coordination, the infrared inactive vibrations of the free ion become infrared active and appear with moderate intensity and the degenerate vibrations are split. Moreover, all the fundamentals are more or less shifted according to their modes of The intensity of the new permitted bands, the vibration. magnitude of the splitting, and the frequency shifts are more pronounced if the anionic group is involved in coordination. Crystal field effects cause the forbidden infrared active modes to appear only weakly and the splittings of the degenerate modes

due to this effect are in general not very well resolved and are comparatively smaller in magnitude.

Some suggestions to explain the five coordination of the tin atom in trialkyltin derivatives have been put forward recently. Janssen, Luijten, and van der Kerk (48) have suggested that in five coordinate tin compounds, the principal interaction involves the donation of d electrons from the filled 4d orbitals of tin into appropriate ligand orbitals, although some donation of ligand electrons into vacant 5d tin orbitals may also be involved. Matwiyoff and Drago (22) consider the use of tin hybrid orbitals ($p_z + d_z 2$) in the bonding of the axial groups to planar R_3Sn .

As discussed earlier, for compounds of the type R_2SnX_2 , the possibility of tin achieving a coordination of six through adduct formation arises. Six coordination of the tin atom is also indicated (49, 50) in compounds of the type R_2SnL_2 (where R = methyl or phenyl and L = chelate ligand such as acetylacetonate, 8-quinolinolate etc.). A large number of such compounds have been reported recently. However, no systematic stereochemical studies of R₂SnX₂ compounds in which X is an anionic group derived from an inorganic acid (other than Cl, Br, or I) have been made, except recently reported studies on dimethyltin dinitrate (51) and dialkyl hydroxide nitrates (45). Dimethyltin dinitrate is a deliquescent crystalline solid, soluble in water and many other polar solvents buttonly slightly soluble in chloroform. The infrared spectrum of this compound in the solid state indicates coordination by the nitrate group and a tetrahedral configuration around the tin atom. Its ultraviolet absorption spectrum in non-

aqueous solvents is also consistent with the presence of the nitrato groups. Dialkyltin hydroxide nitrates are high melting crystalline substances which are soluble in water and methanol, but insoluble in non-polar solvents. The infrared spectra of these compounds also indicate a tetrahedral structure.

The preceding discussion thus shows that in trialkyltin compounds the tin atom tends to increase its coordination from four to five and that there is no evidence for the existence of trialkyltin cations in the solid state. However, no information exists on analogous triaryltin compounds. Existing evidence also indicates coordination of either four or six for the tin atom in dialkyl- and diaryltin compounds, though very little is known about the nature of R_2SnX_2 compounds in which X is a strongly electronegative anion. In view of these conclusions, several questions can be raised:

- 1) Are the organotin cations such as R_3Sn^+ and R_2Sn^{2+} unstable, and if so what is the nature of interaction between the organotin group and the anionic group?
- 2) Is there any similarity between analogous alkyltin and aryltin derivatives, since by analogy with the triphenylcarbonium cation, the triphenyltin cation may well possess greater stability than trialkyltin cations?

In an attempt to answer these questions a wide variety of trimethyl-, triphenyl-, and dimethyltin derivatives of acids including derivatives of very strong acids and transition metal oxyanions were synthesized and examined by infrared spectrosopy in the solid state. While this work was in progress, a report (52) describing an ionic constitution for trimethylantimony dinitrate appeared. The cations $(CH_3)_3Sn^+$ and $(CH_3)_3Sb^{2+}$ are isoelectronic. In view of the accumulated evidence (discussed earlier), as well as evidence based on the findings of this investigation for the non-existence of trimethyltin cation in the solid state, the reported ionic structure of trimethylantimony dinitrate can only be considered anomalous. Therefore a systematic infrared study of trimethylantimony(V) acid derivatives was also made.

Antimony (symbol Sb, atomic number 51) occurs in group Vb and the 5th period of the periodic table. The electronic configuration of a neutral antimony atom is [Kr] $4d^{10}5s^2p^3$. R_3SbX_2 (where R = alkyl or anyl group, X = halogen or any other anionic group) are derived from the Sb(V) oxidation state of the antimony In addition to dihalides, the derivatives containing atom. $(NO_3)_2$, $(CNS)_2$, SO_4 etc. have been described in the literature (2b, 53). However, very little is known about the nature of these compounds except the established stereochemistry of dihalides (Cl, Br, I). From X-ray crystallography, Wells (54) demonstrated that trimethylantimony dichloride, dibromide and diiodide are isomorphous and have a trigonal bipyramidal structure in which three methyl groups are arranged in the plane of the metal atom and the two halogen atoms lie at the apices. The Sb-X bond lengths are greater than their appropriate covalent radii sums. This fact led Wells to suggest that these compounds could be intermediate between the molecular and ionic forms shown as follows.



Jensen (55) assigned a trigonal bipyramidal structure to triphenylantimony dichloride on the basis of a dipole moment determination. This has been confirmed recently by an X-ray structure determination (56). Apart from dihalides, no information exists on the stereochemistry of other R_3SbX_2 compounds, except a recent report on dinitrate and sulphate by Long, Doak, and Freedman (52). From infrared spectroscopic studies, these authors concluded that trimethylantimony dinitrate is an ionic solid and that trialkylantimony sulphates are covalent compounds.

Some solution studies on dihalides have also been made. However, there are divergent views on the species present in solution. Conductivity measurements of both trimethyl- and triphenylantimony dichlorides and dibromides in acetonitrile solution have shown that these compounds are effectively nonelectrolytes in this solvent but the diiodides show a conductance drift due to the formation of triiodide ion (57,58). Coates (2b) has stated that the dihalides are covalently constituted, but when dissolved in water and other polar solvents they appear to ionize as shown below:

 $R_3SbX_2 \longrightarrow R_3SbX^+ + X^-$

Sidgwick (59a) has stated that R_3SbX_2 compounds appear to ionize to give the cations $(R_3Sb)^{2+}$ or more probably R_3SbX^+ . Trimethyl-

antimony dihalides form highly conducting solutions in water. Lowry and Simons (60) have attributed the high conductance values in water due to the presence of ionic hydroxy halides. From a detailed study of hydrolysis of trialkylantimony dibromides, Nylen (61) concluded that these compounds are hydrolysed according to the equations:

 $R_{3}SbBr_{2} + 2H_{2}0 \longrightarrow R_{3}SbBrOH + H_{3}^{+}0 + Br^{-}$ $R_{3}SbBrOH \longrightarrow R_{3}SbOH^{+} + Br^{-}$ $R_{3}SbOH^{+} + H_{2}0 \longrightarrow R_{3}SbO + H_{3}^{+}0$

However, as pointed out by Long, Doak, and Freedman (52), all the hydrolysis equations must be reversible, since trialkylantimony dihalides can be recovered quantitatively by recrystallization from water. These authors have also reported that trimethylantimony dihalides can be converted to dihydroxide by passing an aqueous solution of the dihalide through a column containing an anionic exchange resin.

As mentioned earlier, the present investigation is largely confined to infrared studies in the solid state and in the following chapters, these results are discussed.

CHAPTER 2

TRIPHENYLTIN(IV) DERIVATIVES

In contrast to trimethyltin derivatives of the type $(CH_3)_3SnX$ (where X = a highly electronegative group such as Clo_4 , NO_3 , BF_4 , AsF_6 , or SbF_6), no systematic study of similar triphenyltin derivatives has been made. In the present investigation therefore, two such triphenyltin derivatives, triphenyltin nitrate and perchlorate were synthesized. A comparative study of their infrared spectra with those of analogous trimethyltin derivatives was made in an attempt to elucidate their stereo-chemistry and to determine the effect of phenyl groups on the interaction between R_3Sn and X. While this work was in progress a brief report (62) appeared describing the preparation and and apparent instability of triphenyltin nitrate.

2.1 <u>Triphenyltin Nitrate</u> (C₆H₅)₃SnNO₃

The infrared spectra of nitrates and nitrato complexes have been widely studied and the subject has recently been reviewed (63,64). Recent research has indicated that compounds of elements (M) and the nitrate group can be divided into two classes according to whether the M-NO₃ bond is predominantly ionic or covalent. The term 'nitrate' is usually applied to a compound in which the M-NO₃ bond is ionic, that is, a compound containing the nitrate ion, and the term 'nitrato-compound' is generally used for compounds in which the NO₃ group is covalently bonded through one or more of its oxygen atoms.

A free nitrate ion belongs to the point group D_{3h} and has four fundamental modes of vibration. Two of these are each doubly

degenerate and the other two are nondegenerate. The fundamental vibrational frequencies of the NO3 ion are well established (65a) and are listed in Table 2.1a.

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Vibratio	nal Frequencies of N	0 ₃ Ion (Poinț	Group D _{3h})
Vibrational mode	Assignment	Frequency (cm ⁻¹)	Activity
$\dot{v}_1(A_1)$	NO symmetric stretch	1050	(R)
$ \mathbf{v}_2(\mathbf{A}_2') $	Out-of-plane bend	831	(I.R)
θ 3 (Ε)	Degenerate NO ₂ stretch	1390	(R,I.R)
√ 4 (É)	Degenerate NO ₂ bend	720	(R,I.R)

(R = Raman active; I.R = Infrared active)

The alkali metal nitrates, and certain of the alkaline earth metal nitrates, give infrared spectra which resemble closely the predicted spectrum of a free nitrate ion (66-68). On the other hand, many anhydrous metal nitrates, especially the transition metal nitrates, are largely covalent in character and their infrared spectra resemble those of non-metal nitrates (64). In organic nitrates such as methyl nitrate the bonding is essentially covalent. In metal-nitrato compounds the bond character is expected to vary from largely ionic to near covalent. Addison and Logan (64) have pointed out that metal-nitrato compounds and their derivatives are much less reactive as compared to the nonmetal nitrates such as alkyl nitrates and fluorine nitrate which are highly reactive. These authors consider that some form of back-donation of electrons from the metal atom to the empty orbitals of the nitrate group may make a contribution to the greater stability of metal-nitrato compounds.

Covalent or partial covalent bonding between the metal atom and nitrate group can involve one or two of the oxygen atoms of the nitrate group thereby reducing the symmetry of the nitrate group to either C_S or C_{2v} as shown below:





C_s symmetry

(a) Unidentate nitrato group



C_{2v} symmetry



 C_{2v} symmetry

C_{2v} symmetry

(b) Bidentate or bridging nitrato group

Upon lowering the symmetry of the NO_3 group from D_{3h} to either C_{2v} or C_s , the degeneracy of degenerate modes of the free NO_3^- ion is completely removed and, as such, the nitrato group possessing either C_{2v} or C_s symmetry will give rise to six nondegenerate fundamental vibrations, all of which are both Raman and infrared active. The correlation between the vibrational modes of D_{3h} , C_{2v} and C_s point groups is shown in Table 2.1b. It may be noted that, in a unidentate nitrato group, two of the three N-0 bonds will have double bond character while the remaining N-0 bond will have single bond character.
TABLE	2.	lb
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Correl	ation Table f	or D_{3h} , D_3 , C_3	$2_{\rm V}$, and $C_{\rm S}$ Poi	nt Groups
Point Group	ئ ا	Vibrational v_2	Modes ♪3	v ₄
D _{3h}	$A_1(R)$	$A'_{2}(I.R)$	E(R, I.R)	E(R, I.R)
D3	A ₁ (R)	$A_2(I.R)$	E(R,I.R)	E(R,I.R)
C _{2v}	$A_1(R,I,R)$	$B_1(R,I.R)$	$A_1(R,I.R)$	$A_1(R,I.R)$
			+B2(R,I.R)	+ $B_2(R, I.R)$
Cs	Á(R,I.R)	Á(R,I.R)	Á(R,I.R) +	A(R,I.R) +
			Á(R, I.R)	A(R, I.R)

or bridging nitrato group, as the bond order of the two M-O bonds approaches unity, the terminal NO bond approaches a double bond. Due to the considerable gradation to be expected in the polarity of the metal nitrate bond and therefore a corresponding gradation of the nitrate ion, the actual frequencies for the nitrato group cannot be predicted as for the free ion. The infrared absorption frequencies found experimentally for unidentate and bidentate (or bridging) nitrato groups, by various workers (69,70), are shown in Table 2.1c.

The vibrational modes have been numbered according to the convention that within a point group, vibrational modes are numbered from the highest symmetry species, and, within any given symmetry species, from the highest frequency.

Though many bidentate (or bridging) nitrato-compounds (63, 64, 70, 72) show the highest nitrate frequency at 1630 cm⁻¹ or even higher, it must be noted that absorption frequency in this region cannot be considered a criterion for a bidentate

TABLE	2.	10
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Vibrational Frequencies of Unidentate and Bidentate Nitrato

Group	os (C _{2v} Symm	netry)	ч. т. т.
Assignment	Species	Frequency (Unidentate	cm ⁻¹) Bidentate or bridging
NO2 symmetric stretch	(A1)	$ \mathbf{v}_{1}(1290-1253) $	\overrightarrow{v}_2 (985)
NO stretch	(A ₁)	$\vec{v}_2(1030-970)$	v₁ (1630)
$ ext{NO}_2$ symmetric bend	(A ₁)	$\overline{v}_3 (\sim 739)$	∳ ₃ (785)
NO ₂ asymmetric stretch	(B ₂)	$ egli_4(1550-1480) $	v_4 (1250)
${\tt NO}_2$ asymmetric bend	(B ₂)	\hat{v}_5 (~713)	\overrightarrow{v}_5 (750)
Out-of-plane rock	(B ₁)	\vec{v}_{6} (800–781)	√ ₆ (700)

Note: These authors classified modes $\sqrt[3]{4}$ and $\sqrt[3]{5}$ as belonging to B_1 species and $\sqrt[3]{6}$ to B_2 . This classification has been reversed in conformity with the correlation tables in Wilson, Decius, and Cross (71).

or bridging nitrato group. Cotton, Goodgame, and Soderberg (73) have shown that the highest nitrate frequency in the infrared spectrum of Co $[(CH_3)_3PO]_2(NO_3)_2$, where the presence of bidentate nitrate groups has been established by X-ray crystallography (74), occurs at 1517 cm⁻¹. Similarly uranyl nitrato compounds containing bidentate nitrato groups show the highest nitrate frequency in the region 1560 - 1454 cm⁻¹ (63). SnF₂(NO₃)₂ is reported (75) to be tetrahedral but the infrared absorption frequencies of the nitrato group in this compound are very similar to those of Sn(NO₃)₄ which is reported (70) to contain

bidentate nitrato groups. Since the asymmetric NO_2 stretching frequency of a unidentate nitrato group can appear at frequencies as high as 1550 cm⁻¹, and other nitrate bands appear in similar regions for unidentate and bidentate (or bridging) nitrato groups, it is not, in general, possible to distinguish between a unidentate, bidentate or bridging nitrato group.

The symmetry of the nitrate ion in the solid state can also be lowered if it is subjected to the field of a crystal lattice. Buijs and Schutte (66) consider that, in ionic crystals, the cohesive energy is of the same order as the bond energies of covalent compounds. Though in solid state infrared spectra, the degenerate infrared active modes are usually split, and Raman active modes appear weakly due to the crystal field effects, a survey of the spectra of ionic nitrates (66-68,76) suggests that any interaction with the metal ion is insufficient to restrict the normal vibrations of the nitrate ions. By comparing the spectra of ionic nitrates, metal-nitrato compounds and covalent nitrates, some estimation may be made of the degree of covalent character in the metal-nitrate bond. The following points can be stressed in this connection:

(a) In ionic nitrates the NO stretching vibration ϑ_1 shows only a very weak absorption in the 1050 cm⁻¹ region, even in cases where the site symmetry of the nitrate ion is lowered to C_s, as in potassium nitrate (66,76). In nitrato compounds, the NO stretching vibration appears as a strong band and varies between the observed frequency (1050 cm⁻¹) for an ionic nitrate to that observed (854 cm⁻¹) for methyl nitrate (77). Gatehouse, Livingston, and Nyholm (69) have used this criterion to place a

number of metal-nitrato complexes in the order of the covalent character of the metal-nitrate bond.

(b) The out-of-plane rocking mode in nitrato compounds occurs almost invariably at lower frequency than that for the free nitrate ion (64).

The degenerage mode all_3 of the free nitrate ion is split into (c) $artheta_1$ and $artheta_4$ in the nitrato group and the value of the difference $\Delta \vartheta = (\vartheta_4 - \vartheta_1)$ (in case of bidentate nitrato groups $\Delta \vartheta = \vartheta_1 - \vartheta_4$), increases progressively with an increase in the covalent character of bonding of the nitrate group. The values of $\Delta oldsymbol{\vartheta}$ give the same sequence for covalency as does the variation in the NO stretching frequency (64). Ferraro (67) has suggested that the extent of this splitting $\partial_4 - \partial_1$ is a criterion of the strength of the covalent bond. In methyl nitrate $artheta_4$ and $artheta_1$ are found at 1672 and 1287 cm⁻¹ respectively (77) and $(\partial_4 - \partial_1)$ is 385 cm^{-1} . In metal-nitrato complexes, the value of $(\dot{v}_A - \dot{v}_1)$ is, in general, less than 385 cm⁻¹ (63) but, on the other hand, the observed splitting of v_3 due to crystal field effects are comparatively much smaller. In potassium nitrate no splitting of $artheta_3$ is observed (66,76). The infrared spectra of metal nitrates have also been studied in organic solvents In general, the ϑ_1 and ϑ_4 frequencies of the nitrato (78,79). group are independent of the solvent, but strongly dependent on the metal ion. From a detailed study of the infrared spectra of many metal nitrates dissolved in tributyl phosphate, Katzin (78) concluded that a $(\dot{v}_4 - \dot{v}_1)$ splitting of less than 100 cm^{-1} can be attributed to electrical asymmetry rather than to covalent bonding, but a $(v_4 - v_1)$ splitting greater than 125 cm⁻¹ is undoubtedly due to the effects of partial covalent bonding.

Triphenyltin nitrate was prepared by the metathetical reaction of triphenyltin chloride and silver nitrate under anhydrous conditions, as well as by using an aqueous solution of silver nitrate as described by Shapiro and Becker (62). The infrared absorption bands of triphenyltin nitrate are listed, with their relative intensities and assignments, for both preparations of the compound in Table 2.1d. A portion of the spectrum of anhydrous nitrate is shown in Figure 2.1. As can be seen from Table 2.1d, the anhydrous nitrate does not show any bands due to the free nitrate ion while the bands attributed to the nitrato group are present at 1515-1492, 1288-1257, 978 and 798 cm⁻¹. The other two bands due to the nitrato group cannot be observed due to the presence of two strong phenyl absorptions at 729 and 692 $\rm cm^{-1}$. The nitrate absorption in triphenyltin nitrate is very similar to that shown by trimethyltin nitrate (28, 45). As regards the absorptions of the triphenyltin group, there are no apparent differences between the spectra of triphenyltin chloride (5,8), triphenyltin azide (80), triphenyltin nitrate, and triphenyltin perchlorate (to be discussed later). Triphenyltin chloride is reported (5,8) to be non-associated so that the triphenyltin groups should be non-planar, while triphenyltin azide is considered (81) to contain planar triphenyltin groups bridged by azide groups. Moreover, there is a considerable disagreement concerning the frequencies at which absorption due to the symmetric and asymmetric stretching vibrations of the phenyl-tin bonds should be Griffiths and Derwish (8) have assigned a weak band observed.

 $\mathbf{26}$



TABLE 2.1d

Infrared Absorption Spectra of Anhydrous and Wet

Triphenyltin Nitrate

Anhydr	ous	Wet		
Frequency (cm ⁻¹)	Relative intensity	Frequency (cm ⁻¹)	Relative intensity	Assignment
3060	m)	3060	m)	
2990	, w)	2990) W)	C-H str.
1965	. w)	1965	w)	
1880	w)	1880	w)	Dhanal mina
1815	w)	1820	- w)	Phenyi ring.
1770	w)	1760	w))	
1750	vw			
1515	s)			,
1508	s)			NO_2 asym.
1492	s)			NO str., (\mathbf{v}_4)
		1393	VS	NO2 asym. str., $(\mathbf{\vartheta}_3)$
1483	sh)	1483	m)	
1437	s)	1434	s)	Skeletal C-C
1339	m)	1334) m)	vibrations
1325	m)			
1305	m .	1303	m	(З С-Н
		1278	m	i
1288	s)	•		NO see sta
1271	s)			(v_1)
1257	s)			NO ₂ asym.str. (v_4)

Table 2.	ld continued			
1190	VW			
1155	VW			β С-н
1076	m	1075	m	ВС-Н
		1062	w	NO str., (v_1)
1044	Ψ.			
1024	m	1022	m	ВС-н
996	m	996	m	Phenyl ring
978	m			NO str., (v_2) or
				NO2 sym.str., (ϑ_2)
		826	m	NO_3 out-of-plane bend, (v_2)
798				ONO ₂ out-of- plane rock,(V ₆)
729	S	729	S	C-H vib.
692	S	695	S	C-H_vib.
45 0	S	45 0	S	Sn-Phenyl

m = medium; s = strong; vs = very strong; vw = very weak; w = weak.

at 1164 cm^{-1} in the spectrum of triphenyltin chloride to the phenyl-tin asymmetric stretching mode, but Kriegsmann and Geissler(5) have assigned this mode to the strong band observed at 450 cm^{-1} . The latter is probably more correct, but without more precise information, it is not possible to describe the configuration of the triphenyltin group in triphenyltin nitrate with any certainty. As discussed earlier, no conclusion can be reached about the unidentate, bidentate or bridging nature of the nitrato group from the infrared spectrum. However, the infrared spectrum of triphenyltin nitrate certainly shows that free NO₃ and $(C_6H_5)_3Sn^+$ ions are not present in anhydrous triphenyltin nitrate and therefore an ionic structure is not possible for this compound. Like trimethyltin nitrate, triphenyltin nitrate may have either a tetrahedral, monomeric structure containing a unidentate nitrato group, or a polymeric structure containing five coordinate tin atoms and bridging nitrato groups.

In contrast to the anhydrous compound, the infrared spectrum of triphenyltin nitrate prepared from wet acetone clearly shows the presence of the free nitrate ion. The absorptions at 1515-1492 and 1288-1257 cm⁻¹ in the anhydrous compound are replaced by a single very strong broad band at 1393 cm⁻¹ which is characteristic of the free nitrate ion. The other expected absorptions at 1062 and 826 cm⁻¹ are also present; the band expected at approximately 720 cm⁻¹ is probably masked by strong phenyl absorption. The same spectrum is also observed when anhydrous triphenyltin nitrate is exposed to moist air, the changes in the infrared spectrum being complete after an exposure of 24 hours. Thus there is a constitutional difference between anhydrous and wet triphenyltin nitrate.

Since samples of anhydrous triphenyltin nitrate appeared stable, a confirmation of the reported instability was sought. Shapiro and Becker (62) have reported that triphenyltin nitrate, prepared in wet acetone, decomposes spontaneously at 25⁰ according to the equation

 $(C_6H_5)_3SnNO_3 \longrightarrow C_6H_5NO_2 (87\%) + (C_6H_5)_2SnO (100\%)$

and at higher temperatures, according to the equation

$$(C_6H_5)_3SnNO_3 \longrightarrow C_6H_5NO_2 (33\%) + C_6H_6 (65\%) + (C_6H_5)_2SnO + NO_2$$

All their products were characterized except the oxide of nitrogen. In this investigation the anhydrous nitrate showed no apparent changes in infrared spectrum, as well as in appearance, after storage in the dry box for more than two months. When a sample of anhydrous triphenyltin nitrate was heated under vacuum at 150° for one and one-half hours, some spectroscopic changes were observed in the solid, and a very small amount of vapour was evolved. The infrared spectra of the heated solid and the evolved vapour are recorded in Table 2.1e. In the spectrum of the heated solid, all the phenyl absorptions are unchanged, while the nitrate absorptions occur at 1550, 1277, 965 and 790 cm⁻¹. In addition, two strong bands appear at 606 and 558 which may be possibly associated with tin-oxygen vibrations. Monophenyltin oxide, diphenyltin oxide and bis(triphenyltin) oxide show the characteristic strong absorptions of the tin-oxygen vibration at 572(82), 575(82) and 774(83) cm⁻¹ respectively. None of

TABLE 2.1e

Infrared Absorption Spectra of The Products Obtained

On Heating Anhydrous Triphenyltin Nitrate

Sol	id	Xapour	
Frequency (cm-1)	Relative intensity	Frequency (cm ⁻¹)	Relative intensity
3080	w	3070	m
1550	S	2980	w
1535	S	1685-1665	S
1485	m	1485	w
1335	w	1050	w
1277	S	990	m
1265	sh	850	sh
1075	m	825	S
1065	sh	800	sh
1022	m	685	m
998	m	670	S
965	S	660	m
920	w	615	ım
790	. m	572	w
730	S		
694	S		
655	w		
606	S		
558	S		
450	S		

m = medium; s = strong; sh = shoulder; w = weak.

these absorptions are found in the spectrum of the heated solid.

The infrared spectrum of the vapour indicates the absence of any nitrogen oxides. Some of the absorptions can be assigned to benzene but other bands could not be characterized. From the above spectroscopic data, it may be concluded that decomposition of the anhydrous triphenyltin nitrate under these conditions is slight, and that, although some structural changes must occur, the nitrate group is still apparently retained with either C_{2v} or C_S symmetry.

Even the product obtained from wet acetone is much more stable than the product described by Shapiro and Becker. Samples were always pale yellow in colour, and did not show any change in appearance or spectra over periods of several days. When a sample of the compound was heated with o-dichlorobenzene as described by Shapiro and Becker, decomposition was found to be considerable, the final residue being shown by its infrared spectrum to contain no nitrate, and also, from the reduced intensities of the phenyl absorptions (as compared with those observed for the original compound in a mull of approximately similar concentration), to have lost phenyl groups. No absorptions characteristic of bis(triphenyltin) oxide were observed. It is concluded, therefore, that pure triphenyltin nitrate is stable under anhydrous conditions, and that the instability observed by Shapiro and Becker is associated with the presence of catalytic impurities and, to some degree, with the presence of moisture.

Trimethyltin nitrate, by reaction with ammonia, readily forms a diadduct which is formulated (28) as $(CH_3)_3 Sn(NH_3)_2^+ NO_3^-$. Similar reactions of triphenyltin nitrate with anhydrous ammonia

were carried out. However, no addition compound could be isolated; instead a mixture of ammonium nitrate and bis(triphenyltin) oxide was obtained which was characterized by its X-ray powder photograph and infrared spectrum (83). The reaction of triphenyltin nitrate with ammonia must therefore proceed as follows:

 $(C_6H_5)_3SnNO_3 + NH_3 \longrightarrow (C_6H_5)_3SnNO_3NH_3$

 $2(C_6H_5)_3SnNO_3NH_3 \xrightarrow{H_20} [(C_6H_5)_3Sn]_2^0 + 2NH_4NO_3$

Similar results have been reported by Kupchik and Lanigan (30) who found the products of reaction between triphenyltin bromide and ammonia to be bis(triphenyltin) oxide and ammonium bromide. It seems that, in contrast to ammonia adducts of alkyltin compounds, the ammonia adducts of triphenyltin derivatives have a very low hydrolytic stability, for either kinetic or thermodynamic reasons, and that in the present case hydrolysis occurred even under carefully controlled conditions.

2.2 Triphenyltin Perchlorate (C₆H₅)₃SnCl0₄

The free perchlorate ion $(Cl0_4^-)$ is of tetrahedral(T_d) symmetry (65b) and hence should have nine vibrational modes giving rise to four fundamental vibrational frequencies. These fundamental frequences which have been established (65a) from the Raman spectra of perchlorates are shown in Table 2.2a.

The ϑ_1 mode is nondegenerate, ϑ_2 is doubly degenerate, and ϑ_3 and ϑ_4 are each triply degenerate. In the solid state infrared spectra of ionic perchlorates (68,84), ϑ_1 , which is infra-

Vibr	ational Frequencies of C	$10\overline{4}$ Ion (Point	Group T _d)
Vibrational mode	Assignment	Frequency (cm ⁻¹)	Activity
ϑ_1 (A ₁)	Symmetric stretch	935	(R)
$ \mathbf{v}_2^- $ (E)	Symmetric bend	462	(R)
ϑ_3 (F ₂)	Asymmetric stretch	1102	(R,I.R)
\dot{v}_{4} (F ₂)	Asymmetric bend	628	(R,I.R)

TABLE 2.2a

(R = Raman active; I.R = Infrared active.)

red inactive is usually observed as a very weak absorption at about 930 cm⁻¹. ϑ_3 appears as a broad, strong band, usually split in the 1050-1150 region. Anhydrous copper perchlorate and some other transition metal perchlorates have infrared spectra (85) very different from other metal perchlorates. From a detailed study of their spectra, Hathaway and Underhill (85) showed that, in these compounds, the perchlorate groups are strongly coordinated to the metal atoms. The infrared spectrum of trimethyltin perchlorate (27) also indicates that perchlorate groups act as bridging ligands between the planar trimethyltin groups. The spectroscopic results are completely consistent with a polymeric structure containing five coordinate tin atoms.

If the perchlorate group is involved in such coordination, its symmetry is lowered from T_d to C_{3v} or C_{2v} according to whether one or two of its oxygen atoms participate in such bonding. The correlation between the vibrational modes of the perchlorate group for T_d , C_{3v} or C_{2v} symmetry (85) is shown in Table 2.2b. If



TABLE 2.2b

* denotes oxygen atoms involved in bonding.

the symmetry of the perchlorate group is lowered to C_{3v} , then the ϑ_1 mode of the perchlorate ion becomes infrared active, and modes ϑ_3 , ϑ_4 each split into two modes which are also infrared active. On further lowering of the symmetry to C_{2v} , the ϑ_3 and ϑ_4 modes each split into three infrared active modes.

Ross (84) considers that, in view of the known instability of covalent perchlorates, it is unlikely that covalent bonding can contribute to any extent in metal perchlorates, and that the splittings in the solid state infrared spectra of various perchlorates described by Hathaway and Underhill might be due to the distortion of the perchlorate ion in the crystal lattice. The observed (68,84) infrared spectra of some ionic perchlorates do show lowering of the perchlorate ion symmetry due to the crystal field, however, the observed splittings of the degenerate modes in all these cases are not as well defined and are of a smaller order. Also, the forbidden mode v_1 shows only a weak absorption. For example, in potassium and ammonium perchlorates (84), the perchlorate ion symmetry is distorted to C_{2v} but, in both these cases, the v_3 mode shows a splitting of about 50 cm⁻¹ as compared to the splitting of about 200 cm⁻¹ observed for the same mode in anhydrous copper perchlorate (85) and trimethyltin perchlorate (27). Trimethyltin perchlorate shows four strong, well resolved bands at 1212-1192, 1112, 998 and 908 cm^{-1} and three medium bands at 625, 606 and 468 cm^{-1} . Coordination by the perchlorate group in trimethyltin perchlorate is further supported by its infrared spectrum (28) in methanol solution where crystal field effects are completely absent. While this work was in progress, further evidence of coordination by the perchlorate group has been reported in the following

compounds: Ni(3,5-lutidine)(ClO₄)₂ (86) shows perchlorate group absorptions at 1135, 1030 and 930 cm⁻¹ and the magnetic moment of this compound is in accord with the six coordination of the nickel atom. Ni(CH₃CN)₄(ClO₄)₂ and Ni(CH₃CN)₂(ClO₄)₂ (87) have perchlorate absorption bands at 1135, 1012, 912 cm⁻¹ and 1195, 1106, 1000 and 920 cm⁻¹ respectively, and the coordination by perchlorate groups in these compounds is further supported by their electronic spectra. Thus the preceeding examples demonstrate that the solid state infrared spectrum can be used to distinguish between an ionic and a coordinated perchlorate group.

Anhydrous triphenyltin perchlorate was obtained as a white The observed infrared absorption bands of the anhydrous solid. compound are listed, with their relative intensities and suggested assignments, in Table 2.2c. A portion of the spectrum is shown in Figure 2.2. The bands which can be assigned to the perchlorate group occur at 1200, 1112, 985, 905, 625, 610-604, 455, 449 and 439 cm^{-1} . The remaining bands are identical with those observed in the spectrum of triphenyltin nitrate and can be assigned to the vibrations associated with the triphenyltin group. The four strong perchlorate bands at 1200, 1112, 985 and 905 cm^{-1} are almost identical with those observed for trimethyltin perchlorate (27), and clearly indicate the $\text{C}_{2\,\nu}$ symmetry of the perchlorate group. This is also supported by the bands at 625, and 610-604, which are observed for trimethyltin perchlorate. Trimethyltin perchlorate shows absorption bands at 468 and 450 cm^{-1} . In triphenyltin perchlorate there is a strong absorption band in 450 cm^{-1} region due to the triphenyltin group and this may overlap perchlorate absorption in this region. There is, however,



Т	AE	3I	\mathbf{E}	2		2	С
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The	Infrared	Absorption	Spectrum	\mathbf{of}	Tripheny	yltin	Perchlorate	
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Frequency (cm ⁻¹)	Relative Intensity	Assignment	Frequency (cm ⁻¹)	Relative Intensity	Assignment
3070	m)		1158	m	βС-н
2990) m ()	C-H str.	1112	vs	$C10_2$ sym.str.,
2990	w (*)		1075	S	^{𝔅¹}
1990	vw	Phenyl ring	1020	m	β С−н
1967	w	Phenyl ring	995	sh	Phenyl ring
1905	vw	Phenyl ring	985	vs	$C10^*_2$ asym. str., (v_8)
1884	w	Phenyl ring	905	S	clo_2^* sym. str., (v_2)
1818	.' W	Phenyl ring	728	vs	C-H deform.
1765	w		690	vs	C-H deform.
1644	w		673	. w	
1582	w)	Skeletal C-C	664	w	
1483	m)	vibrations	625	m	$C10_2$ sym. bend, $(\sqrt{3})$
1435	s		610	sh)	
1335	m)		604	sh)	$C10_4$, $(\sqrt[3]{7})$
1300	w	βС-н	455	sh)	Rocking
1200	vs	ClO ₂ asym.	449	s)	$C104, (v_9)?$ $C10^*_2 \text{ sym.}$
		str., (v ₆)	439) sh ⁻)	bend, (v_4) ? and Sn-phenyl.

vs = very strong; s = strong; m = medium; w = weak; vw = very
weak; sh = shoulder. * denotes the two bridging oxygen atoms.

little doubt that the perchlorate symmetry in this compound is not higher than C_{2v} .

Triphenyltin perchlorate, like trimethyltin perchlorate, is highly soluble in ether and methanol and is very hygroscopic. On exposing triphenyltin perchlorate to air, the four intense bands at 1200, 1112, 985 and 905 were replaced by an intense broad band in the 1075-1150 cm⁻¹ region and a very weak band at 940 cm⁻¹. These are characteristic bands of the free perchlorate ion which is formed by the hydrolysis of the anhydrous triphenyltin perchlorate. Identical spectral changes occur in trimethyltin perchlorate (27). Thus in view of the almost identical spectra of triphenyltin perchlorate and trimethyltin perchlorate, and their identical behaviour upon hydrolysis, it can be concluded that both these compounds are almost similar in structure.

Hathaway and Underhill (85) have suggested assignments for the fundamental frequencies of the perchlorato group of C_{2v} symmetry by comparison with the assignments for sulphuryl fluoride, and the bidentate sulphate group. These workers have suggested the following assignments for the ClO_2 and ClO_2 stretching vibrations : 1270 - 1245 cm⁻¹, asymmetric ClO_2^* stretch $(\sqrt[3]{8})$; 948-920 cm⁻¹, symmetric ClO_2^* stretch $(\sqrt[3]{2})$; 1130 cm⁻¹ asymmetric ClO_2 stretch $(\sqrt[3]{6})$; and 1030 cm⁻¹, symmetric ClO_2 stretch $(\sqrt[3]{1})$. However, these assignments are not consistent with the reported assignments for sulphuryl fluoride (88) and dimethyl sulphate (89). Moreover, the bond order of the two Cl-O bonds (involving oxygen atoms not participating in coordination) should be higher than that of the remaining two Cl-O bonds ($(\sqrt[6]{1})$ denotes oxygen atoms participating in coordination). Therefore the ClO₂ stretching vibration should occur at higher frequencies, compared with frequencies for the $Cl_{0,2}^*$ stretching In dimethyl sulphate the stretching vibrations characmodes. terizing the two double sulphur-oxygen bonds occur near 1400 and 1200 cm^{-1} whereas the stretching vibrations of the two single sulphur-oxygen bonds occur at 825 and 752 cm^{-1} (see section 5.4). Therefore in triphenyltin perchlorate the four strong perchlorate absorption bands in the $1200-900 \text{ cm}^{-1}$ region are assigned as 1200 cm⁻¹, ClO₂ asymmetric stretch (\checkmark_6) ; 1112 cm⁻¹, follows: Clo_2 symmetric stretch (v_1) ; 985 cm⁻¹ Clo_2^* asymmetric stretch (v_8) ; and 905 cm⁻¹, Cl ${}^{*}_{2}$ symmetric stretch (v_2) . In the lower frequency region, there is no obvious method to distinguish between the vibrational frequencies of ϑ_3 , ϑ_7 , and ϑ_9 modes and the assignments suggested by Hathaway and Underhill are used.

Trimethyltin perchlorate forms an additional compound with anhydrous ammonia which has been formulated as $(CH_3)_3Sn.2NH_3^+Clo_4^-$ (27). However, the reaction of triphenyltin perchlorate with ammonia resulted in the formation of ammonium perchlorate and bis(triphenyltin) oxide. A similar reaction between ammonia and triphenyltin nitrate has been discussed and the formation of ammonium perchlorate and bis(triphenyltin) oxide in this reaction can be explained in a similar manner.

CHAPTER 3

TRIMETHYLTIN(IV) DERIVATIVES

To seek further information about the nature of the interaction between R₃Sn and the anionic group, some trimethyltin derivatives containing transition metal oxyanions were sought. It was considered that the electronic spectra of such derivatives might provide some information about the electronic description of the interaction.

Perchlorates, tetrafluoroborates, and permanganates of the same cation are frequently isomorphous and the three anions have many similar features including their regular tetrahedral symmetry. Therefore an attempt was made to prepare trimethyltin permanganate, but this compound could not be isolated due to its instantaneous decomposition in the presence of a range of sol-Bis(trimethyltin) chromate, $\left[(CH_3)_3Sn\right]_2Cr0_4$, however, vents. could readily be synthesized. In this compound, formally at least, a doubly charged anion $C_r 04^{2-}$ is present so that the stoichiometry is quite different from that of a trimethyltin derivative containing univalent anion such as perchlorate. Therefore, to provide a comparison, bis(trimethyltin) sulphate $\left[(CH_3)_3 Sn\right]_2 SO_4$ was also studied. Both the sulphate ion and the chromate ion have regular tetrahedral symmetry and belong to the point group T_{d} (47a).

3.1 <u>Bis(trimethyltin) Sulphate</u> [(CH₃)₃Sn]₂SO₄

The infrared and Raman spectra of sulphates have been widely studied (47a). The fundamental vibrational frequencies of the free SO_4^{2-} ion as shown in Table 3.1a, have been established

from the Raman spectra (65b) in aqueous solutions.

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-	Vibrational Frequencies of S	0_4^{2-} Ion (Point (Group T _d)
Vibratio mode	onal Assignment	Frequency (cm-1)	Activity
1 (A ₁)	Symmetric stretch	981	· (R)
2 (E)	Symmetric bend	451	(R)
3 ^{(F} 2)	Asymmetric stretch	1104	(R,I.R)
4 (F ₂)	Asymmetric bend	613	(R,I.R)

TABLE 3.1a

(R = Raman active; I.R = Infrared active.)

In the solid state infrared spectra of ionic sulphates, the infrared inactive mode ϑ_1 shows a weak absorption and the degenerate frequencies ϑ_3 and ϑ_4 appear very strongly and often display splitting due to crystal field effects (90). The crystal field effects observed in the spectra of crystalline ionic sulphates are similar in nature and magnitude to those discussed in connection with perchlorates (90).

From infrared studies, Nakamato and coworkers (91) have shown coordination by the sulphate group in certain ammino-cobalt (III) complexes. Their conclusions have been confirmed by Barraclough and Tobe (92) in an infrared study of ethylenediamine cobalt(III) complexes. Coordination by the sulphate group has also been reported recently in some ethylenediamine and bipyridyl complexes of copper (93,94). The sulphate absorptions in all these sulphato complexes occur in the following frequency (cm^{-1}) ranges:

Unidentate sulphato group	v ₁ 965-978(m)	√2 438(m)	v ₃ 1114-1143(s)	v ₄ 615-645
C _{3v} symmetry			1032-1070(s)	602-625(s)
Didontato			١	
sulphato group	961-995(m)	462(m)	1163 - 1211(s) 1096 - 1176(s)	632-647(s) 602-632(s)

(m = medium; s = strong)

Alkyltin sulphates are well known, but no work has been done to determine their constitution, except earlier studies by Werner and Pfeiffer (95) and a brief study by Gillespie and Robinson (96). Werner and Pfeiffer obtained a low value for the molecular weight of diethyltin sulphate in water, which led them to conclude that the compound was partially dissociated into diethyltin and sulphate ions. As it did not melt or sublime, Werner and Pfeiffer classified the compound as salt-like; however they also stated that the compound should be planar with a cis configuration. Gillespie and Robinson have briefly reported that, in anhydrous sulphuric acid solution, bis(trimethyltin) sulphate is ionized giving four particles for every molecule of $[(CH_3)_3Sn]_2SO_4$. However, neither of these results can be considered as evidence for the existence of free $(CH_3)_3Sn^{\dagger}$ and SO_4^{2-} either in the solid state or in solution, and the results can be interpreted equally well in terms of solvated ions.

In this investigation, trimethyltin sulphate was prepared under anhydrous conditions by the metathetical reaction of trimethyltin bromide and silver sulphate using methanol as

The first product of the preparation was a methanol solvent. [(CH₃)₃Sn] ₂SO₄.2(CH₃OH), from which the methanol was adduct. completely removed by heating under vacuum at 100° for about four hours. Part of the infrared spectra of the adduct (curve 1) and the nonsolvated product (curve 2) are shown in Figures 3.1a and 3.1b. Infrared absorption bands of both the products are listed in Table 3.1b, with their relative intensities and suggested assignments. For both the methanol adduct and the nonsolvated bis(trimethyltin) sulphate, the trimethyltin group shows absorption at 3000-2900, (C-H stretch); 1410-1400, (C-H asymmetric bend); 1205-1195, (C-H symmetric bend); 785-780, $(Sn-CH_3 \text{ rock})$; and 552, $(Sn-C \text{ asymmetric stretch}) \text{ cm}^{-1}$. It may be noted that only the tin carbon asymmetric stretch appears in the spectra, and its frequency is shifted to higher wave number as compared to the value of 545-540 cm⁻¹ observed in trimethyltin chloride (4). This shift to higher frequencies from 545-540 $\rm cm^{-1}$ observed for tetrahedral trimethyltin compounds is observed in other trimethyltin derivatives (27, 28, 33, 45) containing a planar trimethyltin group in a trigonal bipyramidal configuration around the tin atom. In at least one of these derivatives, $(CH_3)_3SnCl.Py$, both the planarity of the trimethyltin group and the five coordination of the tin atom have been conclusively established by an X-ray structure determination and infrared spectroscopic studies (25, 26, 33). Thus the presence of only the Sn-C asymmetric stretch and its shift to a higher frequency indicate that both in bis(trimethyltin) sulphate and its methanol adduct, the trimethyltin group is planar. In the methanol adduct absorption bands due to the sulphate group are observed at 1165, 1095, 1065, 1021, 989, 630, 595, 558 and 447 cm^{-1} . Free





TABLE 3.1b

Infrared Absorption Spectra of Bis(trimethyltin) Sulphate-Methanol

(CH3)3Sn]2 Frequency (cm ⁻¹)	2SO42(CH3OH Relative Intensity	I) [(CH ₃) ₃ Sn Frequency (cm ⁻¹)	SO4 Relative Intensity	Assignment
3150-3100	s,b		•	O-H str.
3020	w	3000	w	C-H asym. str.
2920	W	2900	w	C-H sym.str.
2800	Ŵ			
1410	m,b	1400	m	C-H asym.bend
1195	W .	1205	w	C-H sym. bend
1165	S			SO_2 asym.str., (v_6)
		1100	VS	$\vartheta_3(\mathrm{so_4}^{2^-})$
1095	s,sh		·	
1065	S			SO ₂ sym.str., (v_1)
1021	S			SO_2^* asym. str., $(\sqrt[4]{8})$
989	m .	·		$\begin{array}{c} \operatorname{SO}_2^* \operatorname{sym. str.,} \\ (v_2) \end{array}$
785	S	780	S	CH ₃ rock
		630	S	$\sqrt[3]{4}(\mathrm{SO}_4^2)$
630	S			$SO_4 \text{ rock}, (v_7)$
595	m			SO_2 bend, (v_3)
558	sh			SO_4 rock, (v_9)
552	S	552	S	Sn-C asym. str.
447	m , b			SO_2^{\star} bend, (v_4)

Adduct and Bis(trimethyltin) Sulphate

b = broad; m = medium; s = strong; sh = shoulder; v = very; w = weak. * denotes the oxygen atoms involved in bonding. Assignments for the SO_4 absorption bands in the adduct have been made assuming that SO_4 acts as a bridging group. methanol also has a strong absorption band in the 1100-1000 cm⁻¹ region. However, in the bis(trimethyltin) sulphate-methanol adduct, the 1021 cm⁻¹ band is sharp and of only medium intensity in contrast to the strong broad absorption at 3150-3100 cm⁻¹; therefore this (1021 cm⁻¹) band is unlikely to be due to methanol. The 1095 cm⁻¹ shoulder is probably due to the methanol and the 1100-1000 cm⁻¹ region methanol band is masked by the strong sulphate absorption at 1065 cm⁻¹.

The sulphate absorption in the spectrum of the trimethyltin sulphate-methanol adduct clearly shows that the symmetry of the sulphate group is reduced to C_{2v} . The $\sqrt{3}_3$ and $\sqrt{4}_4$ modes are clearly split each into three frequencies and the \overline{v}_1 and \overline{v}_2 modes appear with moderate intensities. The absorption frequencies are in the same range as reported for $\left[(NH_3)_4 C_0 < \frac{NH_2}{SO_4} > C_0 (NH_3)_4 \right]^3$ ion Therefore it can be concluded that each sulphate group is (91). coordinated to two trimethyltin groups. Moreover the O-H absorption of the methanol is observed as a broad band at 3105-3100 $\rm cm^{-1}$ lowered from the 3400 cm⁻¹ band observed for methanol itself. This indicates that the methanol molecules are also coordinated to the trimethyltin group. The entire spectrum of the methanol adduct of bis(trimethyltin) sulphate is thus consistent with the structure shown in Figure 3.1c, which contains planar trimethyltin groups, a bridging sulphato group and two coordinated methanol molecules, making the tin atoms five coordinate.

The sulphate absorption in the spectrum of non-solvated bis(trimethyltin) sulphate shows only the triply degenerate vibrations ϑ_3 at 1100-1090, and ϑ_4 at 630 cm⁻¹ indicating the presence of the regular tetrahedral sulphate group. As pointed out earlier, only the Sn-C asymmetric stretch is observed at



552 cm⁻¹, indicating the planarity of the trimethyltin groups. The structure shown in Figure 3.1d is proposed to incorporate these features, but this can be interpreted in terms of ions, $(CH_3)_3Sn^4$ and SO_4^{2-} , or equally well in terms of a coordinated model where every oxygen of the sulphate group is coordinated to a tin atom. As a result of the molecular stoichiometry, the infrared spectrum does not differentiate between these two models.

Both the bis(trimethyltin) sulphate-methanol adduct and bis(trimethyltin) sulphate showed marked changes in their infrared spectra on exposure to air. In the bis(trimethyltin) sulphate-methanol adduct, in addition to the appearance of water bands, the splitting of the v_3 and v_4 bands gradually disappeared and finally these were replaced by a strong broad band at 1105 $\rm cm^{-1}$ and a strong sharp band at 613 $\rm cm^{-1}$; both the 989 and 447 cm^{-1} bands gradually disappeared and were replaced by a weak band at 983 cm⁻¹. Again this change in the sulphate spectrum, upon exposing the solid to air, suggests that free sulphate ions and hydrated trimethyltin cations are produced as a result of hydrolysis. Since the position and intensity of the Sn-C asymmetric stretch does not change, it can be concluded that trimethyltin group is still planar and five coordinate. However. in the infrared spectrum of a sample of bis(trimethyltin) sulphate-methanol adduct which was exposed to air for about two months, the Sn-C asymmetric stretch at 552 $cm^{-1}was$ replaced by a strong band at 541 and a medium band at 513 cm^{-1} , probably indicating the formation of a tetrahedral trimethyltin species. Similarly in non-solvated bis(trimethyltin) sulphate, the sulphate absorptions showed gradual changes in the infrared spectrum upon



exposing the solid to air. After a short exposure, in addition to the appearance of water bands, the ϑ_3 mode showed bands at 1140,1100 and 1065, a medium band appeared at 989 cm⁻¹, and 630 cm⁻¹ band became broad, and a strong band at 613 cm⁻¹ and a medium band at 475 cm⁻¹ appeared. After a longer exposure, the ϑ_3 mode appeared at 1100-1090 as a single broad band, the ϑ_1 mode showed only a weak absorption at 885 cm⁻¹ and ϑ_4 appeared strongly at 613 cm⁻¹. This gradual change in the sulphate part of the spectrum indicates that, immediately after exposure of bis(trimethyltin) sulphate to air, the sulphate symmetry is reduced to C_{2v} as a result of partial hydrolysis and, on further hydrolysis, free sulphate ions are produced. This behaviour on hydrolysis is again consistent with a coordinated structure.

3.2 <u>Bis(trimethyltin) Chromate</u> (CH₃)₃Sn₂Cr04

The infrared and Raman spectra of chromates have been studied (68, 97, 98). The earlier assignments for the fundamental frequencies of the chromate ion have been revised by Stammreich, Bassi and Sala (97). The fundamental vibrational frequencies and the revised assignments of the free chromate ion are shown in Table 3.2. It may be mentioned that these authors could not be certain whether the assignment is $\vartheta_2 = 348$, $\vartheta_4 = 368$ or vice versa, but preferred the former. However, Miller and coworkers (98) have reported that the infrared band for the chromate ion in the cesium bromide region is observed at 370-420 cm⁻¹; therefore the assignments shown in Table 3.2 are considered to be correct.

Some chromato complexes of cobalt have been reported and from the electronic spectral studies of these complexes, Shimura

TABLE 3.2

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Vibrational		Frequencies of $C_r 0_4$		(Point Group T _d)	
Vibrational mode	Assignment		Frequency (cm ⁻¹)	Activity	
ϑ_1 (A ₁)		Symmetric stretch		847	(R)
ϑ_2 (E)		Symmetric bend		348	(R)
v_3 (F ₂)		Asymmetric stretch		884	(R,I.R)
\overline{v}_4 (F ₂)		Asymmetric bend		368	(R,I.R)

(R = Raman active; I.R = Infrared active)

and Tsuchida (99) have indicated the early position of $\operatorname{Cr0}_4^{2-}$ in the spectrochemical series, but no infrared studies on coordinated chromates have been reported. However, the symmetry of the chromate group, and therefore the number of infrared active modes, will change upon coordination in a similar manner as that discussed for other tetrahedral anions.

The observed infrared spectrum of bis(trimethyltin) chromate is very similar to that of non-solvated trimethyltin sulphate. The main features of the spectrum are the $\sqrt[3]{3}$ mode of the chromate group at 885 cm⁻¹, the Sn-CH₃ rock at 750 cm⁻¹, and the Sn-C asymmetric stretch at 554 cm⁻¹. No absorption was observed below 554 cm⁻¹. The $\sqrt[3]{4}$ mode usually observed as a weak doublet for crystalline ionic chromates at 368 cm⁻¹ was not observed even in highly concentrated nujol mulls. The spectrum indicates that the chromate group has T_d symmetry and that the trimethyltin group is planar. The structure proposed for the non-solvated trimethyltin sulphate (see Figure 3.1d) is also applicable to trimethyltin chromate and again the infrared spectrum is not helpful in elucidating the nature or the extent of anion-cation interaction. Trimethyltin chromate, in contrast to trimethyltin sulphate, did not form a methanol adduct nor did it hydrolyse on exposure to air.

The ultraviolet and visible diffuse reflectance spectrum of trimethyltin chromate was examined and compared with the spectrum of powdered potassium chromate. Trimethyltin chromate showed absorption maxima at 310 and 420 m/s, showing very little change from the maxima observed at 275 and 375 m/s for potassium chromate. This is in agreement with the reported spectrum of the complex $Co(NH_3)_5Cr0_4^+$ (100), which is very similar to that of $Cr0_4^{2-}$ ion showing that coordination by chromate through an oxygen atom has little effect on the charge transfer band.

CHAPTER 4

DIMETHYLTIN(IV) DERIVATIVES

As mentioned earlier, very little work has been done on structure elucidation of dialkyl- or diphenyltin acid derivatives. In the present investigation, attempts were made to synthesize and examine, by infrared spectroscopy, a wide variety of dimethyltin acid derivatives such as dimethyltin carbonate, chromate, bis(tetrafluoroborate), hexafluorosilicate, bis(hexafluorophosphate), bis(hexafluoroarsenate), bis(hexafluoroantimonate), and the dimethyltin derivative of $B_{12}Cl_{12}^{2}$. In addition, the known compounds, dimethyltin difluoride and sulphate were also studied.

4.1 <u>Dimethyltin Difluoride</u> (CH₃)₂SnF₂

In a comparison of methyltin chlorides, Taimsalue and Wood (4) reported a distinct fall in the Sn-Cl stretching force constants, in the series $SnCl_4$, $(CH_3)SnCl_3$, $(CH_3)_2SnCl_2$ and $(CH_3)_3SnCl$. This sequence follows the increasing inductive effect of the methyl groups, facilitating the ionization of the Sn-Cl bond. A similar comparison of the infrared spectra of dimethyltin difluoride and trimethyltin fluoride was considered desirable. The infrared spectrum of dimethyltin difluoride and the Sn-F vibration frequency in trimethyltin fluoride have not been reported and were measured in this work.

In the infrared spectrum of dimethyltin difluoride, the absorption bands were observed at 3040(w), 2940(vw), 1410(vw,b) 1210(w,sp), 785(m), 595(m,sp) and 373(s) cm⁻¹. These
bands can be assigned as, 3040 cm^{-1} , C-H asymmetric stretch; 2940 cm⁻¹, C-H symmetric stretch; 1410 cm⁻¹, C-H asymmetric bend; 1210 cm⁻¹, C-H symmetric bend; 785 cm⁻¹, CH₃ rock; and 595 cm⁻¹ Sn-C asymmetric stretch. The strong band at 373 $\rm cm^{-1}$ must be associated with the Sn-F bond. In the spectrum of trimethyltin fluoride, a strong band was observed at 355 cm^{-1} which can be assigned to the Sn-F asymmetric stretching vibration. The presence of only one Sn-C stretching frequency in dimethyltin difluoride indicates that the dimethyltin group is linear. Thus dimethyltin difluoride and trimethyltin fluoride apparently have different stereochemistry, and the Sn-F stretching frequency in each compound should arise from a different vibrational mode. Nevertheless, it is interesting to note that Sn-F frequency in dimethyltin difluoride occurs at higher wave number compared to the Sn-F frequency in trimethyltin fluoride.

As mentioned earlier, the crystal structure of trimethyltin fluoride (39) cannot be interpreted as ionic, and strongly suggests that some type of coordinative interaction between trimethyltin groups and fluorine atoms is involved. From a comparison of the Sn-F frequency in dimethyltin fluoride with that of trimethyltin fluoride, and in view of the non-ionic nature of trimethyltin fluoride, it should therefore be considered that dimethyltin difluoride cannot have a purely ionic structure. As was pointed out by Beattie and Gilson (36), dimethyltin difluoride may have a polymeric structure, in which two methyl groups occupy trans positions and the four bridging fluorine atoms occupy the four corner positions in the equatorial plane making the tin atom six coordinate. The effective

symmetry of such a trans octahedral unit would be D_{4h} and five infrared active vibrations of the species $2A_{2u} + 3E_u$ would be expected. Of these five vibrational modes, only two [Sn-C]asymmetric stretch (A_{2u}) , and Sn-F asymmetric stretch (E_u)] would have vibrational frequencies above 300 cm⁻¹. Thus the observed infrared spectrum of dimethyltin difluoride is consistent with such a structure. The Sn-F frequency (373 cm^{-1}) in dimethyltin difluoride compares well with the reported (50) value (400 cm⁻¹) for the Sn-O asymmetric stretching frequency in the dimethyltin acetylacetonato complex, $(CH_3)_2Sn(C_5H_7O_2)_2$ which is also indicated to have a trans octahedral structure, on the basis of its Raman and infrared spectra.

It is known that alkyltin difluorides form complexes with alkali metal fluorides of the type $M_2^+R_2 SnF_4^{2-}(2a)$. If the dialkyltin difluoride contains the free ions $R_2 Sn^{2+}$ and F⁻, i.e. the fluoride ions are outside the coordination sphere of the R_2Sn group, then the formation of a complex, in which four fluoride ions are now within the coordination sphere, can only be considered somewhat of an anomaly.

4.2 <u>Dimethyltin Carbonate</u> (CH₃)₂SnCO₃

The free carbonate ion (CO_3^{2-}) is trigonal planar and belongs to the point group D_{3h} (65a). The infrared and Raman spectra of carbonates have been widely studied (47b) and the fundamental frequencies of the carbonate ion, shown in Table 4.2a are well established (65a).

The spectra of crystalline ionic carbonates fall, generally, into one of two groups according to whether the compound is of the calcite or aragonite type (47b). The difference

Vibra	tional Frequencies of CO_3^{2-}	Ion (Point Group	o D _{3h})
Vibrational mode	Assignment	Frequency (cm-1)	Activity
\mathbf{v}_1 \mathbf{A}_1	CO symmetric stretch	1063	(R)
$ $	Out-of-plane bend	879	(I.R)
ν ₃ ε΄	Degeneratestretch	1430	(R,I.R)
∛ ₄ Е′	Degenerate bend	680	(R,I.R)

TABLE 4.2a

(R = Raman active; I.R = Infrared active)

between the two groups arises mainly from the intermolecular coupling of the out-of-plane bending \ldots mode $\sqrt{2}$ (101), and the lower symmetry of the carbonate ion in the crystal (47b). The site symmetry of the carbonate ion in a calcite type crystal is D_3 , whereas it is C_s in aragonite (47b). As seen from the correlation Table 2.1b, there is no change in the selection rules in going from ${\tt D}_{3{\tt h}}$ to ${\tt D}_3$ symmetry. The spectrum of calcite is very similar to that of a free carbonate ion and the infrared absorption bands appear at 1430 (vs), 874 (s) and 710 (m) cm^{-1} (91). In the infrared spectrum of aragonite, the v_1 mode shows a weak absorption at 1080 cm⁻¹ and the y_4 mode splits into two bands at 710 and 696 cm⁻¹, but there is no splitting of the ψ_3 mode (91). From a study of the solid state infrared spectra of the carbonates of main group and first row transition metals, Ross and Goldsmith (102) have concluded that the crystal field in carbonates cannot be very strong. These authors observed that the splittings of the ϑ_3 and ϑ_4 modes are usually small and sometimes absent. Infrared spectra of anhydrous alkali metal

carbonates also show only small splittings of degenerate modes (103). Only in anhydrous lithium carbonate does the v_3 mode show a splitting of about 60 cm⁻¹, and no splitting for this mode is observed in sodium and potassium carbonates.

Metal-carbonato complexes of cobalt(III) have been known for a very long time. From the existence of $Co(NH_3)_4CO_3^+$ and $Co(NH_3)_5CO_3^+$ it became evident that the CO₃ group sometimes is a bidentate and sometimes a unidentate ligand. The bidentate nature of the carbonate group in $Co(NH_3)_4CO_3^+$ has recently been proved by an X-ray crystal structure determination (104). The carbonate ion can coordinate to the metal atom (M) in one of the following ways:







Unidentate C_S symmetry Bidentate C_{2v} symmetry

C_{2v} symmetry

Bridging

(OI represents oxygen atoms involved in coordination, OII represents oxygen atoms not involved in coordination.)

As discussed in section 2.1, upon lowering the carbonate ion symmetry to either C_s or C_{2v} , the infrared active mode y_1 of the free ion becomes infrared active and the degenerate modes of the free ion are each resolved into two modes thus giving rise to a total of six infrared active vibrations. In the infrared spectra of carbonato complexes, the ϑ_1 mode of the free CO_3^{2-} ion appears with moderate intensity, and the degenerate modes show larger splittings than those causedby crystal field effects. Gatehouse, Livingston, and Nyholm (105) suggested the vibrational modes of a coordinated carbonato group, assuming C_{2v} symmetry which are shown in Table 4.2b.

TABLE 4.2b

Vibrational Modes of The Carbonato Groups of C_{2v} Symmetry

v_1 (A ₁)	CO_2 symmetric stretch
v_2 (A ₁)	CO stretch
v_3 (A ₁)	CO2 bend
v_4 (B ₂)	Asymmetric stretch
v_5 (B ₂)	Planar rock and
•) ₆ (B ₁)	Non-planar rock

Note: These authors classified modes ϑ_4 and ϑ_5 as belonging to the B₁ species, and ϑ_6 to B₂. This classification has been reversed here in conformity with the correlation tables in Wilson, Decius, and Cross (71).

From a solid state infrared study of a number of metalcarbonato complexes containing both unidentate and bidentate carbonato groups, these authors found that the vibrational frequencies of the carbonato group fall in the following ranges: Vibrational mode ϑ_4 ϑ_1 ϑ_2 ϑ_6 ϑ_3 or ϑ_5

					-	
Frequency				(1080-1055	,	
(cm-1)	•	1577-1493	1338-1260	(1050-1021	889-824	809-738

These authors showed that the splitting of the ϑ_3 mode of the free CO_3^{2-} ion increases along the series: basic carbonates < carbonato complexes < acid carbonates < organic carbonates. However, these authors did not differentiate between the vibrational modes of unidentate and bidentate (or bridging) carbonato groups. Nakamoto and coworkers (91) examined the infrared spectra of both unidentate and bidentate carbonato groups and found that the splitting of the ϑ_3 mode is greater for the bidentate than for the unidentate carbonato group, but that there is no significant difference in the frequencies of the four remaining bands.

However, as recently pointed out by Elliot and Hathaway (106) the change from a unidentate to a bidentate carbonate group may be considered to involve an increase in the double bond character of the C-O stretching vibration (ϑ_2) , resulting in an increase in the C-O stretching frequency, and a lowering of the double bond character of the CO₂ group with a consequent lowering of the frequencies of the symmetric and asymmetric CO₂ stretching vibration. The result of this change is to alter the assignments of the first three high frequency bands of the bidentate carbonato group to

v_1 (A ₁)	v_4 (B ₂)	$\sqrt{2}$ (A_1)
C O symmetric stretch	CO ₂ asymmetric stretch	CO ₂ symmetric stretch
1577-1493	1338-1260	(1080-1055 (1050-1021

It can be seen that the vibrational modes suggested by Gatehouse, Livingston, and Nyholm for the carbonato group in fact represent the vibrational modes of a unidentate carbonato group. The

vibrational modes of unidentate and bidentate carbonato groups would be similar to those of unidentate and bidentate nitrato groups and the same convention has been used in numbering the vibrational modes.

Later, Fujita, Martell and Nakamoto (107) reported the results of a normal coordinate analysis of unidentate and bidentate carbonato groups. These authors used models based on C_S as well as C_{2v} symmetry for the unidentate carbonato group. A model based on a four membered chelate ring of C_{2v} symmetry was used for the bidentate carbonato group. Their calculated results are shown in Table 4.2c.

TABLE 4.2c

Calculated Frequencies of Unidentate and Bidentate

	Co(III)	Carbonato Comp	lexes (cm ^{-]}	<u>L)</u>	
		1		:	
Unidentate				·	
Vibrational mode	\boldsymbol{v}_5	ϑ_1	$ \mathbf{v}_2$	J ₃	\mathcal{Y}_{6}
Assignment	(C-0 _{II})	(C-0 _{II})	(C-0 _I)	(0 ₁₁ C0 ₁₁)	$(0_{II}C0_{II})$
	str.	str. + $(C-0_I)$ str.	str. + (C-0 _{II})st	bend t r .	rock
Frequency				•	· ·
Cs	1483	1373	1039	765	711
c_{2v}	1482	1376	1069	772	676
Bidentate					
Vibrational mode	ϑ_1	ϑ_5	\mathbf{v}_2	ϑ_3	ə 6
Assignment	(C-O _{II}) str.	$(C-0_{I})$ str.+ $(O_{I}CO_{II})$ bend	(C-0 _I) str.	Ring def. +(Co-01) str.	(01C011) bend + (C-01)str. +(Co-01) str.
Frequency	1595	1282	1038	771	669

The numbering of modes used by these workers is slightly different because vibrational frequencies involving metal-oxygen bonds have also been included in the above shown assignments. These results confirm the general conclusions, about the infrared spectra of the coordinated carbonato group, reached by earlier workers (91, 105). However, these results show coupling between various vibrational modes in metal-carbonato complexes containing four membered rings. Very recently Elliot and Hathaway (106) have reported the polarization data for single crystals of $Co(NH_3)_4CO_3Br$. Their results confirm the normal coordinate analysis model involving covalent bonding of the carbonate oxygen atoms to the cobalt ion.

The infrared spectrum of dimethyltin carbonate was measured on a mixture of dimethyltin carbonate and silver chloride, which was obtained by the metathetical reaction of dimethyltin dichloride and silver carbonate in methanol followed by removal of the solvent under vacuum. X-ray powder photographs of the mixture were examined and no lines due to either dimethyltin chloride or silver carbonate were found. Therefore it may be considered that the infrared spectrum thus obtained is largely due to dimethyltin carbonate. A portion of the observed spectrum is shown in Figure 4.2, and the frequencies, together with the relative intensities of the absorption bands in the region 2000- 250 cm^{-1} and their suggested assignments, are listed in Table 4.2d. The absorption bands due to the dimethyltin group can be easily distinguished and assigned, i.e. 1415 cm^{-1} , C-H asymmetric bend; 1200 cm^{-1} , C-H symmetric bend; 785 cm⁻¹, CH₂ rock; 576 cm^{-1} , Sn-C asymmetric stretch; and 523 cm^{-1} Sn-C symmetric The absorptions due to the carbonate group occur at stretch.



TABLE 4.2d

Infrared Absorption Spectrum of Dimethyltin

Frequency (cm^{-1})	Relative Intensity	Assignment
1510	VS	$C=0$ sym. str., (v_1)
1415	sh	C-H asym.bend
1385	vs	CO_2 asym.str., (v_4)
1200	m	C-H sym. bend
1105 1068	w) m)	CO_2 sym.str., (v_2)
832	m	CO_3 out-of-plane def., $(\sqrt[4]{6})$
785	S	CH ₃ rock
700	m	CO ₂ sym.bend, (\mathbf{y}_3)
655	S	CO ₂ asym.bend, (v_5)
576	s	Sn-C asym. str.
523	m	Sn-C sym. str.
500 340 275	s) m) m)	Sn-0 asym. str. and
210	ш /	Datifice modes (

Carbonate

m = medium; s = strong; sh = shoulder; v = very; w = weak.Assignments for the carbonate absorption bands have been suggested, assuming that the carbonate group is bridging.

1510, 1385, 1105, 1068, 832, 700, 655, 500, 340 and 275 cm^{-1} . It is evident that the strong bands at 1510 and 1385 cm^{-1} correspond to the doubly degenerate mode v_3 of the free carbonate ion which has split into these two strong bands. The 1105 and 1068 $\rm cm^{-1}$ bands correspond to the infrared inactive mode ∂_1 of the free ion, the 832 cm^{-1} band corresponds to the out-of-plane bending mode $artheta_2$ of the free ion, and the bands at 700 and 655 are the two components of the doubly degenerate mode $oldsymbol{\vartheta}_{\mathtt{A}}$ of the free ion. The absorption bands in the region $500-275 \text{ cm}^{-1}$ are likely to be associated with the Sn-O stretching vibrations as well as with the absorptions of the lattice modes. Similar absorption bands at 450, 375 and 250 $\rm cm^{-1}$ were also observed in the spectrum of trimethylantimony carbonate (to be discussed later). It is known (108) that the carbonates have a lattice-type absorption in this region. Miller and coworkers (98) have reported similar bands in the spectra of some metal carbonates, e.g. lithium carbonate shows strong absorption bands at 498 and 420 cm^{-1} , lead(II) carbonate has a strong broad band at 400 cm^{-1} , and calcite has a strong band at 320 cm^{-1} .

The infrared spectrum of dimethyltin carbonate clearly shows that the symmetry of the carbonate group is lowered from D_{3h} to C_{2v} or C_s , and the magnitude of the splittings observed for degenerate modes indicates that the carbonate group is coordinated to the dimethyltin group. Moreover, the presence of two Sn-C stretching vibrations of medium intensity suggests that the dimethyltin group is non-linear. These two Sn-C stretching frequencies at 576 and 523 cm⁻¹ can be compared with those of dimethyltin dichloride (4) which occur at 567 and 515 cm⁻¹.

Therefore the possibility of any significant amount of dimethyltin dichloride being present in the mixture is very low. Though the observed splitting of the v_3 mode in dimethyltin carbonate is less than that reported (107) for bidentate carbonato complexes, the entire infrared spectrum of dimethyltin carbonate suggests that the tin atom has a tetrahedral configuration which will imply some sort of coordinate bonding between the dimethyltin group and two of the oxygen atoms of the carbonate group. A polymeric structure consisting of non-linear dimethyltin groups and bridging carbonato groups, making the tin atom tetrahedral, is suggested. A monomeric structure containing a bidentate carbonato group coordinated to a non-linear dimethyltin group is also possible, but is considered less likely due to the insolubility and non-volatility of the compound.

4.3 <u>Dimethyltin Chromate</u> (CH₃)₂SnCr0₄

In an attempt to prepare dimethyltin chromate, Rochow, Seyferth, and Smith (16) obtained a basic dimethyltin chromate by the reaction between dimethyltin dichloride and sodium chromate in aqueous solution. In the present investigation, dimethyltin chromate could be prepared by the metathetical reaction between dimethyltin dichloride and silver chromate in acetone or acetonitrile. However, like dimethyltin carbonate, due to the insolubility of dimethyltin chromate in any suitable solvent (from which the compound could be recovered without decomposition), the dimethyltin chromate formed in the metathetical reaction could not be isolated free from silver chloride. Therefore the infrared spectrum of this compound

was studied using the mixture of dimethyltin chromate and silver chloride. A portion of the observed infrared spectrum is shown in Figure 4.3. The absorption frequencies are listed together with their relative intensities and suggested assignments, in Table 4.3.

The fundamental frequencies of the chromate ion $(Cr0_4^{2-})$ have already been given in section 3.2. In the infrared spectrum of dimethyltin chromate, the absorption bands due to the dimethyltin group occur at 2940, (C-H stretch); 1405, (C-H asymmetric bend); 1195 (C-H symmetric stretch); 785, (CH3 rock); 573, (Sn-C asymmetric stretch); and 512, (Sn-C symmetric stretch) cm^{-1} . The bands at 975, 928, 880, 750, 465, 390, 348, and 305 cm^{-1} are due to absorption by the chromate group. Since the spectrum was obtained for a mixture of silver chloride and dimethyltin chromate, the possibility must be considered that some of these bands may be due to some unreacted silver chromate or dimethyltin This can be rejected, however, on the following dichloride. grounds: (a) the quantitative amount of silver chloride was obtained on dissolving the mixture in water acidified with acetic acid; (b) X-ray powder photographs of the mixture did not show any lines due to either silver chromate or dimethyltin dichloride; (c) the Sn-Cl stretching vibrations, which are observed in the infrared spectrum (4) of dimethyltin dichloride at 332 and 307 cm^{-1} as strong bonds, do not appear in the infrared spectrum of the mixture; (d) the observed Sn-C stretching frequencies in the spectrum of the mixture differ slightly from those of dimethyltin dichloride (567 and 515 cm^{-1}). The observed spectrum is therefore due only to dimethyl-



				•
Frequency	(cm ⁻¹)	Relative	Intensity	Assignment
294 0		vw		C-H str.
1405		w		C-H asym.bend
1195		m	5	C-H sym.bend
975		vs		$Cr0_2$ asym. str.,(v_6)
928		vs		$Cr0_2$ sym.str., (ϑ_1)
880	·	vs		$Cr0^*_2$ sym.str., (v_8)
785		vs		CH ₃ rock
750		vs		$Cr0^*_2$ sym.str., (v_2)
573		m		Sn-C asym.str.
512		m		Sn-C sym.str.
465		ms		$Cr0_4$ rock, (b_7)
390		m		$Cr0_2$ bend, (\checkmark_3)
348		m		$Cr0_4$ rock, (v_9)
305		m		$\operatorname{Cr0}_2^*$ sym.bend, (\mathfrak{d}_4)

TABLE 4.3

Infrared Absorption Spectrum of Dimethyltin Chromate

m = medium; s = strong; v = very; w = weak.

Note: The cromate absorption bands have been assigned by analogy with ${\rm SO}_4$ group of ${\rm C}_{2v}$ symmetry.

tin chromate.

The presence of two Sn-C stretching frequencies indicates that the dimethyltin group is non-linear in dimethyltin chromate. The chromate absorption bands in dimethyltin chromate are remarkably different from those of ionic chromates. The ϑ_3 mode observed at 884 cm⁻¹ for the chromate ion is resolved into three strong bands at 975, 928 and 880 cm⁻¹. The ϑ_1 mode observed only as a very weak band at 845 cm^{-1} for the chromate ion, shows strong absorption at 750 $\rm cm^{-1}$ appearing as one of the components of a broad band giving rise to strong absorption in the 800-720 cm^{-1} region; another component is the $Sn-CH_3$ rocking frequency. At lower frequencies, the free chromate ion shows only a weak band due to the triply degenerate mode ϑ_4 , usually observed as a doublet in the $420-370 \text{ cm}^{-1}$ region. The appearance of well defined absorption bands of medium intensity at 465, 390, 348 and 305 cm^{-1} , in the infrared spectrum of dimethyltin chromate, shows that the ϑ_4 mode of the free ion has split into three modes and the v_2 mode has become infrared active, although Sn-0 vibrations may possibly also cause absorption in this region. Certainly the chromate absorption bands in dimethyltin chromate can only be interpreted in terms of a $C_{2v}(\delta r$ possibly lower) symmetry of the chromate group.

As in the case of other solid state spectra, the lower symmetry of the chromate group observed in this spectrum could be attributed to crystal field effects. However, recent studies made by Campbell (109) on a large number of chromates, containing a wide variety of cations, showed that crystal field effects do not cause significant changes in the infrared spectra of

chromates. Not even in ammonium chromate, where hydrogen bonding is known to occur (109) were such large and well defined splittings of the v_3 mode observed, and only minor effects were observed in the 500-250 cm⁻¹ region in contrast to the pronounced splittings observed for dimethyltin chromate. The entire infrared pattern and extent of splittings observed for dimethyltin chromate are quite different from those which could be attributed to crystal field effects. Therefore the infrared spectrum of dimethyltin chromate can only be explained in terms of a coordinated structure in which the chromate group is coordinated to the non-linear dimethyltin group through two of its oxygen atoms, making the tin atom tetrahedral. A polymeric structure similar to that of trimethyltin perchlorate (27) is therefore proposed, the $Cr0_4$ groups acting as bridging groups between non-linear (CH3)2Sn units. A monomeric structure containing a bidentate chromate group is also possible, although less likely in view of the insolubility and non-volatility of this compound.

The ultraviolet and visible diffuse reflectance spectrum of a powdered sample of the dimethyltin chromate and silver chloride mixture was examined. Two absorption bands showing maxima at 280 and 380 m/ were observed. This result is similar to that obtained for bis(trimethyltin) chromate as well as reported (100) for $Co(NH_3)_5Cr0_4^+$.

4.4 <u>Dimethyltin Sulphate</u> (CH₃)₂SnSO₄

In this investigation the preparation of dimethyltin sulphate was attempted in different solvents, and the infrared spectra of the products were examined. Some addition compounds

of dimethyltin sulphate were also prepared and examined by infrared spectroscopy.

The metathetical reaction between dimethyltin dichloride and silver sulphate in aqueous solution resulted in the formation of dimethyltin sulphate and silver chloride, and dimethyltin sulphate was obtained as a non-hygroscopic solid. The infrared absorption spectra (obtained on samples made as mulls in nujol showed absorption bands at 1238 (w,sp), 1095 (vs,b), 805(s), 670 (m,sp), and 600 (s,sp) cm^{-1} . The bands at 1238, 805 and 600 cm^{-1} are due to the dimethyltin group and can be assigned as 1238 cm⁻¹, C-H asymmetric stretch; 805 cm⁻¹, CH₃ rock; and 600 cm^{-1} , Sn-C asymmetric stretch. The band at 1095 cm^{-1} corresponds to the ϑ_3 mode of the SO₄²⁻ ion and the 670 cm⁻¹ band is due to the v_4 mode of the SO_4^{2-} ion. It may be noted that the frequency of the ϑ_4 mode in dimethyltin sulphate is considerably shifted towards higher wave number as compared with the value (\sim 613 cm⁻¹) observed in ionic sulphates. Nevertheless, the symmetry of the sulphate group in this compound is tetrahedral. The dimethyltin group shows only one Sn-C stretching mode and its frequency is almost the same as observed for dimethyltin difluoride. spectrum can be interpreted in terms of $(CH_3)_2 Sn^{2+}$ and SO_4^{2-} ions. However, it can be interpreted equally well in terms of a polymeric sturcture, in which every oxygen of the sulphate group is coordinated to a tin atom making the tin atom six coordinate, as shown below:



In such a structure, the T_d symmetry of the sulphate groups and linearity of the dimethyltin groups are preserved. A three dimensional polymeric structure containing linear dimethyltin and tetrahedral sulphate groups is also possible.

The metathetical reaction between dimethyltin dichloride and silver sulphate was also carried out in acetone, acetonitrile and methanol. In both acetone and acetonitrile, the reaction product was a mixture of silver chloride and dimethyltin sulphate, which was characterized in each case by the results of X-ray powder photographs and the infrared absorption spectra of the However, when the metathetical reaction was carried mixtures. out in methanol, a mixture of silver chloride and a methanol adduct of dimethyltin sulphate was obtained. Though the methanol adduct of dimethyltin sulphate could not be isolated free from silver chloride on account of its insolubility in a range of solvents, except water, its formation and presence in the mixture is demonstrated by infrared spectroscopic evidence. The infrared absorption spectrum of the mixture was found to be very different from that observed for dimethyltin sulphate. The infrared absorption bands, together with the relative intensities and assignments, are listed in Table 4.4a and a portion of the spectrum is shown in Figures 4.4a and 4.4b. (The broken curves refer to the spectrum of the anhydrous sulphate.) Absorption bands due to the sulphate group in the mixture appear at 1210, 1175, 1065, 995, 665, 606, 585 and 475 cm^{-1} . The absorption bands associated with the dimethyltin group appear at 2960, (C-H stretch); 1415, (C-H asymmetric bend); 1230, (C-H symmetric bend); 795, (CH₃ rock); and 595, (Sn-C asymmetric



0.0 Me₂ SnSO₄(Me OH)_x



TABLE 4.4a

The Infrared Absorption Spectrum of The Mixture of Dimethyltin Sulphate-Methanol Adduct and Silver Chloride

Frequency (cm^{-1})	Relative Intensity	Assignment
3110	m	O-H str.
2960	vw	C-H str.
2800	v	
1455	W	C-H asym.bend
1415	vw	
1230	m	C-H sym.bend
1 2 10	m	SO_2 asym.str.,(v_6)
1175	S	SO_2 sym.str., (v_1)
1140	sh	
1065	S	SO_2^* asym.str.,(\mathfrak{v}_8)
995	S	SO_2^* sym.str., (v_2)
795	S	CH ₃ rock
655	s	SO_4 rock, (v_7)
606	S	SO_2 bend, (v_3)
595	S	Sn-C asym.str.
585	sh	$so_4 \operatorname{rock}(v_9)$
475	m	SO_2^* bend, (\mathfrak{d}_4)
m = medium; s = st	rong; sh = shoulder;	v = very; w = weak.
* denotes the oxyge	n atoms (of the SO $_4$ g	roup) involved in bonding
The assignments for	the SO_4 group have be	een suggested assuming
C_{2v} symmetry.	· · · ·	

stretch) cm^{-1} . There is no band which can be attributed to the Sn-C symmetric stretch. The bands at 3110, 2800, and 1455 $\rm cm^{-1}$ are due to methanol. The 0-H stretching frequency has been considerably lowered as compared with methanol, suggesting that the methanol is coordinated to dimethyltin sulphate. A similar shift in 0-H frequency occurs in the methanol adduct of bis(trimethyltin) sulphate, as discussed earlier. The sulphate portion of the spectrum is completely consistent with the presence of coordinated sulphato group of C_{2v} symmetry and indicates that no free SO_4^2 ions are present in the mixture. The entire spectrum of the mixture strongly suggests that a methanol adduct of dimethyltin sulphate is present and that, in this adduct, both the methanol and sulphate group are coordinated to the linear dimethyltin group. However, in view of the uncertainty in the number of methanol molecules present in the adduct, no conclusions can be drawn about its detailed stereochemistry.

The methanol adduct of dimethyltin sulphate was hydrolysed on exposing to air, as shown by changes in its infrared spectrum. However, a sample of the mixture kept in the dry box did not show any changes in infrared spectrum. Similarly, a sample of the mixture did not show any change in infrared spectrum after being pumped for several hours at room temperature. However, when the mixture was heated under vacuum at 100° for about four hours, the methanol was completely removed and the infrared spectrum of the heated solid was identical to that of dimethyltin sulphate. Thus it is evident that, during this treatment, the coordinated methanol is lost from the adduct and dimethyltin sulphate is formed.

Dimethyltin sulphate also formed 1:1 addition compounds with pyridine and dimethyl sulphoxide. These addition compounds are stable and do not hydrolyse in air. A 1:2 addition compound of dimethyltin dichloride with pyridine has been described (33). A similar addition compound of dimethyltin dichloride was obtained with dimethyl sulphoxide. A comparison of the infrared spectra of these compounds is made below.

The infrared spectra of pyridine complexes and pyridinium salts have been studied (110). Coordinated pyridine can be distinguished by the presence of a weak band between 1250 and 1235 cm^{-1} ; by a shift in the strong 1578 cm^{-1} band to 1600 cm^{-1} ; and by shifts of the 601 and 403 cm^{-1} bands to 625 and 420 cm^{-1} respectively (110). The infrared absorption spectra of both dimethyltin sulphate-pyridine monoadduct and dimethyltin dichloride-pyridine diadduct are recorded, together with the relative intensities of the absorption bands and suggested assignments, in Table 4.4b. A portion of each spectrum is shown in Figure 4.4c; curve (a) refers to the dichloride adduct and curves (b) and (c) refer to the sulphate adduct. The pyridine absorption bands in both the compounds occur at almost the same frequencies and are in agreement with the pyridine absorption bands reported for other pyridine complexes. From a comparison of the spectrum of the dimethyltin sulphate adduct with that of the dimethyltin dichloride adduct, the sulphate absorption bands in the dimethyltin sulphate adduct can be distinguished unambiguously. In the dimethyltin dichloride adduct, there are four strong very sharp absorption bands at 1210, 1062, 1037 and 1010 cm^{-1} , due to pyridine. In



TABLE 4.4b

Infrared Absorption Spectra of Pyridine Adducts of Dimethyltin

(CH3)2Sn Frequency (cm-1)	SO ₄ .Py Relative <u>intensity</u>	(CH3) Frequency (cm-1)	2SnCl2.2Py y Relative intensity	Assignment
3100) 3050) 2940)	w	3100) 3040) 2940)	w .	C-H str.
2450 1605	vw s	1605	S	
		1570	vw .	
1492	m	1490	S	
1450	s	1450	S	
1410	w			C-H asym.bend
1360	vw	1360	vw	
1245	sh	1245	w	
1232)) 1217)	m			C-H sym. bend
1208	sh	1210	S	
1200		1185	w	SO ₂ asym.str., (v_6)
1160	vw	1160	VW	
1090	S			SO ₂ sym.str., (v_1)
1066	S	1062	. S	
		1037	S	
1025	S			SO_2^* asym.str.,(ϑ_8)
1013	sh	1010	S	
992	m			SO $_2^*$ sym.str.,(ϑ_2)
		973	vw	

Sulphate and Dimethyltin Dichloride



417 sh

Table 4.4b continued

m = medium; s = strong; v = very; w = weak.

* denotes the oxygen atoms (of the $\rm SO_4$ group) involved in bonding. The assignments for the $\rm SO_4$ group have been made assuming $\rm C_{2v}$ symmetry.

No assignments have been made for the absorption bands due to pyridine.

the dimethyltin sulphate adduct, the bands at 1208, 1066 and 1010 correspond to three of the above four bands while the band at 1037 cm^{-1} is apparently masked by a strong band at 1023 cm^{-1} . Thus the absorption bands at 1200, 1090, 1025 and 992 cm^{-1} in the spectrum of dimethyltin sulphate-pyridine adduct can be attributed to the sulphate group. Similarly, in the lower frequency region, the bands at 655, 590, 576 and 465 cm⁻¹ are due to the sulphate group. As regards the absorption bands due to the dimethyltin group, the bands at 598 and 800 cm^{-1} in the sulphate adduct can be assigned to the Sn-C asymmetric stretch, and CH₂ rocking modes respectively. The corresponding frequencies in the dichloride adduct occur at 560 and 780 cm^{-1} respectively. In both compounds, only the Sn-C asymmetric stretching frequency appears. Therefore the dimethyltin group is apparently linear in both compounds. There is a very weak absorption band at 510 cm^{-1} in the sulphate adduct, it may either be due to a slight deviation from linearity of the (CH₃)₂Sn group, or more likely to a forbidden band, because of its very weak intensity.

Thus the infrared spectrum of dimethyltin sulphate-pyridine monoadduct again indicates that the sulphate group is coordinated to the dimethyltin group and that it acts either as a bidentate or a bridging ligand. The C_{2v} symmetry of the sulphate group and the linearity of the dimethyltin group suggest that the tin atom is five coordinate in this compound. Considering the five coordination of the tin atom, two stereochemical configurations can be suggested. One involves a trigonal bipyramidal arrangement containing the two methyl groups in the apical positions; the pyridine molecule and two oxygen atoms of the sulphate group being coordinated to the central tin atom in the three axial

positions. The other possible configuration can be that of a square pyramid in which the linear dimethyltin group is coordinated to two oxygen atoms in trans positions; the pyridine molecule being coordinated to the tin atom at the apex. However, it must be considered that a trigonal bipyramidal configuration for this compound involves coordinated groups in the axial plane, while the covalently bonded methyl groups are placed at the apical positions. Therefore such a configuration is most unlikely.

The assignments for vibrational frequencies of dimethyl sulphoxide (DMSO) have been made (111) and the S-0 stretching frequency has been well established. It gives rise to a very strong absorption band at 1057 cm^{-1} (in a liquid film). There is another very sharp, much less intense absorption at 950 $\rm cm^{-1}$. and a weaker, broad peak at 915 cm^{-1} , both of them being assigned to CH₂ rock. DMSO has an unshared pair of electrons on both sulphur and oxygen, and can coordinate through the sulphur atom or through the oxygen atom. As Cotton and Francis (112) have pointed out, the S-0 bond in sulphoxides has at least partial double bond character which may be considered to result from the superposition of $p\Pi - d\Pi$ bonding from 0 to S upon the S-0 sigma bond. Therefore coordination through the oxygen atom should decrease pT - dT back bonding and hence lower the S-0 bond order and the stretching frequency. On the other hand, coordination via sulphur would be expected to increase $p \Pi - d \Pi$ back bonding and thus raise the S-0 stretching frequency. Cotton, Francis, and Horrocks (113) have reported that, in sulphoxides, the oxygen atom is the donor in the majority of the metal complexes studied. In such cases, the S-0 stretch

is shifted to lower frequencies. With an acceptor such as Pt(II) or Pd(II), sulphur seems to be the donor atom and the S-0 stretching frequency is higher in the complex than in the free ligand. Though there is hardly any doubt that in DMSO complexes such as $Co(DMSO)_6CoCl_4$ and $SnCl_4(DMSO)_2$, the oxygen atom of DMSO acts as the donor atom, the assignments of the vibrational frequencies have been disputed. In $Co(DMSO)_6CoCl_4$, Cotton, Francis, and Horrocks (113) have assigned the S-0 stretching mode to a very strong band at 950 cm⁻¹ and the CH₃ rocking mode to a strong band in the 1000 cm⁻¹ region. Contrary to these assignments, Drago and Meek (114) have assigned the 950 cm⁻¹ band to the CH₃ rock and 1000 cm⁻¹ band to the S-0 stretch.

The infrared absorption bands of DMSO adducts of dimethyltin sulphate and dimethyltin dichloride are listed, together with their relative intensities and suggested assignments in Table 4.4c, and a portion of the spectrum of the sulphate adduct is shown in Figure 4.4d. The absorption bands due to DMSO in both compounds occur at almost the same frequencies. In addition to the DMSO bands which can be recognized easily, the main features of the spectrum of the dichloride adduct are the absorption bands at 788, 573, 508 (vw), 415, 340, 312 and 255 cm^{-1} . The bands at 788, 578, and 415 cm⁻¹ can be assigned to CH_3 rock $[Sn(CH_3)_2]$ group, the Sn-C asymmetric stretch and Sn-O asymmetric stretch respectively. The very weak band at 508 may be an overtone of the 255 cm^{-1} band. Of the three bands at 340, 312 and 255 cm^{-1} , most probably only one band is due to the Sn-Cl stretching vibration. In DMSO, there are absorption bands at 382 and 333 $\rm cm^{-1}$ which have been assigned (111) to the symmetric and asymmetric



TABLE 4.4c

Infrared Absorption Spectra of DMSO Adducts of Dimethyltin

	Sulpha	te and Dimeth	yltin Dichlo	ride
(CH ₃) ₂ SnS	504.DMSO	CH ₃) ₂ SnCl	2.2DMS0	
Frequency (cm ⁻¹)	Relative intensity	Frequency (cm-1)	Relative intensity	Assignment
3040 2960	w) ŵ)	3030 2930	w) w)	C-H stretch
1455	sh	1457	sh	
1443	ms .	1430	S	
1420	w	1410	m	
		1365	vw	
1323	m	1320	ms	
1300	w	1300) 1295)	m	
1225	m			
1202) 1193)	S			SO ₂ asym. str., (v_6)
1080	s, sh			SO ₂ sym. str., (v_1)
1045	s			
		1034	S	SO_2^* asym.str.,
1000	m	995	S	(v ₈)
989	m			SO ₂ sym.str., (ϑ_2)
945	S	943	S	∂ (S-O) (DMSO)
915	w	910	m	
805	S	788	S	CH ₃ rock
783	sh			
727	m	720	m	

Table 4.4c continued

655	S			$SO_4 \operatorname{rock}(y_7)$
597	S	573	S	Sn-C asym.str.
590	S			SO_2 bend, (v_3)
		508	vw	
468	m			SO_2^* bend ,($artheta_4$)
437	S	415	S	Sn-0 stretch
330	m	340	S	
		312	S	Sn-Cl str.
255	m	255	m	

m = medium; s = strong; sh = shoulder; v = very; w = weak; * denotes the oxygen atoms (of the SO₄ group) involved in bonding. The assignments for the SO₄ group have been made assuming C_{2v} symmetry as in ClO₄. No assignments have been made for DMSO absorption bands except the $\hat{V}(S=0)$.

C-S-O deformation. These bands are shifted to 330 and 255 cm^{-1} in the dimethyltin sulphate adduct. Therefore it is suggested that in the dimethyltin dichloride adduct, the 312 cm^{-1} band is associated with the Sn-Cl stretching vibration and the bands at 340 and 255 cm^{-1} are due to the DMSO ligand. Thus only one frequency is indicated for each of the Sn-C, Sn-O and Sn-Cl stretching vibrations in the infrared spectrum of the dimethyltin dichloride-DMSO diadduct. In view of these spectral features, a trans octahedral structure is suggested for this compound. As regards the assignments for the S-0 stretching frequency, there are two strong bands of almost equal intensity at 995 and 943 $\rm cm^{-1}$ and it is not possible to distinguish which of the two bands corresponds to the S-O stretch. However, in dimethyltin sulphate-DMSO adduct the most intense band due to DMSO appears at 945 $\rm cm^{-1}$ and therefore this band is assigned to the S-O stretch. On this basis, the 943 cm⁻¹ band in the dichloride adduct can be assigned to the S-0 stretch and the 995 cm^{-1} band to CH₃ rock (DMSO).

The main features of the infrared spectrum of the dimethyltin sulphate-DMSO adduct are the absorption bands at 1207-1193, 1080, 1045, 989, 655, 590 and 468 cm⁻¹. Comparing the DMSO part of the spectrum of the sulphate adduct with that of the dichloride adduct, it can be seen that no bands due to DMSO occur in these regions except a band at 1034 cm⁻¹ which is masked by the strong sulphate band at 1045 cm⁻¹. The sulphate absorption bands in the dimethyltin sulphate-DMSO adduct are almost identical to those observed for the dimethyltin sulphate-pyridine adduct. Thus the infrared spectrum of dimethyltin sulphate-DMSO adduct also shows coordination between the sulphate and the dimethyltin groups. The Sn-C and Sn-O vibrations in the dimethyltin sulphate-DMSO adduct appear at 597 and 437 cm⁻¹ respectively. It may be noted that only the Sn-C asymmetric stretching and Sn-O asymmetric stretching vibrations appear. The stereochemical features suggested for dimethyltin sulphate-pyridine adduct can also be suggested for the DMSO adduct because of the almost identical spectrum of the dimethyltin and the sulphate groups in both compounds.

The coordination by the sulphate groups in the adducts of dimethyltin sulphate with methanol, pyridine and DMSO as shown by the above spectroscopic results, is not consistent with an ionic constitution of dimethyltin sulphate and suggests a coordinated structure for this compound.

Proton n.m.r. studies on dimethyltin(IV) compounds have recently been used to estimate the percentage s-character in the tin orbitals directed to the methyl groups, by the measurement of the 117 Sn-CH₃ or 119 Sn-CH₃ coupling constants. Coupling constant data reported (50) for some dimethyltin compounds are shown in Table 4.4d.

TABLE	4.	4d
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Sn-OH3	Coupling	Constants	of Some	Dimethyltin	n(IV)Derivatiyes
Compound	· .	Solvent	J(¹¹⁷ Sn- c.p.s.	-СН _З)	J(¹¹⁹ Sn-CH ₃) c.p.s.
$(CH_3)_2 Sn(C104)$) 2	H20	102		107
$(CH_3)_2 Sn (NO_3)_2$	2	Н ₂ 0	104.3	3	108.7
$(CH_3)_2SnCl_2$		HC1	92.5	5	97.5
(CH3)2Sn(C5H702	2) ₂	CDC13	95.0)	99.3
$(CH_3)_2SnCl_2$		CDC13	66.5	5	69.8
$(CH_3)_2 Sn (OCH_3)$) ₂	CC14	71.3	3.	74.4

Raman and infrared studies on aqueous solutions of dimethyltin compounds (21) indicate the presence of the aquodimethyltin cations with a linear C-Sn-C skeleton and four water molecules coordinated in the equatorial plane. Bis(acetylacetonato) dimethyltin(IV), $(CH_3)_2Sn(C_5H_7O_2)_2$ is also considered, from Raman and infrared and proton n.m.r. studies (50), to be octahedral with trans methyl groups. The configuration of the last two compounds listed above, i.e. dimethyltin dichloride (4) and dimethoxy dimethyltin (115), is reported to be tetrahedral in chloroform solution. As seen from Table 4.4d, the coupling constant values for the octahedral species are markedly different from those of tetrahedral species.

In this investigation the proton n.m.r. spectra of dimethyltin sulphate as well as its adducts with pyridine and DMSO, and dimethyltin chloride-DMSO adduct were determined. The values of the coupling constants obtained are shown in Table 4.4e.

TABLE 4.4e

Sn-CH3 Coupling Constants of Dimethyltin Sulphate, Dimethyltin

Sulphate-Pyridine,	Dimethyltin	Sulphate-DMSO and	l Dimethyltin				
Dichloride-2DMSO							
Compound	Solvent	J(¹¹⁷ Sn-CH ₃) c.p.s.	$J(119Sn-CH_3)$ c.p.s.				
$(CH_3)_2 SnSO_4$	H ₂ 0	104.5	109.5				
$(CH_3)_2 SnSO_4 \cdot Py$	H ₂ 0	91.0	95.0				
$(CH_3)_2 SnSO_4 \cdot DMSO$	н ₂ 0	104.5	109.5				
(CH ₃) ₂ SnCl ₂ .2DMSO	H20	102.0	107.0				
$(CH_3)_2 Sn Cl_2 \cdot 2DMSO$	CHC13	82.5	86.5				

Note: Dimethyltin sulphate and its addition compounds with pyridine and DMSO are not soluble in organic solvents such as $CHCl_3$ or CCl_4 .
The coupling constant values for aqueous solutions of dimethyltin sulphate, the dimethyltin sulphate-DMSO adduct and the dimethyltin dichloride-DMSO adduct are in good agreement with the values reported for dimethyltin perchlorate and nitrate, and it can be inferred that like dimethyltin perchlorate and nitrate, these compounds are also dissociated in aqueous solution to form six coordinate aquodimethyltin cations. The values for the coupling constants of the dimethyltin sulphate-pyridine adduct are lower but they are of the same order as those reported in Table 4.4d for dimethyltin dichloride in hydrochloric acid solution. The coupling constants for dimethyltin dichloride-DMSO adduct are lower compared with those for bis(acetylacetonato)dimethyltin(IV). According to the linear relation (12) between coupling constant and percentage s-character in the tin orbitals directed to methyl groups, s-character in the Sn-CH3 bond is about 40 percent in dimethyltin dichloride-DMSO adduct and 46 percent in bis-(acetylacetonato)dimethyltin(IV). The Sn-0 stretching frequencies in these two compounds occur at 415 and 400 ${\rm cm}^{-1}$ respectively, indicating greater Sn-0 bond strength in dimethyltin dichloride-DMSO adduct. However, the Sn-C stretching frequencies in the two compounds occur at 573 and 570 cm^{-1} respectively, indicating very little change in the Sn-C bond strength in the two compounds.

4.5 <u>Dimethyltin Bis(tetrafluoroborate)</u> $(CH_3)_2 Sn(BF_4)_2$

The tetrahedral symmetry (T_d) of the tetrafluoroborate ion has been established by infrared and Raman studies (116, 117). However, the frequencies of the fundamental vibrations of the

tetrafluoroborate ion reported by two groups of workers (116, 117) are slightly different and both sets of values are listed in Table 4.5a.

Vibrati	onal Fre	quencies of	BF_4 Ion (Point Group T	d)
Vibrational mode	ϑ_1	ϑ_2	√ ₃	\mathbf{v}_4	
	(A ₁)	(E)	(F ₂)	(F ₂)	
	(R)	(R)	(R,I.R)	(R,I.R)	
Frequency (cm ⁻¹)	· .				
(116)	786	369	1100	541	
(117)	769	353	984,1016	524	

TABLE 4.5a

(R = Raman active; I.R = Infrared active)

The detailed infrared spectra of some ionic tetrafluoroborates have been studied (118-120). Crystalline tetrafluoroborates give many absorption bands other than the fundamentals, the most prominent feature being the splitting of the $\sqrt[4]{3}$ mode, a doublet for $\sqrt[4]{4}$ mode and the appearance of the forbidden $\sqrt[4]{1}$ mode. Coté and Thompson (118) considered this splitting to be a result of the lowering of the site symmetry of the anion in the crystal. From an infrared spectroscopic study of potassium tetrafluoroborate containing an enriched isotope ratio of (^{10}B : ^{11}B), Greenwood (120) showed that the splitting and broadening of peaks in potassium tetrafluoroborate is due to a combination of the lowering of site symmetry and the presence of the two isotopes of boron. However, the infrared spectrum (43) of trimethyltin tetrafluoroborate is considerably different from the infrared spectra of the ionic tetrafluoroborates. While in ionic tetrafluoroborates, the $elsiph_3$ mode appears as a very strong broad band in the region $1050-1075 \text{ cm}^{-1}$ showing splitting in the form of fine structure, in trimethyltin tetrafluoroborate, this mode is clearly resolved into three strong bands at 1170, 1070, and 930 cm^{-1} . Similarly, the ϑ_1 mode appears only as a weak "forbidden" transition at 771 cm^{-1} in the spectra of ionic tetrafluoroborates, but in the spectrum of trimethyltin tetrafluoroborate, the $\sqrt{1}$ mode shows a strong absorption at 746 cm⁻¹. Another important feature of the spectrum of trimethyltin tetrafluoroborate is the appearance of a broad band at 446 cm^{-1} . These features of the infrared spectrum of trimethyltin tetrafluoroborate are consistent with the suggested C_{2v} symmetry of the tetrafluoroborate group and indicate strong interaction between the tetrafluoroborate and trimethyltin groups. Coordination by the tetrafluoroborate group has also been reported (86) in Ni(3,5-lutidine)₄ (BF_{4)₂}.

The infrared spectra (121) of Mn(II) and Zn(II) tetrafluoroborate-(methyl cyanide) complexes also differ from the infrared spectra of silver and potassium tetrafluoroborates.

Attempts were made to prepare dimethyltin bis(tetrafluoroborate) by the metathetical reaction between dimethyltin dichloride and silver tetrafluoroborate. However, the metathetical reaction, carried out in methanol as well as in ether, resulted in the formation of dimethyltin bis(tetrafluoroborate), dimethyltin difluoride, boron trifluoride and silver chloride. The evolution of boron trifluoride was confirmed by the formation of boron trifluoride-amine adducts. When the metathetical

reaction was done in methanol, the quantitative amount of silver chloride was precipitated. Upon removal of the methanol from the filtrate, an extremely hygroscopic white solid was obtained. The infrared spectrum, analytical results and the X-ray powder photographs of the solid showed it to be a mixture of dimethyltin bis(tetrafluoroborate) and dimethyltin difluoride. The analytical results indicate that the mixture contained nearly 46 percent dimethyltin bis(tetrafluoroborate) and 54 percent of dimethyltin difluoride. The mixture did not show any change, either spectroscopically or analytically, when it was heated to $60 - 70^{\circ}$ under vacuum for about six hours. Therefore it is concluded that the decomposition of dimethyltin bis(tetrafluoroborate) is not due to its thermal instability under experimental conditions. Quantitative precipitation of silver chloride shows that the metathetical reaction in methanol goes to completion, i.e.

The formation of dimethyltin difluoride can be explained in the following manner:

$$(CH_3)_2 Sn^{2^+}(solvated) + 2BF_4^- \xrightarrow{-CH_3OH} (CH_3)_2 SnF_2 + 2BF_3 . . (2)$$

The formation of dimethyltin difluoride upon removal of the solvent also indicates that dimethyltin bis(tetrafluoroborate) is stable in methanol but partially decomposes upon removal of the solvent according to equation (2).

These results indicate a very strong interaction between $(CH_3)_2Sn$ and BF_4 groups in the solid state, apparently causing this partial decomposition. This interaction is further supported by the spectroscopic results. The metathetical reaction between dimethyltin dichloride and silver tetrafluoroborate was also done in liquid sulphur dioxide but dimethyltin bis (tetrafluoroborate) could not be isolated in the pure form.

Although only a solid mixture of dimethyltin bis-(tetrafluoroborate) and dimethyltin difluoride was obtained, the infrared spectrum of this mixture shows very interesting features and suggests strong interaction between $(CH_3)_2Sn$ and BF_4 groups. The infrared absorption spectrum obtained on a nujol mull sample of the solid is recorded together with the relative intensities and suggested assignments of the absorption bands, in Table 4.5b and part of the spectrum is shown in Figures 4.5a and 4.5b.

The absorption bands at 1280, 1207, 1195, 1157, 1095, 1066, 1047, 1030, 940, 760, 525-510, 455 and 410 cm⁻¹, can be attributed to the tetrafluoroborate group. It is evident that the spectrum is markedly different from that of the free $BF_4^$ ion. The triply degenerate mode ϑ_3 of the free ion is clearly resolved into three strong bands at 1157, 1066, and 940 cm⁻¹; the infrared forbidden mode ϑ_1 of the free ion appears as a strong sharp band at 760 cm⁻¹, and the triply degenerate mode ϑ_4 of the free ion which usually appears as a doublet at 536 and 525 cm⁻¹ now shows one medium absorption band at 525-510 cm⁻¹ and two strong bands at 455 and 410 cm⁻¹. The other absorption bands which are all weak, apparently are due to the isotope





TABLE 4.5b

Infrared Absorption Spectrum of The Mixture of Dimethyltin Bis(tetrafluoroborate) and Dimethyltin Difluoride

Frequency	(cm ⁻¹) Relative	Intensity	Assignment
1280	w		
1225	w ,	sp C-H	sym. bend
1207	vw	•	
1195	vw		
1157	S	$^{ m BF}2$	$\operatorname{asym.str.}, (v_6)$
1095	sh		
1066	S	$^{ m BF}2$	$sym.str., (v_1)$
1047	sh		
1030	sh		
940	S	\mathtt{BF}_2^*	asym.str., $(\sqrt[4]{8})$
815	S	CH ₃	rock
760	s	BF_2^*	sym. str., (v_2)
604	m	Sn-	C asym.str.
525)		
518) m	BF ₂	bend, (v_3)
510			
455	s,	b (BF	4) rock, $(\sqrt[1]{7})$
410	s,	b (BF	4) rock, (v_9)
375-3	350 sh	Sn-	F str., $\left[(CH_3)_2 Sn F_2 \right]$

b = broad; m = medium; s = strong; sh = shoulder; v = very; w = weak. * denotes the fluorine atoms involved in bonding. The assignments for the BF_4 group have been suggested by analogy with Clo_4 group of C_{2v} symmetry. effect as well as to overtones and combination bands. The bands at 1225, 815, and 604 cm⁻¹ can be assigned to the C-H symmetric bend, CH₃ rock and Sn-C asymmetric stretching modes respectively. Dimethyltin difluoride has absorption bands at 1210, 787, 595 and 373 cm⁻¹. These bands are masked by the bands due to dimethyltin bis(tetrafluoroborate). The strong broad band at 410 cm⁻¹ clearly has a shoulder in the 375 cm⁻¹ region and this is probably due to the 373 cm⁻¹ band of dimethyltin difluoride. The observed spectrum is therefore largely due to dimethyltin bis(tetrafluoroborate).

The observed spectrum is almost identical to that reported (43) for trimethyltin tetrafluoroborate and both spectra can only be interpreted in terms of coordinated tetrafluoroborate groups of C_{2v} or lower symmetry. Due to the presence of tetrafluoroborate absorption bands in the 525-510 ${\rm cm}^{-1}$ region, it is difficult to say whether the Sn-C symmetric stretch is also present. However, the Sn-C asymmetric stretching vibration in this compound occurs at almost the same frequency as that observed in dimethyltin difluoride, dimethyltin sulphate, and dimethyltin Since the infrared spectra of these compounds sulphate adducts. suggest the presence of a linear dimethyltin group, it is very likely that the dimethyltin group is linear in dimethyltin bis(tetrafluoroborate). Considering the probable linearity of the dimethyltin group and the presence of coordinated tetra fluoroborate groups of $C_{\ensuremath{2v}}$ symmetry, it can be suggested that in dimethyltin bis(tetrafluoroborate), four fluorine atoms are coordinated to the linear dimethyltin group, in the equatorial plane making the tin atom six coordinate.

Like trimethyltin tetrafluoroborate, dimethyltin bis(tetrafluoroborate) is extremely hygroscopic, and marked changes in the infrared spectrum of the mixture were observed on exposing it to air for a few seconds. The strong bands at 1157, 1066, 940, 760, 455 and 410 cm⁻¹ and the medium band at 525-510 cm⁻¹ disappeared and the spectrum showed characteristic bands of the BF_4^- ion, i.e. a broad strong band at 1110-1025 cm⁻¹ and a doublet at 535 and 520 cm⁻¹. The methyl rocking and the Sn-C asymmetric stretching vibrations were shifted to 790 and 575 cm⁻¹ respectively. The marked changes in the spectrum upon exposing the mixture to air again indicate that free $BF_4^$ ions and hydrated (CH₃)₂Sn^{2,+} cations are produced by hydrolysis of the anhydrous product.

4.6 Dimethyltin Hexafluorosilicate (CH₃)₂SnSiF₆

An attempt to prepare this derivative was not successful. Nevertheless, the reaction products from the attempted preparation are interesting in that they show a very strong interaction between $(CH_3)_2Sn$ and SiF_6 groups. The metathetical reaction between dimethyltin dichloride and silver hexafluorosilicate in methanol resulted in instantaneous precipitation of silver chloride. However, after pumping off the solvent (at room temperature) from the filtered solution, pure dimethyltin difluoride was obtained, as shown by analytical results, infrared spectrum and X-ray powder photographic data. The recovered methanol was highly acidic and contained silicon and fluorine. The results can only be interpreted according to the scheme: $(CH_3)_2SnCl_2 + Ag_2SiF_6 \xrightarrow{CH_3OH} (CH_3)_2Sn^2$ (solvated) + $SiF_6^2 + 2AgCl$ $(CH_3)_2Sn^2$ (solvated) + $SiF_6^2 - \xrightarrow{-CH_3OH} (CH_3)_2SnF_2 + SiF_4$ The metal fluorosilicates are stable, being only about one percent hydrolysed in aqueous solution (59b). The decomposition of the $\operatorname{SiF}_6^{2-}$ ion in aqueous solution is considered to proceed in the following manner (122):

$$\operatorname{SiF}_{6}^{2-} \longrightarrow \operatorname{SiF}_{4} + 2\overline{F} \qquad \dots \qquad (1)$$

followed by the rapid hydrolysis

$$\operatorname{SiF}_4 + \operatorname{3H}_20 \longrightarrow \operatorname{4HF} + \operatorname{H}_2\operatorname{SiO}_3 \qquad \dots \qquad (2)$$

The value of the equilibrium constant K, for the lst reaction is reported (122) to be 1×10^{-6} at 20° . The heat of formation ΔH_f° of SiF_6° ion in aqueous solution is -558.5kcal/mole (123). Although the corresponding values in methanol solution would be different, still it can be seen from these figures that complete decomposition of dimethyltin hexafluorosilicate must involve a very strong interaction between (CH₃)₂Sn and SiF₆ groups.

4.7 Dimethyltin Derivatives of Group V_b Hexafluorides

Phosphorus, arsenic and antimony form stable hexafluoride anions of the formula MX_6 . These anions have octahedral symmetry and belong to point group 0_h . An octahedral molecule, or ion, should have fifteen normal vibrations distributed between six vibrational modes (47c) as shown in Table 4.7a. If the MX_6 group is involved in coordination then its symmetry would be lowered. A correlation between the modes of vibration of a octahedral group, having 0_h , D_{4h} or C_{2v} symmetry is shown in Table 4.7b. If the hexafluoride ion acts as a trans bridging ligand, then the 0_h symmetry of the hexafluoride ion is lowered to D_{4h} and this should result in five infrared active fundamental

TABLE 4.7a

·		
Vibrational mode	Assignment	Activity
ϑ_1 (A _{1g})	M-X symmetric stretch	(R)
√ 2 (E _g)	X-M-X stretch	(R)
\mathbf{J}_{3} (F _{1u})	X-M-X bend	(I.R)
$ \mathbf{y}_4 (\mathbf{F}_{1u}) $	M-X asymmetric stretch	(I.R)
v_{5} (F _{2g})	X-M-X bend	(R)
$ \mathbf{v}_{6} (\mathbf{F}_{2u}) $	X-M-X bend (out-of-plane)	(Inactive)

Vibrational Modes of An Octahedral Group MX₆

(R = Raman active; I.R = Infrared active)

vibrations belonging to $(2A_{2u} + 3E_u)$ species. Moreover, the bond lengths of one pair of trans M-X bonds would be expected to increase, and as a result of this elongation, the infrared active antisymmetric F-M-F stretching mode (corresponding to the A_{2u} fundamental arising from the splitting of the degenerate mode $\vartheta_3 \rightarrow A_{2u} + E_u$) should shift to a lower frequency. This effect has been observed (43) in the infrared spectrum of trimethyltin hexafluoroarsenate, in which the ϑ_3 mode of the AsF_6^- ion splits into two bands at 675 cm⁻¹ and 710 cm⁻¹. If the hexafluoride ion acts as a cis bridging ligand, then its symmetry is lowered to C_{2v} . In that case, the degeneracy of infrared active modes is completely removed and the number of infrared active fundamental modes is increased to thirteen. Complete removal of degeneracy of the ϑ_3 mode has been observed (43) in the infrared spectrum of trimethyltin hexafluoroantimonate in which the ϑ_3 mode of the SbF_6^- ion splits into three modes at 675, 656 and 640 cm⁻¹.

Group of O_h , D_4	h, or C _{2v} Symmetry	!
D _{4h}	o _h	C _{2v}
A _{lg}	Alg	Al
$A_{1g} + B_{1g}$	Eg	$A_1 + B_1$
$2A_{2u^+}$ $2E_u$	2F _{lu}	$2A_1 + 2B_1 + 2B_2$
B _{2g} + E _g	F _{2g}	$A_1 + A_2$
$B_{2u} + E_u$	^F 2u	$A_1 + A_2 + B_1$
Vibrations of species A _{2u} and E _u are infra= red active	Vibrations of species F _{lu} are infrared active	Vibrations of species A ₁ ,B ₁ , and B ₂ are infrared active

TABLE 4.7b

Correlation Between The Vibrational Modes of An Octahedral

Splittings of the degenerate infrared active modes of the octahedral anions due to crystal field effects have also been reported (124) in the solid state infrared spectra of ammonium hexafluorogermanate and barium hexafluorogermanate. The reported (125) splitting of the $\sqrt[3]{3}$ mode of barium hexafluorosilicate probably is also due to the same effect. However, in all these cases, the Raman active modes of the hexafluoride ion do not appear with any significant intensity in the infrared spectra. Unfortunately only very few studies on the vibrational spectra of hexafluoride ions have been made, probably due to great experimental difficulties involved in such studies.

In this investigation an attempt was made to prepare dimethyltin derivatives of hexafluorophosphate, hexafluoroarsenate and hexafluoroantimonate. Derivatives of both hexafluorophosphate and hexafluoroarsenate decomposed partially to give dimethyltin fluoride and the corresponding Lewis acid as described below.

When stoichiometric amounts of silver hexafluorophosphate and dimethyltin dichloride were allowed to react in methanol, silver chloride was precipitated instantaneously. However, upon removal of the methanol under vacuum at room temperature, a sticky solid was obtained which could not be further dried and which was not completely soluble in methanol or water. The infrared spectrum of the solid showed intense bands at 1210, 1110, 1050, 815, 800, 495 and 475 cm⁻¹. The recovered methanol was highly acidic and contained fluorine as well as phosphorus as shown by qualitative tests.

When the above metathetical reaction was performed in liquid sulphur dioxide, the product was a white solid which gave infrared absorption bands at 1260, 1150, 920, 885, 810, 600, 590, 565, 535, and 480 cm⁻¹. An X-ray powder photograph of the solid showed the presence of dimethyltin difluoride, and the recovered sulphur dioxide contained some phosphorus oxytrifluoride, POF₃, which was identified by its infrared spectrum. Since silver hexafluorophosphate can best be prepared from liquid sulphur dioxide (126), POF₃ cannot arise from direct reaction of PF₆ with SO₂. Therefore, the results can only be interpreted in the following manner;

 $(CH_3)_2 SnCl_2 + 2AgPF_6 \xrightarrow{SO_2} (CH_3)_2 Sn(PF_6)_2 + 2Agel$ $(CH_3)_3 Sn(PF_6)_2 \xrightarrow{(CH_3)_2 SnF_2} + 2PF_5$ $PF_5 + SO_2 \xrightarrow{POF_3} + SOF_2$

Similar results have been reported (43) for the reaction between trimethyltin bromide and silver hexafluorophosphate.

The metathetical reaction between dimethyltin dichloride and silver hexafluoroarsenate in methanol resulted in instantaneous precipitation of silver chloride. Upon removal of the solvent from the filtrate a hygroscopic white solid was obtained which gradually turned yellowish. The recovered methanol was highly acidic and contained arsenic and fluorine. An X-ray powder photograph of the solid showed the presence of dimethyltin difluoride. The infrared spectrum of the solid as described below indicated the presence of the hexafluoroarsenate group. These results can be explained in terms of partial decomposition of dimethyltin bis(hexafluoroarsenate) to give dimethyltin difluoride and arsenic pentafluoride.

The infrared spectrum of the mixture in a nujol mull showed absorption bands at 1210, 825, 800, 760, 718, 595, 475, and 375 cm⁻¹. The spectrum in the 850 - 250 cm⁻¹ region is shown in Figure 4.7a. The AsF₆ ion has two infrared active vibrational modes, ϑ_3 and ϑ_4 . The ϑ_3 mode gives a strong, broad, but symmetrical band at approximately 700 cm⁻¹ (127), while the ϑ_4 mode is reported to occur at 400 cm⁻¹ (128). In addition subsidiary bands at 1300, 1065, 970 and 825 cm⁻¹ also appear in the infrared spectrum (127). In the spectrum of the mixture, the bands at 1210, 800, and 595 cm⁻¹ can be assigned to the C-H symmetric band, the CH₃ rock, and the Sn-C asymmetric stretching modes respectively. The bands at 760 and 718 cm⁻¹ are the two components of the ϑ_3 mode of the hexafluoroarsenate group. Similarly the bands at 375 and 475 are probably the two



components of the $\sqrt[4]{4}$ mode, although dimethyltin difluoride will also absorb at 375 cm⁻¹. Thus it appears that the symmetry of the AsF₆ group has been lowered from O_h to D_{4h}. The spectrum of the mixture thus shows features similar to those reported (43) for trimethyltin hexafluoroarsenate. The spectroscopic results and the partial decomposition of the dimethyltin bis(hexafluoroarsenate) both suggest very strong interaction between (CH₃)₂Sn and AsF₆ groups resulting in the partial decomposition of AsF₆ group.

Dimethyltin bis(hexafluoroantimonate) could be prepared by the metathetical reaction between dimethyltin dichloride and silver hexafluoroantimonate in methanol. However, the product could not be obtained free from methanol even after pumping the solid for 24 hours at 60° . When the solid was heated to 120° under vacuum, decomposition of the hexafluoroantimonate occurred and some antimony pentafluoride was formed. The metathetical reaction between dimethyltin dichloride and silver hexafluoroantimonate was also performed in liquid sulphur dioxide. An anhydrous, extremely hygroscopic white solid was obtained. X-ray powder photographs of the solid did not show any lines due to dimethyltin difluoride. However, no analysis of the product was obtained. Nujol mull samples of the solid prepared for the measurements of the infrared spectrum reacted rapidly with salt windows but reproducible spectra could be obtained on nujol mull samples by using silver chloride or polythene sheets.

The infrared spectrum has features similar to those reported for trimethyltin hexafluoroantimonate. The spectrum in the 750 - 250 cm⁻¹ region is shown in Figure 4.7b. Other bands



were observed at 1210(w), 990(m), 910(m), 828(m), 782(w) and 760(vw). Only one infrared active frequency (the v_3 mode) has been reported (128) for the SbF_6 ion. In order to compare the spectrum of dimethyltin bis(hexafluoroantimonate) with that of the SbF_6^- ion, the infrared spectrum of silver hexafluoroantimonate was also measured under comparable conditions. The spectrum showed a very strong broad band at 660 cm^{-1} (with a shoulder at 560 cm⁻¹) and another strong band showing peaks at 310, 290 and 270 cm⁻¹. The 660 cm⁻¹ band is due to the reported $\sqrt{3}$ mode and the band in the 310-270 cm⁻¹ region is evidently due to the u_4 mode which is split due to crystal field effects. In the spectrum of dimethyltin bis(hexafluoroantimonate), the bands at 1210 and 828 cm^{-1} can be assigned to the C-H symmetric band and the CH₃ rocking modes respectively. The spectrum of silver hexafluoroantimonate does not show any bands in the $1000-800 \text{ cm}^{-1}$ The medium bands at 990 and 910 cm^{-1} are therefore the region. vibrational modes, infrared inactive for the octahedral SbF_{6} ion, which have become infrared active as a result of distortion of the SbF_6 group by $(CH_3)_2Sn$. Significantly, as can be seen from the Figure 4.7b, the v_3 mode for dimethyltin bis(hexafluoroantimonate) is split and shows peaks at 675, 650 and 635 cm^{-1} , and additional bands which do not appear in the spectrum of silver hexafluoroantimonate are present at 595, 545, 445 and 365 cm⁻¹. The band at 595 cm⁻¹ can be assigned to the Sn-C asymmetric stretch but the bands at 540 and 445 cm⁻¹ are certainly due to the hexafluoroantimonate group. Thus the hexafluoroantimonate absorption in dimethyltin bis(hexafluoroantimonate) is significantly different from that of the

 SbF_6 ion. The appearance of 540 and 445 cm⁻¹ bands cannot be attributed to crystal field effects, and indicate strong interaction between $(CH_3)_2$ Sn and SbF₆ groups as a result of which the O_h symmetry of the SbF₆ group is distorted (probably to C_{2v}). Although the stereochemistry in this compound cannot be determined with any certainty, the infrared results are consistent with a configuration in which linear $(CH_3)_2$ Sn groups are coordinated in the equatorial plane by cis fluorine atoms of the ${\rm SbF}_6$ group making the tin atom six coordinate. Coordination between $(CH_3)_2Sn$ and SbF_6 is also indicated by the marked changes brought about in the spectrum when the compound was exposed to air. The bands at 990, 910, 782, 760, 545, 445 and 365 cm^{-1} completely disappeared and the bands at 675, 650 and 635 were replaced by a broad band showing a maximum at 660 cm^{-1} . Thus, upon exposure of dimethyltin bis(hexafluoroantimonate) to air, free SbF_6^- ions are produced as a result of hydrolysis.

The dimethyltin derivatives of group Vb hexafluorides are very similar to the analogous trimethyltin derivatives (43). Trimethyltin hexafluorophosphate is unstable, the hexafluoroarsenate and antimonate which are derived from progressively stronger Lewis acids AsF_5 and SbF_5 are stable, the anion in the former acting as a trans, and in the latter as a cis bridging group. The stabilities of corresponding dimethyltin derivatives follow the same sequence though dimethyltin derivatives are apparently less stable than the trimethyltin derivatives.

4.8 The Dimethyltin(IV) Derivative of $B_{12}Cl_{12}^{2-}$

The $B_{12}Cl_{12}^{2}$ ion is considered (129) to have an icosahedral structure similar to that of $B_{12}H_{12}^{2}$. The icosahedral structure of $B_{12}H_{12}^{2}$ has been established (130) by X-ray crystallography. A molecule or ion belonging to point group I_h should give rise to two strongly polarized Raman Lines of species A_g , and four depolarized Raman Lines of species H_g , and three infrared active fundamentals of species F_{1u} . However, only a single strong line at 300 cm⁻¹ is observed in the Raman spectrum of $B_{12}Cl_{12}^{2-}$ (129). It has been suggested (129) that the failure to observe other strong Raman lines may be a consequence of accidental cancellation of polarizability changes of oppositely charged boron and halogen atoms in totally symmetric vibrations. Only one fundamental infrared absorption frequency at 1030 cm⁻¹ has been reported (129) for $B_{12}Cl_{12}^{2-}$ ion.

The dimethyltin derivative of $B_{12}Cl_{12}^{2}$ was obtained as a hygroscopic white solid which contained some methanol. The methanol could not be removed from the solvated product even after heating for 24 hours at 100° under vacuum. The analytical results of the heated solid indicate that the product contained about one to two moles of methanol per mole of $(CH_3)_2SnB_{12}Cl_{12}$. Due to the very high molecular weight of $(CH_3)_2SnB_{12}Cl_{12}$ it is rather difficult to ascertain the exact amount of methanol in the product. However, no decomposition of the $B_{12}Cl_{12}^{2-}$ group occurred and the recovered methanol was neither acidic nor contained any chlorine or boron.

The infrared spectrum of the dimethyltin $B_{12}Cl_{12}$ derivative is recorded in Table 4.8 and part of the spectrum is shown in



TABLE 4.8

Infrared	Absorption Spect	trum of The	e Dimethyltin Derivative	of
		$\frac{B_{12}Cl_{12}^{2}}{B_{12}Cl_{12}}$		
	Frequency	(cm ⁻¹)	Relative Intensity	
	3460	. N.	i s	
	3080		vw	
	2960		vw	
	1600		w	
	1455		m	
	1400		W	
	1250		w	
	1220		VW	
	1170		vw	
	1144		w	
	1040		s	
	1002		m	
	950	·)		
	925	·)	m	
	857		s,sh	
	824		S	
	590		vw	
	535		vs	
	480		m	
	425		W	
	328		W	
m = mediu	m: s = strong:	sh = show	ulder: $v = verv \cdot w = wea$	ե

;

= very; w = weak.

Figure 4.8 (curve b). For comparison, the infrared spectrum of solid $Ag_2B_{12}Cl_{12}$ was also measured and is also shown in Figure 4.8 (curve a). In the spectrum of the dimethyltin derivative, the absorption bands at 1040, 1002, 950, 925, 824, 535, 480, 425 and 328 cm⁻¹ can be attributed to the $B_{12}Cl_{12}$ group. The other absorption bands are due to the methanol and the dimethyltin group. The CH₃ rocking mode of $(CH_3)_2$ Sn group is probably masked by the strong band at 824 cm⁻¹. It may be noted that the Sn-C asymmetric stretch appears at 590 cm⁻¹; however, it is not possible to ascertain whether the Sn-C symmetric stretch is also present.

Comparing the $B_{12}Cl_{12}$ part of the spectrum in the dimethyltin derivative with that of the silver salt it becomes evident that, in the dimethyltin salt, the spectrum of the $B_{12}Cl_{12}$ group is very different from that of the free $B_{12}Cl_{12}^{2}$ -ion. Though it is difficult to derive any definite conclusions about the stereochemistry it can be inferred that the symmetry of $B_{12}Cl_{12}$ has been lowered in this compound as a result of which the infrared inactive modes of the free $B_{12}Cl_{12}^2$ ion have become infrared active. This can be explained either in terms of crystal field effects or in terms of an interaction between the dimethyltin group and the $B_{12}Cl_{12}$ group. In view of the infrared spectroscopic results of other dimethyltin derivatives, it is suggested that the changes in the $B_{12}Cl_{12}$ part of the spectrum of the dimethyltin derivative may be due to some form of coordination between $(CH_3)_2$ Sn and $B_{12}Cl_{12}$ groups. This is further supported by the gradual changes in the infrared spectrum of this compound upon exposure of the compound to air. The bands at 950,

925, 824, 480, 425 and 328 gradually diminished in intensity and after an exposure of three days, these bands disappeared and the CH₃ rocking mode appeared at 790 cm⁻¹.

CHAPTER 5

TRIMETHYLANTIMONY(V) DERIVATIVES

Apart from the crystal structure determination of trimethylantimony dichloride, dibromide and diiodide, very little is known about the stereochemistry of trimethylantimony derivatives of the type R_3SbX_2 . Recently Long, Doak, and Freedman (52) reported infrared spectra of trimethylantimony dihalides, the dinitrate and the sulphate. However, some of the results obtained by these workers appear rather anomalous. In the present investigation, some of the work reported by these workers was repeated. In addition, a wide variety of acid derivatives of trimethylantimony(V) were prepared and their infrared spectra were examined.

5.1 Trimethylantimony Dihalides

Crystal structure determinations (54) of trimethylantimony dichloride,dibromide and diiodide have shown that these dihalides are trigonal bipyramidal molecules containing a planar trimethylantimony group in the equatorial position. The general conclusions of Long, Doak, and Freedman (52) are consistent with the trigonal bipyramidal structure. The main features of the spectra of these dihalides reported by these workers are the C-H asymmetric stretch in the $3020-3010 \text{ cm}^{-1}$ region, the symmetric C-H stretch in the $2928 - 2920 \text{ cm}^{-1}$ region, the C-H asymmetric bend in the $1403-1387 \text{ cm}^{-1}$ region, the CH₃ rock in the $870 - 860 \text{ cm}^{-1}$ region and the Sb-C asymmetric stretch in the $587-554 \text{ cm}^{-1}$ region. However, these authors reported that, in the spectrum of trimethylantimony difluoride, complex bands occur in the 11201050, 730, and 540 - 450 cm^{-1} regions, and the Sb-C asymmetric stretch at 587 cm^{-1} is partially masked. In view of this inconsistency in the spectrum of the difluoride, the spectrum of this compound was studied again.

The observed absorption bands, with their relative intensities and assignments, are listed in Table 5.1. The main features of the spectrum are the C-H asymmetric stretch at 3065 cm^{-1} , the C-H symmetric stretch at 2965 cm^{-1} , the C-H asymmetric bend at 1415 cm^{-1} , the C-H symmetric bend at 1235 and 1221 cm^{-1} , the CH₃ rock at 855 cm^{-1} , the Sb-C asymmetric stretch at 585 cm^{-1} , and the Sb-F asymmetric stretch at 475 cm^{-1} . Contrary to the reports of Long, Doak, and Freedman, the spectrum of the difluoride does not show any complex bands in the 1120-1050, 730, and 540 - 450 cm^{-1} regions. The observed spectrum is completely consistent with a trigonal bipyramidal structure. The additional bands observed by Long, Doak, and Freedman must therefore be associated with impurities present in their sample.

Trimethylantimony difluoride sublimes, at room temperature under vacuum, and is soluble in organic solvents such as methanol, acetone and chloroform. It is therefore largely covalent like other dihalides. A comparison of the Sb-F stretching frequency (475 cm⁻¹) in trimethylantimony difluoride with the Sn-F stretching frequency (355 cm⁻¹) in trimethyltin fluoride also indicates the covalent nature of trimethylantimony difluoride.

5.2 <u>Trimethylantimony Dinitrate</u> (CH₃)₃Sb(NO₃)₂

Long, Doak, and Freedman (52) described the infrared spectrum of trimethylantimony dinitrate and from it concluded

Frequency	(cm ⁻¹)	Relative Intensity	Assignment
3065		w	C-H asym. str.
2965		w	C-H sym. str.
24 50		vw	
2 110		vw	
1812		w	
1768		w	
1415		m	C-H asym. bend
1235)		
1221	·) ·)	m,sp	C-H sym.bend
855		vs	CH3 rock
585		s,sp	Sb-C asym. str.
475		VS	Sb-F asym. str.

TABLE 5.1

Infrared Absorption Spectrum of Trimethylantimony Difluoride

m = medium; s = strong; sp = sharp; v = very; w = weak.

that this compound has an ionic structure. They observed the nitrate absorption frequencies at 1516(s), 1457(s), 1050(vw), 834(s), and 728(w) cm⁻¹. In view of the recently accumulated evidence for the nonexistence of the trimethyltin cation in the solid state, the ionic structure for trimethylantimony dinitrate seems rather surprising. Therefore, in this work, trimethylantimony dinitrate mony dinitrate was prepared under anhydrous conditions, and the infrared and ultraviolet spectra of this compound were studied.

Reliable infrared spectra of trimethylantimony dinitrate could only be obtained on samples made as mulls and placed between silver chloride sheets. When the spectra were measured either on mulls placed between potassium bromide plates or on samples made in potassium bromide pellets, considerable exchange occurred between trimethylantimony dinitrate and potassium bromide. The spectra measured by using silver chloride sheets were always reproducible. The spectrum of trimethylantimony dinitrate in the 1650-650 cm⁻¹ region obtained in a nujol mull is shown in Figure 5.2. The absorption frequencies (in the $4000 - 400 \text{ cm}^{-1}$ region) together with their relative intensities and assignments, are listed in Table 5.2. The absorption bands due to the nitrate group occur at 1550-1510, 1290-1275, 965, 795, 730, and 708 cm⁻¹. It can be clearly seen that the nitrate group in trimethylantimony dinitrate shows infrared absorption characteristic of a nitrato group (see section 2.1). The characteristic bands of a free nitrate ion are absent in the observed spectrum. Therefore trimethylantimony nitrate must have a non-ionic structure and the nitrate groups are apparently coordinated to the trimethylantimony



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Infrared	Absorption	Spectrum	of	Trimethy	lantimony	y Dinitrate
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Frequency (cm ⁻¹)	Relative Intensity	Assignment
3070	m	C-H asym. str.
2960	m	C-H sym. str.
2820	w	
2260	W	
1990	W	
1820	w	
1765	w	
1675	w	· ·
1530	s,b	NO ₂ asym. str., (v_4)
1415	m	C-H asym. str.
1290	s)	
1275	s)	NO $_2$ sym. str., $(\boldsymbol{\mathfrak{d}}_1)$
1245	m)	
1230	m	C-H sym. bend
965	S	NO str., (v_2)
865	S	CH ₃ rock
795	m	NO ₃ out-of-plane rock, (v_6)
728	S	NO ₂ sym. bend, (v_3)
708	m	NO ₂ asym.bend, (ϑ_5)
580	ms	Sb-C asym. str.
520	w,b	Sb-C sym. str.?

b = broad; m = medium; s = strong; w = weak.

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Nitrate absorption bands have been assigned assuming that the nitrate group is unidentate.

group. The absorptions due to the trimethylantimony group can be assigned by comparison with the spectra of trimethylantimony dibromide, and difluoride, i.e. 3070 cm^{-1} , C-H asymmetric stretch; 2960 cm⁻¹, C-H symmetric stretch; 1415 cm⁻¹, C-H asymmetric bend; 1245, 1230 cm⁻¹, C-H symmetric bend; 865 cm⁻¹, CH₃ rock; and 580 cm⁻¹, Sb-C asymmetric stretch. The presence of only one Sb-C stretching frequency of medium strong intensity, indicates that the trimethylantimony group is planar. A non-planar configuration of the trimethylantimony group would give rise to a symmetric Sb-C stretching band of medium intensity in addition to the asymmetric Sb-C stretching band with an intensity ranging from medium to strong.

Long, Doak, and Freedman (52) observed a weak band at 528 cm⁻¹ in the infrared spectra of $\left[(CH_3)_3SbC1\right]_2^0$ and $\left[(CH_3)_3SbC10_4\right]_2^0$. These authors have suggested that this band may be associated with the antimony-oxygen stretching vibration or may represent the distortion of the plane containing the carbon and antimony atoms. Very recently Cullen, Deacon, and Green (131) examined the infrared and Raman spectra of $(CH_3)_4$ Sb HgI₃ and found that the infrared forbidden Sb-C symmetric stretch appears weakly at 529 cm-1 in the infrared spectrum. In trimethylantimony dinitrate and in other trimethylantimony derivatives such as carbonate and chromate which will be described later, a similar weak absorption occurs in the 530-520 cm^{-1} region. Though a Sb-0 stretching frequency can also occur in this region in these compounds, it is more likely that the weak absorption in this region is associated with the Sb-C symmetric stretching vibration which may appear as a symmetry forbidden mode. Alternately, the presence of this weak band may be due to the slight distortion of the

plane containing the carbon and antimony atoms. Thus the entire spectrum of trimethylantimony dinitrate can be interpreted in terms of a trigonal bipyramidal structure in which each nitrate group occupies the apical position and is bonded through one oxygen atom to the trimethylantimony group situated in the equatorial plane.

Further evidence of partial covalent bonding between nitrate groups and the antimony atom is provided by the ultraviolet absorption spectrum which was measured in aqueous and chloroform solutions. In aqueous solution, the absorption maximum occurs at 302 m $_{\mathcal{M}}$, and in chloroform solution, at 280m $_{\mathcal{M}}$. The absorption maximum at 302 m μ in aqueous solution is characteristic of the free nitrate ion and is attributed to the symmetry forbidden $n \rightarrow \overline{n} *$ transition in the nitrate ion (64). All such $n \longrightarrow \pi^*$ transitions show a blue shift (i.e. the absorption maximum is displaced to higher frequency) in a series of solvents with increasing dielectric constant (132). Since chloroform has a lower dielectric constant (D = 4.8)than water, the free nitrate ion in this solvent would be expected to show an $n \rightarrow \pi^*$ transition at longer wave lengths than in water. The observed maximum at $280m\mu$ in chloroform solution indicates that trimethylantimony dinitrate dissociates in aqueous solution to produce nitrate ions, but in chloroform solution, no nitrate ions are present. Similar shifts of absorption maxima in going from water to a solvent of lower dielectric constant have been observed for other nitrato compounds, e.g. transition metal nitrates, in t-butyl alcohol, show absorption maxima at 270-275 m (133), and dimethyltin nitrate in ethyl alcohol shows absorption maximum at $285m\mu$ (51).

The proton resonance spectrum of trimethylantimony dinitrate in chloroform solution shows one peak, at γ 7.85. Under the same conditions, trimethylantimony dibromide shows a peak at γ 7.3.

5.3 <u>Trimethylantimony Carbonate</u> (CH₃)₃SbCO₃

The vibrational frequencies of the carbonate ion and the carbonato group have been discussed earlier. The infrared spectrum of trimethylantimony carbonate was measured on samples made as mulls, as well as on samples made as pellets in potassium bromide. Both methods gave identical results. A portion of observed spectrum is shown in Figure 5.3, and the absorption frequencies, together with their relative intensities and suggested assignments, are listed in Table 5.3. The absorption bands due to the trimethylantimony group appear at 2950. (C-H asymmetric stretch); 2880, (C-H symmetric stretch); 1405-1385, (C-H asymmetric bend); 1225, (C-H symmetric bend); 875, (CH₂ rock); and 575, (Sb-C asymmetric stretch) cm^{-1} . Since only one absorption band of medium intensity appears in the region $575-500 \text{ cm}^{-1}$, the trimethylantimony group is apparently planar in this compound. The absorption bands which can be attributed to the carbonate group occur at 1730, 1280, 1115, 1110, 790, 740, 632, 450, 375, and 250 cm^{-1} . The weak bands at 1460, 1075, 1040 and 510 cm are probably overtones and combination bands. The appearance of the weak band at 525 cm^{-1} has already been discussed in connection with trimethylantimony dinitrate. The carbonate absorption bands in this compound clearly show that the carbonate group is involved in partial



Frequency (cr	m ⁻¹) Relative Intensity	Assignment
2950	m	C-H asym.str.
2880	sh	C-H sym. str.
1730	S	$C == 0 \text{sym. str.,} \\ (v_1)$
1460	W	
1405-138	85 w	C-H asym.bend
1280	S	CO_2 asym. str., (v_4)
1225	w	C-H sym.bend
1115	s)	() and at ()
1100	s)	CO_2 Sym. Str., (v_2)
1075	vw	
1040	VW	
875	vs	CH ₃ rock
7 90	vs	$CO_3 \text{ out-of-plane} $ def., (v_6)
740	S ,	CO_2 sym.bend, (v_3)
632	S	CO_2 asym.bend, (v_5)
575	S	Sb-C asym. str.
525	w	Sb-C sym. str.?
510	w	
450 375 250	m) . m) . s)	Sb-Ostr. ? Lattice modes ?

Infrared Absorption Spectrum of Trimethylantimony Carbonate

m = medium; s = strong; v = very; w = weak.

Assignments for the carbonate group have been suggested assuming that the CO_3 group is bridging.
covalent bonding with the trimethylantimony group and that its symmetry cannot be higher than C_{2v} . The doubly degenerate mode ϑ_3 observed in ionic carbonates at 1415 cm⁻¹ has split into two strong well defined bands at 1730 and 1280 cm^{-1} . In fact these two frequencies can be compared with the C=0 and C- 0_2^{\star} (* represents oxygen atoms involved in bonding) stretching frequencies of dimethyl carbonate which occur at 1750 and 1280 $\rm cm^{-1}$ respectively Similarly, the Raman active mode ϑ_1 of the free ion now (134). appears as an intense band, split into a doublet at 1115 and 1100 cm^{-1} ; the corresponding band in dimethyl carbonate occurs at 965 cm⁻¹ and at 1078 cm⁻¹ in ethylene carbonate (solid) (135). The splitting of this mode is also observed in metal-carbonato complexes (105). The other degenerate mode v_4 of the free ion has split into two strong bands at 740 and 632 cm^{-1} and the out-ofplane mode \dot{v}_2 of the free ion shows a strong absorption at 790 cm⁻¹. The bands at 450, 375 and 250 cm⁻¹ are similar to those observed in dimethyltin carbonate and may be due to the lattice modes, although Sb-0 vibrations may possibly also cause absorption in 500 - 400 cm^{-1} region. The infrared spectrum of trimethylantimony carbonate undoubtedly indicates that this compound contains a penta-covalent antimony atom, and the spectrum can only be interpreted in terms of a polymeric structure in which each carbonato group is bonded to planar trimethylantimony groups through two oxygen atoms. The other possible arrangement in which a carbonato group is bonded to any two corner positions of a trigonal bipyramidal monomer, would involve a highly strained structure and may be ruled out. Similarly a monomeric structure in which the carbonate group is

unidentately bonded to the trimethylantimony group would not be consistent with the planarity of the trimethylantimony group as well as with the observed frequencies of the carbonate group.

5.4 Trimethylantimony Sulphate

The infrared spectrum of trimethylantimony sulphate was reported recently by Long, Doak, and Freedman (52). These authors concluded, from their infrared results, that trimethylantimony sulphate is covalent. However, these authors remarked that the observed infrared bands do not correspond well with those given for sulphato complexes containing either unidentate or bidentate sulphato groups, and that the spectrum is difficult to interpret. These authors also reported that pronounced changes occurred in the spectrum very rapidly when a potassium bromide pellet containing trimethylantimony sulphate was exposed to the atmosphere. In view of this inconclusive report, the infrared spectrum of trimethylantimony sulphate was studied again The infrared spectra were measured on anhydrous in this work. samples made as mulls in the dry box, as well as on samples which were exposed to air and made as mulls or potassium bromide pellets. Both the anhydrous samples and samples exposed to air gave identical spectra by both methods (i.e. as mulls or potassium bromide pellets). A portion of the spectrum obtained on a nujol mull sample is shown in Figure 5.4. The absorption frequencies together with their relative intensities and suggested assignments are listed in Table 5.4a. The absorption bands due to the trimethylantimony group occur at 3050, (C-H asymmetric stretch); 2950, (C-H symmetric stretch); 1415, (C-H asymmetric bend); 1230, (C-H symmetric bend); and 860,



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Infrared Absorpt	tion Spectrum of I	rimethylantimony Sulphate
Frequency (cm ⁻¹)	Relative Intensi	ty Assignment
3050	W	C-H asym. str.
2950	W	C-H sym. str.
2120	vw	
1760	VW	ν.
1415	m	C-H asym. bend
1285	S	SO_2 asym.str., (v_6)
1230	m	C-H sym. bend
1145	S	SO ₂ sym. str., $(\boldsymbol{\vartheta}_1)$
980	sh	
950	S	SO $_2^*$ asym. str., (ϑ_8)
860	, S	CH ₃ rock
825	S	SO_2^* sym.str., (\mathfrak{d}_2)
650	S	SO $_4$ rocking,(ϑ_7)
600	S	SO ₂ bend, (v_3)
495	m	$Rocking(SO_4)$, (v_9)
428	Ŵ	SO_2^* bend, (ϑ_4)
250	S	Lattice mode ?

m = medium; s = strong; sh = shoulder; sp = sharp; w = weak; v = very. * denotes the oxygen atoms involved in bonding.

(CH₃ rock) cm⁻¹. The absorption bands at 1285, 1145, 980, (sh), 950, 825,650, 600, 495 and 428 can be attributed to the vibrations of the sulphate group. The number of sulphate absorption bands observed in the spectrum of trimethylantimony sulphate clearly shows that this compound does not contain free $S0_4^{2-}$ ions and that the symmetry of the sulphate group in this compound cannot be higher than C_{2v} . It is true that the observed bands do not correspond well with those reported (91) for metal sulphato complexes containing unidentate or bidentate sulphato group. However, it must be considered that the changes in the vibrational frequencies of the ligand upon coordination to a metal atom, would depend upon the degree of covalent interaction between the ligand and the metal atom. It has already been shown that the C-O stretching frequencies in trimethylantimony carbonate correspond to the C-0 stretching frequencies observed in organic carbonates, rather than to those observed in metal-carbonato complexes. The situation in trimethylantimony sulphate seems to be very similar. In order to make a comparison, the infrared spectrum of dimethyl sulphate The observed absorption frequencies with their was measured. relative intensities are listed in Table 5.4b. The infrared active vibrational modes of the sulphate group of C_{2v} symmetry are similar to those of $C10_4$ group of C_{2v} symmetry described in Table 2.1b. In dimethyl sulphate, two of the four S-O bonds in the sulphate group should have double bond character while the remaining two S-0 bonds will essentially have single bond character. The (0=S=0) and (0-S=0) vibrations in dimethyl sulphate have been reported (89) to occur at 1400, [asymmetric (0=S=0) stretch]; 1200, [symmetric (0=S=0) stretch]; 875, [asymmetric (0-S-0) stretch; and 752, symmetric (0-S-0) stretch cm⁻¹. The value of the (0-S-O) asymmetric stretching frequency seems

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Intrar	ed Absorption	Spectrum of Dimethyl Sulphate
Frequency (cm-1)	Relativ e intensity	Assignment (SO4 group)
3100	m	
1460	m	· · ·
1395	S	(O=S=O) assymetric stretch (V ₆)
1200	S	$(0=S=0)$ symmetric stretch (v_1)
1010	sh	
985	S	
825	S	(O-S-O) asymmetric stretch (V ₈)
752	m	(O-S-O) symmetric stretch (v_2)
615	sh	·
592	m	SO_4 rocking (ϑ_7)
573	m	$(0=S=0)$ bend (v_3)
52 0	sh	· · · · ·
502	S	SO_4 rocking $(\cancel{9}_9)$
428	m	(0-S-0) bend (y) .

to be erroneous because no band was observed at 875 $\rm cm^{-1}$ in the spectrum of dimethyl sulphate. Instead a band is observed at 825 cm^{-1} and it is now suggested that the value of the (O-S-O) asymmetric stretching frequency is 825 cm^{-1} . The infrared spectrum of dimethyl sulphate has not been reported previously for the potassium bromide region. From a comparison with the infrared spectrum of sulphuryl difluoride (88), the four observed bands in this region can be assigned as follows: 592 cm⁻¹, SO₄ rocking; 573 cm⁻¹, (0=S=O) bend; 502 cm⁻¹, SO₄ rocking; and 428 cm⁻¹, \therefore (0-S-0) bend.

The four sulphate absorption bands at 1285, 1145, 950, and 825 cm^{-1} observed in the spectrum of trimethylantimony sulphate correspond to the four sulphate bands at 1395, 1200, 825 and 752 $\rm cm^{-1}$, observed in the spectrum of dimethyl sulphate. Therefore, these bands can be assigned to the same vibrational modes, i.e. 1285 cm⁻¹, SO₂ asymmetric stretch; 1145 cm⁻¹, SO₂ symmetric stretch; 950 cm⁻¹, SO₂ asymmetric stretch; and 825 cm⁻¹, SO₂ symmetric stretch (* denotes the oxygen atoms involved in bonding with the antimony atom). Similarly, the four sulphate absorption bands in low frequency region can be assigned as 650 cm⁻¹, rocking; 600 cm⁻¹, SO₂ bend; 495 cm⁻¹, rocking; and 428 cm⁻¹, SO₂^{*} bend. The broad band in the 250 cm^{-1} region is probably due to a lattice mode. It is evident from the sulphate absorption bands that trimethylantimony sulphate is largely covalent. There is no absorption band in the region $600-495 \text{ cm}^{-1}$. This indicates that the trimethylantimony group is planar, the Sb-C asymmetric stretch being apparently masked by the strong sulphate band at 600 cm^{-1} . The infrared spectrum of trimethylantimony sulphate is thus completely consistent with a polymeric structure containing bridging sulphato groups, each group being bonded through two of its oxygen atoms to the planar trimethylantimony group, making the antimony atom five coordinated. As mentioned in connection with trimethylantimony carbonate, the possibility of a monomeric structure containing a bidentate sulphate group can be ruled out due to the large strain involved in such a structure.

The potassium bromide pellet containing trimethylantimony sulphate was exposed to air and no change in the spectrum was observed on short exposure. However, after about four hours exposure to air, additional bands due to ionic sulphate and a band at

565 cm⁻¹ appeared. After twenty-four hours, the intensity of the ionic sulphate bands had increased considerably while the bands due to the sulphato group became less intense. This change in the spectrum of the potassium bromide pellet of trimethylantimony sulphate, on exposure to air, must be due to the exchange reaction between trimethylantimony sulphate and potassium bromide. Long, Doak, and Freedman (52) consider that the Sb-C asymmetric stretching frequency in trimethylantimony sulphate occurs at 564 cm⁻¹. However, this absorption is due to the Sb-C asymmetric stretching vibration of the trimethylantimony dibromide (which is formed in the pellet) and not due to the Sb-C asymmetric stretching mode of trimethylantimony sulphate because this band appears only after the exchange reaction in the pellet takes place.

5.5 Trimethylantimony Chromate

Trimethylantimony chromate was obtained by the metathetical reaction of trimethylantimony dibromide and silver chromate in water. The infrared spectrum of this compound was measured on samples made as mulls, as well as on potassium bromide pellets. Identical spectra were obtained by these methods. A portion of the observed spectrum is shown in Figure 5.5. The absorption frequencies, together with their relative intensities and suggested assignments, are listed in Table 5.6. The absorption bands at 3040, 2940, 1410, 1230, 852, and 575 cm⁻¹ can be assigned to the C-H asymmetric stretch, C-H symmetric stretch, C-H asymmetric bend, C-H symmetric bend, CH₃ rock and Sb-C asymmetric stretch, respectively. The weak band at 530 is probably due to the forbidden Sb-C asymmetric stretching mode. The absorption bands due to the chromate group occur at 964, 940, 838, 700, 420, 390



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Frequency (cm ⁻¹) Relative Intensity	Assignment
3040	vw	C-H asym. str.
2940	vw	C-H sym. str.
1410	W	C-H asym. bend
1230	m	C-H sym. bend
.964	S	$Cr0_2$ asym. str., (v_6)
940	S	$Cr0_2$ sym. str., (v_1)
852	S	CH ₃ rock
838	s(sh)	$Cr0_2^*$ asym. str., (v_8)
700	vw, b	$Cr0_2^*$ sym. str., (v_2)
575	ms	Sb-C asym. str.
530	W	Sb-C sym. str. ?
420	m	$Cr0_4$ rock, (v_7)
390	m	$Cr0_2$ bend, (v_3)
355	m	$Cr0_4$ rock, (v_9)
313	m	$\operatorname{Cr0}_2^*$ bend, (v_4)

TABLE	ວ.ວ	

Infrared Absorption Spectrum of Trimethylantimony Chromate

b = broad; m = medium; s = strong; sh = shoulder; v = very; w = weak. * denotes the oxygen atoms involved in bonding. The assignments for the $Cr0_4$ group have been suggested by comparison with the SO₄ group of C_{2v} symmetry. 355 and 313 cm⁻¹. It can be noticed that the infrared spectrum of the chromate group in trimethylantimony chromate is almost identical to the chromate spectrum observed in dimethyltin chromate. The eight observed bands show clearly that the symmetry of the chromate group has been lowered from T_d to C_{2v} (or lower). The ϑ_3 mode of the free chromate ion is resolved into three strong bands at 964, 940 and 838 cm⁻¹. Though the 838 cm⁻¹ band is partly masked by the strong band at 852 cm⁻¹ (CH₃ rocking mode), nevertheless the bands at 852 and 832 show two absorption maxima.

The Raman active mode \boldsymbol{a}_1 of the free ion now shows very strong absorption at 700 cm⁻¹. The three medium bands at 420, 390 and 355 cm⁻¹ correspond to the triply degenerate mode ϑ_A of the free ion and the Raman active mode v_2 of the free ion shows medium absorption at 313 cm^{-1} . The presence of only one sharp band of medium intensity in the region 575-500 again indicates the planarity of the trimethylantimony group. The chromate absorption in this compound evidently shows that free $Cr0_{4}^{2-}$ ions The entire infrared spectrum of trimethylanare not present. timony chromate is again consistent with a polymeric structure identical to that proposed for trimethylantimony sulphate. Like trimethylantimony sulphate, the infrared spectrum of trimethylantimony chromate did not show any change upon exposing the compound to air. Both the compounds are insoluble in organic solvents but soluble in water, are perfectly stable, and are non-volatile.

5.6 Trimethylantimony Oxalate (CH₃)₃SbC₂0₄

The structure determination of sodium oxalate (136) indicates that the oxalate ion is planar and has the following interatomic distances and bond angles:



However, it is considered (137-139) that the oxalate ion has V_h symmetry and the different values for the angles C-C-OI and C-C-OII might be due to errors in the X-ray analysis (138). An oxalate ion of V_h symmetry should have twelve normal vibrations as shown in Table 5.6a (65c).

TABLE 5.6a

Vibrational Modes of $C_2 O_4^{2-}$ Ion (Point Group V_h)

Vibration mode	al <u>Activity</u>	Assignment	
ϑ_1 (Ag)	R	symmetric (O-C-O) stretch	
ϑ_2 (A _g)	R	C-C stretch	
ϑ_3 (A _g)	R	symmetric (O-C-O) bend	
v_4 (A _u)	Inactive	C-C torsion	
v_{5} (B _{1g})	R	<pre>symmetric(0-C-0) stretch</pre>	
ϑ_6 (B _{1g})	, .R	CO_2 rock or symmetric (C-C-O)	bend
v_7 (B _{1u})	I.R	Out-of-plane CO_2 wagging	
v_8 (B _{2g})	R	Out-of-plane CO_2 wagging	
v_9 (B _{2u})	I.R	Asymmetric (O-C-O) stretch	
$\vartheta_{10}(B_{2u})$	I.R	CO_2 rock or symmetric (C-C-O)	bend
$\mathcal{Y}_{11}(B_{3u})$	I.R	Symmetric (O-C-O) stretch	
$V_{12}(B_{3u})$	I.R	Asymmetric (0-C-0) bend	
	(R = Raman active;	$I_R = Infrared active)$	

Assignments of the fundamental frequencies of the oxalate ion have been reported by several workers (137-139), but there are some differences in the reported results. Murata and Kawai (137) reported that the rule of mutual exclusion holds in the Raman and infrared spectra of the oxalate ion, and therefore the oxalate ion should have Vh symmetry. Schmelz and coworkers (139) have also reported V_h symmetry for the oxalate ion. However, these workers have reported two additional Raman bands at 1600 and 1310 cm^{-1} in aqueous solutions of potassium oxalate monohydrate and have assigned them to the $v_{1,1}(B_{3u})$ and $v_9(B_{2u})$ modes which are forbidden in the Raman spectrum by the selection rules for V_h symmetry. Hence these workers concluded that the symmetry of the oxalate ion in aqueous solution is changed to V, i.e. the oxalate ion is no longer planar, and consequently, the ϑ_{11} and ϑ_9 modes become Raman active. In addition to this, there is disagreement in the assignments of the lower frequency vibrations. Murata and Kawai reported the V_6 (B_{1g}) Raman frequency at 545 cm^{-1} while Schmelz and coworkers reported that this frequency occurs at 317 cm^{-1} . Murata and Kawai, and Schmelz and coworkers, from a normal coordinate analysis, calculated the frequency for the $\dot{v}_{10}(B_{2u})$ mode to be 295 and 222 cm⁻¹ respectively, while Fujita, Nakamoto and Kobayashi (138) have assigned the 518 cm^{-1} infrared band to this mode. Schmelz and coworkers have also reported a strong infrared band at 514 cm⁻¹ in sodium oxalate but have not suggested an assignment for In view of these conflicting results the infrared spectrum it. of sodium oxalate was measured. The observed values are in agreement with the values reported by Fujita, Nakamoto and

Kobayashi. Therefore the assignments made by Fujita, Nakamoto and Kobayashi are preferred and are recorded in Table 5.6b.

Vibr	ational Frequ	encies (cm^{-1})	of the $C_2 0_4^2$ Ion
ibration mode	Raman (Aqueous solution)	Infrared (Solid)	Assignment
) 1	1485, 1450	Inactive	Symmetric (C-O) stretch
ϑ_2	898	Inactive	(C-C) stretch
\rightarrow_3	443	Inactive	Symmetric (O-C-O) bend
ϑ_4	Inactive	Inactive	
1 5	1664	Inactive	Asymmetric (C-O) stretch
∂ ₆	545	Inactive	Asymmetric (C-C-O) bend
ϑ_7	Inactive	· 	· ·
4 <mark>8</mark>	· 	Inactive	
ϑ_9	Inactive	1630	Asymmetric (C-O) stretch
ϑ_{10}	Inactive	518	Symmetric (C-C-0) bend
ϑ_{11}	Inactive	1335,1316	Symmetric (C-O) stretch
$\boldsymbol{\vartheta_{12}}$	Inactive	768	Asymmetric (O-C-O) bend

TABLE 5.6b

The oxalate group is a very common ligand and numerous metal oxalato complexes are reported in the literature (140). In metal oxalato complexes in which the oxalate group is bidentate (with unidentate carboxylic groups), and in cis diakyl oxalates, the symmetry of the oxalate group is lowered to C_{2v} as shown below:



(OI represents the oxygen atoms involved in bonding.)

The correlation between the point groups V_h and C_{2v} (138) is shown in Table 5.6c. Thus an oxalato group of C_{2v} symmetry will have ten infrared active fundamental vibrations. The infrared spectra of metal-oxalato complexes have been studied by several workers (47d). Fujita, Martell, and Nakamoto (141) have done a normal coordinate analysis for metal-oxalato complexes, using Urey-Bradley force field approximations. The oxalate group acts as chelating ligand in these complexes forming a four membered chelate ring. The results of Fuita, Martell and Nakamoto show strong coupling between various vibrational modes due to the presence of the chelate ring. However, it is expected that if both the O_{I} oxygen atoms in the oxalate group participate in bonding, the C-O_I bond length will increase and the C-O_{II} bond will be shortened, resulting in the shifts of the C-OI and C-OII stretching frequencies to lower and higher frequencies respectively. An X-ray structure determination of $K[CrC_20_4(H_20)_2]3H_20$ (142) indicates that the two C-O_I bonds coordinated to the metal atom are lengthened (1.39Å) and the two C-O_{II} bonds shortened (1.17\AA) . In metal-oxalato complexes the frequencies of the $C-0_{II}$ stretching vibrations (1700-1600 cm^{-1} region) increase, and those of the C-O_I stretching vibrations $(1450-1350 \text{ cm}^{-1} \text{ and } 1300-1200 \text{ cm}^{-1} \text{ regions})$ decrease as the

TABLE 5.6c

The	Vibrational	Modes of	The	Free	Oxalate	Ion	(V _h)	Symmetry
			1					

		and Th	e Oxalato	Group (C _{2v}	Symmetry)
	v _h		C _{2v}	· . ·	Assignmentein C _{2v} C
3	A _g (R)	3	A ₁ (R,I.R)		\checkmark (C-O), \checkmark (C-C), sym.
1	A _u (Inactiv	e) 1	A ₂ (R)		Out-of-plane
2	B _{lg} (R)	2	B ₁ (R,I.R))	♦(C-0), asym. §(C-C-0)
1	B _{lu} (I.R)	1	B ₂ (R,I.R)) •	Out-of-plane
1	B _{2g} (R)	1	A ₂ (R)	ļ	Out-of-plane
2	B _{2u} (I.R)	2	A _l (R,I.R)		♦(C-O); sym. δ(C-C-O)
2	B _{3u} (I.R)	2	B ₁ (R,I.R)	•	$\sqrt[4]{(C-0)}$, asym. $(0-C-0)$

frequency of the metal-oxygen stretching vibration increases.

In cis dimethyl oxalate, each O_I oxygen atom in the oxalate group is covalently bonded to a methyl group and the C-O_{II} and C-O_I stretching frequencies appear at 1776, 1770 and 1325, 1165 cm⁻¹ respectively. Other frequencies are also shifted, e.g. the (IO-C-O_{II}) bend (A₁) and the (IO-C-O_{II}) bend (B₁) frequencies appear at 404 and 851 cm⁻¹ respectively and the C-C stretch (A₁) appears at 862 cm⁻¹ (139).

A portion of the infrared spectrum of trimethylantimony oxalate is shown in Figure 5.6, and the frequencies, together with their intensities and probable assignments are listed in Table 5.6d. The spectra were obtained on samples made as mulls, as well as on potassium bromide pellets. Both the methods gave identical spectra. The trimethylantimony part of the spectrum can be easily assigned, i.e. 3035 cm^{-1} , C-H



Infrared Absor	ption Spectrum of Trimet	chylantimony Oxalate
Frequency (cm ⁻	¹) Relative Intensity	Assignment
3035	W	C-H asym. str.
2950	m	C-H sym. str.
2570	· w .	
1665	vs	$(C-0_{II}) \text{ str.}, (B_1)$
1620	s,sh	$(C-0_{II}) \text{ str.}, (A_1)$
1375	m	$(C-0_{I}) \text{ str., } (A_{1})$
1250)		
1227)	VS	$(C-0_{I}) \text{ str.}, (B_{I})$
1215)	·.	• •
855		CH3 rock
827	s, sh	C-C str., (A_1)
755	S	(O _I -C-O _{II}) asym. bend, (B ₁)
585	w	(C-C-O) asym. bend, (B ₁)
575	m	Sb-C asym. str.
525	S	(C-C-O) sym. bend, (A ₁)
420	S	$(0_{I}-C-0_{II})$ sym.

TABLE 5.6d

m = medium; s = strong; sh = shoulder; v = very; w = weak.OI denotes oxygen atomsinvolved in bonding. asymmetric stretch; 2950 cm⁻¹, C-H symmetric stretch; 855 cm⁻¹ CH₃ rock; and 575 cm⁻¹, Sb-C asymmetric stretch. Absorption bands due to the oxalate group occur at 1665, 1620, 1375, 1250-1215, 827, 755, 585, 525 and 420 cm⁻¹. The infrared absorption bands in sodium oxalate occur at 1640(s,b), 1420(w), 1340-1315(s,b), 777(s,sp) and 515(s,b) cm⁻¹.

By comparison with the spectrum of the free oxalate ion it can be seen that the spectrum of trimethylantimony oxalate is quite different from that of the $C_2 O_4^2$ ion. The absorption bands at 1665 and 1250-1215 cm^{-1} correspond to the C-O_{II} and $C-0_{T}$ stretching frequencies observed in metal-oxalato complexes. Moreover the Raman active modes for the free $C_2 O_4^{2-}$ ion now appear with moderate or strong intensity. The oxalate spectrum in trimethylantimony oxalate is completely in accord with the presence of an oxalato group of C_{2v} symmetry. Though nothing conclusive can be said about the presence of the Sb-C symmetric stretch due to the presence of a strong band in the 525 cm^{-1} region, it may be noted that the Sb-C asymmetric stretching frequency in this compound appears in the same frequency region and with almost the same intensity as in trimethylantimony carbonate, the dinitrate, and the dibromide, which indicates that the geometry of the trimethylantimony group in trimethylantimony oxalate is not significantly different from that found in these latter compounds. Considering the planarity of the trimethylantimony group and the C_{2v} symmetry of the oxalate group, it is suggested that the oxalate groups act as bridging ligands between planar trimethylantimony groups making the antimony atom five coordinate. Therefore a polymeric structure

similar to that proposed for trimethylantimony carbonate, sulphate and chromate can also be proposed for the oxalate. The alternative monomeric structure containing a chelate ring would involve a considerable distortion of the trimethylantimony group to a non-planar arrangement as well as lengthening of the C-C bond to a great extent; it is very unlikely that such a structure could be possible. Like trimethylantimony sulphate and chromate, the oxalate is insoluble in organic solvents and is non-volatile.

In a polymeric structure involving planar trimethylantimony groups and bridging oxalato groups, the coupling between the various vibrational modes of the oxalate group may not be so strong as compared with metal-oxalato complexes containing a chelate ring. Therefore the following assignments, based on the correlation between the vibrational modes of the free oxalate ion and the coordinated oxalato group of C_{2v} symmetry, are suggested for the absorption frequencies of the oxalate group in trimethylantimony oxalate:

(a) The bands at 1375, 827 and 420 cm⁻¹ correspond to the three Raman active modes of A_{1g} species in the oxalate ion (i.e. 1485-1450, 898 and 443 cm⁻¹). These bands are therefore assigned to the C-O_I stretch (A₁), the C-C stretch (A₁) and the symmetric (O_I-C-O_{II}) bend (A₁) respectively.

(b) The two Raman active modes of B_{1g} species in the V_h point group become infrared active modes of B_1 species in the C_{2v} point group, therefore the bands at 1665 and 585 cm⁻¹ are assigned to the C-O_{II} stretch (B₁) and the asymmetric (C-C-O) bend (B₁) respectively.

(c) The bands at 1620 and 525 cm⁻¹ correspond to the two infrared active modes (B_{2u}) at 1640-1630 and 515 cm⁻¹ of the oxalate ion. Therefore these bands are assigned to the $(C-0_{II})$ stretch (A_1) and the symmetric (C-C-0) bend (A_1) respectively.

(d) The bands at 1250-1215, and 755 cm⁻¹ correspond to the two infrared active B_{3u} modes of the free ion and are assigned to the C-O_I stretch (B₁), and the asymmetric (IO-C-O_{II}) bend (B₁) respectively.

5.7 Trimethylantimony Bis(tetrafluoroborate) (CH₃)₃Sb(BF₄)₂

The metathetical reaction between trimethylantimony dibromide and silver tetrafluoroborate in methanol resulted in instantaneous precipitation of silver bromide. Upon removal of the methanol, a white solid was obtained. The recovered methanol contained boron trifluoride which was identified by its infrared spectrum and qualitative tests. The infrared spectrum of the solid indicated the presence of the tetrafluoroborate group, but the analytical results do not correspond to $(CH_3)_3Sb(BF_4)_2$. An X-ray powder photograph of the solid showed the presence of trimethylantimony difluoride. On the basis of spectroscopic, analytical, and X-ray powder photographic results, it is concluded that the solid is an approximately 1:1 mixture of trimethylantimony bis(tetrafluoroborate) and trimethylantimony difluoride. The mixture sublimed readily at 50° under vacuum and the infrared spectrum, analytical results and X-ray powder photographs of the sublimed product were identical to that of the unsublimed mixture, indicating that no further decomposition had occurred during sublimation.

These results can be explained in the following manner:

$$(CH_{3})_{3}SbBr_{2} + 2AgBF_{4} \xrightarrow{CH_{3}OH} (CH_{3})_{3}Sb^{2+}(solvated) + 2BF_{4}^{-} + 2AgBr \quad . . (1)$$

$$(CH_{3})_{3}Sb^{2+}(solvated) + 2BF_{4}^{-} \xrightarrow{-solvent} (CH_{3})_{3}SbF_{2} + 2BF_{3} \quad . . . (2)$$

In the infrared absorption spectrum of the mixture, no bands were observed in the 4000-1500 cm^{-1} region except weak bands at 3050-2900 cm⁻¹ due to C-H stretching vibrations. The absorption bands (in $1500-250 \text{ cm}^{-1}$ region), together with their relative intensities and suggested assignments, are listed in Table 5.7 and part of the spectrum is shown in Figure 5.7. The absorption bands at 1410, 1235, 885 and 587 are associated with the trimethylantimony group and can be assigned as 1410 cm^{-1} , C-H asymmetric bend; 1235 cm^{-1} , C-H symmetric bend; 880 cm^{-1} , CH₃ rock; and 587 cm⁻¹, Sb-C asymmetric stretch. The bands at 1287, 1150, 1100, 1053, 1040, 1015, 760, 572, 545, 515 and 400 cm^{-1} can be attributed to the tetrafluoroborate group. The absorption bands due to trimethylantimony difluoride would be expected to occur at 1415, 1235, 855, 586 and 475 cm^{-1} . Apparently the bands at 855 and 475 cm^{-1} are masked by strong bands at 880 and 400 cm⁻¹. The broad shoulder in the 475 cm⁻¹ region indicates the presence of a band in this region. The strong bands at 1100 and 1053 cm^{-1} correspond to the triply degenerate mode ϑ_3 of BF₄ ion and the weak band at 760 cm⁻¹. corresponds to the Raman active mode ϑ_1 of the free ion. In the low frequency region, the bands at 572 and 515 cm^{-1} are



Frequency (cm⁻¹)

Infrared Absorption Spectrum of The Mixture of Trimethylantimony

Bis(tetrafluoroborate) and Trimethylantimony Difluoride

Frequency	(cm ⁻¹)	Relative Intensi	ty Assignment
1410		w	C-H asym. bend
1287		m	
1235		m	C-H sym. bend
1150		sh	
1100		S	B-F str., $(\sqrt[4]{4})$
1053		S	BF_3 sym. str., (v_1)
1040		sh	
1015		sh	
880		S	CH3 rock
7 60		w	$B-F^*$ str., (v_2)
587		ms	Sb-C asym. str.
572		S	BF_3 asym.bend, (v_5)
545		w	
515		ms	BF_3 sym.bend, (v_3)
475		sh	S-F asym. str., $\left[(CH_3)_3 SbF_2 \right]$
400		S	BF_4 rocking, (v_6)
m = mediur	n; s =	strong; sh = sh	oulder; v = very; w = weak.

* F represents the fluorine atom involved in bonding. Math.

probably two components of the triply degenerate mode v_4 . The broad band at 400 cm⁻¹ may be correlated with the Raman active mode v_2 of the free ion.

On exposing the mixture to air, the absorption bands attributed to the tetrafluoroborate group showed marked changes. The bands at 1100 and 1053 were replaced by a very strong broad band at 1055 cm⁻¹ which is characteristic of the free BF_4^- ion. The bands at 760 and 573 cm⁻¹ disappeared and the intensity of 400 cm⁻¹ band was diminished. New bands appeared in the 500-450 region.

The spectroscopic results thus suggest that trimethylantimony bis(tetrafluoroborate) is present in the mixture and that the tetrafluoroborate groups are coordinated to the trimethylantimony group through one of the fluorine atoms. The volatility of the mixture also indicates a non-ionic constitution for trimethylantimony bis(tetrafluoroborate). Considering the resulting C_{3v} symmetry of the tetrafluoroborate group, the following assignments for the absorption bands of the tetrafluoroborate groups are suggested: 1100 cm^{-1} , B-F stretch $\vartheta_4(E)$; 1053 cm⁻¹, BF₃ symmetric stretch $\vartheta_1(A_1)$; 760 cm^{-1} , B-F* stretch $\psi_2(A_1)$; 572 cm⁻¹, BF₃ asymmetric bend $v_5(E)$; 515 cm⁻¹, BF₃ symmetric bend $v_3(A_1)$; and 400 cm⁻¹, rocking mode \dot{v}_6 (E). (F* represents the fluorine atom involved in coordination.) These assignments have been suggested by comparison with the vibrational assignments reported (143,144) for the perchloryl fluoride, Cl03F.

5.8 <u>Trimethylantimony Hexafluorosilicate</u> $(CH_3)_3$ SbSiF₆

The hexafluorosilicate ion $(SiF_6)^2$ - is octahedral and

belongs to point group O_h . The vibrational modes of an octahedral group have already been discussed. Only three fundamental vibrational frequencies ϑ_1 , ϑ_3 , and ϑ_4 of the SiF $_6^{2-}$ ion are known. Raman active frequency ϑ_1 occurs at 656 cm⁻¹ (145) and the infrared active frequencies ϑ_3 and ϑ_4 occur at 726 and 480 cm⁻¹ respectively (128). Crystalline potassium and ammonium hexafluorosilicates show no splitting of the degenerate modes but, in barium hexafluorosilicate, the ϑ_4 mode shows a splitting of about 20 cm⁻¹ (125). No example of coordination by the SiF $_6^{2-}$ ion has been reported so far.

The metathetical reaction between trimethylantimony dibromide and silver hexafluorosilicate in methanol resulted in instantaneous precipitation of silver bromide. Upon removal of the solvent under vacuum, a white crystalline, hygroscopic solid was obtained. X-ray powder photographic data infrared spectrum and analytical results of the solid showed it to be a mixture of trimethylantimony hexafluorosilicate and trimethylantimony difluoride containing about 52 percent hexafluorosilicate and 48 percent difluoride. The recovered methanol was highly acidic and contained silicon and fluorine. The solid sublimed readily under vacuum at 50° and the infrared spectrum, X-ray powder photograph and analytical results of the sublimate were identical to those of unsublimed mixture indicating that no further decomposition had occurred during sublimation. The partial decomposition of trimethylantimony hexafluorosilicate can be explained in a manner similar to that suggested for the partial decomposition of the trimethylantimony bis(tetrafluoroborate), i.e.

$$(CH_3)_3 SbBr_2 + Ag_2 SiF_6 \xrightarrow{CH_3 \Theta H} (CH_3)_3 Sb^{2+} (solvated) + SiF_6^{2-} + 2AgBr . . . (1)$$
$$(CH_3)_3 Sb^{2+} (solvated) + SiF_6^{2-} \xrightarrow{- solvent} (CH_3)_3 SbF_2 + SiF_4 . . . (2)$$

The infrared spectrum of the mixture is recorded, together with the relative intensities of the absorption bands, in Table 5.8. Part of the spectrum is shown in Figure 5.8. Except for the C-H stretching vibrations in the region 3050-2900 cm^{-1} , no bands were observed in the 4000-1500 cm^{-1} region. The absorption bands at 1410, 1240, 880-855, and 586 cm^{-1} can be assigned to the C-H asymmetric bend, the C-H symmetric bend, the CH₃ rock, and the Sb-C asymmetric stretch respectively. The 475 $\rm cm^{-1}$ band can be attributed to the Sb-F asymmetric stretching vibration of the trimethylantimony difluoride. The remaining medium or strong bands are therefore associated with the hexafluorosilicate group. This is further supported by the change in the spectrum when the mixture was exposed to air. A sample of the mixture exposed to air showed characteristic infrared absorption bands of the SiF_6^{2-} ion, i.e. a strong broad band at 735 cm⁻¹ and a strong band in the 480 cm⁻¹ region. Thus spectroscopic results indicate the presence of trimethylantimony hexafluorosilicate in the mixture. Since the hexafluorosilicate spectrum in the anhydrous mixture is significantly different from that of the SiF_6^2 ion, it can be concluded that trimethylantimony hexafluorosilicate is non-ionic, but on exposure to air, it is hydrolysed to produce free SiF_6^{2-} ion. The volatility of



Infrared Absorption Spectrum of The Mixture of Trimethylantimony

	······································	
Frequency (cm ⁻¹)	Relative Intensity	Assignment
3050-2900	w	C-H str.
1495	m ·	
1410	w	C-H asym. bend
1288	ms	
1240	w	C-H sym. bend
1057	w	
997	ms	r
880	sh)	OW 1
855) s)	CH ₃ rock
785	s	
720	m	
586	m	Sb-C asym. str.
555	s	
533	w	
475	S	Sb-F asym. str.
445	m	
350	m	

Hexafluorosilicate and Trimethylantimony Difluoride

m = medium; s = strong; sh = shoulder; v = very; w = weak. No assignments are suggested for the absorption bands due to the SiF_6 group.

the mixture also indicates a non-ionic constitution. However, due to the presence of a large number of bands in the spectrum, no conclusions can be reached about the possible stereochemistry of trimethylantimony hexafluorosilicate.

5.9 Trimethylantimony Bis(hexafluoroantimonate) (CH₃)₃Sb(SbF₆)₂

This compound was obtained, as an extremely hygroscopic white solid, by the metathetical reaction between trimethylantimony dibromide and silver hexafluoroantimonate in liquid sulphur dioxide. X-ray powder photographs of the solid did not show any lines due to either trimethylantimony difluoride or the dibromide; however, the fluorine percentage in the sample was found to be five percent lower than the calculated value. The substance reacted rapidly with salt windows, but reproducible spectra could be obtained by using silver chloride and polythene sheets. A portion of the infrared spectrum, on a nujol mull sample, is shown in Figure 5.9. Other bands were observed at 1180(m) and 880(m) cm⁻¹. The 880 cm⁻¹ band can be assigned to the CH₂ rocking mode. The other band which can be attributed to the trimethylantimony group occurs at 585 cm^{-1} and can be assigned to the Sb-C asymmetric stretch. The rest of the bands must therefore be associated with the hexafluoroantimonate group. As can be seen from Figure 5.9, the spectrum in this region shows additional bands of medium intensity at 550 and 445 $\rm cm^{-1}$, and a shoulder in the 370 cm⁻¹ region. Moreover, the v_3 mode which appears as a broad, symmetrical band at 660 $\rm cm^{-1}$ in the spectrum of the SbF_6 ion, is now split, and shows peaks at 665 and 640 cm^{-1} . As described earlier, almost similar spectroscopic



features are observed for dimethyltin bis(hexafluoroantimonate). However, in dimethyltin bis(hexafluoroantimonate), the $\sqrt[4]{3}$ mode shows three peaks. Thus it appears that, in trimethylantimony bis(hexafluoroantimonate), the octahedral symmetry of the SbF₆ group is lowered to probably C_{4v} or D_{4h} . The almost similar spectroscopic effects observed for trimethyltin hexafluoroantimonate, dimethyltin bis(hexafluoroantimonate), and trimethylantimony bis(hexafluoroantimonate) strongly suggest that these spectroscopic effects are due to coordination. This is further supported by the change in the infrared spectrum when the anhydrous compound was exposed to air. The bands at 1180, 550, and 445 disappeared, and the $\sqrt[3]{3}$ mode showed a single broad symmetrical peak at 660 cm⁻¹.

5.10 <u>Trimethylantimony(V)</u> Derivative of $B_{12}Cl_{12}^{2}$

The trimethylantimony(V) derivative of $B_{12}Cl_{12}^{2}$ was obtained as a crimson red, hygroscopic solid. The colour of the solid changed to white on exposure of the anhydrous solid to water or methanol vapour. The aqueous or methanol solution of $Me_3SbB_{12}Cl_{12}$ was also colourless. However, the recovered solid from these solutions was always coloured. The infrared spectrum of the anhydrous solid is recorded in Table 5.10 and part of the spectrum is shown in Figure 5.10. The absorption bands due to the trimethylantimony group appear at 3000-2900, (C-H stretch); 1405, (C-H asymmetric bend); 1245, (C-H symmetric bend); 865, (CH₃ rock); and 570, (Sb-C asymmetric stretch) cm⁻¹. The absorption bands at 1030, 1000, 827, 532, 450, and 320 cm⁻¹ can be attributed to the $B_{12}Cl_{12}$ group. By comparing the spec-



TABLE 5.10

Infrared Absorption Spectrum of $Me_3SbB_{12}Cl_{12}$

Frequency (cm ⁻¹)	Relative intensity	Assignment
3000 - 2900	. vw	C-H stretch
1405	vw	C-H asymmetric bend
1307	vw	
1245	w	C-H asymmetric bend
1030	vs	
1000	m	
865	S	CH ₃ rock
827	S	
570	W	Sb-C asymmetric stretch
532	VS	
45 0	m, b	
320	m, b	

b = broad; m = medium; s = strong; v = very; w = weak

No assignments have been suggested for the absorption bands due to the $B_{12}Cl_{12}$ group

trum of Me₃SbB₁₂Cl₁₂ with that of $Ag_2B_{12}Cl_{12}$ it becomes evident that in Me₃SbB₁₂Cl₁₂ the symmetry of $B_{12}Cl_{12}$ group is reduced. There is no appreciable change in the trimethylantimony part of the spectrum as compared with trimethylantimony dibromide, though it is difficult to determine whether the Sb-C symmetric stretch is also present in the spectrum of Me₃SbB₁₂Cl₁₂.

The bands at 827, 450 and 320 cm⁻¹ disappeared on exposing $Me_{3}bB_{12}Cl_{12}$ to air for 24 hours. Thus it is reasonable to conclude that the symmetry of the $B_{12}Cl_{12}$ group is appreciably distorted in $Me_{3}SbB_{12}Cl_{12}$ and that this effect is most likely due to the coordination between $Me_{3}Sb$ and $B_{12}Cl_{12}$ groups.

CHAPTER 6 CONCLUSION

The results of this investigation demonstrate the existence of an intense interaction between the organometal group, i.e. $(C_6H_5)_3Sn$, $(CH_3)_3Sn$, $(CH_3)_2Sn$, or $(CH_3)_3Sb$ and the anionic group in all the organotin(IV) or organoantimony(V) acid derivatives studied. The decomposition of the organometal derivatives of strong Lewis acids such as BF_3 and SiF_4 , into the organometal fluoride and the corresponding Lewis acid, indicates this strong interaction. The infrared spectra of all the compounds uniformly show marked changes in the spectrum of the anionic group, i.e. significantly large splittings of the degenerate modes and the appearance of the Raman active modes with moderate to strong intensities. From a comparison with the infrared spectroscopic data of a large number of corresponding ionic salts, it becomes obvious that these spectroscopic observations cannot be attributed to crystal field effects. In view of the possibility of unknown factors in interpreting the spectra of solids, the results of a single spectrum may be open to question. However, the probability of almost identical effects occurring in a wide variety of compounds is exceedingly slight. The observed spectroscopic effects can therefore be attributed to coordination or partial covalent bond formation between the organometal and the anionic groups. Alternatively, a very strong polarization by the organometal cation may produce these effects. However, there is no obvious reason why these simple cations of low charge density should be more polarizing than any other known cation. Consequently, it
is concluded that these spectroscopic effects are due to coordination or partial covalent bonding between the organometal and the anionic groups. Unfortunately, there is no obvious experimental method which will distinguish unambiguously between terms such as 'strong polarization', 'partial covalent bonding' and coordination. However, none of these compounds appear to contain free organometal cations, i.e. $(C_{6}H_{5})_{3}Sn^{+}$, $(CH_{3})_{3}Sn^{+}$, $(CH_{3})_{2}Sn^{2+}$ or $(CH_{3})_{3}Sb^{2+}$, although it must be stressed that the bonding between the metal atom and the anionic group cannot be described in the same covalent terms as that between the metal and the organic groups. The bonding between the metal atom and the anionic group is presumably less covalent than the metal-carbon bond.

The instability of the organotin cations in the solid state probably arises partly from the tendency of the tin atom to increase its coordination number. The findings of this investigation, as well as other recent studies on organotin compounds, demonstrate the tendency of the tin atom to increase its coordination readily to five or six. Tetrakis(8-quinolinato)tin(IV) has been reported (146) to be an eight coordinate tin(IV) compound. In trimethyltin(IV) derivatives five coordination of the tin atom is attained through a polymeric structure involving bridging anionic groups and a trigonal bipyramidal configuration around the tin atom. Dimethyltin(IV) derivatives are apparently either tetrahedral or six coordinated, and polymeric structures involving bridging anionic groups are also indicated for these derivativés. The insolubility in non-polar solvents and nonvolatility of such derivatives are not suitable criteria for considering these compounds as ionic and these physical properties

can be attributed to polymeric structures.

Like trimethyltin(IV) derivatives, a trigonal bipyramidal configuration is also indicated for trimethylantimony(V) deriva-These results are consistent with the general stereotives. chemistry of group Vb elements. From n.m.r. studies of a variety of five coordinate compounds including a number of mono-, di- , and trisubstituted pentahalides of group Vb elements, Muetterties and coworkers (147,148) have shown that a trigonal bipyramidal configuration with the most electronegative groups occupying the apical positions is the most favoured configuration for such Compounds of the type R_3SnX_2 such as trimethylantimony compounds. dihalides and dinitrate are monomeric. In compounds of the type R3SbY, such as trimethylantimony carbonate, sulphate, chromate and oxalate, the trigonal bipyramidal configuration can be attained through a polymeric structure involving bridging anionic groups in a manner similar to that in R₃SnX derivatives. The instability of the R_3Sb^{2+} cation again reflects the preference of the antimony atom to attain a higher coordination.

However, the electronic description of bonding in these compounds is not known with any certainty. The most widely used explanation of the penta- and hexacoordinated molecules is given by assuming the hybridization of the available s and p orbitals with one or two d orbitals respectively (149), i.e. the trigonal bipyramidal configuration can be explained by sp^3d hybridization and an octahedral configuration by sp^3d^2 hybridization. Both tin and antimony have empty d orbitals available in their valence shells and hence are capable of accepting more than four electrons. For trigonal bipyramidal compounds, it has been suggested (22,147) that the three hybrid orbitals of the central atom in the equatorial plane may be constructed from a combination of the s and p orbitals (5s and 5p in the case of tin or antimony) and those on the apical axis from a $(p_z + d_z^2)$ combination $(5p_z \text{ and } 5d_z^2 \text{ in the case of tin and antimony})$. Janssen, Luijten, and van der Kerk (48) consider that, in five coordinate tin compounds, the principal interaction involves the donation of electrons from filled d orbitals of the metal atom into suitable orbitals of the ligand. On the other hand, McGrady and Tobias (50) consider that in dimethyltin chelate complexes (R₂SnL₂) the tin 5s and 5p_z orbitals are involved almost entirely in the two tin-carbon bonds and the bonding orbitals in the equatorial plane are mainly derived from $5p_x$ and $5p_y$ orbitals according to the molecular orbital treatment of Rundle (150).

CHAPTER 7

EXPERIMENTAL

General Preparation of Compounds

The compounds studied in this investigation were synthesized by the metathetical reaction between an organometal halide and the appropriate silver salt in a suitable solvent.

Organotin halides were obtained from M & T Chemicals. Trimethylantimony dibromide was synthesized by the reaction of a Grignayd reagent on antimony trichloride and subsequent reaction with bromine. Anhydrous silver salts were obtained from the following sources:

Silver	Perchlorate		- Frederic Smith Chemical
Silver	Nitrate)	
Silver	Sulphate))	- B.D.H., A.R. grade
Silver	Carbonate	$\sum_{i=1}^{n}$	- Mallinckrodt, A.R.grade
Silver	Chromate	•)	- Fisher Scientific Co.
Silver	Oxalate		– K & K Laboratories
Silver	Permanganate)	
Silver	Hexafluorosilicate	•),	- Alfa Inorganics, Inc.
Silver	Tetrafluoroborate	•)	
Silver	Hexafluorophosphate	Ś	- Ozark Mahoning Co.
Silver	Hexafluoroarsenate	ý	viern menoning out
Silver	Hexafluoroantimonato		
DIIVEI	nexal fuor oan timona te	,	
Silver	Salt of $B_{12}Cl_{12}^{2-}$		- Gift from Dr. E. L. Muetterties, Central Research Laboratory,
			E.I. du Pont de Nemours

Organic solvents were of either anhydrous A.R. Mallinckrodt or A.R. Spectro grade. Methanol was further dried by the method described by Vogel (151) and acetone was dried over drierite.

Co., Wilmington, Delaware.

The sulphur dioxide and ammonia used were Matheson anhydrous grade. Sulphur dioxide was further dried over sulphuric acid and then fractionated, and ammonia was dried over sodium metal.

Except where otherwise stated, compounds were prepared and handled in an atmosphere of dry nitrogen in the dry box which was constantly flushed with nitrogen, dried first over sulphuric acid, then sodium hydroxide and finally silica gel. Fresh phosphorus pentoxide was maintained in the dry box at all times. The reactants were weighed in air-tight weighing bottles which were transferred to the dry box. Sintered glass funnels with Quickfit joints were used for filtration. Mixing of the reactants and filtration of insoluble silver halide were performed in the dry box and solvents were removed under vacuum; then the evacuated flasks were transferred again to the dry box.

Conventional vacuum techniques were used for the manipulation of volatile substances. An apparatus described by Parry, Schultz and Girardot (152) was used for carrying out reactions in liquid sulphur dioxide. The apparatus was first evacuated, then transferred to the dry box where organometal halide and silver salt were added. The closed apparatus was then evacuated again and anhydrous sulphur dioxide was condensed on to the reactants. The mixture was shaken and then the sulphur dioxide was frozen. The apparatus was inverted and precipitated silver halide was filtered off and retained on the sintered glass filter. Finally, the sulphur dioxide was removed under vacuum and the evacuated apparatus was transferred to the dry box.

Analysis

C, H, N, S, and F analyses were performed either in the

microanalytical laboratory of this department or at Microanalytisches Laboratorium im Max-Planck-Institut, Mülheim (Ruhr), Germany, or at the Schwarzkopf Microanalytical Laboratory, New York. B and Cl analyses were obtained by courtesy of Dr. E.L. Muetterties at the Central Research Laboratory of E.I. du Pont de Nemours Co., Wilmington, Delaware. Other analyses were performed according to the methods described by Vogel (153) or Scott (154). Most of the analyses were done in duplicate.

Measurement of Spectra

Infrared absorption spectra in the range 4000-700 cm⁻¹ were recorded on a Perkin Elmer model 21 spectrophotometer. Spectra in the region 2000-250 cm⁻¹ were measured on a Perkin Elmer model 421 grating spectrophotometer. Perkin Elmer model 137 infracords fitted with sodium chloride or potassium bromide optics were also used for a few measurements. Except where otherwise stated, samples were prepared in the dry box as mulls in nujol, hexachlorobutadiene or halocarbon oil. Samples were placed between plates of cesium iodide, potassium bromide or 0.1 cm. thick sheets of silver chloride or polythene. Salt plates were wrapped with polyvinyl tape. Specially designed cells with teflon rings were used to mount silver chloride and polythene sheets. Several spectra of each substance were recorded at varying concentrations. Spectra were also recorded after exposing the substance to air. Blanks were often run on cell windows and mulling agents. In a few cases, spectra of finely powdered samples could be obtained without any mulling agents. Spectra of some compounds were also measured in potassium bromide pellets using freshly dried potassium bromide. Infra-

red spectra of volatile substances were measured using potassium bromide or silver chloride gas cells.

Electronic spectra in the ultraviolet and visible region were recorded on a Cary Model 14 spectrophotometer.

The proton n.m.r. measurements were made with a Varian A60 spectrometer at 60 Mc/sec.

X-ray Powder Photographs

X-ray powder photographs were obtained by using copper $K \triangleleft$ radiation with a nickel filter on a General Electric X-ray unit. Quartz Capillary tubes of either 0.5 mm. or 0.3 mm. diameter were filled with samples in the dry box and the open ends of the capillary tubes were sealed. Photographs were taken in a 14.32 cm. diameter camera.

Triphenyltin Nitrate

(a) Triphenyltin chloride (2.26 g.) and silver nitrate (1.00 g.) were mixed in 50 ml. of acetone and the mixture was shaken for three days. The precipitated silver chloride was filtered off and acetone removed under vacuum. The same reaction was also performed, more rapidly and without shaking, in methanol owing to the greater solubility of silver nitrate in this solvent. The product was a white solid. <u>Analysis</u>, calcd. for $C_{18}H_{15}SnNO_3$: C, 52.42; H, 3.67; N, 3.39. Found: C, 51.90; H, 3.70; N, 3.32.

(b) Triphenyltin nitrate was also prepared by mixing solutions of triphenyltin chloride (3.855 g.) in 50 ml. acetone and silver nitrate (1.698 g.) in 5 ml. of water. Silver chloride was filtered off and the solvent removed under vacuum. The product and the removed solvent were both yellow in color suggesting some

decomposition. <u>Analysis</u>, calcd. for $C_{18}H_{15}SnNO_3$: C, 52.42; H, 3.67; N, 3.39. Found: C, 53.53; H, 4.40; N, 3.23.

(c) Stability of Triphenyltin Nitrate: Anhydrous triphenyltin nitrate was found to be stable at room temperature in the dry box for more than two months. After this time, there was no change in appearance, nor in the infrared spectrum. However, exposure of the anhydrous compound to air caused marked changes in the infrared spectrum. Some changes also occurred when a sample of the anhydrous compound was heated to 150° in vacuum for one and one half hours. A sample of the nitrate prepared from wet acetone was heated in o-dichlorobenzene as described by Shapiro and Becker (62) and the infrared spectra of the residue and of the yellow distillate were recorded.

Reaction with Ammonia: Anhydrous ammonia was condensed on (d) to a sample of the anhydrous triphenyltin nitrate and on to a solution of triphenyltin nitrate in methanol. Both mixtures were kept at -70° for 24 hours, after which the excess ammonia and solvent were removed under vacuum, to leave white solids. Analytical results of the solids were not reproducible but were always of the same order, a typical result being as follows. Analysis, calcd. for C₁₈H₁₅SnNO₃(NH₃)₂: C, 48.44; H, 4.75; N, 9.42. Calcd. for $C_{18}H_{15}SnNO_3(NH_3)$: C, 50.35; H, 4.23; N, C, 50.31; H, 4.76; N, 5.88. X-ray powder photo-6.53. Found: graphs and the infrared spectra of the products showed them to be mixtures containing ammonium nitrate and bis(triphenyltin)oxide.

Triphenyltin Perchlorate

(a) Triphenyltin chloride (2.030 g.) and silver perchlorate (1.092 g.) were mixed in a flask with 50 ml. of ether and the mixture was shaken for three days. Precipitated silver chloride was filtered off and the filtrate was removed under vacuum, at room temperature to leave a white solid. <u>Analysis</u>, calcd. for $C_{18}H_{15}SnClO_4$: C, 48.20; H, 3.34. Found: C, 48.9; H, 3.38. Triphenyltin perchlorate is very soluble in methanol and ether. It is very hygroscopic and hydrolyses immediately on exposure to air as shown by marked changes in the infrared spectrum.

(b) Reaction with Ammonia: Triphenyltin perchlorate as an anhydrous solid or in methanol solution, was allowed to react with excess ammonia, under the same conditions as described earlier for triphenyltin nitrate. The products were white solids which likewise gave non-reproducible analytical results, the following being typical: <u>Analysis</u>, calcd. for $C_{18}H_{15}SnCl0_4(NH_3)_2$: C, 44.75; H, 4.35; N, 5.79. Calcd. for $C_{18}H_{15}SnCl0_4(NH_3)$: C, 46.35; H, 3.86; N, 3.00. Found: C, 44.63; H, 4.63; N, 3.99. X-ray powder photographs and the infrared spectra of the products showed them to be mixtures containing ammonium perchlorate and bis(triphenyltin)oxide.

Trimethyltin Permanganate

Attempts to prepare this compound were not successful. The metathetical reaction between trimethyltin bromide or chloride and silver permanganate, using methanol, acetone, or water as solvent, resulted in the precipitation of the silver halide but the reaction was accompanied by the decomposition of the permanganate. No reaction occurred when t-butyl alcohol, chloroform, acetonitrile, or ether was used as solvent. Attempts to react solid trimethyltin halide and potassium permanganate or silver permanganate at 50° in a closed system were also unsuccessful.

Bis(trimethyltin) Sulphate

Trimethyltin bromide (1.220 g.) and silver sulphate (0.781 g.) were mixed in 50 ml. of methanol, and the mixture was shaken for three days. The precipitated silver bromide was filtered off (0.949 g., calcd. 0.941 g.) and, on removal of the methanol under vacuum at room temperature, white crystals of bis(trimethyltin) sulphate-methanol adduct were obtained. Analysis, calcd. for (C₃H₉Sn)₂SO₄(CH₃OH)₂: C, 19.68; H, 4.13; SO₄, 19.70. Found: C, 19.00; H, 4.59; SO₄, 20.48. On heating the methanol adduct at 100° under vacuum for about four hours, the methanol was completely removed and anhydrous bis(trimethyltin) sulphate was obtained as a white solid. Analysis, calcd. for (C₃H₉Sn)₂SO₄: C, 17.01; H, 4.25. Found: C, 17.55; H, 4.46. Both bis(trimethyltin) sulphate and its methanol adduct are soluble in water and methanol, but insoluble in solvents such as acetone, ether, and acetonitrile. Both the compounds are hydrolysed on exposure to air as shown by changes in their infrared spectra.

Bis(trimethyltin) Chromate

Trimethyltin bromide (2.793 g.) and silver chromate (1.901 g.) were allowed to react in 50 ml. of methanol. Precipitated silver bromide (2.142 g., calcd. 2.152 g.) was immediately filtered off. The methanol was quickly removed under vacuum at room temperature and yellow crystals of bis(trimethyltin) chromate were obtained. <u>Analysis</u>, calcd. for $(C_3H_9Sn)_2Cr0_4$: C, 16.24; H, 4.06; Cr0₄, 26.17. Found: C, 16.08; H, 4.00; Cr0₄, 25.46. Bis(trimethyltin) chromate is soluble in water and methanol but decomposes slowly in solution as shown by the gradual darkening of colour. It is only slightly soluble in acetone and insoluble in ether or chloroform. Unlike bis(trimethyltin) sulphate, it is not hydrolysed on exposure to air. Samples exposed to air for three days showed no changes spectroscopically.

Dimethyltin Difluoride

Dimethyltin difluoride was prepared by the reaction of potassium fluoride (2.8206 g.) and dimethyltin dichloride (5.332 g.) in 50 ml. of water. The precipitated solid was filtered and washed with water and ethanol. The product was recrystallized from a 40 percent aqueous solution of hydrofluoric acid in a platinum dish. <u>Analysis</u>, calcd. for $C_2H_6SnF_2$: C, 12.90; H, 3.23. Found: C, 12.98; H, 3.60.

Dimethyltin Carbonate

Dimethyltin dichloride (1.0850 g.) and silver carbonate (1.3624 g.) were mixed in 50 ml. of methanol and the mixture was shaken for three days. After removal of the solvent under vacuum at room temperature, a mixture of silver chloride and dimethyltin carbonate was obtained which was characterized by its infrared spectrum and X-ray powder photograph. No lines due to either dimethyltin dichloride or silver carbonate appeared in the powder photograph. However, dimethyltin carbonate could not be isolated free from silver chloride due to its insolubility in a suitable solvent. It is insoluble in methanol, acetone, acetonitrile or dimethyl sulphoxide but dissolves in hot water with decomposition to give dimethyltin oxide as the final product. The infrared spectrum of a sample of the mixture exposed to air did not show any change indicating that dimethyltin carbonate is not hydrolysed on exposure to air.

Dimethyltin Chromate

(a) Dimethyltin dichloride (1.800 g.) and silver chromate (2.718 g.) were allowed to react in 50 ml. acetone, as well as in 50 ml. of acetonitrile in the same manner as described for dimethyltin carbonate. After removal of the solvent under vacuum at room temperature, in each case a yellow mixture of silver chloride and dimethyltin chromate was obtained, as shown by infrared spectra and X-ray powder photographs of the solids. X-ray powder photographs did not show any lines due to either dimethyltin dichloride or silver chromate. On addition of the mixture to water acidified with acetic acid, there was no precipitation, only the previously formed silver chloride settled and was recovered in quantitative amounts. From the filtrate, the quantitative weight of barium chromate was precipitated, confirming that there had been no reduction of chromium. The mixture of dimethyltin chromate and silver chloride did not show any spectroscopic changes on exposure to air, indicating that dimethyltin chromate is not hydrolysed in air. On treating the mixture with hot water, dimethyltin chromate dissolved to give a yellow solution, but pure dimethyltin chromate could not be recovered from the aqueous solution due to partial decomposition

of the chromate.

(b) The above metathetical reaction was also done in methanol. Silver chloride was precipitated instantaneously, but the dimethyltin chromate formed reacted with the solvent as shown by a rapid darkening in colour.

Dimethyltin Sulphate

(a) Dimethyltin dichloride (1.2300 g.) and silver sulphate (1.7454 g.) were allowed to react in 50 ml. of water, and precipitated silver chloride was filtered off (1.6036 g., calcd. 1.6040 g.). The filtrate was evaporated on a water bath to give a white solid which was dried under vacuum. <u>Analysis</u>, calcd. for $C_2H_6SnSO_4$: C, 9.80; H, 2.47. Found: C, 9.67; H, 2.46. Dimethyltin sulphate is soluble in water but insoluble in organic solvents such as methanol, acetone, acetonitrile, and dimethyl sulphoxide. It is not hydrolysed in air, a sample exposed to air for 24 hours showed no change in the infrared spectrum.

(b) Dimethyltin dichloride (1.0346 g.) and silver sulphate (1.4690 g.) were mixed in 50 ml. of methanol and the mixture was shaken for three days. An insoluble mixture was precipitated which was recovered by evaporating the solvent under vacuum at room temperature. The infrared spectrum and an X-ray powder photograph of the dried solid showed it to be a mixture of silver chloride and a methanol adduct of dimethyltin sulphate. However, the dimethyltin sulphate-methanol adduct could not be isolated free from the silver chloride due to its insolubility in a suitable solvent. The infrared spectrum of the mixture showed marked changes when the solid was exposed to air indicating hydrolysis of the dimethyltin sulphate-methanol adduct. The methanol adduct dissolved in water and upon evaporating the aqueous solution, pure dimethyltin sulphate was recovered. When a portion of the methanol adduct and silver chloride mixture was heated to 100° under vacuum for about four hours, the methanol was completely removed leaving a mixture of dimethyltin sulphate and silver chloride, as shown by the infrared spectrum of the heated mixture.

(c) Dimethyltin dichloride and silver sulphate were allowed to react in acetone, as well as in acetonitrile, in the manner described above. Insoluble silver chloride and dimethyltin sulphate were formed in each case, as shown by the infrared spectra and X-ray powder photographs of the anhydrous mixtures obtained after removing the solvent under vacuum.

(d) Reaction with Pyridine: Solid dimethyltin sulphate was refluxed with excess pyridine for 24 hours. Insoluble white solid was filtered off, washed with chloroform and dried under vacuum. The product was found to be dimethyltin sulphatepyridine monoadduct. The same product was also precipitated when excess pyridine was added to an aqueous solution of dimethyltin sulphate. The precipitate was dissolved in water and dimethyltin sulphate-pyridine monoadduct was crystallized, washed with chloroform and dried under vacuum. Analysis, calcd. for C₂H₆SnSO₄(C₅H₅N): C, 27.64; H, 3.91; N, 4.61. Found: C, 26.14; H, 3.74; N, 4.40. Dimethyltin sulphate-pyridine adduct is insoluble in pyridine and organic solvents such as

methanol, acetone, acetonitrile, and chloroform, but soluble in water.

(e) Reaction with Dimethyl Sulphoxide (DMSO): Solid dimethyltin sulphate was shaken with excess DMSO for 24 hours. The insoluble solid was filtered off, washed with chloroform and dried under vacuum. The product was found to be dimethyltin sulphate-DMSO monoadduct. Another preparation of dimethyltin sulphate-DMSO adduct was performed in aqueous solution, and crystalline dimethyltin sulphate-DMSO monoadduct was obtained in a similar manner as described above. <u>Analysis</u>, calcd. $C_2H_6SnSO_4(CH_3)_2SO$: C, 15.34; H, 3.86; S, 20.50. Found: C, 15.59; H, 3.84; S, 20.56. Dimethyltin sulphate-DMSO adduct is insoluble in DMSO and organic solvents such as methanol, acetone, acetonitrile, and chloroform, but soluble in water.

Dimethyltin Dichloride Adducts

(a) Dimethyltin dichloride-pyridine diadduct was prepared by the method described by Beattie and McQuillan (33).

(b) Dimethyltin dichloride-DMSO diadduct was prepared by adding excess DMSO to a solution of dimethyltin dichloride in chloroform, followed by addition of excess of ether. A white crystalline precipitate was obtained which was washed with ether and recrystallized from chloroform. <u>Analysis</u>, calcd. for $C_{2H_6}SnCl_2[(CH_3)_2SO]_2$: C, 19.16; H, 4.82; S, 17.07. Found: C, 19.14; H, 4.64; S, 16.97. Dimethyltin dichloride-DMSO adduct is soluble in polar solvents such as water and methanol as well as in non-polar organic solvents such as chloroform.

Dimethyltin Bis(tetrafluoroborate)

(a) Dimethyltin dichloride (0.6470 g.) and silver tetrafluoroborate (1.470 g.) were allowed to react in about 25 ml. of methanol. Precipitated silver chloride was filtered off (0.8370 g. calcd. 0.8440 g.) and the filtrate was removed under vacuum at room temperature to give a white solid (1). <u>Analysis</u>, calcd. for for $C_2H_6Sn(BF_4)_2$: C, 7.44; H, 1.87; F, 47.14. Found: C, 10.47; H, 2.82; F, 32.47. As indicated by the analysis, partial decomposition of dimethyltin bis(tetrafluoroborate) occurred to give boron trifluoride and dimethyltin difluoride. This was confirmed by the following experimental results:

i) A portion of the recovered methanol was condensed on to about 10 ml. of pyridine. Upon evaporation of the mixture under vacuum, a white solid (II) was left, whose infrared spectrum was identical to that reported (155) for the boron trifluoride-pyridine adduct, $BF_3.Py$.

 ii) Another portion of the recovered methanol gave a positive test for fluorine and boron and was found to be markedly acidic.

iii) Upon redissolving the solid (I) in methanol, about one-half of the solid was found to be insoluble in methanol. This insoluble solid was identified (from its infrared spectrum, X-ray powder photograph and analytical results) to be dimethyltin difluoride. <u>Analysis</u>, calcd. for $C_2H_6SnF_2$: C, 12.90; H, 3.23. Found: C, 12.85; H, 3.21.

iv) The infrared spectrum of the solid (I) was very similar to that reported (43) for trimethyltin tetrafluoroborate. Upon exposure of the solid to air for a few seconds, the infrared spectrum showed characteristic absorption bands of the free BF_4^- ion.

(b) The thermal stability of the mixture of dimethyltin bis(tetrafluoroborate) and dimethyltin difluoride (solid I) was examined by heating the solid at $60 - 70^{\circ}$ under vacuum for about 6 hours. The solid did not sublime nor did it show any change in its infrared spectrum and analysis (found: C, 10.57; H, 2.60). No boron trifluoride was evolved.

(c)Dimethyltin dichloride (0.8444 g.) and silver tetrafluoroborate (1.4968 g.) were mixed in about 25 ml. of ether. This resulted in precipitation of silver chloride and an insoluble product. After shaking the mixture for five minutes, the ether was removed under vacuum at room temperature. The residue was sticky and the qualitative analysis showed the presence of silver chloride in it. The infrared spectrum of the residue showed all the absorption bands shown by the mixture of dimethyltin bis(tetrafluoroborate) and dimethyltin difluoride (solid I described above), and, on exposing the residue to air, the same changes were observed in the infrared spectrum as described above for the previous mixtures. About 5 ml. of trimethylamine was condensed onto the recovered ether, and the ether and excess trimethylamine were removed under vacuum at room temperature. A white solid was obtained. The infrared spectrum of this solid was found to be identical to that reported (155, 156) for boron trifluoride-trimethylamine adduct, BF3.N(CH3)3.

(d) Dimethyltin dichloride (0.7708 g.) and silver tetrafluoroborate (1.2774 g.) were allowed to react in about 20 ml. of liquid sulphur dioxide. The insoluble product was filtered off and the sulphur dioxide was pumped off. Only a trace of solid was left behind after removal of sulphur dioxide from the filtered solution. A portion of the filtered residue gave a positive test for silver chloride. The infrared spectra of the residue, under anhydrous conditions as well as after exposure to air, were identical to those obtained for the previously described mixture of dimethyltin bis(tetrafluoroborate) and dimethyltin difluoride (solid I).

Dimethyltin Hexafluorosilicate

An attempt to prepare this compound was not successful. When dimethyltin dichloride (0.6402 g.) and silver hexafluorosilicate (1.0426 g.) were mixed in about 25 ml. of methanol, silver chloride was precipitated. Upon removal of the methanol, under vacuum at room temperature, the product was found to be dimethyltin difluoride which was characterized by its X-ray powder photograph, infrared spectrum, and analytical results. <u>Analysis</u>, calcd. for $C_2H_6SnF_2$: C, 12.90; H, 3.23. Found: C, 12.82; H, 3.07. The recovered methanol was highly acidic and contained silicon and fluorine which were identified by the qualitative analysis of hydrolysis products of the recovered. methanol.

Dimethyltin Bis(hexafluorophosphate)

(a) Attempts to prepare this compound were not successful. The metathetical reaction between dimethyltin dichloride (1.542 g.) and silver hexafluorophosphate (3.505 g.) in 25 ml. of methanol

resulted in the precipitation of silver chloride. Upon removal of the solvent from the filtered solution under vacuum at room temperature, a white product was obtained which was insoluble in methanol. The infrared spectrum of this product was measured but the product could not be characterized by its infrared spectrum. The recovered methanol was highly acidic and contained both fluorine and phosphorus. This identification was accomplished by qualitative analysis.

(b) The above metathetical reaction was also performed in a sulphur dioxide solution. The precipitated silver chloride was shown by an X-ray powder photograph to contain dimethyltin difluoride. Fractionation of the volatile material from the sulphur dioxide solution gave a sample rich in phosphorus oxytrifluoride, POF_3 , as shown by its infrared spectrum. The solid remaining on removal of the sulphur dioxide under vacuum also contained dimethyltin difluoride which was identified by an X-ray powder photograph.

Dimethyltin Bis(hexafluoroarsenate)

Dimethyltin dichloride (0.7790 g.) and silver hexafluoroarsenate (2.1044 g.) were mixed in 25 ml. of methanol and the precipitated silver chloride was filtered off. The methanol was removed from the filtered solution under vacuum at room temperature to give a hygroscopic white solid which gradually turned yellowish-white. The infrared spectrum of the solid was very similar to that reported (43) for trimethyltin hexafluoroarsenate, indicating the presence of the hexafluoroarsenate group in it. An X-ray powder photograph of the solid showed the presence

of dimethyltin difluoride. Thus the solid was a mixture of dimethyltin difluoride and the bis(hexafluoroarsenate). When the solid was exposed to air, its infrared spectrum showed the characteristic strong band of AsF_6^- ion at 720 cm⁻¹. The recovered methanol was highly acidic and contained both fluorine and arsenic as shown by qualitative tests.

Dimethyltin Bis(hexafluoroantimonate)

(a) The metathetical reaction between dimethyltin dichloride (1.0606 g.) and silver hexafluoroantimonate (3.3178 g.) was performed in 25 ml. methanol in the manner described above. The product was a hygroscopic white solid which contained some methanol as shown by its infrared spectrum. The recovered methanol was not acidic and did not show presence of any fluorine or antimony indicating that no decomposition of hexafluoroantimonate had occurred. When the recovered solid was heated up to 120° under vacuum to remove the methanol, decomposition of the solid occurred and oily drops of antimony pentafluoride, SbF_5 were condensed in the trap. Qualitative tests on this oil showed the presence of antimony and fluorine.

(b) Dimethyltin dichloride (1.038 g.) and silver hexafluoroantimonate (3.2476 g.) were allowed to react in 25 ml. of liquid sulphur dioxide and the precipitated silver chloride was filtered off. Removal of sulphur dioxide under vacuum gave a very hygroscopic solid. X-ray powder photographs of the solid and the silver chloride did not show any lines due to dimethyltin difluoride. The infrared spectrum of the solid showed similar features to those reported (43) for trimethylantimony hexafluoroantimonate and the infrared spectrum of a sample of the solid

exposed to air showed characteristic band of the SbF_6^- ion at 660 cm⁻¹. However, no analysis of the solid was obtained.

The Dimethyltin Derivative of $B_{12}Cl_{12}^2$

Dimethyltin dichloride (0.2030 g.) and $Ag_2B_{12}Cl_{12}$ (0.7118 g.) were allowed to react in 25 ml. methanol. Precipitated silver chloride was filtered off and the solvent was removed under vacuum at room temperature to give a white product which contained methanol as shown by its infrared spectrum. The methanol could not be removed from the solid even after heating it under vacuum at 100° for 24 hours. The recovered methanol was not acidic and gave negative tests for boron and chlorine indicating that no decomposition of the $B_{12}Cl_{12}$ group had occurred. Analysis, calcd. for C₂H₆SnB₁₂Cl₁₂(CH₃OH): B, 17.6; Cl, 57.8; calcd. for C₂H₆SnB₁₂Cl₁₂(CH₃OH)_{1 5}: B, 17.26; Cl, 56.6; calcd. for C₂H₆SnB₁₂Cl₁₂(CH₃OH)₂: B, 16.9; C1, 55.4. Found: B, 16.4; Cl, 57.8. The dimethyltin derivative of $B_{12}Cl_{12}^{2-}$ is soluble in polar solvents such as methanol and water but insoluble in chloroform. It is very hygroscopic and hydrolyses on exposure to air as shown by changes in its infrared spectrum.

Trimethylantimony Dibromide

This was prepared by the method described by Morgan and Davies (157). Trimethylstibine was prepared from freshly distilled A.R. grade antimony trichloride and methyl magnesium iodide. The trimethylstibine and ether were co-distilled in a nitrogen atmosphere and the distillate treated with a carbon tetrachloride solution of bromine. Precipitated trimethylantimony dibromide was filtered off and recrystallized from water. <u>Analysis</u>, calcd. for $C_3H_9SbBr_2$: C, 11.20; H, 2.80; Br, 48.92.

Found: C, 11.09; H, 2.46; Br, 48.90.

Trimethylantimony Difluoride

An aqueous solution of silver fluoride was made by dissolving silver carbonate in 40 percent aqueous solution of hydrofluoric acid in a platinum dish. 20 ml. of this solution which contained 0.7160 g. of silver fluoride, was allowed to react with 0.9214 g. of trimethylantimony dibromide. Silver bromide was filtered off and the filtrate was evaporated to dryness. The product was then recrystallized from ethanol and further purified by sublimation under vacuum at room temperature. <u>Analysis</u>, calcd. for $C_{3}H_{9}SbF_{2}$: C, 17.58; H, 4.39. Found: C, 17.00; H, 4.29. Trimethylantimony difluoride is a white crystalline solid. It is soluble in water, methanol and chloroform and is not hydrolysed in air.

Trimethylantimony Dinitrate

Trimethylantimony dibromide (0.6472 g.) and silver nitrate (0.6732 g.) were allowed to react in 25 ml. of methanol. Precipitated silver bromide was filtered off and the solvent removed under vacuum at room temperature. White flakes of trimethylantimony dinitrate were obtained which were recrystallized from chloroform. <u>Analysis</u>, calcd. for $C_{3}H_{9}Sb(NO_{3})_{2}$: C, 12.40; H, 3.10; N, 9.63. Found: C, 12.78; H, 2.95; N, 9.89.

Trimethylantimony dinitrate is soluble in water, methanol and chloroform. It is hydrolysed slowly in the presence of moisture. However, the hydrolysis is reversible and the hydrated product was converted into anhydrous dinitrate by drying under vacuum. The hydration and dehydration could be followed by

observing the changes in the infrared spectrum.

Trimethylantimony Carbonate

Trimethylantimony dibromide (0.9712 g.) and silver carbonate (0.8200 g.) were allowed to react in 20 ml. of liquid sulphur dioxide. Silver bromide was filtered off and, after removal of sulphur dioxide under vacuum, white trimethylantimony carbonate was obtained. <u>Analysis</u>, calcd. for $C_3H_9SbCO_3$: C, 21.17; H, 4.00. Found: C, 21.37; H, 4.23. It is soluble in liquid sulphur dioxide, water and methanol, but insoluble in chloroform. It did not sublime under vacuum up to 100° and no changes were observed in the infrared spectrum on exposing the solid to air.

Trimethylantimony Sulphate

Trimethylantimony dibromide (0.6274 g.) and silver sulphate (0.5992 g.) were allowed to react in about 25 ml. water. Precipitated silver bromide was filtered off and the filtrate evaporated to dryness on a steam bath. A white crystalline solid was obtained which was recrystallized from water and dried under vacuum. <u>Analysis</u>, calcd. for C₃H₉SbSO₄: C, 13.70; H, 3.45. Found: C, 13.78; H, 3.87. Trimethylantimony sulphate is insoluble in organic solvents such as methanol, acetonitrile and chloroform, but soluble in water. It is not hydrolysed in air.

Trimethylantimony Chromate

Trimethylantimony chromate was obtained as a yellow crystalline solid from trimethylantimony dibromide (1.0706 g.) and silver chromate (1.0872 g.) using the same method as that described for trimethylantimony sulphate. Analysis, calcd. for

 $C_{3}H_{9}SbCr0_{4}$: C, 12.73; H, 3.20; $Cr0_{4}$, 41.03. Found: C, 12.66; H, 3.12; $Cr0_{4}$, 41.29. It is also insoluble in methanol and acetonitrile and is not hydrolysed in air.

Trimethylantimony Oxalate

This compound was prepared from trimethylantimony dibromide (1.1064 g.) and silver oxalate (1.0280 g.) in the manner described for trimethylantimony sulphate. <u>Analysis</u>, calcd. for $C_3H_9SbC_2O_4$: C, 23.55; H, 3.56; C_2O_4 , 34.54. Found: C, 23.51; H, 3.68; C_2O_4 , 34.36. Trimethylantimony oxalate is soluble in water but insoluble in methanol and acetonitrile. It is not hydrolysed in air.

Trimethylantimony Bis(perchlorate)

Trimethylantimony dibromide (0.5410 g.) and silver perchlorate (0.6868 g.) were allowed to react in 25 ml. of methanol and silver bromide was filtered off. Most of the methanol was removed under vacuum at room temperature but the last traces were removed by warming to about 60° . An anhydrous solid was obtained which exploded violently on scratching with a nickel spatula. Consequently, no further work was done on it.

Trimethylantimony Bis(tetrafluoroborate)

Trimethylantimony dibromide (0.5614 g.) and silver tetrafluoroborate (1.0268 g.) were allowed to react in 25 ml. of methanol. Silver bromide was filtered off. After removing the solvent under vacuum at room temperature, a white solid was obtained which was sublimed under vacuum at 50° . The analytical results and infrared spectra of both unsublimed and

sublimed products were identical. Analysis, calcd. for C₃H₉Sb(BF₄)₂: C, 10.57; H, 2.66. Found: C, 14.28; H, 3.60. As indicated by the analytical results, partial decomposition of the tetrafluoroborate group had occurred. This was confirmed in the following manner: X-ray powder photographs of the sublimed solid showed the presence of trimethylantimony difluoride. The recovered methanol was highly acidic and contained boron trifluoride, which was identified by its infrared spectrum and by the presence of boron and fluorine in a portion of the recovered methanol. Thus the product was a mixture of trimethylantimony bis(tetrafluoroborate) and difluoride. The presence of the tetrafluoroborate group in the product was inferred from the infrared spectrum.

Trimethylantimony Hexafluorosilicate

Trimethylantimony dibromide (1.0160 g.) and silver hexafluorosilicate (1.1132 g.) were allowed to react in 25 ml. of methanol and a colourless, deliquescent, crystalline solid was obtained after removal of the methanol as described above. The solid was sublimed under vacuum at 50°. The analytical results and infrared spectra of both the unsublimed and sublimed solid were identical. Analysis, calcd. for $C_3H_9SbSiF_6$: C, 11.65; H, 2.93, F, 36.90. Found: C, 14.99; H, 3.71; F, 28.00 X-ray powder photographs of the sublimed solid showed the presence of trimethylantimony difluoride. Thus the product was a mixture. The infrared spectrum of a sample of the mixture exposed to air showed the characteristic absorption bands of the SiF_6^{2-} ion at 735 and 480 cm^{-1} . The recovered methanol was highly acidic and and gave positive tests for both silicon and fluorine.

Trimethylantimony Bis(hexafluoroantimonate)

(a) Trimethylantimony dibromide (0.7240 g.) and silver hexafluoroantimonate (1.5236 g.) were allowed to react in 25 ml. of methanol. The silver bromide was filtered off and most of the methanol was removed from the filtrate under vacuum at room temperature. The last traces of the methanol could not be removed even on prolonged pumping at 100° , and the product could not therefore be isolated in a pure state. However, the recovered methanol neither showed any acidity nor gave a positive test for either fluorine or antimony, indicating that no decomposition of hexafluoroantimonate had occurred.

(b) The metathetical reaction between trimethylantimony dibromide (1.1080 g.) and silver hexafluoroantimonate (2.3304 g.) in 25 ml. of liquid sulphur dioxide gave, following removal of the precipitated silver bromide and evaporation of the sulphur dioxide, an extremely hygroscopic white solid. <u>Analysis</u>, calcd. for $C_{3}H_{9}Sb(SbF_{6})_{2}$: F, 35.72. Obtained: F, 30.90. X-ray powder photographs of the solid did not show any lines due to trimethylantimony difluoride and the infrared spectrum of the solid confirmed the presence of hexafluoroantimonate group in it.

The Trimethylantimony Derivative of $B_{12}Cl_{12}^{2-}$

Trimethylantimony dibromide (0.3320 g.) and $Ag_{2B12}Cl_{12}$ (0.7836 g.) were allowed to react in methanol. After filtering off the precipitated silver bromide, a colourless solution was obtained, which was evaporated under vacuum at room temperature to give a pink red solid which contained some methanol as indicated by its infrared spectrum. The recovered methanol was not

acidic and gave negative tests for boron and chlorine, indicating that no decomposition of the $B_{12}Cl_{12}$ group had occurred. The solid was then heated at about 60° under vacuum for about 6 hours. <u>Analysis</u>, calcd. for $C_{3}H_{9}SbB_{12}Cl_{12}$: B, 17.9; Cl, 58.9. Calcd. for $C_{3}H_{9}SbB_{12}Cl_{12}(CH_{3}OH)$: B, 17.3; Cl, 56.4. Found: B, 17.3; Cl, 56.0. However, the infrared spectrum of the heated solid did not show any absorption bands due to methanol. The compound dissolved in water or methanol to give a colourless solution but the recovered solid from these solutions was always coloured.

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