

THE STEREOCHEMISTRY OF TRIMETHYLTIN DERIVATIVES

by

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H.C. Clark and R.J. O'Brien, Can.J.Chem. 37,
436 (1959).

Co-ordination Compounds of Nickel (II), Part II.
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H.C. Clark, K. MacVicar and R.J. O'Brien, Can.J.
Chem. 40, 822 (1962)

The Crystal Structure of Trimethyltin Fluoride.
H.C. Clark, R.J. O'Brien and J. Trotter, Proc.
Chem.Soc. 1963, 85

Covalent Bonding in Fluoro- Salts of the Trimethyltin
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1963, 113

Trimethyltin Perchlorate, Trimethyltin Nitrate, and
Their Infra-red Spectra. H.C. Clark and R.J.
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Fluoro- Salts of the Trimethyltin Group. H.C. Clark
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ABSTRACT

An X-ray crystallographic study of trimethyltin fluoride has shown that this compound can best be described as a linear polymer containing a five co-ordinate tin atom, instead of the trimethyltin cation as believed earlier. Such trimethyltin compounds as the nitrate, perchlorate, trifluoromethyltrifluoroborate, tetrafluoroborate, hexafluoroarsenate and hexafluoroantimonate were synthesized, and their structural characteristics were determined spectroscopically from their infra-red spectra.

All but one of these compounds were found to be linear polymers with five co-ordinate tin. The data indicated that the nitrate is most likely a discrete non-ionic molecule with essentially a four co-ordinate tin. The di-ammine and di-pyridine adducts of the perchlorate, and the di-ammine adduct of the nitrate are found to contain the $(\text{Me}_3 \text{Sn B}_2)^+$ cation (B = nitrogen base molecule). The same structure also applies in the case of the di-ammine adducts of the bromide and the chloride.

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INTRODUCTION

Tin (Symbol-Sn) is element number 50 and has a gram atomic weight of 118.70 g. It occurs as the fourth member of Group IVb, and can have oxidation numbers two and four. Although organo-tin compounds of both oxidation states are known, the latter is more commonly encountered.

One characteristic feature of organo-tin compounds has been considered to be the existence of the R_3Sn^+ ion(1,2,3,4). However, in spite of the many references to its occurrence the results of this research (5,6), as well as other very recent reports (7,8,9), have shown beyond a reasonable doubt that, under the conditions investigated, this ion does not exist.

In view of this complete revision of the stereochemical concepts for the R_3Sn group, and to place this work in its proper perspective, it seems appropriate to present a precis of the old ideas, followed by the now revised theories. The complete history of stereochemical considerations for three separate categories of organo-tin compounds, "salts", nitrogen base adducts, and hydroxides, will be critically reviewed.

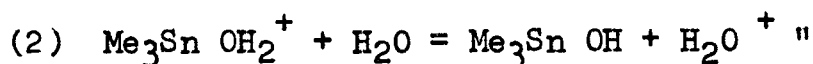
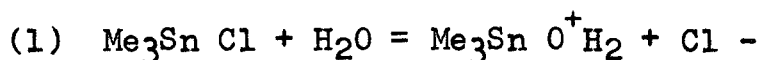
It must be stated that many classes of compounds are not encompassed by these new findings. R_4Sn , $R_3Sn R'$ etc. (R = alkyl or aryl) have without question a monomeric, tetrahedral configuration. Electron diffraction studies (10) of the volatile derivatives of $R_2Sn A_2$ and $R_3Sn A$ (where A = mono

valent anions) have shown that in the gaseous state these compounds also have a tetrahedral configuration. It is in the solid state or in solution that uncertainty existed for all compounds of the above two classes, i.e. $R_2Sn A_2$ and $R_3Sn A$, particularly for the non-volatile compounds.

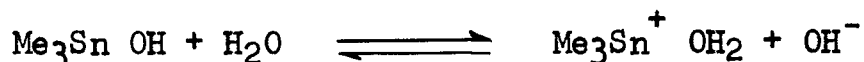
A very complete review of organo-tin compounds was published in 1960 by G.E. Coates (4) in which all the important types of compounds were mentioned. After discussing the solvolysis of the covalent monohalides $R_3Sn Cl$, Coates states that, "Compounds in which R_3Sn or R_2Sn is combined with a highly electronegative group, such as fluoride, nitrate, sulfate, or sulfonate, have quite different properties.

Their high melting points and low volatility (trimethyltin fluoride decomposes about 360° without melting) indicate a 'salt-like' constitution. When they dissolve in water, they do so not as the ionic R_3Sn^+ or R_2Sn^{++} , but co-ordinated with water e.g. $R_3Sn(OH_2)^+$. This follows from the resolving of methylethyl-n-propyltin camphosulfonate. Since the ion R_3Sn^+ would have an sp^2 configuration and be planar, it would lead to immediate racemization.

Aqueous solutions of the mono-and di-halides are slightly acidic; this is due to the co-ordinated water behaving as an acid, as it does in many hydrated ions(e.g. $Cu(H_2O)_4^{++}$). Two equilibria obtain in an aqueous solution of trimethyltin chloride.



In his discussion of trimethyltin hydroxide, Coates states that, "It is readily soluble in water, and has a dissociation constant of 1.7×10^{-5}



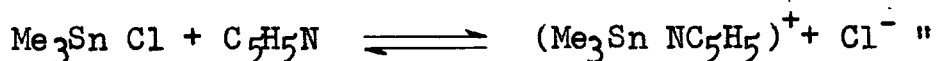
Addition of acids to a solution of trimethyltin hydroxide has afforded a variety of derivatives, some, like the acetate, being covalent and volatile, others like the sulfate being ionic and involatile."

A number of nitrogen base adducts are also discussed: "The mono- and di-halides, in contrast to the tetra-alkyls, form coordination compounds, particularly with nitrogen bases, e.g. $\text{Me}_3\text{Sn I} (\text{C}_5\text{H}_5\text{N})$, m.p. 60.5° , $\text{Me}_2\text{Sn Cl}_2 (\text{C}_5\text{H}_5\text{N})_2$. They are covalent compounds and the lower members are soluble both in water and alcohols, and in non-polar solvents (particularly the iodides). Oxygen is a weaker donor than nitrogen and does not afford isolable complexes with the mono- or di-halides. However, trimethyltin chloride gives a weakly conducting solution in water and alcohol, and this is due to co-ordination by oxygen:



The equilibrium constant for the reaction in ethyl alcohol is 3.5×10^{-5} at 25° . Solutions of trimethyltin chloride in nitrobenzene, which has a higher dielectric constant than ethyl alcohol, are virtually non-conducting,

but the conductance rises markedly on addition of pyridine, due to the reaction

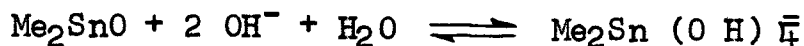


With ammonia a similar species is found, for example, with trimethyltin bromide an ionic solid $(\text{Me}_3\text{Sn} - \text{NH}_3)^+\text{Br}^-$ can be isolated.

In contrast to the four co-ordinated trialkyltin derivatives, the dialkyltin compounds form six co-ordinate complexes. $\text{Me}_2\text{Sn F}_2$, which results from the addition of a soluble fluoride to an aqueous solution of any dimethyltin compound, can combine with two more fluoride ions to give a salt.



This six covalency is also shown by the oxide $(\text{Me}_2\text{Sn O})_n$ when it is dissolved in alkali.



Coates further comments that, "It is amphoteric since it gives salts, e.g. dimethyltin sulfate $\text{Me}_2\text{Sn SO}_4$ (soluble in water, but not in alcohol or non-polar solvents) with acids." "The sulfide, $(\text{Me}_2\text{Sn S})_3$ m.p. 148° , is soluble in organic solvents and in aqueous ammonia sulfide, but not in water. The diacetate, etc., are covalent and volatile like the dichloride, but derivatives of more electronegative anions are salts."

Thus, the following generalizations seemed valid in 1960. For the trialkyltin derivatives, covalent molecules have a characteristic high volatility, while "salts" e.g. $\text{Me}_3\text{Sn}^+ \text{F}^-$,

have a low volatility. The cations that exist in solution, as a result of attack by solvent or by nitrogen base molecules, are four co-ordinate species.

In the case of dialkyltin compounds, four co-ordinate, covalent molecules exist for anions of low or moderate electronegativity, while the cation R_2Sn^{++} is present with highly electronegative anions. Complexes and adducts all have a uniform six co-ordinate state.

However, as a result of an intensive study by many workers, new stereochemical concepts are being established. The non-volatile nature of some trialkyltin derivatives can be correlated with a polymeric configuration. In these compounds a five co-ordinate tin atom occurs as a result of bridging by the "anion."

In the following historical review of the growth of these concepts, it will be noted that many of the results reported were not highly specific and could have more than one interpretation. Also, the role of the solvent molecules had not been fully understood and has led to erroneous interpretations.

As Gilman's superb review of organo-tin compounds(11) surveyed the physical properties of all classes of tin compounds as well as describing general preparative techniques, no attempt will be made to cover these topics.

The very early work in this field was conducted in the latter part of the nineteenth century. Many chemists such

as Cahours (12, 13, 14), Pfeiffer (15) and Frankland (16) not only prepared a large number of compounds, but also attempted to correlate their physical properties with their chemical constitution.

Pfeiffer (15) noted that molecular weight measurements of diethyltin diiodide in boiling benzene indicated a molecular compound. However, the low molecular weight found for diethyltin sulfate in water led him to conclude that the compound was partially dissociated into the diethyltin ions and the sulfate ions. As it did not melt or sublime, Pfeiffer classified the compound as "salt-like". This does not imply that he thought the compound to consist of the diethyltin cation and the sulfate radical, as he later states that the compound should be planar with a cis configuration.

Hjorldahl (17, 18) attempted some crude correlations from crystallographic studies, but was unable to arrive at any useful conclusions. Zelinsky and Krapwin (19), on the other hand, made a useful contribution in their conductivity studies of diethyltin diiodide and triethyltin iodide in absolute methanol. Both of these compounds were found to obey the dilution laws for a weak electrolyte. No statement was made concerning the species present in the solution upon ionization. They were the first to note the susceptibility of these compounds to hydrolysis.

The next work, which was to have far reaching effects, was the attempted resolution of optically active organo-tin

isomers by Pope and Peachey (20, 21). In 1900 these authors published two preliminary notes, but never followed with a full paper giving all the experimental data. The first of these notes contained many curious details. They attempted to resolve methylethyl-n-propyltin iodide by reacting it with silver dextro camphorsulfonate to obtain the methylethyl-n-propyltin dextro camphorsulfonate. Upon slow evaporation of the filtered solution, they found the dextro salt. Further evaporation only yielded more of the dextro salt, and no trace could be found of the levo derivative. This was attributed to a dynamic inter-conversion of the two forms as the more insoluble dextro salt crystallized from solution. A dilute aqueous solution of this dextro methylethyl-n-propyltin dextrocamphorsulfonate gave a molecular rotation ($M_D = [\alpha]_D \times \frac{\text{Mol. Wt.}}{100}$) of $+95^\circ$. From this value, in what seems an arbitrary manner, the methylethyl-n-propyltin group was given a molecular rotation of $+45^\circ$. Upon addition of potassium iodide, the methylethyl-n-propyltin iodide was obtained as a yellow oil. The highest specific rotation of this iodide in an ethereal solution was $[\alpha]_D = +23^\circ$. However, they state that the observed rotation for different preparations was very variable, and in some cases, under conditions which they did not understand, the separated iodide was optically inactive.

It should be noted that as the methylethyl-n-propyltin iodide separated as an oil, its purity can be verified only with difficulty, and a derivative other than the iodide should have been found.

An anomaly is present which can be viewed from two aspects. The first is that the absence of the levo salt in the initial separation of the camphorsulfonate derivative requires rapid interconversion of these two isomers, i.e. racemization. Yet, the aqueous solution, from which the final iodide was isolated, was considered to contain predominantly the dextro isomer.

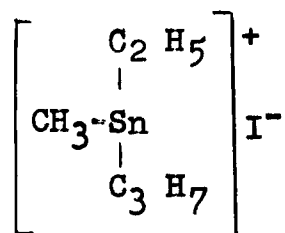
However, the more serious criticism of this work results from a simple calculation. Pope and Read (22) reported the resolution of ammonium d-camphorsulfonate giving the molecular rotation as $M_D = +171.6$. Then, if the organotin derivative contained two optically active components in the solution, the following relationship will not hold (23).

$$\frac{M_D S_n}{M_D NH_4^+} = \frac{\text{Mol. Wt. } NH_4^+}{\text{Mol. Wt. } S_n}$$

Using the molecular weight of methylethyl-n-propyltin camphorsulfonate, (Mol. Wt. S_n), as the unknown, and substituting $M_D S_n = +95$, $M_D NH_4^+ = +171.6$, and Mol. Wt. $NH_4^+ = 248$ gm. a value of 447 gm. is obtained for the tin derivative. This is only in 2% error from the value of 436 gm. obtained from the formula $Sn(CH_3)(C_2H_5)(C_3H_7)(C_{10}H_{15}OSO_3)$. Consequently, it may be stated without qualification that a racemic mixture existed in the aqueous solution before the regeneration of the iodide.

This is supported by the failure of two other attempts to resolve the same compound (24, 25).

Kipping (26) also tried unsuccessfully to resolve phenylbenzyl-p-tolyltin hydroxide, phenylbenzyl-n-butylin iodide and benzylethyl-n-butylin iodide using d, α -bromo- π -camphorsulfonate, d-tartrate, and d-camphorsulfonate. It is interesting to note that Gilman (27) reports the resolved methylethyl-n-propyltin iodide as having the following constitution.



The positive results obtained by Pope and Peachey were, unfortunately, taken as conclusive evidence for a four coordinate species existing in solutions of trialkyltin derivatives. All further stereochemical considerations were either directly or indirectly related to these results.

In 1918 Krause (28) reported some interesting observations in a study of the organo-tin fluorides. He found that triethyltin fluoride and di-n-propyltin difluoride sublimed at 180° and 205° respectively. Melting points were also found for tri-n-propyltin fluoride and diethyl-n-propyltin fluoride at about 270°. Although these results do not give specific information concerning the chemical constitution of these fluorides, the sublimation of a compound at such low temperature is not a

property attributable to ionic compounds. Krause also found that the dialkyltin difluorides formed complexes with alkali metal fluorides of the type $M_2^+ R_2 SnF_4^-$. If the dialkyltin difluoride contains the free ions $R_2 Sn^{++}$ and F^- , i.e. the fluoride ions are outside the co-ordination sphere of the $R_2 Sn$ group, then the formation of a complex, in which four fluoride ions are now within the co-ordination sphere, can only be considered somewhat of an anomaly. There are no chemical phenomena that require the fluoride ions to co-ordinate in an aqueous potassium fluoride solution (from which the complex was isolated) and not in the parent compound.

Although the majority of the early workers recorded the properties of some non-volatile compounds as "salt-like". Kraus (29, 30) was the first to definitely state that the $R_3 Sn^+$ ion existed in solution.

In his study of the conductivity of trimethyltin chloride in non-aqueous solvents, Kraus confirmed the earlier report (19) of the weak electrolytic character of the halides, and speculated that the organotin cation, which arose from ionization, resulted from the transfer of the chloride ion to the solvent molecule.

Later, Kraus in a lecture published in the Journal of the American Chemical Society (31) stated that he considered the $Me_3 Sn$ group to be related to the hydrogen atom, both in their possible oxidation states, e.g. H_2 and $Me_6 Sn_2$, H^+ and $Me_3 Sn^+$,

and Na^+H^- and $\text{Na}^+\text{Me}_3\text{Sn}^-$, as well as their chemical reactivity. There seems to be sufficient data quoted to make this suggestion of some value in predicting possible reaction products. These considerations led Kraus to postulate that compounds of trimethyltin with strongly electronegative groups are then non "salt-like" substances. This does not seem consistent with his earlier statements concerning Me_3Sn^+ .

Except for dipole moment studies of some organotin chlorides in carbontetrachloride (32), very little work was done until Skinner and Sutton (10) reported their electron diffraction investigation. Their results showed that all of the volatile alkyltin halides were tetrahedral in the gaseous state. The extension of this configuration to the solid state cannot be made without an experimental investigation of this phase.

In 1954 a remarkable paper was published by Anderson and Vasta (33) entitled " 'Conversion Series' for Triethyltin derivatives". This series is quoted below with the available data on their boiling points.

Et_3SnX	S	I	Br	CN	NCS	Cl
B.P.	$188^\circ/20\text{mm}$	234°	224°	130°	160°	210°

Et_3SnX	O	NCO	OCOCH_3	F
B.P.	272°	(m.p. 214°)	224°	294°

These authors found that if the silver salt of an ion lying in the above series to the right of that contained in the

triethyltin derivative was heated under anhydrous conditions with the organotin compound, a sublimate or distillate was obtained of the converted triethyltin compound. Thus, if triethyltin bromide is heated with silver fluoride, a white sublimate of triethyltin fluoride is found. Similar results were obtained in this present investigation by heating trimethyltin bromide and potassium fluoride. In the above series it will be noted that the boiling points of the compounds from bis (triethyltin) sulfide to triethyltin cyanide decrease, and the results do not need further comment. However, the boiling points of the succeeding members are not consistent with these findings. The high volatility of triethyltin fluoride from an anhydrous melt is a strong indication that a discrete (volatile) form exists, in addition to the non-discrete (non-volatile) product isolated from solution. Moreover, the volatility of triethyltin acetate is only second to the fluoride, yet dibutyltin dicarboxylates have been found to exist as high molecular weight polymers (34).

Although the above results are inconsistent with the presence of ions, Rochow and his co-workers were strong proponents for the R_3Sn^+ and R_2Sn^{++} ions (35). They claim that $(CH_3)_2Sn^{++}$ ions may be retained on a cation exchange resin (36) and have used this fact for the preparation of new compounds by eluting the resin with the appropriate acid (37). Undoubtedly a cation exists, but the co-ordination of the (aqueous) solvent cannot be neglected. This is emphasized by the fact that many compounds were isolated as mixed oxides. Of equal importance

in this connection is the characterization of divinyltin dichloride dihydrate by Langer (38).

Various non-aqueous solution studies were conducted at this time, but added very little to the determination of the constitution of these compounds. Conductivity measurements in N,N dimethylformamide (39, 40) of the diorgano- and triorganotin chlorides reconfirmed the two earlier studies (30, 19) that these compounds are weak electrolytes. Proton magnetic resonance spectra were recorded in D_2O of $(CH_3)_3 Sn Cl$, $(CH_3)_2 Sn Cl_2$ and $CH_3 Sn Cl_3$ by Van der Kelen (41). The conclusion that the ions $(CH_3)_3 Sn^+$, $(CH_3)_2 Sn^{++}$, and $CH_3 Sn^+$ exist in solution is not very realistic as the solutions would be acidic and consequently would contain some hydroxides.

A detailed study of trimethyltin hydrogensulfate and bis (trimethyltin) sulfate in anhydrous sulfuric acid by Gillespie and Robinson (42) indicated complete dissociation. The authors favour the unsolvated ion, but acknowledge that the possibility of a mono-solvate cannot be excluded from their results. A transfer of a proton from the anhydrous acid to the sulfate in the "salt" would produce the same results.

The first investigation that yielded some direct information concerning the stereochemistry of these compounds was a series of infra-red studies conducted by Okawara et. al. (43, 44, 1). From considerations of the shifts in the C-O stretching absorption of dimethyltin diacetate and trimethyltin acetate, they concluded that an ionic acetate group was present.

For the trimethyltin group, the infra-red shows deformation, rocking, and stretching modes from the tin-methyl vibrations. Okawara selected the Sn-C symmetric and asymmetric stretching fundamental as indicator frequencies. If a planar arrangement occurred, the symmetric, Sn-CH₃ stretching vibration should be infra-red inactive. For any other symmetry, it should be recorded. In trimethyltin acetate, this fundamental was not present. Thus, they state that the compound consists of the planar trimethyltin cation and the acetate anion. Similarly, in trimethyltin fluoride this symmetrical stretching mode is absent, and as a result an ionic constitution was postulated.

The selection of the acetate group as an indicator was unfortunate, as its symmetry is identical for both ionic and bridging groups. Beattie and Gilson (45) were the first to illustrate this fact in a short study of the shifts of the carbonyl stretching frequency of some inorganic acetates, and they concluded that the infra-red spectrum of the acetate group cannot be used diagnostically. Referring to a note on the crystal structure of SnF₄ (46), where bridging fluorine atoms occurred rather than the supposed ions (47), these authors speculated that in dimethyltin difluoride an octahedral arrangement existed.

Kriegsmann and Pischtschan (48) extended these suggestions to some trimethyltin derivatives by a simple consideration of melting points (see below)

Me ₃ SnH	M.P. -70°C.
Me ₃ Sn OH	118°

$\text{Me}_3 \text{Sn F}$	360°C
$\text{Me}_3 \text{Sn Cl}$	39.5°
$\text{Me}_3 \text{Sn Br}$	27.5°

If discrete molecules existed, there should be a gradual increase with molecular weight. This is obviously not the case. From the observation that the O-H stretching band in the infrared spectrum of trimethyltin hydroxide is sharp, they state that the association occurred via oxygen bridging rather than Sn-O-HSn. Both trimethyltin chloride and trimethyltin bromide were felt to contain Sn-hal-Sn chains, although no further details were given. They did not consider trimethyltin fluoride to be in the same category, as an ionic structure was postulated.

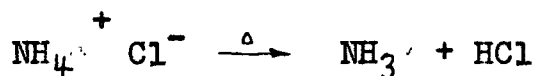
In the same year, Burg and Spielman (49) reported the isolation of trimethyltin tetrafluoroborate as an incidental preparation in a kinetic study. Although the melting point of this compound was 89° , they found no reason not to consider it ionic.

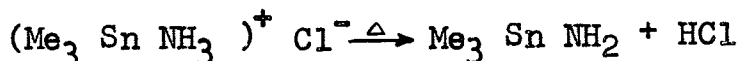
From all the preceding results on the trimethyltin "salts", it is clear that one or more X-ray crystal structure determinations will be required to finally solve the problem of the configuration about the tin atom.

The second aspect of organo-tin chemistry to be reviewed is the stereochemistry of the nitrogen base adducts. Although this forms a minor segment, it is an interesting one.

For the dialkyltin halides (excluding the fluoride) little doubt exists concerning the configuration of the ammine adducts. Both di (15) and tetra (50) adducts have been prepared, the former being highly hygroscopic. In view of the tendency for the dialkyltin derivatives to attain a six co-ordinated configuration, the stereochemistry of these adducts can be easily rationalized. The diadducts will be covalent molecules with the halide atoms within the co-ordination sphere. This is supported by some conductivity studies by Thomas and Rochow (39). The tetra adduct, on the other hand, will consist of a hexa co-ordinated divalent cation with two halide ions outside the co-ordination sphere.

With the nitrogen base adducts of trimethyltin halides, however, a great deal of uncertainty has existed. Pfeiffer (15) isolated the diammine and dipyridine adducts of trimethyltin iodide and considered them to be hexa co-ordinated molecules. Kraus and Greer (51) found that, although the diammine adduct of the chloride and bromide could be isolated, a volatile mono-ammine formed after long pumping. Similarly, a di-pyridine adduct can be isolated from a pyridine solution of the trimethyltin halide, but it immediately loses one molecule of pyridine to form the stable mono-adduct. Kraus's often reiterated statement that the trimethyltin group is chemically related to the hydrogen atom may have minor significance, but his attempt to correlate the volatility of the mono-ammine adduct to ammonium chloride (31), i.e.



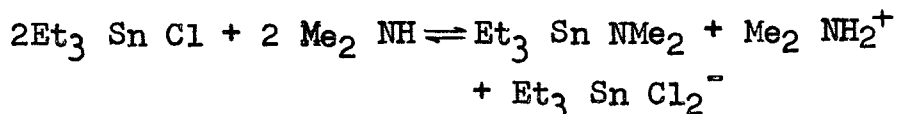


does not have any experimental foundation.

Recently renewed interest in adduct chemistry has thrown further light on this problem. Joshi and Wyatt (52) have reacted triethyltin chloride with methylamine, dimethylamine and trimethylamine. They found indications of a 2:1 complex, i.e. $2\text{Et}_3 \text{ Sn Cl} : 1 \text{NHMe}_2$, from vapour pressure, melting point, and conductivity measurements on the intimate mixture. The conductivity rapidly increases until the 2:1 ratio is reached and then gradually decreases. To explain this 2:1 adduct, they formulated the following equilibrium.



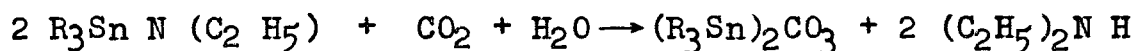
The existence of this particular anion is given additional credibility by the isolation of $(\text{Ph}_3 \text{ P-CH}_2 - \text{Sn} (\text{CH}_3)_3)^+ (\text{CH}_3)_3 \text{ Sn Br}_2^-$ (53). They then stated that a similar equilibrium may exist for the 1:1 adduct i.e.



Besides many other factors, the decrease they recorded for the conductivity at a 1:1 ratio is not compatible with this equilibrium.

Further information concerning the Sn-N bond has been gained from the isolation of triethyl (dimethylamine) tin (54, 55) as well as numerous other derivatives. The exceptional

reactivity of the four co-ordinate tin compound was demonstrated by Sisdo and Kozema (56) who reported that the following reaction occurred almost immediately upon exposing the sample to the atmosphere.



This high reactivity, which is characteristic of the ammino stannanes, is not found in derivatives of imidazole and trimethyl tin (57, 9). In imidazole, the nitrogen atoms are situated in the 1, 3 positions. Consequently, a linear polymer can be formed with a five co-ordinate tin atom. The trimethyltin group will be planar and the imidazole will be acting as a bridging ligand. Their stability may be related to the fact that the tin atom is co-ordinately "saturated."

Thus, the formulation of the mono-amine adduct of trimethyltin chloride, which is stable in the open atmosphere, as $(\text{Me}_3\text{ Sn NH}_3)^+ \text{ Br}^-$ is not consistent with the properties of the amino stannanes. A better configuration would be the molecular species $\text{Me}_3\text{Sn (NH}_3\text{) Cl}$.

This has been substantially verified by Beattie's (58) and Hulme's (59) crystal structure determination of the related trimethyltin chloride mono-pyridine, where a five co-ordinate tin atom with a planar Me_3Sn group was found. The configuration of the di-ammonia and di-pyridine adducts will be discussed with some experimental results later in this thesis.

The final class of compounds are the hydroxides, but as no active research was undertaken on them, their properties will only be dealt with to illustrate some general properties.

As in the two previous categories, it is only recently that the problem of the stereochemistry of these compounds has been fully realized. Early workers in this field tacitly assumed that a "normal" hydroxide was present (60). However, a recent infra-red study (61) has shown that in trimethyltin hydroxide a hydrated oxide exists, the trimethyltin group being planar and the bridging is $\text{Sn} - \underset{\text{H}}{\underset{|}{\text{O}}} \dots \text{Sn}$ not $\text{Sn}-\text{O}-\text{H} \dots \text{Sn}$.

These results place the numerous hydroxy halides isolated by Harada (62, 63, 64) in their proper prospective as possible polymers. Due to the complicated nature of these compounds, Harada has only been able to obtain meager information suggesting that one of these compounds is a trimer (65).

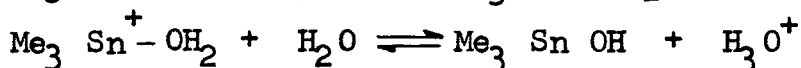
Some recently reported hydrolysis studies are of particular interest. Di-n-butyltin dichloride was first reported to form dichlorotetrabutyl-distannane (66) when acted upon by sodium ethoxide in ethanol. However, Alleston and Davies (67) obtained evidence that the compound was in reality bis (dibutyl-chlorotin) oxide. This was substantiated by the isolation of tetrabutyl-distannane diacetate (67). Sn^{119} magnetic resonance spectra of the oxide in benzene (69) shows that the molecule contains two non-equivalent types of tin atoms. The authors then revised their earlier monomeric configuration (67) for a

cyclic structure.

Tobias et. al. (70) in a definitive hydrolysis study of dimethyltin diperchlorate found that over the pH range of 1.0 to 8.0, five complex hydroxides had to be postulated to explain their results. The point of maximum polymerization was reached at pH 5.5. Above this value, moderately concentrated solutions yielded the polymeric dimethyltin oxide.

In view of all the above results, the solvolysis study by Prince (71) should be re-evaluated. In this work the only species that was deemed present in an aqueous - dioxane mixture (20% w/w H₂O) was $\text{H}-\text{O}-\overset{\text{H}}{\underset{|}{\text{Sn}}}^+\text{R}_3$ in addition to the undissociated

halide. Kriegemann and Pischtschan (48) reported that a 1.052 molar solution of trimethyltin chloride had a pH of 2.8. Using the equations:



and the ionization constant for trimethyltin hydroxide ($K_i = 1.7 \times 10^{-5}$) reported by Kraus (72), a simple hydrolysis calculation using the pH value of 2.8 gives the ($\text{Me}_3\text{Sn}^+-\text{OH}_2$) concentration as 2,100 molar. Some doubt, therefore, exists as to the applicability of the above equation.

Although the triaryltin derivatives have not been mentioned in this historical review of hydroxides, recent publications have demonstrated that these compounds have some interesting properties. The characterization of triphenyltin

hydroxide and bis (triphenyltin) oxide has only recently been accomplished (73, 74). The first report (73) considered the hydroxide to be associated, while the second (74) formulates a free hydroxide. The latter supposition is supported by Smith and Kipping's (75) finding that a very similar compound, tri-benzyltin hydroxide has a high molecular weight in boiling benzene.

As stated earlier, when this research project was undertaken, the R_3Sn^+ ion was believed present in the compound trimethyltin fluoride and an X-ray crystallographic study of this compound was completed. Using the results of this investigation to interpret the infra-red spectrum of this fluoride, further work was undertaken with univalent trigonal planar (NO_3^-) and tetrahedral (ClO_4^-) oxyanions as well as tetrahedral (BF_4^-) and octahedral (AsF_6^- , SbF_6^-) fluoroanions. In addition, the nitrogen base adducts were studied to investigate some anomalies that seemed present in previous studies.

In addition to the anomalous volatility of trimethyltin fluoride from a melt of trimethyltin bromide and silver fluoride (33), two experiments with this compound in solution should be recorded.

When trimethyltin fluoride is dissolved in liquid ammonia, the product obtained upon removal of the solvent is the original fluoride. When trimethyltin chloride is treated in a similar manner, an ionic di-adduct, $(\text{Me}_3 \text{Sn} (\text{NH}_3)_2)^+ \text{Cl}^-$, is formed. If the fluoride contained the $\text{R}_3 \text{Sn}^+$ ion and it dissolves in liquid ammonia, then the solvated cation should exist in solution. Removal of the solvent should leave $(\text{Me}_3 \text{Sn} (\text{NH}_3)_2)^+ \text{F}^-$ as a residue. The inherent stability of the $\text{Me}_3 \text{Sn} (\text{NH}_3)_2^+$ cation will be demonstrated later in this thesis.

If potassium fluoride is added to a saturated aqueous solution of trimethyltin fluoride, there is no precipitation. Should simple ions be present in solution, the addition of fluoride ion ought to affect the equilibrium concentration of trimethyltin fluoride.

It is understood that these experiments are not highly specific and many effects could cause the same results, but they do indicate that a full investigation of the structure or the nature of the bonds within this compound is warranted. Consequently, single crystals were prepared for an X-ray crystallographic study. The required data were obtained as

SECOND FOURIER PROJECTION FOR TRIMETHYLTIN FLUORIDE

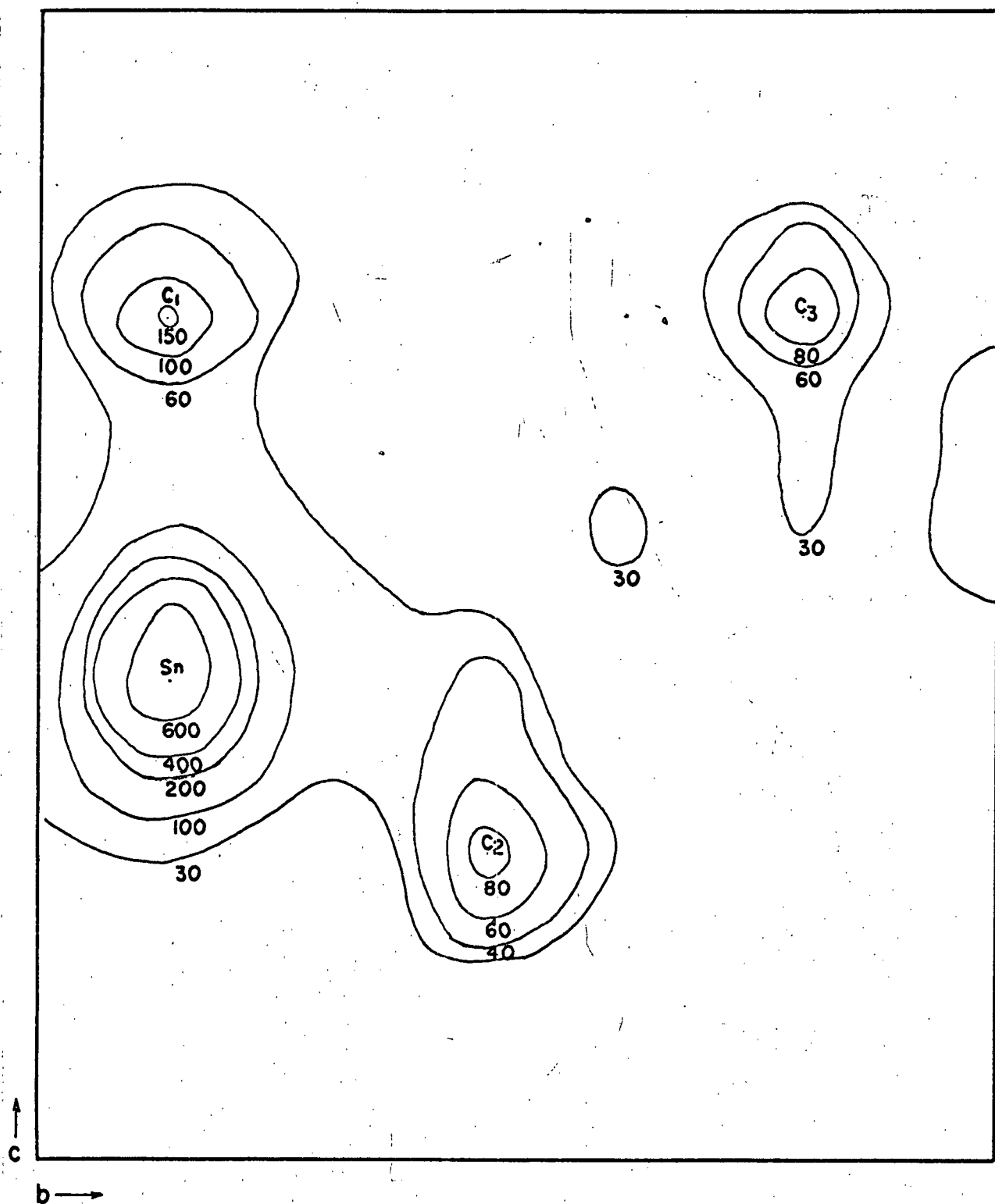


FIGURE 1

described in Chapter 10, and its interpretation is as follows.

From the a axis Patterson projection, the y and z parameters of the tin atom were determined, and a Fourier series was summed using signs based only on the tin contribution. On the resulting electron-density map, three light atoms (probably carbon) were well resolved, and were situated at the corners of an equilateral triangle with the tin atom at the centre. Structure factors were recalculated with inclusion of these three extra atoms, and a second Fourier synthesis was completed. This map (Fig. 1) showed improved resolution of these atoms. The triangular arrangement of the light atoms suggested a structure with planar trimethyltin groups situated in a mirror plane at $X=\frac{1}{4}$ of the space group $\underline{Pm} \underline{c} \underline{n}$, with the fluorine atoms situated midway between successive tin atoms along the a axis.

Parameters based on this structure are shown in Table 1 as well as the general crystal data. The structure factors were calculated from these parameters for all the h k l reflections using the scattering factors listed by Sagel (76) for uncharged tin, fluorine, and carbon atoms. The very good agreement between measured and calculated structure factors (Table 2), and the normal interatomic distances suggested that this structure was a very plausible one.

However, there were one or two anomalies:

- (i) The peak electron-density at one of the carbon atoms, C_1 , was considerably higher than those of the other two.

- (ii) The a axis electron-density projection contained some diffuse density along the lines between tin and the two lower-density carbon atoms.
- (iii) The integrated electron density of the tin peak was 50.08 electrons, so that even allowing for possible errors in the electron count (77), it seemed that the fluorine atom was not situated on top of the tin atom in projection.

To account for these anomalies, the three-dimensional electron-density distribution was calculated. The Sn and C₁ atoms were represented by well resolved spherical peaks, but both of the other carbon atoms were split into two half-atoms, one on each side of the mirror plane. The electron density distribution at the fluorine atom was even more remarkable, being spread out over parts of the surface of a sphere with the tin atom as centre. The density was greatest in positions above the C₁-Sn-C₂ and C₁-Sn-C₃ angles, but was absent above the C₂-Sn-C₃ angle. Typical sections of the three-dimensional Fourier illustrating these features are shown in Figures 2,3,4.

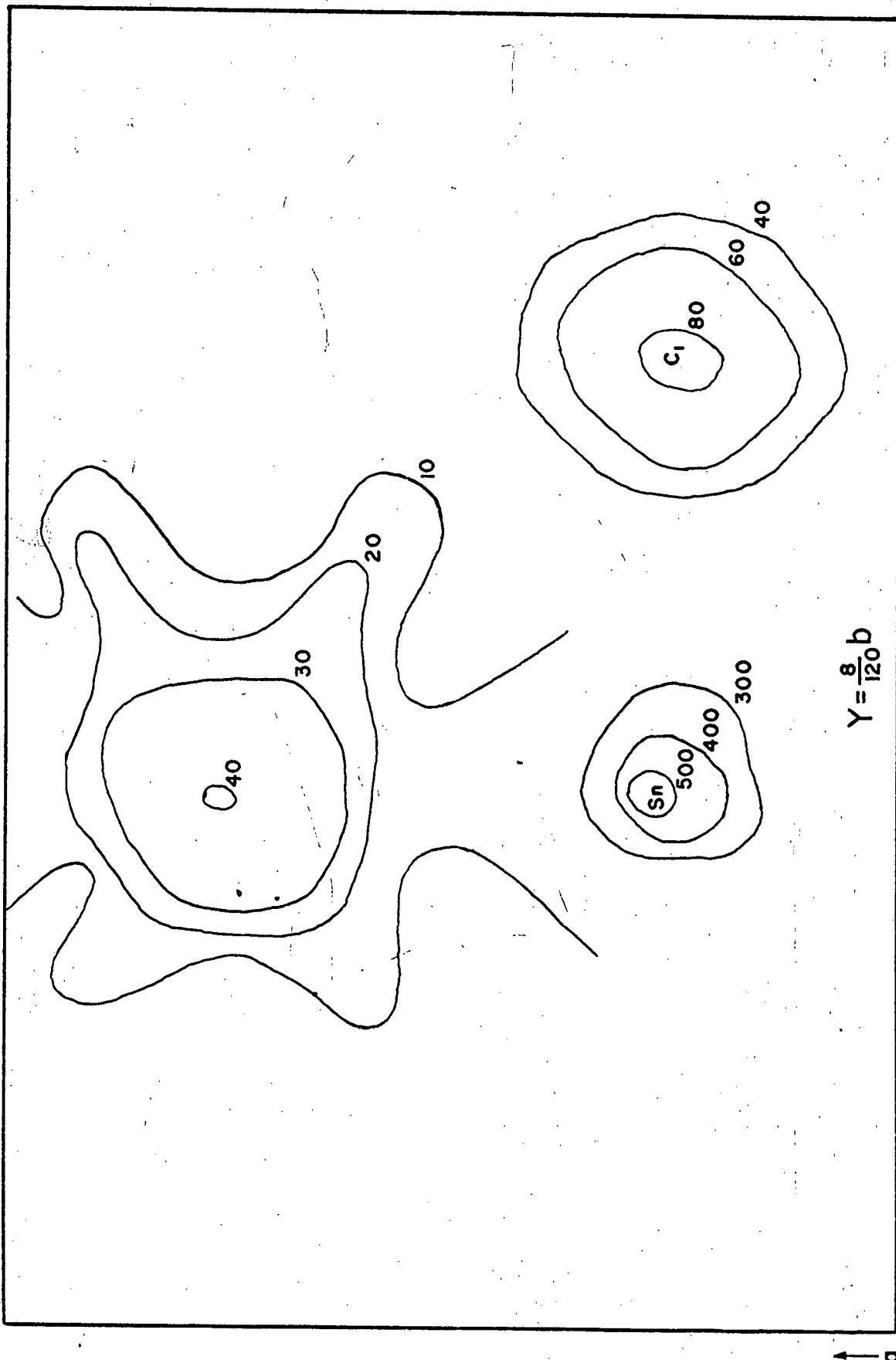


FIGURE 2

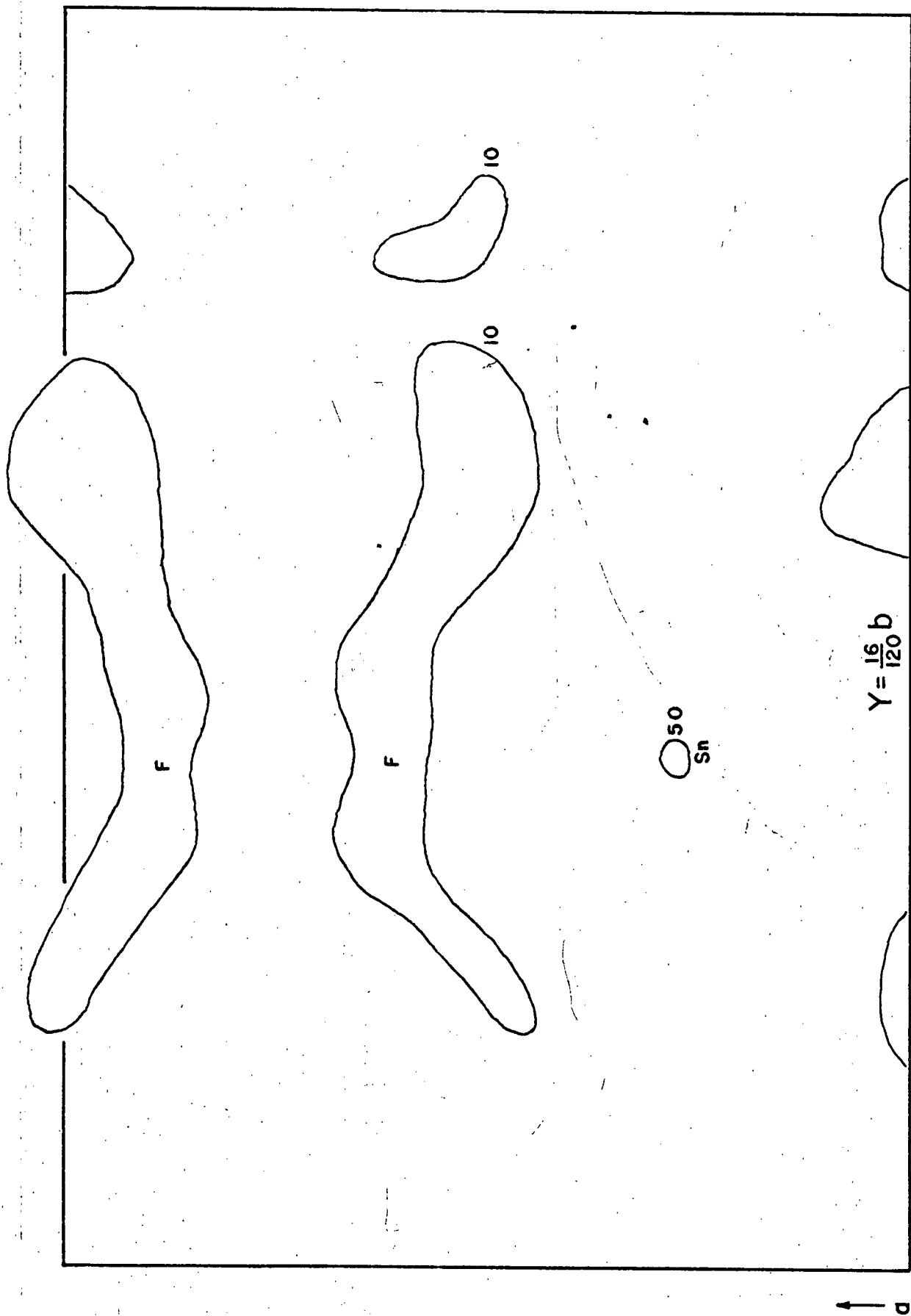


FIGURE 3

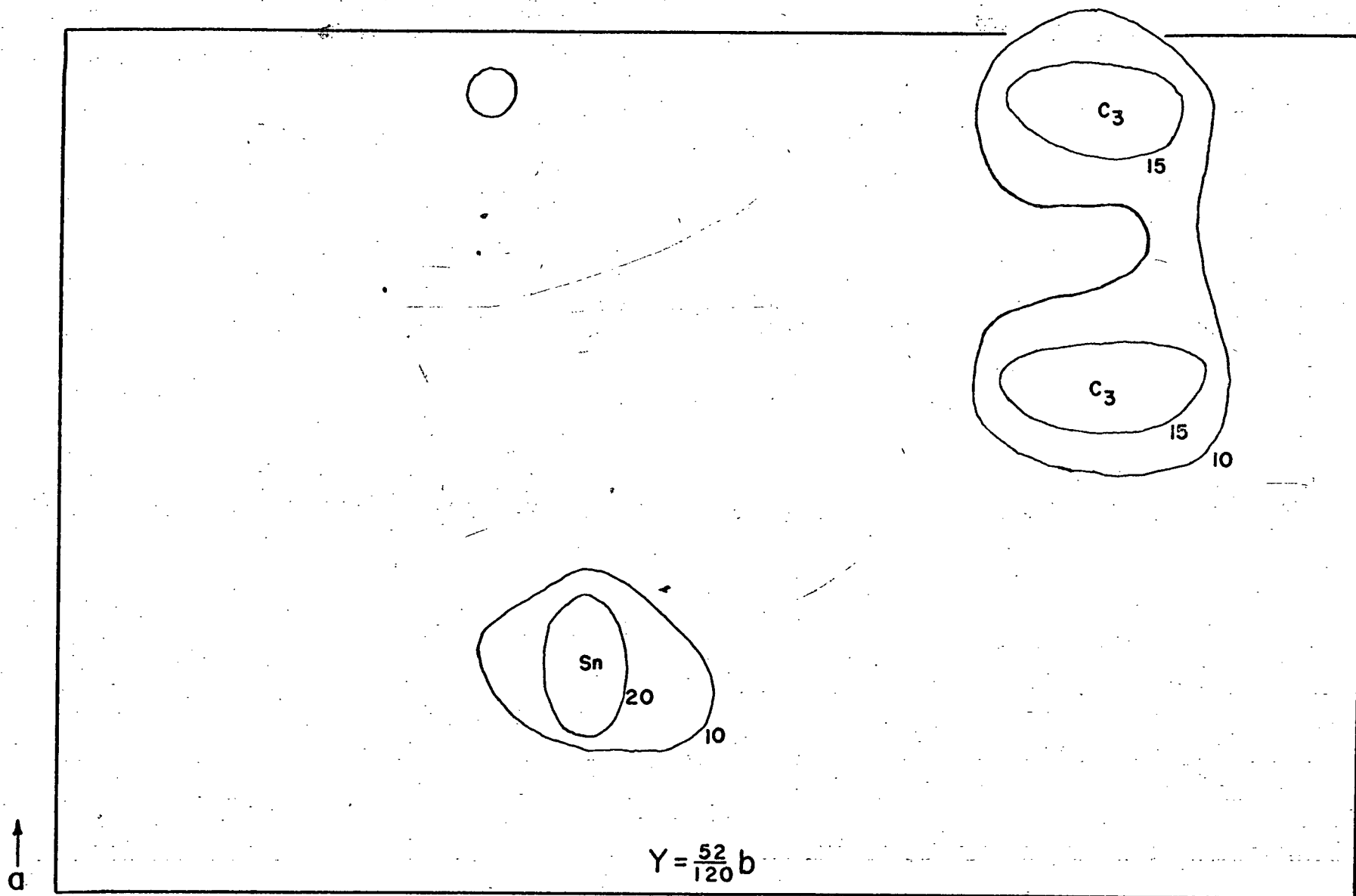


FIGURE 4

TABLE 1.

PARAMETERS BASED ON CRYSTAL STRUCTURE OF
TRIMETHYLTIN FLUORIDE.

(a) General Crystal Data.

$$\begin{aligned}\text{Orthorombic} \quad a &= 4.32 \pm 0.01 \text{ \AA}, \\ b &= 10.85 \pm 0.02 \text{ \AA} \\ c &= 12.84 \pm 0.02 \text{ \AA}\end{aligned}$$

$$U = 601.6 \text{ \AA}^3$$

$$D_x = 2.015 \text{ gm.cm}^{-3} ; \quad D_m = 2.01 \text{ gm.cm}^{-3}$$

$$F_{(000)} = 344$$

$$\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA} ; \quad \lambda_{\text{MoK}\alpha} = 0.7107 \text{ \AA}$$

Absorption coefficient for $\text{CuK}\alpha$ X-rays , $\mu = 352 \text{ cm}^{-1}$

Absent reflections: $\underline{h} \ 0 \ \underline{l}$ when \underline{l} is odd

$\underline{h} \ \underline{k} \ 0$ when $(h + k)$ is odd

Space group is $\bar{P} \ 2, c \ n \ (C_{2v}^9)$ or $Pm \ c \ n \ (D_{2h}^{16})$.

(b) Positional and thermal parameters

From \underline{a} -axis projection:

Atom	Position	x	y	z
Sn	4 (\underline{C})	$\frac{1}{4}$	0.0654	0.2114
C ₁	4 (\underline{C})	$\frac{1}{4}$	0.0654	0.3676
C ₂	4 (\underline{C})	$\frac{1}{4}$	0.02323	0.1308
C ₃	4 (\underline{C})	$\frac{1}{4}$	-0.1152	0.1308
F	4 (\underline{C})	$\frac{3}{4}$	0.0654	0.2114

Final disordered structure:

	Position	x	y	z	B (\AA^2)
Sn	4 (\underline{C})	$\frac{1}{4}$	0.0654	0.2114	6.0
C ₁	4 (\underline{C})	$\frac{1}{4}$	0.0654	0.3676	6.0
C ₂	8 (\underline{d}) \pm 0.20		0.2323	0.1308	6.0
C ₃	8 (\underline{d}) \pm 0.20		-0.1152	0.1308	6.0
F	(4 (\underline{C}) $\frac{3}{4}$		0.0654	0.2114)	6.0

TABLE 2.

(a) Fo and Fc for the final structure of trimethyltin fluoride.

h	k	l	F OBS	F CALC
0	0	2	180.8	-195.7
0	0	4	33.6	53.2
0	0	6	7.2	- 7.9
0	0	8	20.2	- 14.7
0	0	10	47.0	36.1
0	0	12	42.6	- 36.1
0	0	14	20.7	19.2
0	1	1	43.6	48.5
0	1	2	42.0	- 37.4
0	1	3	113.6	-113.9
0	1	4	71.1	54.7
0	1	5	132.1	124.2
0	1	6	47.5	- 49.1
0	1	7	115.2	- 93.2
0	1	8	21.8	31.1
0	1	9	44.2	49.6
0	1	10	10.0	- 13.3
0	1	11	13.4	- 16.7
0	2	0	128.7	138.2
0	2	1	144.4	-143.8
0	2	2	99.0	-115.3
0	2	3	90.1	96.5
0	2	4	50.3	62.2
0	2	5	29.1	- 34.9
0	2	6	7.2	- 8.9
0	2	7	10.0	- 9.2
0	2	8	18.5	- 20.0
0	2	9	24.6	26.3
0	2	10	16.7	25.4
0	2	11	24.6	- 25.0
0	2	12	21.8	- 19.4
0	2	13	17.9	16.6
0	2	14	11.8	11.2
0	3	1	0.0	1.2
0	3	2	25.7	- 35.4
0	3	3	22.4	- 22.1
0	3	4	111.9	104.3
0	3	5	42.0	44.1
0	3	6	134.4	-116.8
0	3	7	25.2	- 34.7
0	3	8	61.6	66.3
0	3	9	12.3	13.7
0	3	10	21.3	- 21.2
0	F	0	6.2	- 12.9
0	F	1	136.0	-149.6

h	k	l	F OBS	F CALC
0	4	2	6.2	9.4
0	4	3	98.5	98.2
0	4	4	5.1	- 3.7
0	4	5	29.1	- 34.9
0	4	6	6.2	0.6
0	4	7	11.2	- 9.0
0	4	8	0.0	1.1
0	4	9	25.7	28.0
0	4	10	0.0	- 2.0
0	4	11	26.9	- 28.4
0	4	12	0.0	2.0
0	4	13	22.4	19.3
0	5	1	14.6	- 13.3
0	5	2	54.9	- 53.1
0	5	3	31.9	33.8
0	5	4	89.0	74.0
0	5	5	39.7	- 39.0
0	5	6	73.3	- 65.1
0	5	7	24.1	30.2
0	5	8	51.0	44.0
0	5	9	15.1	- 16.5
0	5	10	21.8	- 21.3
0	6	0	100.2	- 92.8
0	6	1	89.5	- 71.9
0	6	2	83.9	67.5
0	6	3	35.2	34.1
0	6	4	21.3	- 25.8
0	6	5	6.7	- 7.4
0	6	6	0.0	3.8
0	6	7	0.0	- 0.7
0	6	8	7.2	7.6
0	6	9	10.6	8.8
0	6	10	13.4	- 16.0
0	6	11	12.9	- 14.1
0	6	12	14.0	15.8
0	6	13	8.4	10.6
0	6	14	6.7	- 8.6
0	7	1	18.5	- 15.9
0	7	2	6.2	- 8.9
0	7	3	43.6	42.8
0	7	4	9.5	13.8
0	7	5	57.7	- 52.6
0	7	6	10.6	- 13.0
0	7	7	49.8	42.6
0	7	8	7.9	8.9
0	7	9	21.8	- 23.2
0	8	0	64.9	- 57.3
0	8	1	6.7	9.6
0	8	2	57.7	50.0
0	8	3	0.0	- 4.8

h	k	l	F OBS	F CALC
0	8	4	23.5	- 29.1
0	8	5	0.0	1.2
0	8	6	0.0	4.6
0	8	7	0.0	0.2
0	8	8	7.9	11.2
0	8	9	0.0	- 1.3
0	8	10	0.0	- 14.4
0	8	11	0.0	2.2
0	8	12	9.5	11.2
0	9	1	7.2	- 4.1
0	9	2	0.0	8.4
0	9	3	21.8	17.8
0	9	4	15.7	- 16.0
0	9	5	26.9	- 29.9
0	9	6	19.0	17.2
0	9	7	24.1	25.6
0	9	8	12.9	- 11.1
0	9	9	9.5	- 11.4
0	10	0	19.0	- 19.7
0	10	1	24.6	27.4
0	10	2	13.4	16.1
0	10	3	21.8	- 17.7
0	11	1	0.0	- 1.9
0	11	2	10.6	11.0
0	11	3	0.0	3.7
0	11	4	17.4	- 16.3
0	11	5	0.0	- 2.6
0	11	6	18.5	15.5
0	11	7	0.0	2.0
0	11	8	9.5	- 11.0
0	12	1	21.3	17.9
0	12	2	0.0	- 3.0
0	12	3	11.2	- 9.6
1	0	2	77.5	- 73.5
1	0	4	101.3	88.6
1	0	6	91.3	- 73.9
1	0	8	56.0	51.9
1	0	10	29.2	- 26.8
1	0	12	10.7	5.8
1	1	0	53.0	- 65.1
1	1	1	112.1	-137.1
1	1	2	39.1	44.8
1	1	3	55.3	64.4
1	1	4	10.0	- 15.3
1	1	5	13.0	- 16.0
1	1	6	0.0	2.4
1	1	7	0.0	- 2.9
1	1	8	0.0	4.8
1	1	9	23.8	18.0
1	1	10	10.0	- 10.1
1	1	11	29.9	- 24.9
1	1	12	0.0	9.9

h	k	l	F OBS	F CALC
1	1	13	20.0	18.2
1	1	1	4.6	- 6.5
1	2	2	8.4	- 16.4
1	2	2	31.5	38.6
1	2	4	48.4	52.8
1	2	5	69.1	- 66.7
1	2	6	71.4	- 61.1
1	2	7	53.0	53.6
1	2	8	36.8	35.6
1	2	9	27.6	- 23.7
1	2	10	10.7	- 11.8
1	3	0	89.0	- 95.5
1	3	1	24.6	- 30.5
1	3	2	83.7	87.4
1	3	3	17.7	27.8
1	3	4	52.2	- 54.3
1	3	5	0.0	- 12.3
1	3	6	0.0	8.2
1	3	7	0.0	- 3.7
1	3	8	19.2	19.4
1	3	9	0.0	9.0
1	3	10	29.9	- 23.4
1	3	11	0.0	- 7.1
1	3	12	25.3	17.5
1	3	13	0.0	4.6
1	4	1	6.1	- 11.9
1	4	2	0.0	3.0
1	4	3	43.8	46.5
1	4	4	0.0	- 4.6
1	4	5	87.5	- 71.0
1	4	6	0.0	4.4
1	4	7	67.5	57.3
1	4	8	0.0	- 2.9
1	4	9	29.2	- 27.3
1	4	10	0.0	1.4
1	4	11	0.0	7.9
1	4	12	0.0	- 0.2
1	5	0	90.6	- 89.5
1	5	1	36.8	41.3
1	5	2	60.6	62.6
1	5	3	17.7	- 22.1
1	5	4	18.4	- 21.1
1	5	5	0.0	6.3
1	5	6	0.0	3.1
1	5	7	0.0	1.2
1	5	8	0.0	6.0
1	5	9	0.0	- 6.5
1	5	10	15.4	- 15.3
1	5	11	0.0	8.8
1	5	12	16.9	16.0
1	6	1	8.4	- 13.3

h	k	l	F OBS	F CALC
1	6	2	23.8	25.0
1	6	3	21.5	28.3
1	6	4	31.5	- 35.3
1	6	5	26.9	- 26.7
1	6	6	31.5	32.4
1	6	7	20.7	21.1
1	6	8	20.7	- 22.9
1	6	9	10.7	- 14.3
1	6	10	0.0	11.6
1	6	11	20.0	5.9
1	7	0	13.0	- 16.0
1	7	1	58.3	53.7
1	7	2	9.2	12.0
1	7	3	29.9	- 31.3
1	7	4	0.0	- 4.8
1	7	5	10.0	10.0
1	7	6	0.0	0.7
1	7	7	0.0	2.3
1	7	8	0.0	1.6
1	7	9	14.6	- 10.0
1	8	1	0.0	1.8
1	8	2	17.7	10.8
1	8	3	0.0	- 3.9
1	8	4	29.2	- 27.3
1	8	5	0.0	4.1
1	8	6	33.8	32.7
1	8	7	0.0	- 3.3
1	8	8	25.3	- 20.4
1	8	9	0.0	2.2
1	9	0	18.4	17.5
1	9	1	26.1	24.6
1	9	2	15.4	- 14.3
1	9	3	18.4	- 19.7
1	10	1	0.0	3.6
1	10	2	0.0	4.9
1	10	3	0.0	- 10.7
1	10	4	0.0	- 9.2
1	10	5	17.7	14.9
1	11	0	20.0	20.3
1	11	1	0.0	4.4
1	11	2	16.9	- 14.9
2	0	2	115.8	107.4
2	0	4	36.7	- 39.2
2	0	6	19.3	5.7
2	0	8	0.0	11.0
2	1	1	23.2	- 25.5
2	1	2	15.4	20.7
2	1	3	59.8	65.0
2	1	4	30.9	- 32.2
2	1	5	71.4	- 75.1
2	1	6	19.3	30.3
2	1	7	59.8	58.2

h	k	l	F OBS	F CALC
2	1	8	0.0	- 19.6
2	2	0	77.2	- 79.2
2	2	1	81.0	82.4
2	2	2	48.2	66.4
2	2	3	48.2	55.7
2	2	4	28.9	35.8
2	2	5	0.0	20.5
2	2	6	0.0	5.4
2	2	7	0.0	5.5
2	2	8	0.0	12.3
2	3	1	0.0	- 3.1
2	3	2	30.9	28.0
2	3	3	0.0	15.4
2	3	4	61.7	63.5
2	3	5	0.0	25.9
2	3	6	73.3	69.8
2	3	7	0.0	21.2
2	3	8	25.1	42.4
2	4	0	0.0	7.4
2	4	1	100.3	89.8
2	4	2	0.0	5.6
2	4	3	63.7	59.0
2	4	4	0.0	2.4
2	4	5	0.0	21.3
2	4	6	0.0	- 0.3
2	4	7	0.0	5.7
2	4	8	0.0	- 0.7
2	5	1	0.0	8.0
2	5	2	34.7	31.0
2	5	3	34.7	20.4
2	5	4	48.2	45.6
2	5	5	23.2	24.7
2	5	6	48.2	42.5
2	5	7	0.0	19.8
2	5	8	25.1	29.3
2	6	0	59.8	56.0
2	6	1	42.4	43.2
2	6	2	44.4	41.8
2	6	3	0.0	22.1
2	6	4	0.0	17.4
2	6	5	0.0	5.8
2	6	6	0.0	2.5
2	6	7	0.0	0.8
2	6	8	0.0	5.4
2	7	1	0.0	10.1
2	7	2	0.0	5.6
2	7	3	0.0	27.5
2	7	4	0.0	8.9
2	7	5	25.1	34.9
2	7	6	0.0	8.8
2	7	7	0.0	28.6

h	k	l	F OBS	F CALC
2	7	8	0.0	- 6.0
2	8	0	50.2	- 38.6
2	8	1	0.0	- 6.1
2	8	2	44.4	- 33.0
2	8	3	0.0	- 3.4
2	8	4	0.0	- 18.9
2	8	5	0.0	- 0.8
2	8	6	0.0	- 2.9
2	8	7	0.0	- 0.1
2	8	8	0.0	- 7.1
2	10	0	0.0	- 13.4
3	0	2	24.3	- 23.8
3	0	4	38.3	- 35.4
3	0	6	31.3	- 33.8
3	1	0	19.1	- 23.0
3	1	1	48.7	- 49.4
3	1	2	0.0	- 17.3
3	1	3	31.3	- 28.1
3	1	4	0.0	- 7.6
3	1	5	0.0	- 8.7
3	1	6	0.0	- 1.1
3	2	1	0.0	- 5.3
3	2	2	0.0	- 10.3
3	2	3	0.0	- 17.9
3	2	4	0.0	- 21.9
3	2	5	0.0	- 26.9
3	2	6	0.0	- 24.8
3	2	0	43.5	- 41.9
3	2	1	0.0	- 13.8
3	2	2	41.7	- 35.6
3	2	3	0.0	- 10.3
3	2	4	0.0	- 20.2
3	2	5	0.0	- 4.3
3	2	6	0.0	- 3.1
3	2	1	0.0	- 6.5
3	2	2	0.0	- 1.1
3	2	3	0.0	- 20.8
3	2	4	0.0	- 2.0
3	2	5	0.0	- 30.2
3	2	6	0.0	- 1.9
3	0	0	36.5	- 35.3
3	0	1	0.0	- 16.8
3	0	2	19.1	- 26.4
3	0	3	0.0	- 10.0
3	0	4	0.0	- 11.1
3	0	5	0.0	- 3.1
3	0	6	0.0	- 1.6

(b) Structure factor agreement.

No. of reflections included
in refinement.

	Observed	Unobserved	R (ordered structure)	R (approximation to final dis- ordered structure)
0k1	116	18	0.125	0.125
1k1	69	36	0.132	0.132
2k1	34	37	0.130	0.130
3k1	10	26	0.103	0.090
hk1	229	117	0.122	0.119

Thus, as a result of these peculiarities in the three-dimensional electron-density distribution, the structure of trimethyltin fluoride is not uniquely defined and must be best interpreted from these maps. A difficulty arises in a structure consisting of linear polymers, as each chain may assume an independent configuration. The electron-densities are not, therefore, specific for a particular position of any one atom but are a summation of all positions of that atom.

For trimethyltin fluoride, a projection on the ab plane for a single chain will give a complete diagram (Fig.5) in which all possible positions of C_2 , C_3 and F are evident.

Since the compound has a very high melting point (360°C), it is assumed that the apparent disorders do not result from atomic vibrations at room temperature, but rather from superposition of the electron-densities of two or more types of chains. In any systematic structure, the four fluorine positions F_a , F'_a , F_b and F'_b must be reduced in an individual chain to either F_a and F'_a or F_b and F'_b , and the five carbon positions to a planar or non-planar trigonal configuration for the three carbon atoms. Since it is highly improbable that both trigonal planar and trigonal non-planar arrangements occur in the compound, two crystal structures become plausible.

In the trigonal non-planar case, both carbon atoms (C_2 and C_3) are displaced from the plane $x = \frac{1}{4}$ in the direction opposite to the tin fluorine bond, and the fluorine atom is completely disordered occupying either a primed or unprimed position. Then, the composite electron density distribution may be completed using two chains (Fig.6) differing only in

A PROJECTION OF ALL POSSIBLE ATOMIC POSITIONS ON ab PLANE

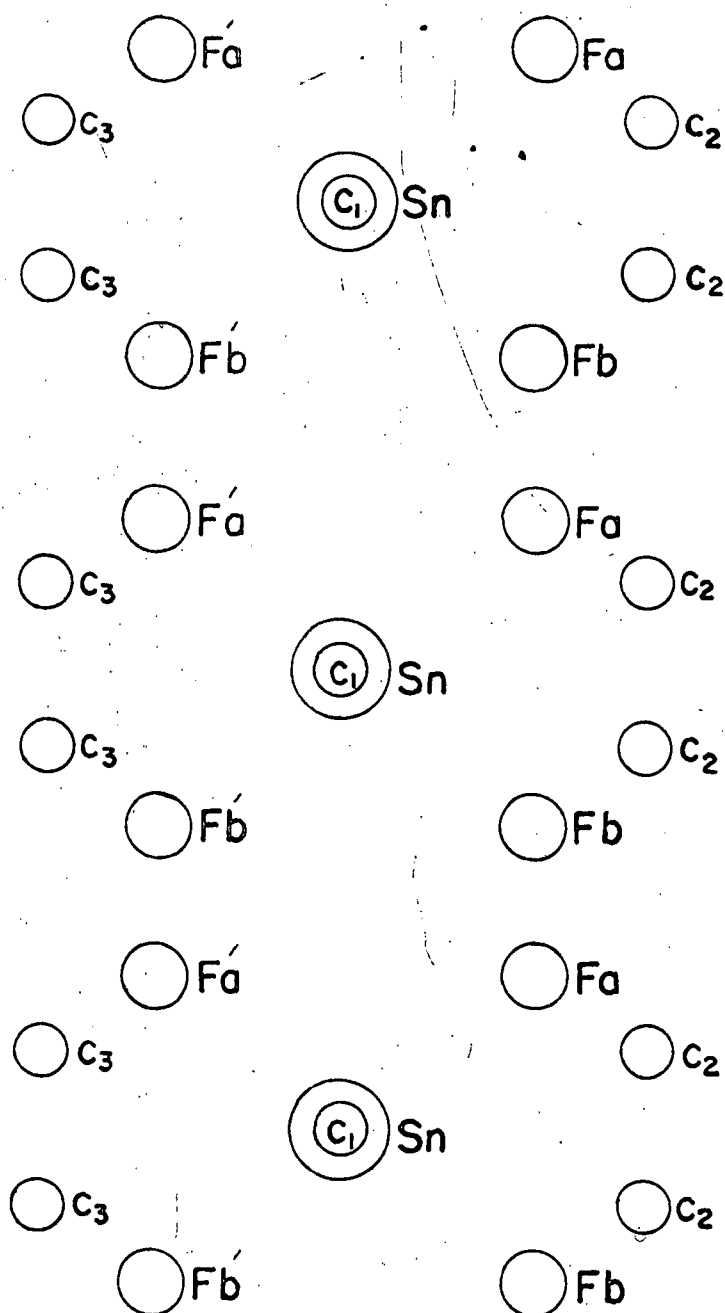


FIGURE 5

FIRST POSSIBLE STRUCTURE OF TRIMETHYLTIN FLUORIDE

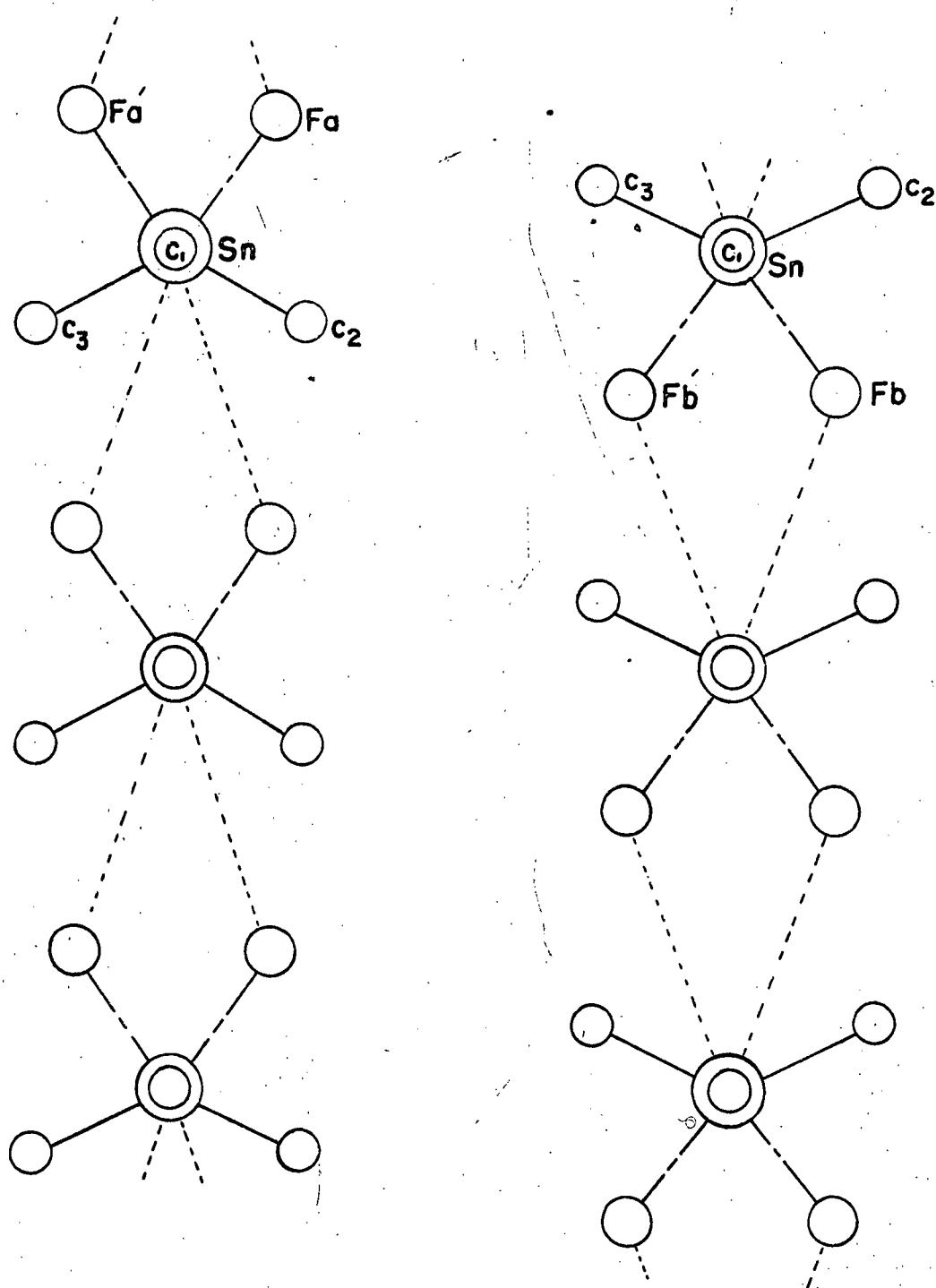


FIGURE 6

Fa or Fb fluorine atom positions.

The lack of planarity of the trimethyltin group is supported by the observance of the previously unreported symmetric Sn - C stretching vibration at $500-515\text{cm}^{-1}$ in the infrared spectrum of Me_3SnF in very concentrated nujol mulls. Alternatively, however, there remains the possibility that this is a forbidden transition of low intensity.

The second structure assuming planarity of the Me_3Sn group should require the fluorine atom to occupy positions which will give the five co-ordinated tin atoms a distorted trigonal bipyramidal configuration. Again, only one type of fluorine position (a or b) may be used in any one chain, but now because of alternate primed and unprimed occupation, any one fluorine atom need not be considered disordered between two positions. The two chains necessary for the composite electron-density are shown in Fig. 7.

Although in any one chain the repeat distance is twice the cell length, the entire crystal will have the recorded a axis because of its composite character. It will be noted that in both structures one chain may be converted into the second by inversion of the entire chain.

Of the two possibilities, the latter is preferred if only for the fact that the fluorine atoms are not disordered. However, independent of the form preferred, it is very conclusively shown that trimethyltin fluoride is not a purely ionic solid.

SECOND POSSIBLE STRUCTURE OF TRIMETHYLTIN FLUORIDE

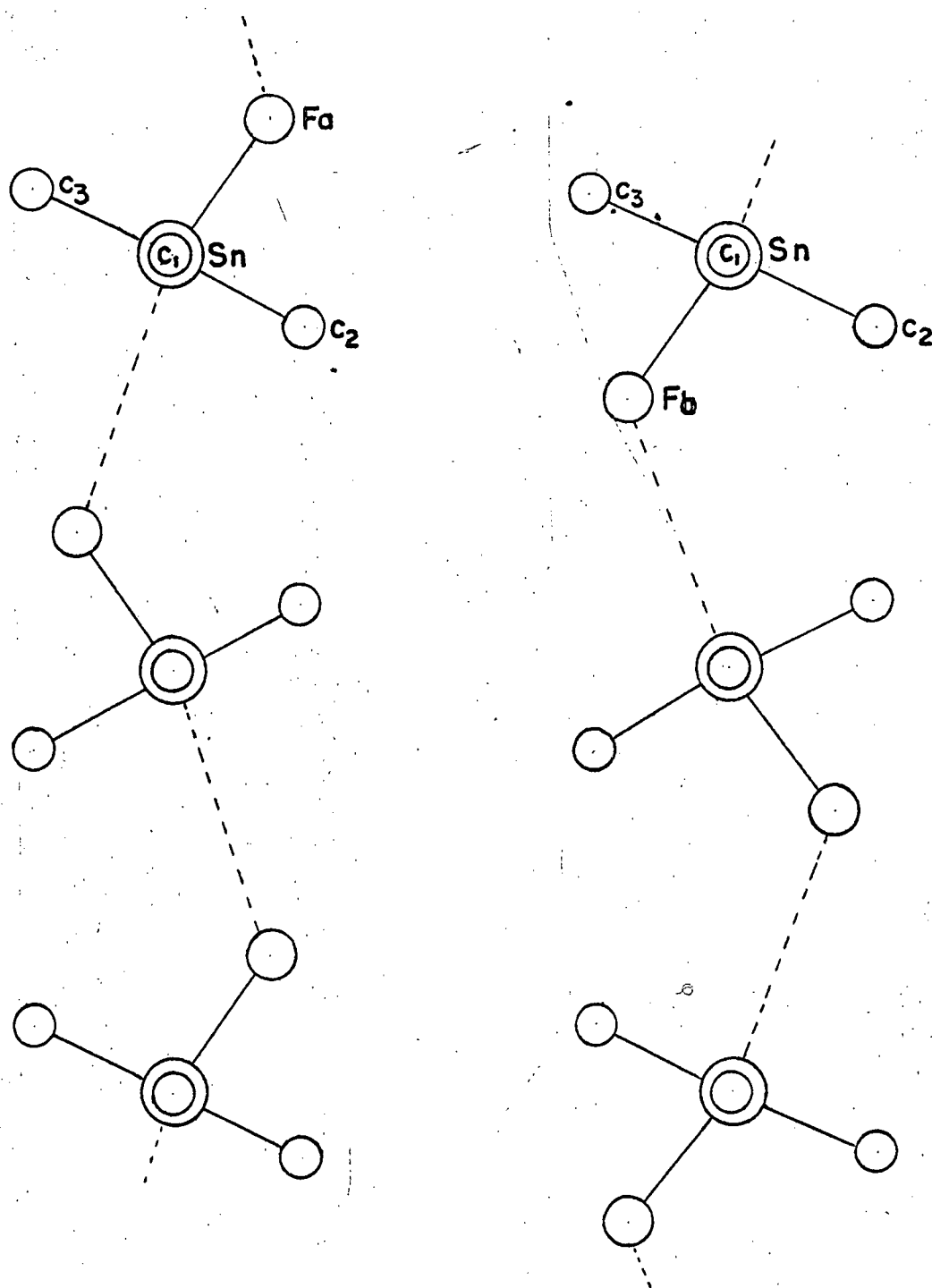


FIGURE 7

If ionic species were present, the fluorine ion would be expected to lie mid-way on the axis between two tin atoms, and the planar trimethyltin cation would be expected to lie parallel to some crystal plane. None of these requirements are found. In fact, the non-linear, non-equidistant Sn-F.....Sn arrangement is a definite indication of some covalent interaction.

The chemical and physical properties of trimethyltin fluoride are consistent with a polymeric chain structure. Its high melting point, low solubility in organic solvents, and only moderate solubility in hydrolytic solvents are a result of the inherently high lattice energy.

Evidence that trimethyltin fluoride can exist in a discrete form is suggested from the fact that if anhydrous potassium fluoride and trimethyltin bromide are heated together to 170°C a white sublimate is evolved which analyses as $C_3H_9Sn F$. It is possible that this species results from the decomposition of a complex fluoride, possibly $KMe_3 Sn F_2$. The fact that the solid condensate cannot be resublimed after it has stood for some time may be due to the formation of a chain polymer.

CHAPTER 3:

INTRODUCTION TO THE INFRA-RED STUDY OF TRIMETHYLTIN DERIVATIVES

The tetra organo-tin compounds and their halogen derivatives have been thoroughly studied by infra-red spectroscopy (78, 79, 80). As these papers were mainly concerned with establishing the positions of the fundamental vibrations for a four co-ordinate, tetrahedral configuration, little doubt exists in the assignment of the spectra for methyl-tin compounds, and their characteristic frequencies are given below.

3000 cm ⁻¹	C-H asym. [⊕] str.
2900 "	C-H sym. str.
1410 "	CH ₃ asym. def.
1220 "	CH ₃ sym. def.
780 "	CH ₃ rocking
550 "	Sn-C asym. str.
520 "	Sn-C sym. str.

[⊕] asym., asymmetric; sym., symmetric; str. stretching; def., deformation.

Okawara (1) had unsuccessfully attempted to deduce the stereochemistry of some compounds containing the trimethyltin group on the basis of the presence or absence of the Sn-C sym. stretching mode, but the difficulties encountered by these authors can be traced to their inappropriate selection of compounds. For a compound Me₃ Sn X, where X is a singly charged

anionic group, three possible configurations can be postulated: one composed of discrete ions, the discrete molecular structure, and a linear polymeric structure. If ions exist, the three methyl groups will be planar, inactivating the Sn-C symmetric stretching mode in the infra-red, and the anionic portion of the spectra should indicate that the highly symmetrical form of X exists. In the second case, when the solid contains discrete molecules, there are two possible co-ordination numbers for the tin atom.

A four co-ordinate tetrahedral arrangement about the tin atom will now activate the Sn - C symmetric stretching fundamental, and the infra-red spectrum for the monodentate ligand, X, should be observed. On the other hand, five co-ordination would require the ligand, X, to act as a bidentate group resulting in two more configurations. The two co-ordination sites can either be both in the trigonal plane, or one in the trigonal and the other in the apical position.

Although a bidentate ligand is possible, the more probable configuration for five co-ordination is a polymeric one in which X behaves as a bridging group, e.g. trimethyltin fluoride. In such cases, the trimethyltin group will be planar as in a purely ionic configuration, but the spectrum of the anionic portion should now indicate that a bridging ligand, X, is present.

Okawara unfortunately attempted to determine the configuration of trimethyltin acetate and trimethyltin formate solely on the basis of their infra-red spectra (1). The very low symmetry of these anionic groups will not permit a distinction to be made between the free ion, and the bridging ligand (45). Final conclusions regarding the stereochemistry of any compound rests in a definitive analysis of the anionic portion of the spectrum.

In the above work, trimethyltin bromide and trimethyltin chloride were selected as typical tetrahedral compounds. In these two derivatives, the asymmetric Sn-C stretching mode is about five times more intense than that of the Sn - C symmetric fundamental. In view of the possibility of Sn - hal. - Sn bridging and of any other extraneous effects on the spectra, the spectrum of Me_3SnCF_3 was studied in the gas phase. The observed relative intensities of these two bands were the same as the bromide (liq.). Thus the appearance of a bond of only medium intensity in the $500 - 530\text{ cm}^{-1}$ region will signify a tetrahedral configuration. Moreover, as this bond is not very intense, the second order distortions possible in the solid phase should not give rise to a significant absorption.

In many inorganic compounds, establishing the distinction between absorptions caused by distortion of the anion by crystal field effects (81) from those caused by covalent interaction is the major spectroscopic problem. Co-ordination will usually

cause both the appearance of new bands and splitting of the degenerate modes as well as shifts in frequency of the bands already present in the spectrum of the free ion. Of these three phenomena, only the first two are of any aid in interpretation. Although the appearance of new bands, i.e. activation of infra-red fundamentals, is the most significant, as splitting of the degenerate modes can arise from other sources (81), the accurate assignment of absorptions resulting from both phenomena should be regarded as giving the highest credibility possible for an infra-red study.

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. The probability of a spurious effect occurring in six or more derivatives, however, is exceedingly slight. Consequently, the validity of the data used for the description of any one compound should be evaluated only after inspection of all the related compounds.

CHAPTER 4:

TRIMETHYLTIN NITRATE.

Although the theoretically predicted fundamentals (82) for the free nitrate ion (D_{3h}) and the nitrate ligand (C_{2v}), as given below, do not seem to be contested in the literature, their application in specific cases has been questioned (83).

Nitrate ion (D_{3h}) :- NO_3

ν_3	1390 cm^{-1}	NO_2 asym. str.
ν_1^*	1050 "	NO_2 sym. str.
ν_2	831 "	out of plane vibration
ν_4	720 "	NO_2 bend.

*not infra-red active.

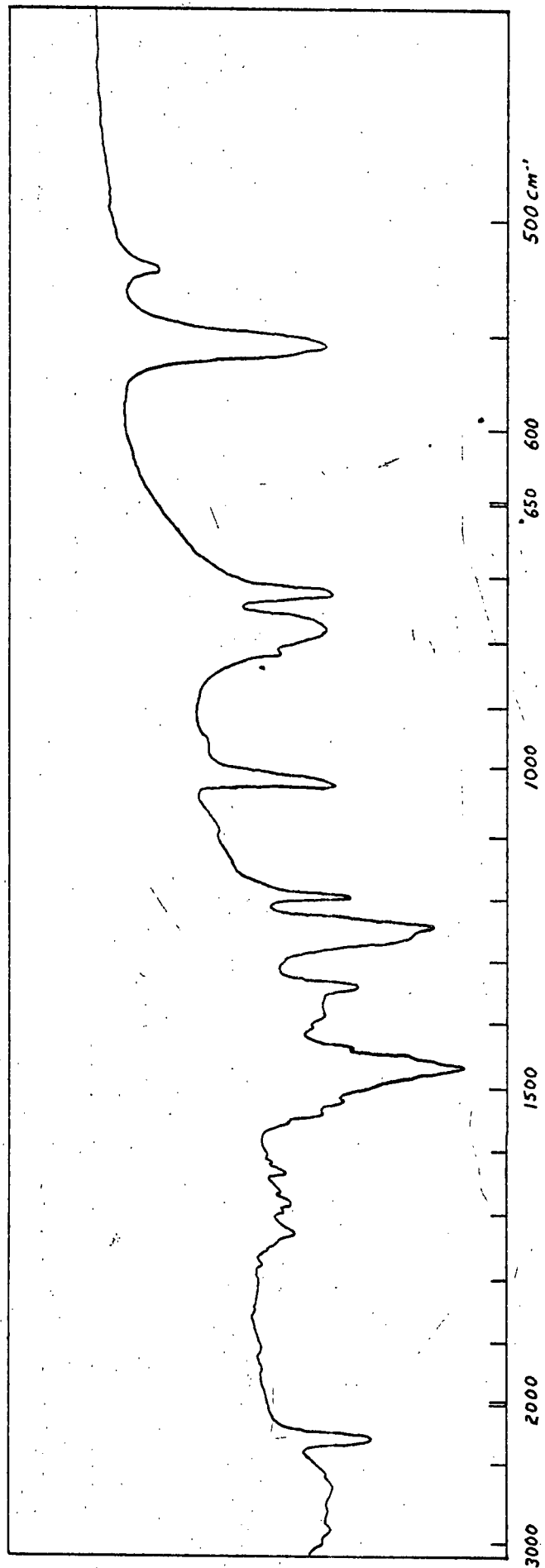
Nitrate ligand (C_{2v}) :- $-O^*-NO_2$

ν_4	1530 - 1481 cm^{-1}	NO_2 asym. str.
ν_1	1290 - 1253 "	NO_2 sym. str.
ν_2	1030 - 970 "	NO^* str.
ν_6	800 - 780 "	out of plane vibration
ν_3	739	NO_2 asym. bend.
ν_5	713	NO_2 sym. bend.

This controversy arises from the fact that no criterion has been established to separate distortion effects from covalent interactions. Buijs (83) has extended to the nitrate ion Halford's concept (84) that the symmetry of the lattice site affects the symmetry of the ion.

Although this principle seems sound, this predicted activation of infra-red fundamentals into significant absorptions is not found in practice. Ferraro (85) approaches the problem in a different manner and makes no statement concerning the reason for the lowering of the symmetry from D_{3h} to C_{2v} . The spectra are simply tabulated according to the charge on the cation, and the symmetry assigned on the extent of splitting of the ν_3 nitrate band, i.e. $\nu_4 - \nu_1$. However, Katzen (86) found some splitting of this band in all inorganic nitrates he investigated with the exception of KNO_3 and $NaNO_3$. Thus, it is somewhat difficult to justify the use of $\Delta = \nu_4 - \nu_1$ as a criterion for covalent interactions. Gatehouse, Livingstone and Nyholm (87) in their investigation of nitrate complexes of cobalt, nickel, palladium, and platinum, tested the criterion that activation of the "forbidden transition" ν_1 to a major absorption could be used to designate covalent interaction and found it completely applicable. Addison and Gatehouse (88) recorded this band as a strong absorption for the four compounds they considered covalent, $(Mn(NO_3)_2, Cu(NO_3)_2, Zn(NO_3)_2$ and $Hg(NO_3)_2$), but do not stress this principle.

The nitrate studied in this work was the anhydrous trimethyltin nitrate and its spectrum is shown in Fig. 8. The bands arising from the Me_3Sn portion (Table 3) of the molecule; 3000, 2900, 780 and 557 cm^{-1} , are given the same assignment as those previously described, although it is clear that the 780 cm^{-1} band is overlapped by at least one absorption at 825 cm^{-1} and possibly another.



THE INFRA-RED SPECTRUM OF TRIMETHYLTIN NITRATE

FIGURE 8

TABLE 3.

Infra-red assignments for Trimethyltin Nitrate.

3000 (W)	[⊗] cm ⁻¹)	C - H str.
2900 (W))	
1488 (S)	asym. str. of NO ₂	
1355 (M)	asym. def. of CH ₃	
1268 (S)	sym. str. of NO ₂	
1208 (M)	sym. def. of CH ₃	
1031 (M)	str. of NO*	
825 (M)	out of plane def. of NO ₃	
780 (S)	rocking mode of CH ₃	
727 (M)	bending mode of NO ₂	
557 (M)	asym. str. of Sn-C	
520 (W)	sym. str. Sn-C	

* W, weak; M, medium; S, strong.

The band at 520 cm^{-1} is, as before, assigned to Sn-C symmetric stretch, this band approaches in intensity a similar one in trimethyltin chloride (1). As a result, the $(\text{CH}_3)_3\text{Sn}$ group cannot be considered planar.

The absorptions attributed to the nitrate group, of which only the strong and medium bands are recorded, are consistent with the presence of a nitrate group of C_{2v} symmetry. Hence, the strong band at 1488 cm^{-1} is assigned to the NO_2 asymmetric stretch. (ν_4), the split maxima at 1268 cm^{-1} to the NO_2 symmetric stretch. (ν_1), and the band at 1031 cm^{-1} to the NO^* stretch. (ν_2). The out of plane vibration usually observed in the $800\text{--}781\text{ cm}^{-1}$ region is either overlapped by the 780 cm^{-1} band due to the CH_3 rocking, or less likely is observed as the 825 cm^{-1} band. The NO_2 symmetric and asymmetric bending vibrations do not seem to be resolved and probably appear as the 727 cm^{-1} band.

The infra-red spectrum therefore indicates that trimethyltin nitrate is a largely covalent, and presumably monomeric substance, containing a nitrate group. It must, however, be pointed out that both a monodentate $-\text{O}^*-\text{NO}_2$ group and a bidentate $\begin{array}{c} -\text{O}^* \\ \diagdown \\ \text{N}-\text{O} \\ \diagup \\ -\text{O}^* \end{array}$ group have essentially the same symmetry and could well give similar spectra. However, the relative intensities of the bands due to NO stretching and NO^* stretching vibrations would probably be reversed for a bidentate NO_3 group.

The uncertainty noted above concerning the co-ordination of the nitrate ligand cannot occur in nitratopentacarbonylmanganese (I) where a six co-ordinate metal atom is present. Consequently, the spectrum recorded by Addison, et. al. (89), ($\nu_4=1486\text{ cm}^{-1}$, $\nu_3=1010\text{ cm}^{-1}$ and $\nu_6=805\text{ cm}^{-1}$) which is in close agreement with that found for anhydrous trimethyltin nitrate, lends further credibility to the existence of the nitrate ligand. In addition, basic beryllium nitrate (90), which contains a bidentate nitrate group, gives an infra-red spectrum appreciably different from the manganese derivative (91).

The physical properties of trimethyltin nitrate give some information concerning its inter-molecular association. The compound sublimes at 100° in vacuo. As with many organic compounds, the crystals of the anhydrous nitrate can be easily deformed without fracture indicating that only weak van der Waals forces exist between molecules. These properties are in contrast to the hard brittle crystals of trimethyltin fluoride. However, the relatively high melting point (123°C) of the nitrate as well as its low solubility in organic solvents are properties which are not completely consistent with the presence of discrete molecules.

The characterization of trimethyltin nitrate completes the series ($\text{R}_3\text{M}-\text{NO}_3$) for Group IVb, and it is of interest to record the trends in their physical properties. Tert-butyl nitrate (92) is a low boiling liquid which is very unstable and decomposes upon distillation. Similarly, trimethylsilyl nitrate

(93) decomposes at room temperature to NO_2 , O_2 and $(\text{Me}_3\text{Si})_2\text{O}$ even in the absence of moisture. The third member, trimethylgermanium nitrate (94, 95) is also a liquid, but increased thermal stability renders the compound stable under normal conditions in the absence of moisture. Trimethyltin nitrate, as already seen, is a white sublimable solid which is not readily attacked by moisture. The properties of trimethyllead nitrate have not been extensively studied (96), but interpretation of reported properties indicate that it can be recrystallized from an aqueous alcohol solution. Thus, although the thermal and hydrolytic stabilities increase as the molecular weight of the compound increases, there is a marked difference in physical properties between the first three members and the last two. No completely adequate explanation for this fact is at present available.

CHAPTER 5:

TRIMETHYLTIN PERCHLORATE.

Because the symmetry of the tetrahedral perchlorate ion (T_d) is much higher than that of the trigonal planar nitrate group (D_{3h}), any interaction with the oxygen atoms will have a more marked influence on the infra-red spectrum. As a result, Hathaway (97) was able to establish the constitution of $Cu(ClO_4)_2$ and the hydrates of transition metal perchlorates by a careful inspection of the major absorption bands in their spectra. His correlation diagram is recorded in table 4.

The simple perchlorate ion of regular tetrahedral structure has nine vibrational degrees of freedom giving four infra-red fundamental frequencies. Of these only two will be infra-red active, ν_3 and ν_4 . The former (ν_3) is observed in solid ionic perchlorates as a broad strong band, usually split, in the $1050 - 1150 \text{ cm}^{-1}$ region, while ν_4 is observed at approximately 630 cm^{-1} .

The breathing frequency ν_1 which is theoretically infra-red inactive is usually observed as a very weak absorption at 930 cm^{-1} . Aqueous solutions of ionic perchlorates give, in their infra-red spectra, one band each for ν_3 and ν_4 , and ν_1 is not observed (98).

In the case of anhydrous trimethyltin perchlorate, the infra-red spectrum (Fig.9a, Table 5) shows considerable structure between $900 - 1225 \text{ cm}^{-1}$ which is markedly different

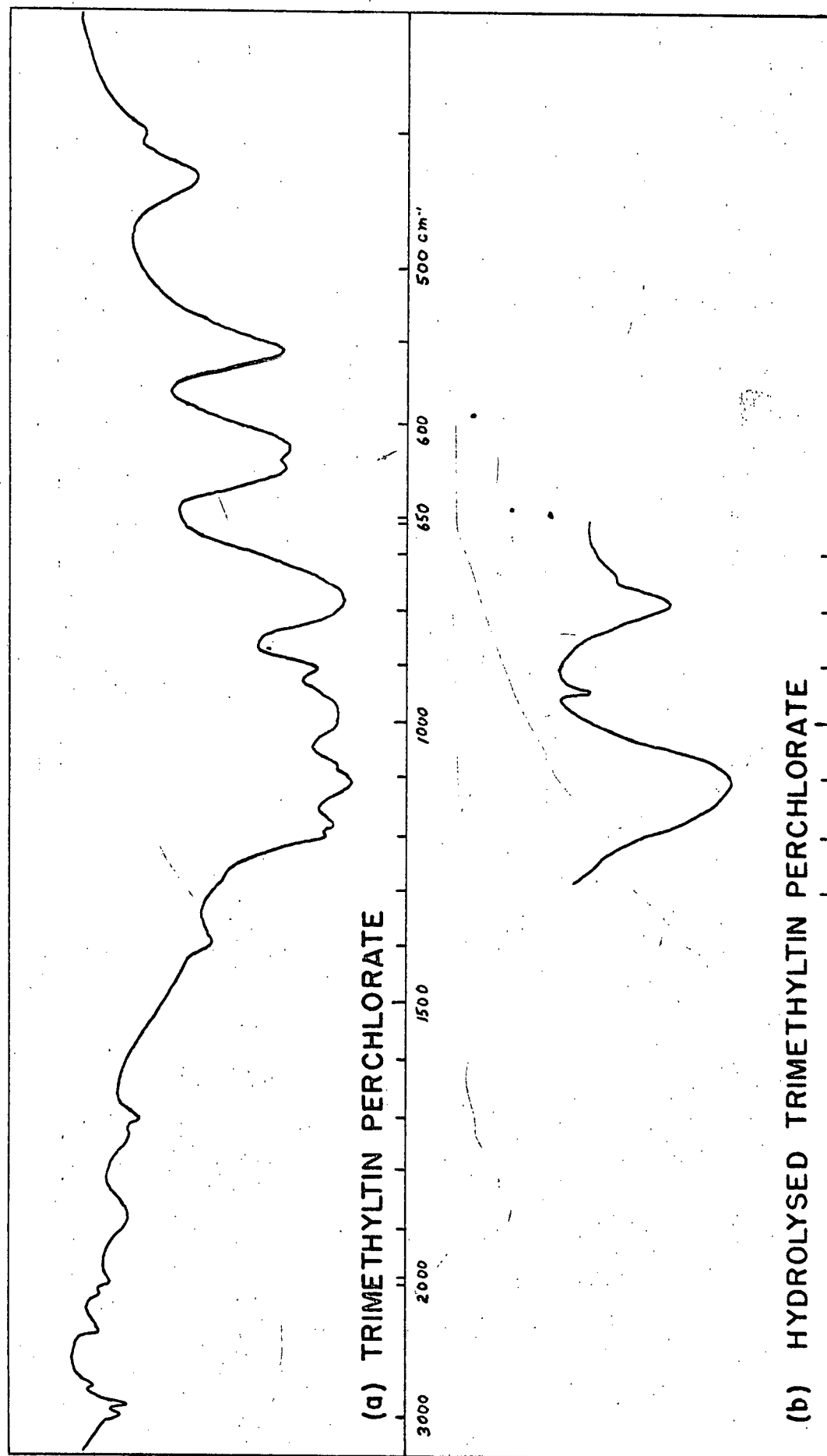
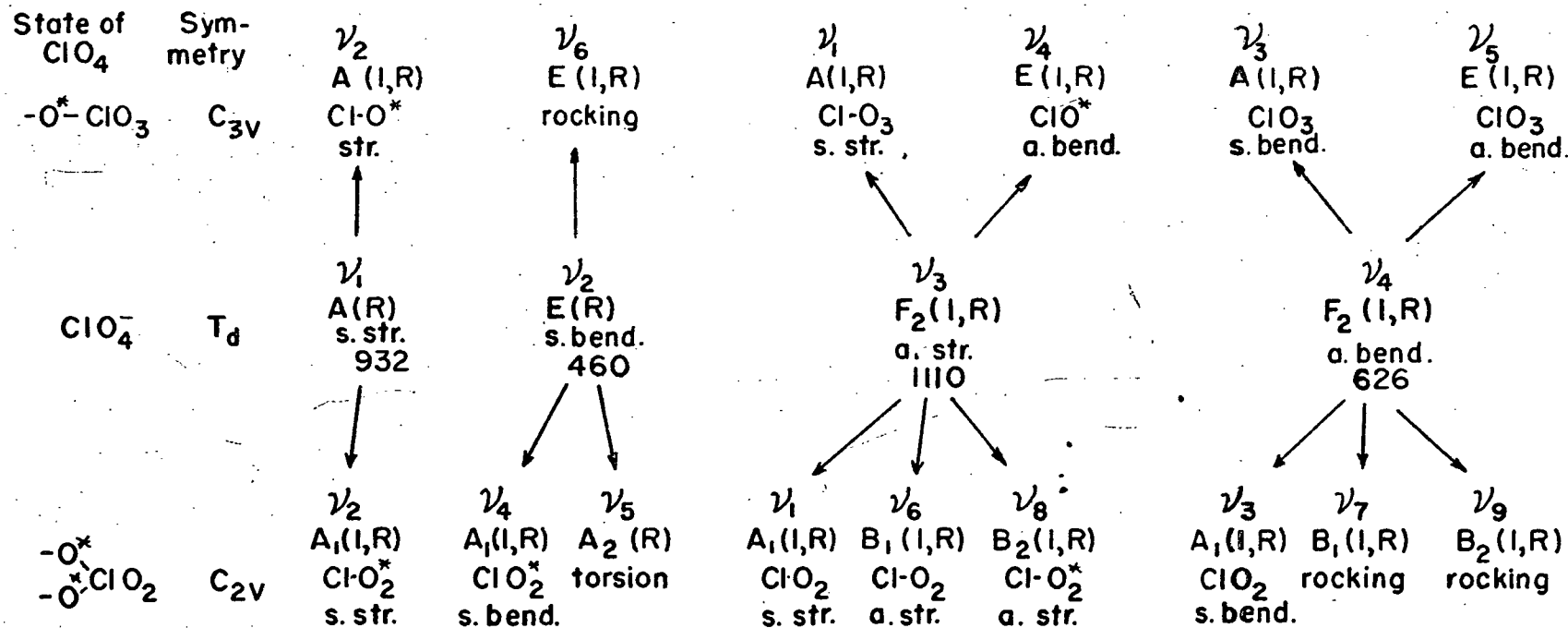


FIGURE 9

A CORRELATION DIAGRAM FOR THE PERCHLORATE GROUP



A and B, non-degenerate. E, doubly degenerate. F, triply degenerate. I, infra-red active. R, Raman active. s., symmetric. a., antisymmetric. O*, oxygen co-ordinated to tin.

TABLE 4

TABLE 5.

Infra-red assignments for trimethyltin perchlorate.

3000 cm^{-1}	(W)	}	C - H str.
2910	(W)		
1405	(M)		CH_3 asym. def.
1212	(S)		CH_3 sym. def.
1192	(S)		ClO_2^* asym. str.
1112	(S)		ClO_2 asym. str.
1078	(W, Sh)		?
998	(S)		ClO_2 sym. str.
908	(S)		ClO_2^* sym. str.
780	(S)		CH_3 rocking.
625	(M)		ClO_2 sym. bend.
606	(M)		ClO_4 rock.
552	(M)		Sn - C asym. str.
468	(M)		ClO_4 rock.
450	(W)		ClO_2^* sym. bend.

from that observed for solid ionic perchlorates. After brief exposure to moist air, however, the compound gives a spectrum (Fig.9b) with absorption maxima at 1095 (s) and 940 (V.W.) cm^{-1} , characteristic of ionic perchlorates. Hydrolysis therefore must produce the free ClO_4^- ion.

The absorptions arising from the trimethyltin group are readily separated from those of the perchlorate. The two weak bands at 3000 and 2910 cm^{-1} are assigned to the C-H stretching of the CH_3 group, and the medium intensity band at 1405 cm^{-1} to the methyl asymmetric deformation mode in accordance with previous assignments (78). The strong band at 780 cm^{-1} is characteristic of the Sn-CH_3 rocking mode. In the 500-560 cm^{-1} region only one band at 552 cm^{-1} is observed, although with a nujol mull of very high concentration an extremely weak band at approximately 515 cm^{-1} can also be noted. The observation of only one infra-red active band in this region is consistent with a planar Me_3Sn group, the 552 cm^{-1} band being assigned therefore to the Sn-C asymmetric stretching vibration. The very weak band at 515 cm^{-1} may be due to a forbidden transition, or it may indicate a slight departure from planarity of the Me_3Sn group. Thus, the perchlorate portion of the molecule must be examined to determine the stereochemistry, as two possible configurations exist. Either simple ions are present, or a bridging perchlorate ligand exists, together with a five co-ordinate tin atom.

Hathaway and Underhill (97) have pointed out that as the perchlorate group becomes involved in partial covalent banding, its symmetry is lowered from T_d to C_{3v} or C_{2v} according to whether one or two of its oxygen atoms are involved in such bonding. The spectra of anhydrous transition metal perchlorate show strong absorptions at 1270-1245, 1130 and 948 - 920 cm^{-1} and a weaker one at 1030 cm^{-1} ; the conclusion is drawn that the perchlorate groups are acting as bidentate ligands and so have C_{2v} symmetry. Although there is a general shift of 30 - 40 cm^{-1} to lower frequencies, the spectrum of trimethyltin perchlorate in the 900 - 1225 cm^{-1} region is very similar to those of anhydrous transition metal perchlorates, and is different from the spectra of lower hydrates of the latter compounds in which the ClO_4 group is considered to behave as a monodentate co-ordinating group.

From a comparison with $\text{Cu}(\text{ClO}_4)_2$, the following assignments are suggested. The broad peak with maxima at 1212 cm^{-1} and 1192 cm^{-1} is assigned as ν_6 , the ClO_2^* asymmetric stretching frequency. However, it should also be noted that either the 1212 or the 1192 cm^{-1} band can be assigned as the symmetrical deformation mode of CH_3 . The 1112 cm^{-1} absorption is assigned as the ClO_2 asymmetric stretching frequency ν'_3 . The 998 cm^{-1} peak which has the same intensity as the 1112 cm^{-1} band, is matched with the unexpectedly weak 1030 cm^{-1} band in $\text{Cu}(\text{ClO}_4)_2$ and is assigned as the ClO_2 symmetric stretching frequency ν_1 . Finally the 908 cm^{-1} peak, like the 948-920 cm^{-1}

peak in $\text{Cu}(\text{ClO}_4)_2$ is assigned as the ClO_2^* symmetric stretching frequency ν_2 . Using the criterion established for the nitrate group, i.e. activation of forbidden transition, in this case ν_2 , the perchlorate is not present as an ion but as a co-ordinating ligand. The symmetry of the ligand should be C_{2v} , to be consistent with the spectrum of the trimethyltin group. The three bands ν_1 , ν_6 and ν_3 in the $950\text{--}1250\text{ cm}^{-1}$ region and the ν_2 (902) absorption are in agreement with this interpretation.

Further support for C_{2v} symmetry is found in the $350\text{--}650\text{ cm}^{-1}$ region. Ionic perchlorate shows one band (ν_4) at 630 cm^{-1} , which for solid ionic perchlorate may display fine structure (98). For a bidentate or bridging ClO_4 group, four bands would be expected theoretically in this region. Anhydrous copper perchlorate shows six peaks so some distortion must be involved. Trimethyltin perchlorate shows the expected four bands in this region, at 625, 606, 468, and 450 cm^{-1} . By analogy with $\text{Cu}(\text{ClO}_4)_2$ the 625 cm^{-1} peak is tentatively assigned to the ClO_2 symmetrical bending mode ν_8 , the 606 cm^{-1} band to rocking frequency ν_9 , and the weak band at 450 cm^{-1} , observed as a shoulder, to the ClO_2^* symmetrical bending frequency ν_4 .

Ross(98,99) contends that the splittings in the spectra of various perchlorates described by Hathaway and Underhill in earlier papers (100, 101) are attributable to crystal field effects rather than to partial covalent bonding. Certainly the splittings of ν_3 and ν_4 and the appearance of the weak ν_1

frequency in the spectra of solid alkali metal perchlorates can be attributed to crystal field effects and are consistent with the observed distortion (102) of the ClO_4 group in crystalline potassium perchlorate. However, the later and more detailed discussion by Hathaway and Underhill (97) clearly shows that the splittings of the infra-red bands of anhydrous transition metal perchlorates are of a considerably greater order of magnitude than those observed for salts such as K ClO_4 . The same can be said for the multiplicity of peaks and the large splittings as well as the activation of ν_2 observed for trimethyltin perchlorate. Moreover, the spectrum of a very concentrated solution of trimethyltin perchlorate in methanol, in which crystal field absorptions can be ignored showed absorption bands at 1175, 1115, 1020 and 912 cm^{-1} .

Hence, in the anhydrous compound, covalent interaction occurs between the $\text{Me}_3\text{ Sn}$ and ClO_4 groups. The $\text{Me}_3\text{ Sn}$ groups are planar, being bridged by ClO_4 ligands.

Reports by Hathaway et. al. (7, 8) in the Proceedings of the Chemical Society concurred with these findings for trimethyltin nitrate and trimethyltin perchlorate, as well as those for trimethyltin tetrafluoroborate given in the next chapter.

The observed physical properties of trimethyltin perchlorate are completely consistent with the above interpretations. It sublimes in vacuo at 120°C to give a colorless crystalline solid. The fact that the compound sublimes near its melting

point (127°) is an indication that the polymeric unit must be thermally disrupted to give a sublimable species. The molecules are then deposited as linear polymers in a narrow band immediately outside the hot zone. In contrast to the nitrate, these have well developed crystal faces, and shatter on the application of stress. However, the major difference is the case of hydrolytic attack. Trimethyltin nitrate is not appreciably hygroscopic, but trimethyltin perchlorate requires rigid dry box conditions to be isolated as the anhydrous compound.

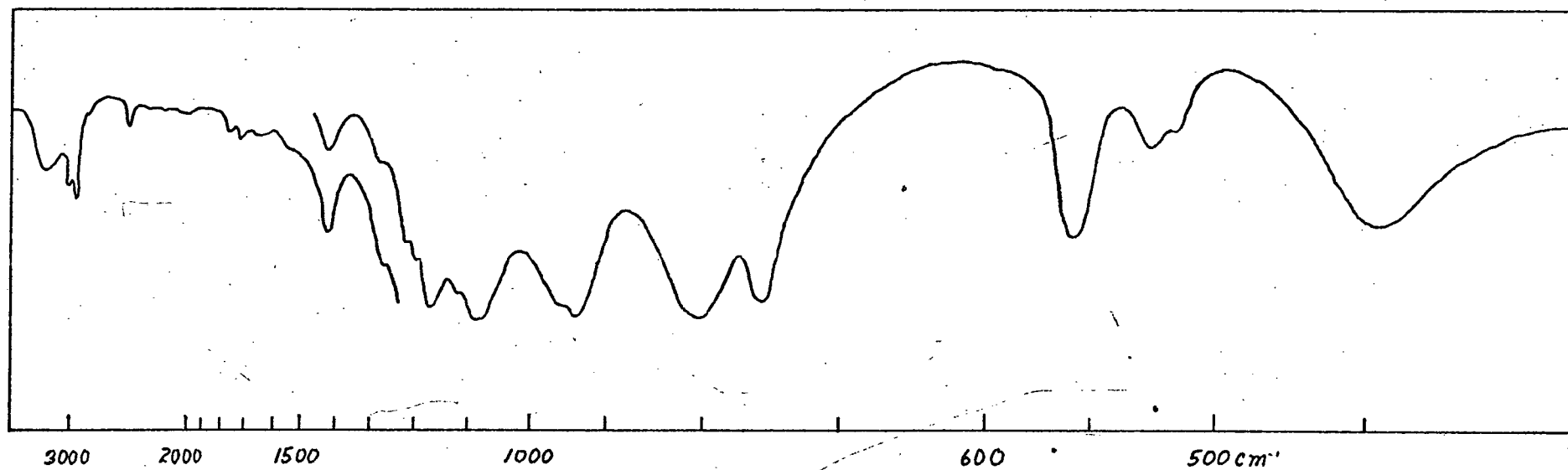
Again, it is interesting to trace the change in physical properties of perchlorate derivatives for members of Group IVb. The alkyl perchlorates (103) are extremely unstable and sensitive to shock. However, under carefully controlled conditions, they may be distilled under reduced pressure. Trimethylsilyl perchlorate (104, 105) is a colorless liquid which fumes in the open air. Although it has greater thermal stability than its carbon analogue, it will detonate upon rapid heating. The reports published for trialkylgermanium perchlorate (106) indicate properties comparable to silicon. As with trimethyltin nitrate, trimethyltin perchlorate is the first solid in the series. Its increased thermal stability may possibly be related to the bidentate nature of the perchlorate ligand. The final member, trimethyllead perchlorate has not been reported, although no serious difficulties should exist in its preparative procedure.

CHAPTER 6:

TRIMETHYLTIN TETRAFLUOROBORATE
AND TRIMETHYLTIN TRIFLUOROMETHYL-
TRIFLUOROBORATE.

Trimethyltin tetrafluoroborate was first reported by Burg (49) as an incidental preparation. The melting point was found to be 87°C and above 100°C decomposition of the product gave borontrifluoride and trimethyltin fluoride. They found no reason not to give this compound an ionic configuration, i.e. $\text{Me}_3\text{Sn}^+ \text{BF}_4^-$. In this work, silver tetrafluoroborate and trimethyltin bromide were reacted in liquid sulfur dioxide. The colorless crystals, obtained upon removal of the solvent from the filtered solution, were extremely hygroscopic and rigid dry box conditions were required to obtain the anhydrous product. This susceptibility to hydrolytic attack is also shown by trimethyltin perchlorate and a close inspection of the spectrum for trimethyltin tetrafluoroborate (Fig. 10), reveals a distinct similarity to that of the perchlorate derivative. The possibility of a similar configuration therefore exists.

As in trimethyltin perchlorate, the portion of the spectrum attributed to the anionic group is markedly altered from that of the free BF_4^- ion (107, 108, 109). The triply degenerate ν_3 (asymmetric B-F stretch) vibration of the ion is clearly resolved into three strong bands at 930, 1070, and 1170 cm^{-1} . Furthermore, the ν_1 fundamental (symmetric B-F



THE INFRA-RED SPECTRUM OF TRIMETHYLTIN TETRAFLUOROBORATE

FIGURE 10

stretch which is infra-red inactive in the symmetrical BF_4^- ion), although it appears as a weak "forbidden" transition at 771 cm^{-1} in the spectra of ionic tetrafluoroborates, is now an intense band at 746 cm^{-1} . The criterion stated earlier for the existence of covalent interaction between the cationic and anionic species, i.e. activation of a forbidden transition, is now applicable. Moreover, the complete removal of the degeneracy of the ν_3 absorption is consistent with a C_{2v} symmetry for the BF_4 group indicating that a bridging ligand may exist.

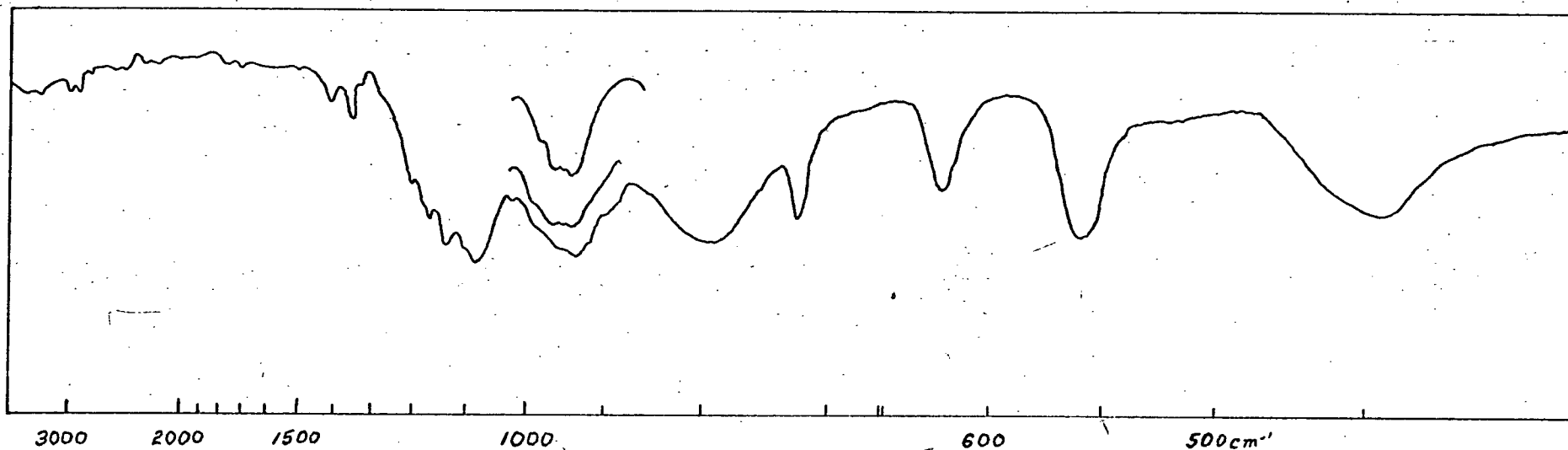
The secondary features of the spectrum in this region ($900 - 1200 \text{ cm}^{-1}$) are also readily explained. There are at least five minor shoulders on the previously mentioned major bands. One of these at approximately 1210 cm^{-1} will be the CH_3 symmetric deformation, while those at 960, 1115 and the second shoulder at 1200 cm^{-1} are probably due to the B^{10}F stretching modes.

In the potassium bromide region ($600 - 400 \text{ cm}^{-1}$), a complete assignment is not possible since some of the fundamental modes may well lie below 400 cm^{-1} . The moderately intense band at 558 cm^{-1} is the Sn - C asymmetric stretching vibration, but it is difficult to determine whether the Sn - C symmetric stretching absorption is also present.

Silver tetrafluoroborate gives a sharp doublet at 526 and 536 cm^{-1} which has been assigned (107) to the asymmetric bending mode (ν_4), the splitting again being due to the two isotopes of

boron. Trimethyltin tetrafluoroborate gives an unresolved band, involving possibly two maxima at approximately 525 and 512 cm^{-1} ; these could arise from splitting of the ν_4 mode, or alternately one at least may be the Sn - C symmetric stretching vibration. The decision regarding the existence of this Sn - C mode will be left until after the discussion of the trimethyltin trifluoromethyltrifluoroborate spectrum. Finally, the band appearing at 446 cm^{-1} can be assigned to one of the bands arising from the removal of the degeneracy of the ν_4 fundamental, and may be either a rocking mode or a symmetrical bending vibration of the BF_4 group with C_{2v} symmetry.

The result concerning the constitution of trimethyltin tetrafluoroborate throws some light on the previous report concerning the preparation of $\text{Me}_3\text{SnCF}_3\text{BF}_3$ (110). This compound which was not prepared in completely anhydrous conditions was formulated as $\text{Me}_3\text{Sn}^+\text{CF}_3\text{BF}_3^-$. However, it seemed likely that, if prepared under absolutely dry conditions, this compound might have a structure similar to that of the anhydrous tetrafluoroborate derivative. This work was therefore repeated and the spectrum (Fig. 11) of the anhydrous product was found to be completely analogous to the parent tetrafluoride. Thus, a bridging CF_3BF_3 ligand is present. Although the introduction of the trifluoromethyl group lowers the symmetry from C_{2v} to C_s for this ligand, no significant change in the spectrum is expected as only the ν_7 torsion mode may be activated. The absorptions resulting from the B - C and C - F stretching modes can be assigned without great



THE INFRA-RED SPECTRUM OF
TRIMETHYLTIN TRIFLUOROMETHYLTRIFLUOROBORATE

FIGURE II

difficulty. Table 6 contains the significant bands for $\text{Me}_3\text{Sn BF}_4$, $\text{Me}_3\text{Sn CF}_3\text{ BF}_3$ and $\text{K}^+\text{CF}_3\text{ BF}_3^-$. As the correlation between the two tin compounds is complete, only the bands arising from C - F and B - C will be discussed at length.

The C - F asymmetric and symmetric stretching modes are found at 984 and 957 cm^{-1} respectively in trimethyltin trifluoromethyltrifluoroborate. These absorptions are in close agreement with the analogous bands at 985 and 963 cm^{-1} for $\text{K}^+\text{CF}_3\text{ BF}_3^-$. Consequently, even in the anhydrous compound, the transfer of the perfluoromethyl group from the tin to the boron atom must have occurred. The suggestion that the shift of the C - F stretching modes from the usual range of 1100 - 1350 cm^{-1} is due to the existence of free ions is not necessarily valid (110). However, the force constants of the B - F bond in the trifluoromethyltrifluoroborate anion must be radically changed from that in BF_4^- as the B - F asymmetric bend is no longer observed in the 600 - 400 cm^{-1} region. The substitution of a perfluoromethyl group onto the boron will lower the T_d symmetry of the BF_4^- ion to C_{3v} for the $\text{CF}_3\text{ BF}_3^-$ ion. Although the asymmetric B - F stretching band has been resolved into three peaks (1041, 1063, and 1090 cm^{-1}), the expected activation of ν_1 to a major absorption is not found. A definite explanation cannot be given for its absence.

In trimethyltin trifluoromethyltrifluoroborate, the shift of the B - F asymmetric bending vibration to lower wave numbers leaves the 500 - 550 cm^{-1} region unobstructed. The

TABLE 6.

Infra-red assignments for trimethyltin tetrafluoroborate, trimethyltin trifluoromethyltrifluoroborate, and potassium trifluoromethyltinfluoroborate.

$\text{Me}_3\text{Sn BF}_4$	$\text{Me}_3\text{Sn CF}_3 \text{ BF}_3$	$\text{K}^+\text{CF}_3 \text{ BF}_3$	Assignments.
1210 (M) cm^{-1}	1220 (M) cm^{-1}		CH_3 sym. def.
1200 (Sh.)	1178 (M)		$\oplus \text{B}^{10}\text{-F}_2^*$ asym. str.
1170 (S.)	1147 (S)		$\text{B}^{11}\text{-F}_2^*$ asym. str.
		1090 (Sh)	?
1115 (Sh.)	1107 (Sh)	1063 (S)	$\text{B}^{10}\text{-F}_2$ asym. str.
1070 (S.)	1083 (S)	1041 (S)	$\text{B}^{11}\text{-F}_2$ asym. str.
	1023 (W)		?
	984 (Sh)	985 (M)	C-F asym. str.
	957 (Sh)	963 (M)	C-F sym. str.
960 (Sh.)	947 (Sh)		$\text{B}^{10}\text{-F}_2$ sym. str.
930 (S)	932 (S)		$\text{B}^{11}\text{-F}_2$ sym. str.
780 (V.S.)	798 (VS)		CH_3 rocking.
730 (S)	745 (S)	737 (W)	BF_2^* sym. str.
	689 (W)		?
	628 (S)	635 (M)	B - C str.
558 (S)	558 (S)		Sn-C asym. str.
536 (W)			?
526 (W)			?
446 (V.S.)	447 (S)		Rocking and/or sym. bend of BF_2^*

$\oplus \text{BF}_2^*$ denotes vibrations involving the F atom which interacts with the Sn.

absence of the Sn - C symmetric stretching fundamental requires the trimethyltin group to be planar, which supports the conclusion drawn from the "anionic" portion of the spectrum that a bridging ligand is present. Thus, in both of these boron derivatives, a linear polymer exists comparable to that earlier described for trimethyltin perchlorate.

An attempt was made to examine the F^{19} nuclear magnetic resonance spectra of concentrated solution (approx. 2 gm./ml. solutions) of $Me_3 Sn BF_4$ in liquid sulphur dioxide. Only a single sharp absorption was observed. Even when the samples were slowly warmed from $-196^\circ C$ to room temperature, no fine structure would be detected. However, it is significant that the chemical shift for $Me_3 Sn BF_4$ was $+57.5$ ppm to high field from the trifluoroacetic acid standard.

The BF_4^- ion in aqueous solution (110) shows a chemical shift of $+72.3$ ppm and a quartet is observed owing to the $B^{11} - F^{19}$ coupling. Even allowing for the effects of different media, the difference in chemical shift is appreciable, and it appears likely that the single absorption for $Me_3 Sn BF_4$ is a consequence of a dynamic equilibrium between BF_4^- and some other BF_4 species.

Of related interest is that the isolation and characterization of anhydrous trimethyltin trifluoromethyltrifluoroborate may have some value in interpreting the mechanism of Brinkman and Stone's (112) preparation of alkyl dihaloboranes.

In their preparation, the tetraalkyltin compound and the trihaloborane were heated in the gas phase to about 70°C. The resulting products, $R_3 \text{ Sn X}$ and REX_2 were separated in vacuo. In the present work, trimethyltrifluoromethyltin and boron trifluoride were condensed into a trap containing anhydrous carbontetrachloride. Large clear plates formed and these were transformed into a very fine, white powder upon removal of the solvent. The clear colourless plates may be some borontrifluoride adduct, $\text{R}_f\text{R}_3 - \text{Sn} - \text{BF}_3 \text{ X CCl}_4$, containing a Sn - F - B configuration and removal of the solvent may have initiated the transfer of the perfluoromethyl group.

CHAPTER 7:

TRIMETHYLTIN DERIVATIVES OF GROUP V₆ HEXAFLUORIDES.

In contrast to the detailed studies that have been conducted for anions with trigonal planar and tetrahedral configuration, the changes in skeletal modes of vibration of an octahedral anion with lowering of symmetry have been relatively ignored. The infra-red studies that have been conducted on hexa co-ordinate complexes, in particular the cobalt derivatives (113, 114, 115), have only attempted to establish an empirical relationship between the fundamental vibrations of the ligands (NH_3 , NO_3^- etc.) and the geometrical configuration of the complex. It is possible that the highly complicated spectra of these complexes have discouraged any attempt to make a more detailed study.

Beattie (116) has specifically studied this problem in an infra-red investigation of $\text{MCl}_4 \cdot 2\text{Py}$ (where Py = pyridine). In these compounds, both cis - and trans-configurations are possible if the presence of discrete, six co-ordinate octahedral species is assumed. His analysis of the spectral changes are as follows: "The trans-adduct is thus considered to be similar to a perturbed square planar MCl_4 unit, so that only one infra-red active fundamental M-Cl stretching vibration is predicted (117) of symmetry type Eu. For the cis-configuration there would be at least two fundamentals associated with M-C stretching modes and expected to be observed (118) in the region under

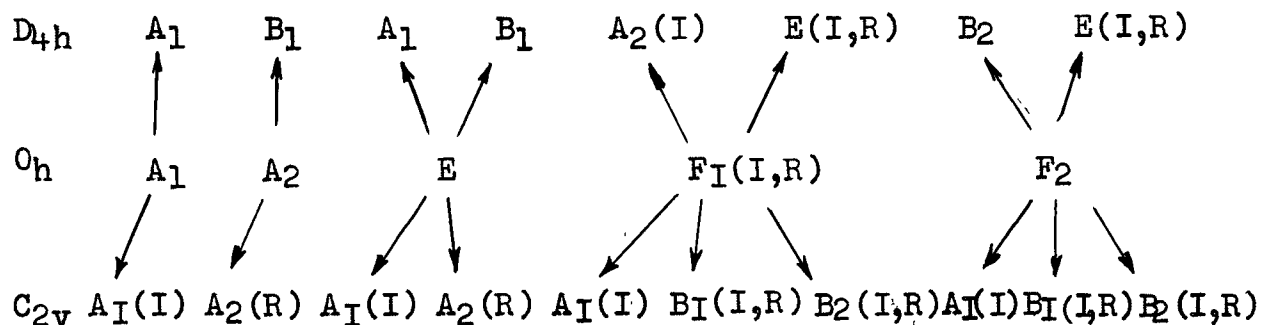
discussion (i.e. the potassium bromide region)." As will be developed later, these statements are correct, though not complete.

In this investigation of the compounds derived from the hexafluoro anions of the group Vb elements and trimethyltin, the "anionic" portion of the infra-red spectra indicates that associated species exist. Trimethyltin fluoride, trimethyltin perchlorate, trimethyltin tetrafluoroborate, and trimethyltin trifluoromethyltrifluoroborate, have spectra which are consistent with the presence of bridging ligands. Thus, if any interaction occurs with these octahedral anions, the first possibility to be considered should be existence of a bidentate anionic group. Should two fluorine atoms interact with different trimethyltin groups, two possible configurations, i.e. cis - trans, can occur, and distinct changes in the entire infra-red spectrum should be found. However, in view of the lack of experimental infra-red data for differentiating cis-trans isomers, only the triply degenerate M-F asymmetric stretching vibration (ν_3) will be considered in detail.

If a trans-bridging ligand is present, the O_h symmetry of the original hexafluoride is lowered to D_{4h} . As seen from the correlation diagram given in Table 7, the triply degenerate ν_3 fundamental will thus be split into a doubly degenerate and a non-degenerate mode. A cis-configuration, on the other hand, will completely remove all degeneracy and three distinct absorptions should be recorded (119).

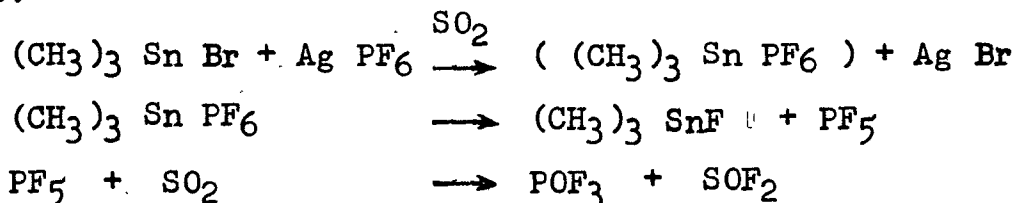
TABLE 7.

The Correlation Diagram for Octahedral Molecules.



In this study of the hexafluoro anions of Group Vb, attempts were made to prepare the hexafluorophosphate, hexafluoroarsenate and the hexafluoroantimonate derivatives of trimethyltin. The pure trimethyltin hexafluorophosphate, $\text{Me}_3 \text{Sn PF}_6$, could not be obtained. The reaction products from the attempted preparation are nonetheless interesting in that they suggest very strong interaction between $\text{Me}_3 \text{Sn}^+$ and the PF_6^- anion.

The results can only be interpreted according to the scheme.

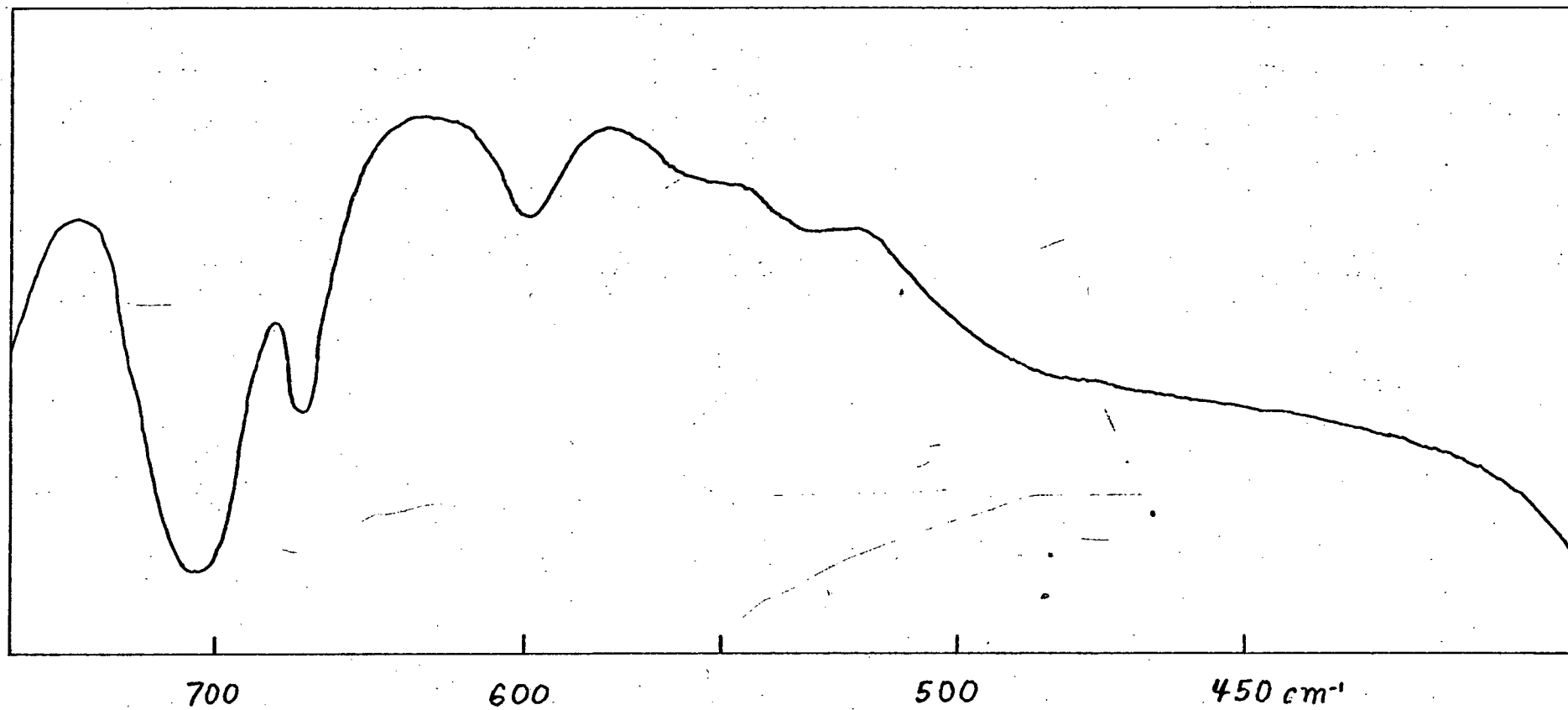


This is supported by the fact that silver hexafluorophosphate can best be prepared from liquid sulphur dioxide (120), so that POF_3 cannot arise from direct reaction of PF_6^- with SO_2 .

The stability of the PF_6^- ion, and the considerable Lewis acidity of PF_5 also emphasizes the strong interaction between Me_3Sn^+ and PF_6^- .

The second compound in this series, trimethyltin hexafluoroarsenate, is obtained as a sulphur dioxide adduct, $(\text{CH}_3)_3\text{SnAsF}_6 \cdot \text{SO}_2$, from which the non-solvated species can be obtained by the slow removal of the sulphur dioxide in vacuo. The infra-red spectrum of $\text{Me}_3\text{SnAsF}_6$ showed the expected absorptions at 2900 - 3000 (C-H stretch), 1405 (CH_3 asym. deformation), and 1215 cm^{-1} (CH_3 sym. deformation). The CH_3 rocking mode is at 792 cm^{-1} and is seen as an unsymmetrical band, with an unresolved component at slightly higher frequencies. The spectrum in the 400 - 800 cm^{-1} region is shown in Fig. 12. The octahedral AsF_6^- ion gives a strong absorption, seen as a rather broad, but symmetrical band at approximately 700 cm^{-1} , with secondary peaks at 1300, 1065, 970 and 825 cm^{-1} (121). The band at 700 cm^{-1} is assigned as ν_3 , while the ν_4 vibration is reported as occurring at 400 cm^{-1} (122). In the spectrum of $\text{Me}_3\text{SnAsF}_6$, no bands could be resolved at frequencies below approximately 550 cm^{-1} , a new band is seen at 603 cm^{-1} and ν_3 is clearly split into two components at 675 and 710 cm^{-1} , the latter being about twice as intense as the former. The Sn - C vibrations (symmetric and asymmetric) are not observed in the usual 500 - 560 cm^{-1} region.

The 603 cm^{-1} band is considered to be due to the asymmetric Sn - C stretching vibration as it is always a major absorption in this region. The shift of 50 cm^{-1} to higher



THE INFRA-RED SPECTRUM OF TRIMETHYLTIN HEXAFLUOROARSENATE

FIGURE 12

frequencies is a result of very strong interactions with the AsF_6^- group. A very weak, poorly resolved band appearing at 535 cm^{-1} may possibly be the Sn - C symmetric vibration. The crystal structure of trimethyltin fluoride has shown that unless this vibration causes a reasonably intense absorption, the trimethyltin group is essentially planar. As stated earlier, the splitting of ν_3 into two components is significant in that the symmetry is lowered to D_{4h} by the interaction of trans fluorine atoms with two five co-ordinate tin atoms. The most likely configuration is thus a linear polymer.

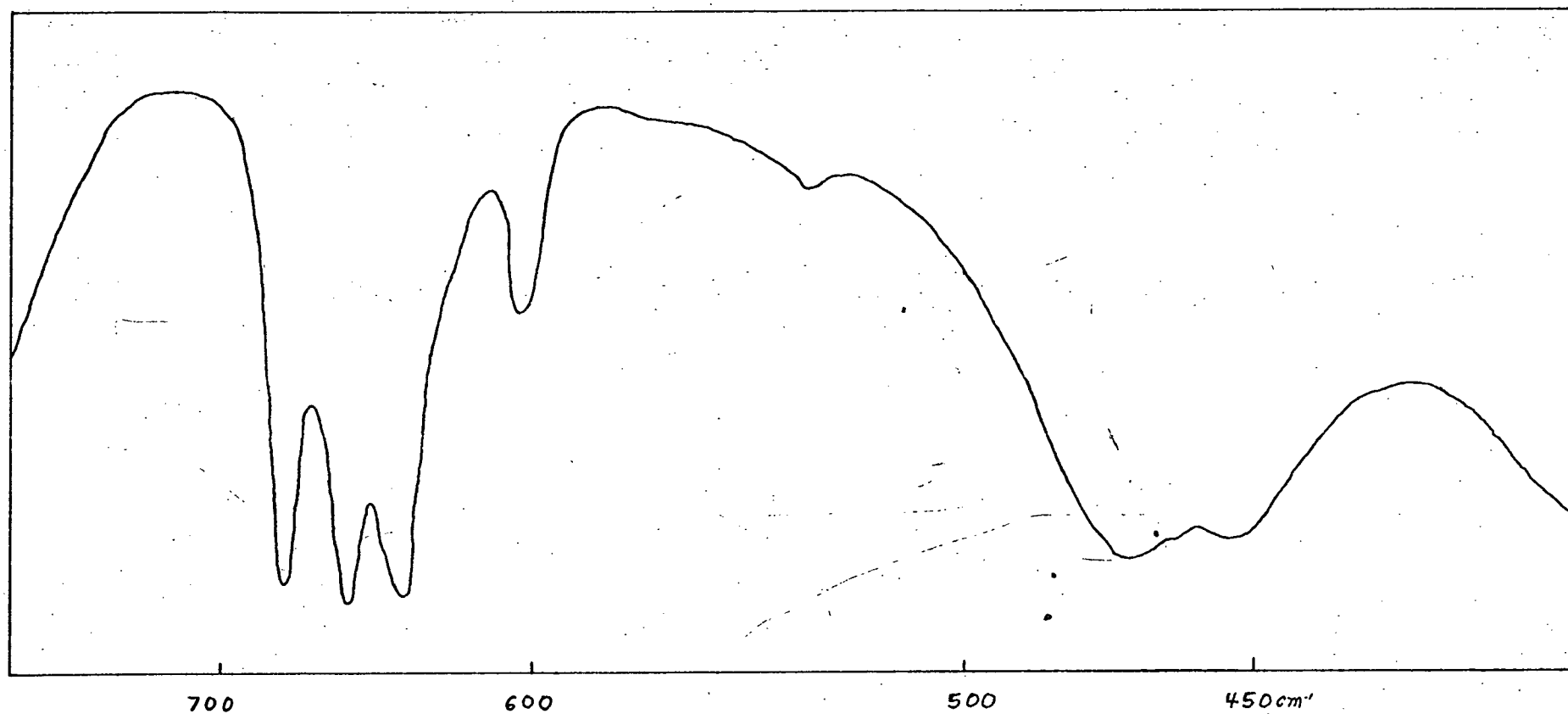
Additional evidence that the ν_3 fundamental is split into a doublet for trans compounds of the class MA_4B_2 is found in the infra-red of trans $(\text{CF}_3)_2\text{SF}_4$ where two strong bands are found at 858 and 904 cm^{-1} (123). These are related to the single ν_3 absorption found at 932 cm^{-1} for SF_6 (124).

The final compound in this series, trimethyltin hexafluoroantimonate shows some features in the infra-red spectrum that are similar to the hexafluoroarsenate derivative. The C-H vibrations, and the CH_3 deformations are observed at 2900 , 3000 , 1405 and 1210 cm^{-1} respectively. New bands of comparable intensity to the CH_3 rocking mode at 810 cm^{-1} are observed at 870 and 990 cm^{-1} . The spectra of "normal" hexafluoroantimonates (e.g. Ag SbF_6^-) (121,122) do not show bands in the $800 - 1000\text{ cm}^{-1}$ region. Therefore, these must be vibrational modes, infra-red inactive for the octahedral SbF_6^- ion, which have become activated as a result of distortions of the SbF_6^- group

by $\text{Me}_3 \text{Sn}$. It is interesting that these bands at 870 and 990 cm^{-1} are comparable to the subsidiary peaks found at 825 and 970 cm^{-1} for AsF_6^- (9).

The ν_3 vibration of SbF_6^- is observed at 660 cm^{-1} , but, as can be seen from Fig. 13, this band for $\text{Me}_3 \text{Sn SbF}_6$ is well resolved into three components at 675, 656, and 640 cm^{-1} . Such a complete removal of the degeneracy of the ν_3 mode of a symmetrical, octahedral ion is consistent with a lowering of the symmetry to C_{2v} . The symmetry expected if two cis F atoms are interacting with $\text{Me}_3 \text{Sn}$ groups. This configuration is also found in liquid SbF_5 where N.M.R. results indicate association via cis fluorines (125). The infra-red spectrum of SbF_5 gives comparable absorptions at 721, 710, and 684 cm^{-1} (126).

Moreover, for $\text{Me}_3 \text{Sn SbF}_6$ a new intense band, not reported for the SbF_6^- ion, is now found in the 440-480 cm^{-1} region, consisting of two components at 454 and 472 cm^{-1} . The triply degenerate ν_4 mode has not been reported for the free SbF_6^- ion, and these bands may well be two of the three possible components. An extension of the spectroscopic studies to lower frequencies is necessary to confirm this. In the 500 - 620 cm^{-1} region, two bands are observed, one being very poorly resolved at 535 cm^{-1} possibly is due to the Sn - C symmetric vibration. The other is a sharp well-defined band at 606 cm^{-1} which is identical to the 603 cm^{-1} band in the $\text{Me}_3 \text{Sn AsF}_6$ spectrum, and is therefore tentatively assigned as the Sn-C asymmetric stretch. Hence, the spectroscopic evidence, in particular the splitting of ν_3 and the appearance of new peaks



THE INFRA-RED SPECTRUM OF TRIMETHYLTIN HEXAFLUOROANTIMONATE

FIGURE 13

at a lower frequency, is consistent with a structure in which essentially planar Me_3Sn groups are bridged by *cis* fluorine atoms of distorted SbF_6^- groups, so that the Sn atom is again five co-ordinate.

There thus appears to be an interesting sequence in the compounds $\text{Me}_3\text{SnMF}_6^-$ where $\text{M} = \text{P}, \text{As}$ or Sb . The hexafluorophosphate is unstable, the PF_6^- groups losing a fluoride ion to the Me_3Sn^+ group. Trimethyltin hexafluoroarsenate and antimonate, which we derived from the 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.

It should be emphasized that the difference in the splittings of ν_3 for the AsF_6^- and SbF_6^- compounds are considered genuine and not just due to a lack of resolution of ν_3 for $\text{Me}_3\text{SnAsF}_6^-$. The two compounds were prepared from reactants of similar purity, their spectra recorded under the same conditions and several preparations of each compound give the same spectrum.

Of related interest is a preliminary study of trimethyltin trifluoromethylpentafluoroantimonate. From the reaction of antimony pentafluoride and trimethyltrifluoromethyltin in the absence of solvent a cream white solid could be isolated. The infra-red spectrum gives the characteristic bands for $\text{Sn}-\text{CH}_3$, $\text{C}-\text{F}$ and $\text{Sb}-\text{F}$ indicating that the desired reaction has taken place, however, many additional bands were also

present. The analysis obtained for this product, while not completely satisfactory, does demonstrate that the molar ratio is probably 1:1. A further study using a suitable solvent will probably yield the pure product. Characterization of the product could be accomplished by a reaction of potassium fluoride in aqueous hydrogen fluoride to give the insoluble trimethyltin fluoride and the potassium salt $K^+ CF_3SbF_5^-$. The extension of this reaction to AsF_5 and PF_5 would also be interesting.

CHAPTER 8:

NITROGEN BASE ADDUCTS OF TRIMETHYLTIN DERIVATIVES

As outlined in the introduction, some discrepancies exist in earlier descriptions of the mono - and di-adducts of the trialkyltin halides. The mono-adducts were thought to contain a quaternary nitrogen atom giving the compounds an ammonium chloride-type constitution (51), while the di-adducts were assigned an octahedral configuration (50). These formulations are not completely consistent with the properties of the compounds. Trimethyltin mono-pyridino chloride is highly soluble in organic solvents and volatile while the di-ammine adduct is insoluble in these solvents and non-volatile.

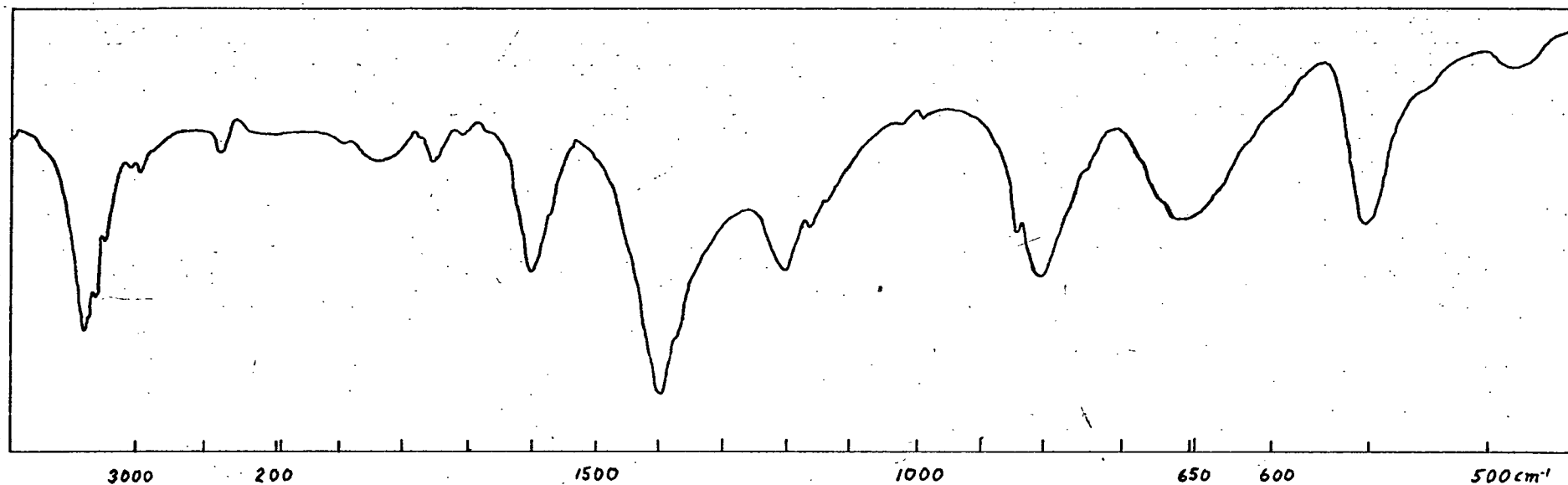
In view of all the recent results, the possibility of a five co-ordinate configuration should be considered. The di-adducts would then consist of a cation containing the five co-ordinate tin atom, $(\text{Me}_3 \text{Sn} (\text{NH}_3)_2)^+$, and the halide anion. A molecular arrangement could be given to the mono-adducts.

An infra-red spectrum of $\text{Me}_3 \text{Sn Cl} \cdot 2 \text{NH}_3$ or $\text{Me}_3 \text{Sn} (\text{NH}_3)\text{Br}$ in the $4000-400 \text{ cm}^{-1}$ region will not give any information on the status of the halogen atom as the tin - halogen stretching vibrations are below 400 cm^{-1} . Consequently, the co-ordination number of the tin atom is in doubt. However, for the adducts $\text{Me}_3 \text{Sn ClO}_4 \cdot 2\text{NH}_3$ and $\text{Me}_3 \text{Sn NO}_3 \cdot 2\text{NH}_3$, the portion of the spectrum attributable to the anion should indicate whether or

not the completely free and highly symmetrical anion exists.

$\text{Me}_3\text{SnNO}_3 \cdot 2\text{NH}_3$ gives a spectrum (Fig. 14) whose principal absorption regions (Table 8) are 3100 - 3300 (N-H str), 3000 - 2900 (C-H str.), 1610 (asym. deformation NH_3), 1360 (NO_2 str.), 1210, 1160 (CH_3 and NH_3 sym. deformation), 827 (NO_3 out of plane vibration), 785 (CH_3 rocking), 720 (shoulder: NO_2 bend.), 650 (NH_3 rocking), 552 (Sn-C asym.str.), and 475 cm^{-1} (Sn-N stretch). Clearly, the observed frequencies of 1360, 875, and 720 cm^{-1} together with the band at 1035 cm^{-1} are those associated with a free NO_3^- ion and are very different from those observed for the nitrate group in anhydrous trimethyltin nitrate. The Me_3Sn group is presumed planar as only a very weak shoulder is found at 520 cm^{-1} in comparison with an intense band at 552 cm^{-1} . The bands at 3200-3100, 1610, 1210, and 650 cm^{-1} are probably those associated with the co-ordinated NH_3 groups, although some of these bands tend to differ in shape from those reported (128) for other amines. For example, the 1600 cm^{-1} band is usually broad, but in this compound it is sharp.

The perchlorate derivatives, $\text{Me}_3\text{Sn}(\text{NH}_3)_2\text{ClO}_4$, gives an infra-red spectrum (Fig. 15 and Table 9) that is comparable to that of the nitrate di-amine. The trimethyltin group is again considered planar from the absence of a significant absorption in the $500 - 530\text{ cm}^{-1}$ region. In contrast to anhydrous $\text{Me}_3\text{SnClO}_4$, only one absorption is found in the 1100 cm^{-1} region and no maximum (ν_1) at 930 cm^{-1} . Moreover, in the



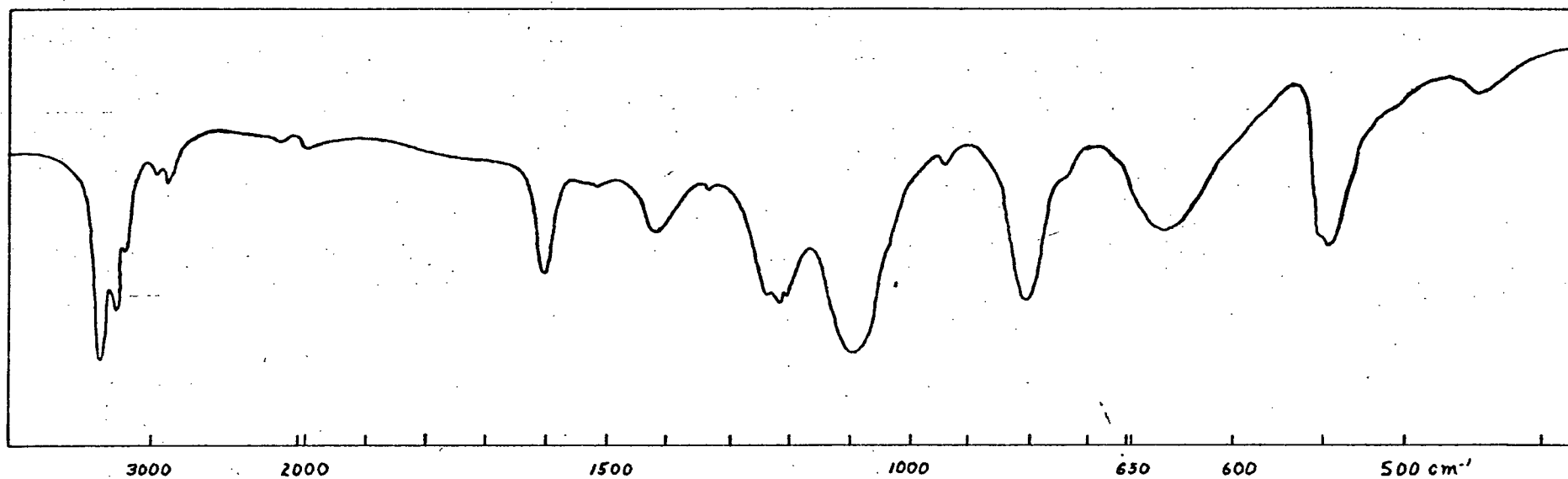
THE INFRA-RED SPECTRUM OF TRIMETHYTIN DI-AMMINO NITRATE

FIGURE 14

TABLE 8.

Infra-red assignments for the di-ammine adduct of trimethyltin nitrate.

3310 cm^{-1}	(S))	
3215	(M))	N-H str.
3120	(M))	
3000	(W))	
2900	(W))	C-H str.
1610	(M)		NH_3 asym. def.
1360	(S)		NO_2 str.
1210	(M))	
1160	(M))	CH_3 and NH_3 sym. def.
827	(M)		NO_3 out of plane vibration
785	(S)		CH_3 rocking
720	(W)		NO_2 bend.
650	(S)		NH_3 rocking
552	(S)		Sn-C asym. str.
475	(W)		Sn-N str.



THE INFRA-RED SPECTRUM OF TRIMETHYLTIN DI-AMMINO PERCHLORATE

FIGURE 15

TABLE 9.

Infra-red assignments for the di-ammine adduct of trimethyltin perchlorate.

3350	(S)	cm ⁻¹)	N-H str.
3260	(S))	
3200	(M))	
2990	(W))	C-H str.
2900	(W))	
1610	(M)		NH ₃ asym. def.
1425	(M)		CH ₃ asym. def.
1240	(M))	NH ₃ , CH ₃ sym. def.
1220	(M))	
1207	(Sh))	
1150	(S)		ClO ₄ ⁻ asym. str.
935	(W)		ClO ₄ ⁻ sym. str.
792	(S)		CH ₃ rock.
625	(S)		NH ₃ rock or ClO ₄ asym. bend.
551	(S)		Sn-C asym. str.
490	(W, Sh)		Sn-N str.
441	(W)		ClO ₄ sym. bend.

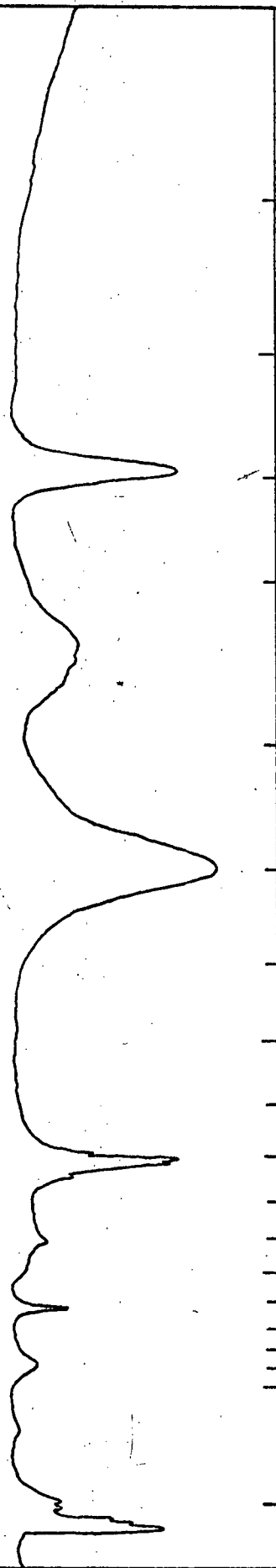
350 - 650 cm^{-1} region, the only band that can be associated with the ClO_4 group is observed at 625 cm^{-1} . These absorptions are identical with those found (81) for solutions of ionic perchlorates and clearly indicate the presence of the undistorted ClO_4^- anion. The spectrum is therefore consistent with the configuration $(\text{Me}_3 \text{Sn} (\text{NH}_3)_2)^+ \text{ClO}_4^-$ with the tin atom having a trigonal bipyramidal configuration and the two ammonia molecules in the apical positions.

It is interesting that both the nitrate and perchlorate adducts show weak bands at approximately 500 cm^{-1} , in good agreement with previous assignments for metal-nitrogen stretching vibrations in amines (127).

Trimethyltin diammine bromide and chloride can be given the same configuration and are stable if prepared under rigidly controlled conditions. It was found that if the halide was sublimed in vacuo, the di-adduct was again found upon condensation of the vapour in a trap cooled to -76°C . However, if this adduct was heated at atmospheric pressure in an air cooled reflux apparatus, the mono-adduct was deposited on the lower portions of the condenser. It is not to be inferred that atmospheric pressure is required to obtain the mono-adduct, but that the cooling required to trap the sublimate in vacuo reforms the di-ammine.

The infra-red spectra of the di-ammine (Fig.16a) and mono-ammine (Fig.16b) adducts of trimethyltin bromide show remarkable similarity, although a difference can be noted in the

(a) TRIMETHYLTIN DI-AMMINO BROMIDE



(b) TRIMETHYLTIN MONO-AMMINO BROMIDE

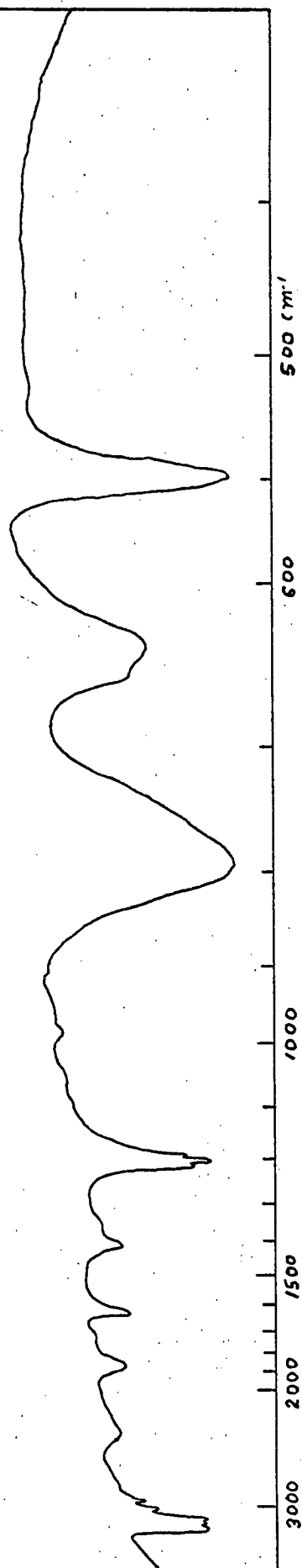


FIGURE 16

N-H stretching and symmetrical deformation absorptions. Assignments for both adducts of trimethyltin bromide are given in Table 10. As the absorptions resulting from Sn-Br vibrations are not observable in the region investigated, the bands given by groups attached to the five co-ordinate tin atom are identical to those found for the nitrate and perchlorate derivatives.

The planarity of the trimethyltin group in both of these adducts i.e. $\text{Me}_3\text{Sn}(\text{NH}_3)_2^+ \text{X}^-$ and $\text{Me}_3\text{Sn}(\text{NH}_3)\text{X}$, give them almost identical symmetry. Consequently, this similarity in spectra is not surprising. However, in order to make a definite differentiation between these two adducts, their crystal class and unit cell dimensions were determined by X-ray crystallography. Using a single crystal, the di-ammine adduct of trimethyltin bromide was found to have a monoclinic unit cell.

For the mono-adduct, only an X-ray photograph of the powder (Table 11) was required as a cesium chloride type crystal was found. ($a = 4.050\text{\AA}$).

Of related interest is Kraus's (51) statement that the di-ammine adducts of trimethyltin bromide and chloride are unstable and readily lose one molecule of ammonia to form the mono-adduct. Pfeiffer (50), on the other hand, found that the similar di-adduct of trimethyltin iodide was stable. However, he noted that conversion of the tetra-ammine derivatives of the dialkyltin dihalide to the di-adduct was initiated by a

TABLE 10.

Infra-red assignments for the mono and di-ammine adducts of trimethyltin bromide.

$(\text{Me}_3 \text{ Sn}(\text{NH}_3)_2)^+ \text{Br}^-$	$\text{Me}_3 \text{ Sn NH}_3 \text{ Br}$	Assignment
3270 cm^{-1} (S)	3220 cm^{-1} (S)	N-H str.
3150 (S)	3150 (S)	
3090 (S)	3090 (S)	
3000 (M)	3000 (M)	C-H str.
2900 (M)	2900 (M)	
1840 (W)	1820 (W)	?
1600 (M)	1600 (M)	N-H ₃ asym. def.
1405 (M)	1400 (M)	C-H ₃ asym. def.
1240 (Sh.)		
1200 (S)	1200 (S)	NH ₃ or CH ₃ sym.def.
1190 (S)	1185 (S)	
1175 (Sh.)	1175 (Sh.)	
793 (VS)	787 (VS)	CH ₃ rocking
625 (M)	625 (M)	NH ₃ rocking
645 (Sh.)	640 (Sh.)	?
544 (S)	541 (S)	Sn-C asym. str.
	503 (VW)	Sn-C sym. str., or Sn-N str.

TABLE 11.

Data from the Powder X-ray Photograph of Trimethyltin
monoammino bromide.

d	$\frac{1}{d^2_{\text{obs.}}}$	$\oplus \frac{1}{d^2_{\text{calc.}}}$	$(h^2+k^2+l^2)$
4.091	0.0572	0.06096	1
2.855	0.1227	0.1219	2
2.336	0.1833	0.1829	3
2.021	0.2448	0.2438	4
1.809	0.3056	0.3048	5
1.654	0.3655	0.3658	6
1.431	0.4877	0.4877	8
1.351	0.5479	0.5486	9
1.281	0.6094	0.6096	10
1.221	0.6708	0.6706	11

\oplus using $a = 4.050$ with a cesium chloride
lattice structure.

trace of moisture.

Regardless of the role played by the water molecule in initiating this conversion, the equation would be as follows:



If the escape of the NH_3 molecule rather than any inherent instability of the di-ammine adduct is the critical factor in the conversion, then the preparation of a compound containing an anion which would not easily form the molecular species $\text{Me}_3 \text{ Sn} \text{NH}_3 \text{X}$ would give some valuable information. Should the conversion now occur under anhydrous conditions, then the instability of the $(\text{Me}_3 \text{ Sn} (\text{NH}_3)_2)^+$ ion would be suggested. If no conversion took place even upon admission of atmospheric moisture, then the critical factor could well be the formation of the molecular mono-adduct and the subsequent escape by thermal diffusion of the ammonia.

With these considerations in mind, the di-ammine derivatives of trimethyltin perchlorate and trimethyltin nitrate were studied, and both were found to be unattached by atmospheric moisture. Consequently, the instability of the di-adduct is not a factor in this conversion.

A second class of adducts is formed by pyridine. Pfeiffer (50) found that a di-pyridine adduct of trimethyltin iodide could be isolated, but unlike the ammine derivative, a mole of pyridine was lost even under the most rigid conditions.

The stable mono-pyridine adduct of trimethyltin chloride has been shown by infra-red measurements (58) and by X-ray crystallography (59) to be molecular with a five co-ordinate tin atom. The infra-red spectra of both trimethyltin bromide and chloride mono-pyridine were recorded and found to be simply the pyridine spectrum (128) superimposed upon that given by the planar trimethyltin group.

The di-pyridine adduct of trimethyltin perchlorate was prepared. It is comparable in all aspects to the di-ammine adduct as both the ClO_4^- ion and a planar trimethyltin group are present. The assignments for the spectrum of this di-pyridine adduct are given in Table 12 as well as that of the mono-pyridine adduct of trimethyltin bromide and pure pyridine.

Attempts were made also to prepare the ammine and pyridine adducts of triphenyltin iodide, bromide, and chloride. Although some adduct is initially formed, ammonia or pyridine is lost upon standing in a vacuum desiccator. This had been reported earlier by Pfeiffer (129). From a study of the ultra-violet of triphenyltin iodide, Prince (130) suggested that the d orbitals are in some manner interacting with the phenyl rings. Thus, these orbitals may not be available for the formation of a five co-ordinate species.

An entirely new type of adduct was found upon investigation of a report by Kriegsmann and Pischtschan (48) that trimethyltin chloride was precipitated from a saturated aqueous solution of this chloride by the addition of concentrated hydrochloric acid.

TABLE 12.

Infra-red for the pyridine adducts of trimethyltin
bromide and trimethyltin perchlorate.

Pyridine	Me ₃ Sn Br·Py	Me ₃ Sn ClO ₄ ·2Py	Assignments
		3200(W) cm ⁻¹	?
3076(M)cm ⁻¹		3150(W)	
	2900(M)cm ⁻¹	3055(W)	} C-H str.
	2850	2950(W)	
1991(M)		2040(M)	
1600(S)	1595(S)	1600(S)	
1574(S)			
1485(S)	1465(M)	1480(M)	
1440(S)	1455(M)	1450(S)	
	1455(W)	1410(W)	CH ₃ asym. def.
1375(W)	1375(W)	1360(W)	
	1215(W)	1215(M)	CH ₃ sym. def.
1210(W)	1185(W)		
1139(W)	1152(W)	1160(W)	
		1100(VS)	ClO ₄ asym.str.
1035(S)	1065(M)	1050(M)	
1028(S)	1033(M)	1010(M)	
990(S)	1003(M)	990(M)	
941(M)		955(W)	
881(W)		890(W)	
	780(VS)	785(VS)	CH ₃ rocking
	785(Sh)	770(Sh)	?
695(S)	695(S)	695(S)	
652(M)			
604(M)	617(M)	618(S)	also ClO ₄ asym.bend.
		565(Sh)	?
	544(S)	546(S)	Sn-C asym. str.
	507(VW)	512(VW)	Sn-C sym. str.
404(M)	417(M)	424(S)	

Analysis of this product showed that in fact the dihydrate was present. For reasons that are not clear, the water was lost upon standing. However, in view of the results for the diammine adducts, no comment can be made regarding the actual stability of the $(\text{Me}_3 \text{Sn} (\text{OH}_2)_2)^+$ cation. Attempts to prepare trimethyltin nitrate dihydrate from trimethyltin nitrate and nitric acid were not successful since cleavage of a methyl group occurred yielding dimethyltin dinitrate.

The importance of this isolation of a dihydrate is that in solution a di-solvate may well exist rather than the monosolvate reported by Prince (71). If this is the case, then the polyhydroxides found by Tobias (70) for dimethyltin diperchlorate will be present in an aqueous solution.

CHAPTER 9:

CONCLUSION

Interest in the stereochemical aspects of organo-tin chemistry has been increasing at a remarkable rate. The recent reports in the literature (since 1962) uniformly indicate that five co-ordination can exist for the tin atom in the trimethyltin compounds.

If a four co-ordinate tin atom is present in a compound of the general class R_3SnA (where R= alkyl, and A= univalent "anion"), the molecule will have a tetrahedral configuration. The special feature observed for the R_3Sn group, however, is that the highest co-ordination number is apparently five and not six, and this co-ordination number may occur as a result of bridging by "anion", A, to give a polymeric type of structure. Consequently, non-volatility cannot be used as a criterion for the presence of an ionic solid.

The occurrence of this unusual co-ordination number can be given a partial explanation. If the trimethyltin group attains a planar configuration at any stage of a reaction, then further co-ordination by the tin atom will take place in the apical positions giving a trigonal bipyramidal arrangement. There is no chemical phenomenon (e.g. crystal field stabilization energy) that would require further co-ordination. Thus, the solvolysis products will be $(Me_3Sn (OH_2)_2)^+ X^-$ or $(Me_3Sn (OHR)_2)^+ X^-$. The nitrogen base adducts will be either

covalent mono-adducts, Me_3SnBX , or ionic di-adducts, $(\text{Me}_3\text{SnB}_2)^+ \text{X}^-$, (where B is a nitrogen base molecule).

In addition the members of the class R_3SnA will either be monomeric tetrahedral molecules, or polymeric chains. There is, however, no obvious reason which will predict that the R_3Sn group will become planar during a reaction. Indeed, it would have seemed more reasonable to anticipate, in the compound R_3SnA , that A would be simply replaced by solvent giving $\text{R}_3\text{Sn S}^+$ maintaining the tetrahedral environment of the tin atom.

Although the dialkyltin derivatives were not studied experimentally, one or two features concerning their stereochemistry can be inferred from this investigation. The free R_2Sn^{++} ion as a discrete species must have definite experimental verification before its existence can be accepted. Beattie's suggestion that an octahedral arrangement may occur in Me_2SnF_2 (45) via fluorine bridging is certainly consistent with the observed crystal structure of trimethyltin fluoride, and six co-ordination may well occur in many R_2Sn compounds.

This difference in co-ordination number between the R_3Sn and R_2Sn groups can be rationalized in the following manner. The "free" R_2Sn group will be linear, and further co-ordination will occur in the plane through the tin atom and perpendicular to the R-Sn-R axis. In this case, the four positions that would be occupied to complete the octahedral configuration are all equivalent and readily filled. Consequently, a hexa-co-ordinate molecule should form rather

than the penta-co-ordinate species found for the R_3Sn group.

In many areas of chemistry, experimental data have accumulated to the extent that the distinction between covalent and ionic species can be made from gross physical properties. However, for complex organo-metallic molecules in the solid state, and certainly for the compounds of the class R_3SnA , this is not the case. If discrete ions are assumed to be present in a solid, then a knowledge of electrostatic forces and atomic sizes permits accurate predictions to be made of the results for many experiments. Should marked deviations from these predictions occur, then covalent interaction is generally assumed, but it is exceedingly difficult to obtain direct evidence as to the positioning of the electron pair. The result of this uncertainty is that the precise definition of covalent bonding has been and still is a subject of extensive debate. In fact, only if the compound melts, sublimes, or distills at a moderate temperature can any positive qualitative statement be made. The compounds trimethyltin fluoride and trimethyltin perchlorate illustrate this point.

The crystal structure of trimethyltin fluoride shows that the Sn-F-Sn angle is not 180° , nor is the fluorine atom situated midway between the two tin atoms. In addition, trimethyltin fluoride may be sublimed from a melt of trimethyltin bromide and potassium fluoride. The first two facts are consistent with a non-ionic solid, and the

third, the volatility of Me_3SnF , supports the assumption that the Sn-F bond may contain a considerable degree of covalent character.

For trimethyltin perchlorate, the infra-red results indicate that two of the oxygen atoms of the acid group differ from the other two. As it is a low melting, easily sublimable solid, the interaction between the tin and oxygen atoms must be extensive, and the suggestion that a degree of covalent bonding occurs between these two atoms is not unreasonable. The stability of trimethyltin diammino perchlorate gives some additional information. If the ammonia molecules were not within the inner co-ordination sphere of the tin atom then they would not be so strongly retained in the formation of the very stable $(\text{Me}_3\text{Sn}(\text{NH}_3)_2)^+$ ion.

If the above three examples are sufficient to demonstrate that covalent interaction occurs in these compounds, then a similar conclusion must be made for all the remaining derivatives. Where five co-ordination is present, the planarity of the Me_3Sn and placing of the two ligands in the apical positions can be interpreted in terms of $4s\ 4p^3 4d$ hybridization of the orbitals in the tin atom. It should also be noted that this trigonal bipyramidal configuration is the expected symmetry for five co-ordination.

Another aspect of the chemistry of the trimethyltin group is that although it is possible to interpret the existence of a

five co-ordinate rather than a six co-ordinate configuration, the non-existence of the R_3Sn^+ ion is not readily explained. There seems no reason why the R_3Sn^+ ion should not exist as a stable entity in the solid state. The obvious fact that the trimethyltin group requires a certain charge density before it is "satisfied", and that if the interacting atom does not donate sufficient charge, the tin will accept, if possible, a fifth atom to make up this deficiency is not an explanation.

CHAPTER 10:

EXPERIMENTALTrimethyltin fluoride

(a) Preparation and Properties.

Trimethyltin fluoride was prepared by adding trimethyltin bromide (Orgmet), dissolved in 50% aqueous ethanol, to a stoichiometric quantity of potassium fluoride. The micro-crystalline trimethyltin fluoride was filtered and recrystallized from a saturated methanol solution by slow evaporation at room temperature. The colorless needles thus obtained (m.p. with decomposition, 360°C) were insoluble in organic solvents and only slightly soluble in hydrolytic solvents.

It was found that heating trimethyltin fluoride to 140°C in a high vacuum caused sublimation. In addition, if trimethyltin bromide was added to an excess of anhydrous potassium fluoride, a fine white powder sublimed at 170° under atmospheric pressure which analyzed as $\text{C}_3\text{H}_9\text{SnF}$ (calc. for $\text{C}_3\text{H}_9\text{SnF}$: C, 19.70%; H, 4.94%; found C, 19.78%; H, 5.00%). Resublimation was possible immediately after preparation, but not possible three days later.

The carbon and hydrogen analyses quoted above were completed with a Sargent Micro Combustion Apparatus as were all the following analyses.

(b) X-ray Crystallography.

The crystals obtained from 95% methanol consisted of bundles of very fine colourless needles, elongated along the a axis. Almost all of the crystals were multiple twins, but it was possible to obtain one or two suitable single crystals by breaking up the bundles, and searching carefully for a very small fragment. The crystal used for recording the x-ray data had a cross-section of 0.02 X 0.02 m.m.

This crystal was mounted on a chuck and placed in a Weissenberg Camera. Using $\text{Cu}_{K\alpha}$ radiation from a G.E. X-ray Unit, a rotation film, and a four film series of Weissenberg films for the $h\ k\ 0$, $h\ k\ 1$, $h\ k\ 2$, and $h\ k\ 3$ zones were taken.

By carefully measuring these films, the crystal was found to have an orthorhombic unit cell with the dimensions $a=4.32\text{\AA}$, $b=10.85\text{\AA}$, and $c=12.84\text{\AA}$. The density of trimethyltin fluoride (2.01 gm. cm^{-3}) was measured by flotation in aqueous silver nitrate and calculations showed that four molecules are in one unit cell.

The possible space groups were determined from the Weissenberg and Precession films by noting the following systematic absences:

$h\ 0\ l$ when l is odd.

$h\ k\ 0$ when $(h+k)$ is odd.

These absences were found consistent (131) with the space groups $P \underline{2}_1 \underline{c} \underline{n}$ (C_{2v}^9) or $Pm\bar{c}n$ (D_{2h}^{16}).

The structure amplitudes were derived from the usual formulae using the intensities of the $h\ k\ l$ reflections which had been measured visually from the Weissenberg films. Absorption was considered negligible and no corrections were considered necessary. The absolute scale was established separately for each level by comparison with the calculated structure factor at each stage of the analysis.

Preparation of Compounds $Me_3\ Sn\ A$ (where A = a monovalent anion.

General

The trimethyltin halides have been known for a very long time, and have been used as convenient intermediates to many trimethyltin derivatives. Cahours (12) used trimethyltin chloride and silver nitrate to prepare trimethyltin nitrate in 1860. More recently, Seyferth and Kallen (132) used trimethyltin iodide and silver cyanide to prepare trimethyltin cyanide.

The compounds in this investigation were prepared from trimethyltin bromide and the appropriate silver salt ($Ag\ BF_4$, $Ag\ PF_6$, $Ag\ AsF_6$, and $Ag\ SbF_6$ were obtained from Ozark - Mahoning Co.). Schwartz - Bergkamf filter - breakers (133) were used to remove the precipitated silver bromide when absolute methanol (134) was used as a solvent while an apparatus

described by Parry (135) was used for liquid sulphur dioxide. The solvent was removed in vacuo, and the anhydrous product was opened only under a nitrogen atmosphere in a dry box. The portion used for infra-red spectra was usually prepared either as Nujol or hexachlorobutadiene mull, and the spectrum was obtained with a Perkin - Elmer model 21 double beam recording spectrophotometer, fitted with sodium chloride or potassium bromide optics. A Perkin - Elmer model 137-K Br Spectrometer was also used for some far infra-red spectra.

Preparations

Trimethyltin Perchlorate.

1.804g. (8.69 mmoles) of anhydrous silver perchlorate (G.F. Smith Chemical Co.), and 2.177g. (8.73 mmoles) of trimethyltin bromide were dissolved in absolute methanol giving 1.640 g. (8.73 mmoles) of silver bromide. After filtration, the major portion of the methanol was removed under vacuum at room temperature. When about 3ml of methanol remained, the mixture solidified but melted again on further pumping. The last traces of methanol were removed in vacuo at 120° to give a white crystalline solid which sublimed from the reaction flask. (Analysis: Calc. for $C_3 H_9 ClO_4 Sn : ClO_4$, 38.0%. Found: ClO_4 , 38.2%). Carbon and hydrogen could not be determined owing to the explosive nature of the compound at high temperatures.

The melting point of trimethyltin perchlorate is 125-127°C (sealed tube). It is extremely soluble in polar solvents such as methanol, and it is very hygroscopic, being converted to a

liquid in less than a minute on exposure to moist air.

To further characterize this product a di-ammonia adduct was formed by condensing anhydrous ammonia on to trimethyltin perchlorate and removing the excess ammonia in vacuo

(Analysis: Calc. for $C_3 H_{15} Cl N_2 O_4 Sn$: C, 12.11%; H, 5.01%, N, 9.42%. Found C, 12.30%; H, 4.87%; N, 9.48%).

This ammonia adduct has very low solubility in organic solvents and is stable in air.

A pyridine adduct was prepared in a manner similar to that for the di-ammine derivative. However, in this case, the excess pyridine was tenaciously held by the product and heating to 50 C for four hours was required to remove the last trace of the nitrogen base. (Analysis: Calc. for $C_{13} H_{19} Cl N_2 O_4 Sn$: C, 37.05%; H, 4.52%; N, 6.66%; ClO_4 , 23.62%. Found: C, 37.14%; H, 4.98%; N, 7.07%; ClO_4 , 23.65%.)

The perchlorate analysis above and the nitrate analysis in the following preparation were completed by the nitron method as described by Scott (136).

Trimethyltin Nitrate.

Trimethyltin bromide (3.166g., 13.00 mmoles) and anhydrous silver nitrate (2.213g., 13.02 mmoles) were allowed to react (with shaking on account of the low solubility of silver nitrate) in dry methanol. Removal of the silver bromide (2.43gm., 12.96m.moles) and evaporation of the methanol in vacuo gave a white solid which was purified by sublimation at

100 C in vacuo. (Analysis: Calc. for $C_3 H_9 NO_3 Sn$: C, 15.59%; H, 3.99%; NO_3 , 27.4%. Found: C, 16.12%; H, 4.33%; NO_3 , 27.50%).

The sublimed trimethyltin nitrate melted at 127-128°C in a sealed tube and was unaffected by exposure to moist air. It was very soluble in polar solvents such as methanol, but has low solubility in non-polar organic solvents. The di-ammine adduct was prepared by reaction of the anhydrous nitrate with liquid ammonia as described above. (Analysis: Calc. for $C_3 H_{15} N_3 O_3 Sn$: C, 13.89%; H, 5.79%; NO_3 , 23.93%. Found: C, 14.03%; H, 5.58%; NO_3 , 24.60%).

Trimethyltin tetrafluoroborate.

Trimethyltin bromide (5.348gm., 22.0m.moles) and silver tetrafluoroborate (4.275gm., 21.9m.moles) were allowed to react in liquid sulphur dioxide solution, and the precipitated silver bromide was removed by filtration. Evaporation in vacuo of the sulphur dioxide solution gave trimethyltin tetrafluoroborate. (Analysis: Calc. for $C_3 H_9 B F_4 Sn$: C, 14.41%; H, 3.60%; F, 30.4%. Found: C, 14.24%; H, 3.39%; F, 29.8%), as a white crystalline solid, which is extremely hygroscopic and very soluble in liquid sulphur dioxide. The fluorine analyses were conducted in the manner described by Willard and Winter

Trimethyltin hexafluoroantimonate.

This compound was prepared from trimethyltin bromide (1.718g., 7.05m.moles) and silver hexafluoroantimonate (2.412g., 7.00m. moles) in liquid sulphur dioxide. Other preparations using methanol as a solvent gave an identical

product. Removal of the precipitated silver bromide (7.14m.moles) and the solvent gave the white crystalline trimethyltin hexafluoroantimonate (Analysis: Calc. for $C_3 H_9 SbF_6 Sn$: C, 9.1%; H, 2.20%; E, 28.5%. Found: C, 9.21%; H, 2.25%; F, 27.5%)

Trimethyltin hexafluoroarsenate.

Trimethyltin bromide (2.981gm. 12.3m.moles) and silver hexafluoroarsenate (3.453gm., 1.17m.moles) gave, following removal of precipitated silver bromide (11.0 m.moles) and evaporation of the sulphur dioxide solvent, a white solid identified as the sulphur dioxide adduct, $C_3H_9 Sn AsF_6 \cdot SO_2$ (Analysis: Calc. for $C_3 H_9 As F_6 O_2 S Sn$: C, 8.66%; H, 2.16%. Found: C, 8.67%; H, 2.18%). Prolonged pumping removed the sulphur dioxide to give the crystalline trimethyltin hexafluoroarsenate (Analysis: Calc. for $C_3 H_9 As F_6 Sn$: C, 10.3%; H, 2.56%. Found: C, 10.3%; H, 2.68%).

Trimethyltin hexafluorophosphate.

An attempt was made to prepare this compound from trimethyltin bromide and silver hexafluorophosphate in a sulphur dioxide solution. The precipitated silver bromide was shown by an X-ray diffraction powder photograph to contain trimethyltin fluoride. Fractionation of the volatile material from the sulphur dioxide solution gave a sample rich in phosphorous oxytrifluoride, POF_3 . The identification was accomplished from the infra-red spectrum of the sample. The solid remaining on removal of the sulphur dioxide was clearly

a mixture, and pure trimethyltin hexafluorophosphate could not be obtained.

Trimethyltin chloride dihydrate.

Recently Kriegsmann and Pischtschan (48) stated without supporting analytical data that if to a very concentrated aqueous solution of trimethyltin chloride some concentrated hydrochloric acid was added, precipitation of trimethyltin chloride occurred. This work was repeated, and it was found that the precipitate was in reality the dihydrate. (Analysis: Calc. for $C_3 H_{13} ClO_2 Sn$: C, 15.30%; H, 5.52%. Found: C, 15.07%; H, 5.55%).

Trimethyltin bromide ammonia adducts.

Kraus and Greer (51) stated that if ammonia was passed over solid trimethyltin bromide or into a benzene solution of the bromide, the di-ammoniate, $Me_3 Sn Br \cdot 2 NH_3$, was formed which rapidly converted to the mono-ammonia adduct. This work was repeated, and it was found that the di-ammine was indeed formed in both cases, but it was not unstable. It remained unchanged after 2 hours pumping and standing for four days. (Analysis: Calc. for $C_3 H_{15} Br N_2 Sn$: N, 10.01%; Found: N, 10.20%) X-ray powder photographs of the two preparations, i.e. from the solid bromide and from a benzene solution, showed a single phase. Sublimation of the di-ammoniate in vacuo and condensation in a trap maintained at -76° by a methanol - dry ice slurry, gave a product whose X-ray powder photograph showed the same single

phase. Sublimation at atmospheric pressure and condensation at room temperature gave the mono-ammonia adduct whose X-ray powder photograph showed a single phase differing from that of the di-adduct. (Analysis: Calc. for $C_3 H_{12} BrN Sn$: C, 13.80%; H, 4.68%; N, 5.37%. Found: C, 13.79%; H, 4.62%; N, 5.41%).

Trimethyltin bromide mono-pyridine.

This compound was prepared by addition of pyridine to a petroleum ether solution of trimethyltin bromide. Partial precipitation occurred at room temperature and cooling to $0^\circ C$ in an ice bath gave additional product. Purification by recrystallization was completed in sodium dried benzene. (Analysis: Calc. for $C_8 H_{14} Br N Sn$: C, 29.90%; H, 4.35%. Found: C, 29.65%; H, 4.26%.)

Trimethyltin chloride mono-pyridine.

This compound was prepared and purified in a manner similar to the bromide. (Analysis: Calc. for $C_8 H_{14} Cl N Sn$: C, 34.51%; H, 5.01%. Found: C, 36.47%; H, 5.47%.)

Triphenyltin halides.

The triphenyltin chloride used in the following reactions was obtained from Eastman Organic Chemicals. The other halides were obtained by a simple conversion process (4). A weighed quantity of triphenyltin chloride was dissolved in 150 ml. of diethylether and shaken for three hours in a 500 ml. separatory funnel with 50 ml. of 6N sodium hydroxide. The organic solvent

containing the triphenyltin hydroxide was removed from the separatory funnel and washed with two portions of distilled water. A six-fold excess of either hydrobromic or hydroiodic acid was added to the washed ether solution and thoroughly mixed for three hours. The organic phase was washed, dried, and evaporated to yield the crude product. Recrystallization from chloroform gave large colorless crystals.

(a) Triphenyltin bromide:- m.p.= 119-120°C. Analysis:

Calc. for $C_{18}H_{15}BrSn$: C, 50.31%; H, 3.50%.

Found: C, 50.61%; H, 3.46%.

(b) Triphenyltin iodide:- m.p.= 120-121°C. Analysis:

Calc. for $C_{18}H_{15}ISn$: C, 46.17%; H, 3.21%.

Found: C, 45.65%; H, 3.35%.

The unstable ammine adducts were prepared by condensing ammonia into a trap maintained at - 76°C containing the triphenyltin halide and then evaporation of the solvent under vacuum. The product was pumped for four hours to remove the last trace of adhering ammonia. Analysis proved that the unchanged halide was present.

The attempted preparation of the pyridine adducts was conducted in a similar manner as the ammine adducts.

Trimethyltin trifluoromethyltrifluoroborate.

This compound was previously prepared by Clark And Willis (110), and it was repeated only to establish the constitution of the anhydrous product by infra-red measurements. An all

glass, self contained system with the usual break seals and capillary constrictions for the movement of reactants and isolation of the product was used. In this preparation 1.195gm (5.15m.moles) of trimethyltrifluoromethyltin (138), 50 ml. of carbontetrachloride (previously dried over P_2O_5), and 0.424gm. (6.25m.moles) of boron trifluoride (Matheson Co. Inc.) were condensed in succession into the reaction vessel with liquid nitrogen. The system was permitted to warm slowly to room temperature, and the product in the carbontetrachloride solvent consisted of clear colorless plates. On removal of the solvent only a white powder remained. This product was extremely hygroscopic and even under the best obtainable dry box conditions slow hydrolysis took place.

Trimethyltin trifluoromethylpentafluoroantimonate.

The reactant antimony pentafluoride was prepared from antimony trioxide and fluorine (139) using the normal fluorination techniques, and purified by repeated distillation. For trimethyltrifluoromethyltin, the procedure outlined by Clark and Willis (138) was used. Final purification of this compound should be a vapour phase chromatographic separation at $50^\circ C$ of the trace quantities of trimethyltin iodide from the desired product.

This reaction was to be conducted in the same manner as trimethyltrifluoromethyltin and boron trifluoride, however, a preliminary experiment showed that antimony pentafluoride reacted with the intended solvent trichlorofluoromethane.

For this reason, the reaction was conducted in the absence of solvent. The antimony pentafluoride (2.79gm., 12.9m.moles) was condensed on the lower sides of the reaction trap and trimethyltrifluoromethyltin (3.34gm., 14.3m.moles) on the upper portion. When the acetone-dry ice coolant was slowly lowered, the tin compound moved down the reaction tube. At the point of contact extensive decomposition took place, but a pure cream white solid was obtained in the lower portions of the vessel (Analysis: Calc. for $C_4 H_9 Sb F_5 Sn$: C, 10.70%; H, 2.01%. Found: C, 11.5%; H, 2.08%.)

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