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SOME REACTIONS OF TIN(II)CHLORIDE IN NON-AQUEOUS SOLUTION

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BY

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James L. Morrison

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INTRODUCTION

The reactions of tin(II)chloride in aqueous solution have been extensively investigated. Most of the early work was concerned with the reactions of tin(II)chloride in dilute hydrochloric acid with an aromatic or aliphatic amine, or with an amino-acid in the same solvent[1-5]. More recently, Davies and co-workers[6] prepared some tin(II)chloride complexes of the platinum metals in which the $SnCl_3^-$ anion acts as an electron pair donor.

Tin(II)chloride is also an excellent reducing agent and as such has wide application in a number of organic reactions[50]. From an inorganic viewpoint, however, the reactions of tin(II) chloride in non-aqueous solution have been largely neglected. Compounds have been reported with diethyl ether[51], and 1,4-dioxane[52]. Two recent papers have been concerned with some novel complexes. The first[7] was on the reaction of carbonyl - π - cyclopentadienyl complexes of iron, molybdenum, and tungsten with tin(II)chloride. In the second[31], a series of phthalocyano-tin complexes was prepared using tin(II)chloride as a starting material.

There has been no systematic study, however, of the reactions of this compound with donor molecules. The purpose of this present study, then was twofold. First, it was desired to determine the scope of the reactions of tin(II)chloride with

donor species in a variety of non-aquecus solvents. Second, the properties of a number of the resulting complexes were to be studied using infra-red, x-ray powder diffraction, and conductance techniques.

This work is divided into three chapters and an appendix. The first two chapters deal with the reactions of tin(II)chloride with particular types of compounds: Chapter I, reactions with alcohols; Chapter II, reactions with nitrogen and oxygen-containing compounds. Each of the chapters includes preparation, properties, and structural studies of the complexes, and also includes an experimental section for detailed preparations of complexes prepared in that chapter. Chapter III is a general experimental section where techniques applicable to the whole study are included. The appendix contains tables of data not included in the main body of the thesis. Also included in the appendix is a section on the preparation and properties of ammonium hexafluorostannate, and a survey of the reactions of tin(IV) compounds with 9,10-phenanthrenequinone.

CHAPTER I

SOME ALKOXIDE COMPOUNDS OF DIVALENT TIN

The metal alkoxides constitute an important class of compounds containing a metal-oxygen-carbon bonding system. Two excellent reviews of metal alkoxides have been written by Bradley[10-11]. Prior to the start of this work, Bradley[12] had reported on the alkoxides of tetravalent tin but there was only one mention of an alkoxide compound of tin(II). Meerwein and Geschke[13], in a study of the pyrolysis of tetraethoxy tin reported the formation of tin(II)ethoxide according to the equation

$$Sn(OC_2H_5)_4 \xrightarrow{\Delta} Sn(OC_2H_5)_2 + CH_3CHO + C_2H_5OH \qquad (1)$$

While our work was in progress, Amberger and Kula[8-9] reported the preparation of tin(II)methoxide by the following reaction:

$$SnBr_2 + 2Na(OCH_3) \longrightarrow Sn(OCH_3)_2 + 2NaBr \qquad (2)$$

Prior to the appearance of these reports, we had attempted unsuccessfully to prepare tin(II)methoxide using this reaction but had decided to look for another method because large volumes of methanol were needed to wash the sodium bromide out of the methoxide. Also, the product we obtained from reaction (2) was not the simple methoxide but a hydrolysis product.

Accordingly, it was decided to try the reaction

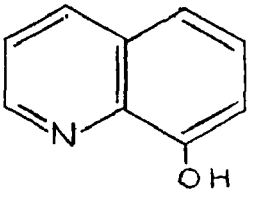
$$SnCl_2 + 2(C_2H_5)_3N + 2CH_3OH \longrightarrow Sn(OCH_3)_2 + 2(C_2H_5)NHCl \qquad (3)$$

Using this reaction we were able to prepare tin(II)methoxide, and, by substituting ethanol for the methanol, successfully

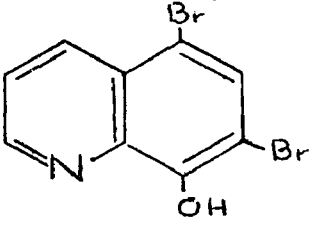
prepared tin(II)ethoxide. This eliminated the need for extensive washing of the alkoxide since the amine hydrochloride formed is quite soluble in a minimum amount of alcohol.

It was found that small amounts of water in the reaction mixture resulted in the formation of a hydrolyzed product, bis-[alkoxidetin(II)] oxide, and that an excess of water resulted in the formation of tin(II)oxide.

By taking advantage of the apparent ease with which tin(II)methoxide reacts with compounds containing a readily replaceable hydrogen, it was used as a starting material to prepare tin(II)acetate, and chelate compounds with 8-quinolinol,



and its 5,7-dibromo derivative,



Preparation of the Compounds

For the alkoxides, anhydrous tin(II)chloride was dissolved in an excess of the alcohol and anhydrous triethylamine was added dropwise with stirring until a permanent precipitate formed. The precipitates were filtered, washed with the appropriate alcohol until the filtrate gave a negative chloride test, washed with ether, and dried with suction. All manipulations were carried out in a glove bag continuously flushed with extra dry nitrogen. These compounds were analyzed immediately for tin content.

The bis-[alkoxidetin(II)]oxide compounds were prepared in the same way except that no special precautions were taken to exclude all traces of moisture from the reaction mixture, or in the case of the ethoxide, by using 95 per cent ethanol in the reaction. Again, tin analysis was done as soon as practical after drying.

Triethylammonium chloride was recovered from the alcohol filtrate of the above reactions by addition of ether. It was purified by repeated precipitation from chloroform solution by ether. It was identified by its x-ray powder diffraction pattern and infra-red spectrum. These data are given in Tables XII and XIII in the appendix.

A bis-[alkoxidetin(II)]oxide compound also resulted from the reaction of tin(II)bromide in methanol with sodium methoxide. Sodium bromide was washed out of the alkoxide with a large volume of methanol and precipitated from the filtrate by addition of ether. It was identified by its x-ray powder pattern given in Table XIV in the appendix.

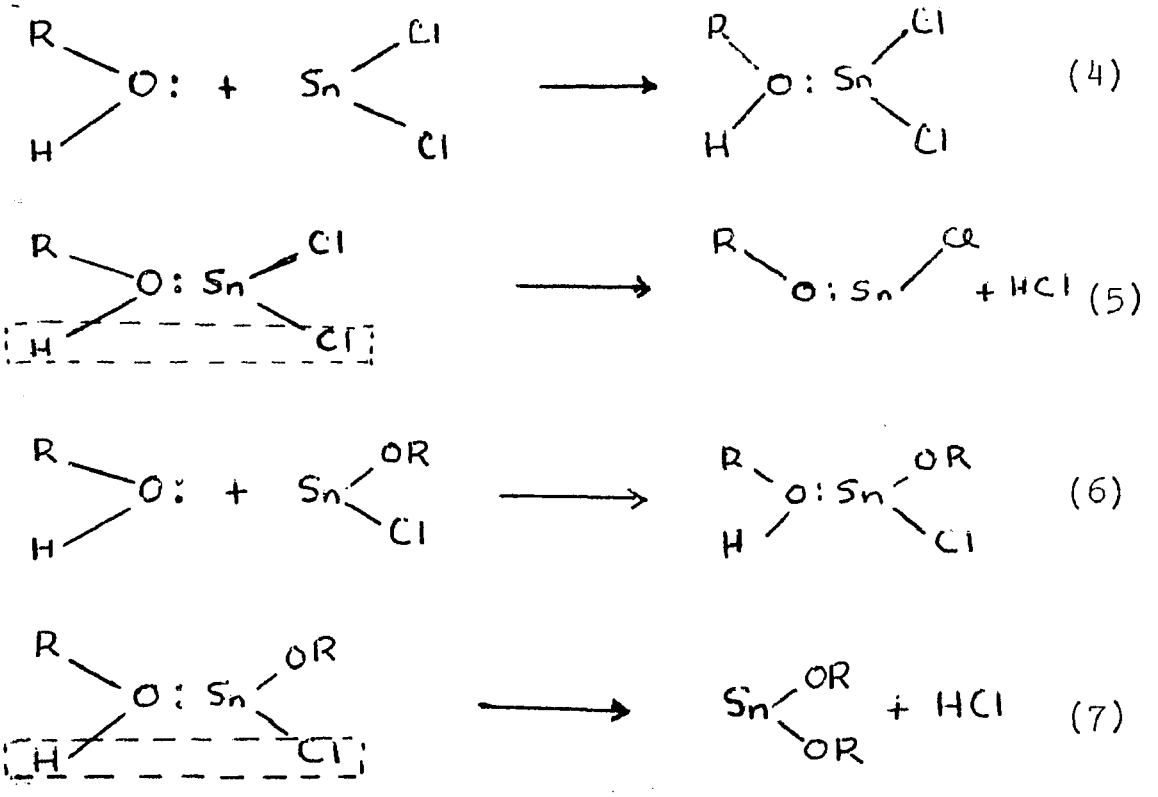
The same compound was formed when tin(II)bromide in methanol was reacted with triethylamine in methanol. Triethylammonium bromide was precipitated as above and identified by its infra-red spectrum and x-ray powder pattern. These data are also given in the appendix in Tables XII and XIII.

The reactions of tin(II)methoxide were carried out by slurrying freshly prepared tin(II)methoxide in an appropriate solvent and adding an estimated excess of the other reactant. This mixture was either stirred mechanically at room temperature or refluxed. The resulting precipitate was filtered, washed

with an appropriate solvent, then ether, and dried. Identification of the compound formed was by elemental analysis, infrared spectra, and x-ray powder diffraction.

Discussion and Results

In view of the products formed in the reaction between tin(II)chloride and the alcohols in the presence of triethylamine, it is felt that the following reactions occur:



$$HCl + (C_2H_5)_3N \longrightarrow \left[(C_2H_5)_3NH\right]Cl \qquad (8)$$

$$SnCl_2 + 2ROH + 2(C_2H_5)_3N \longrightarrow Sn(OR)_2 + 2\left[(C_2H_5)_3NH\right]Cl \qquad (9)$$

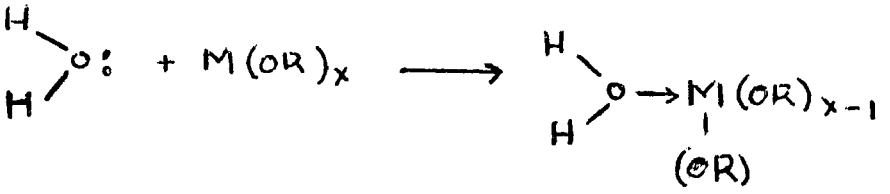
Nelles[14] has used this reaction scheme to explain the products formed in the reaction of titanium(IV)chloride, alcohol, and ammonia, equation 10.

$$TiCl_4 + 4ROH + 4NH_3 \longrightarrow Ti(OR)_4 + 4NH_4Cl \qquad (10)$$

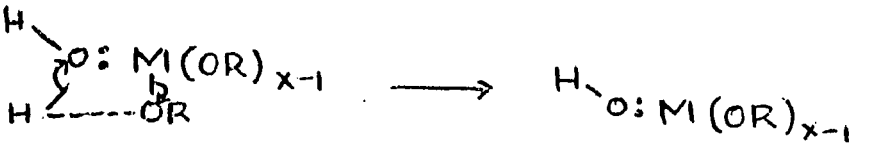
Bradley, Wardlaw and their co-workers have also applied this "ammonia method" to a large number of metal alkoxides of zirconium[15], hafnium[16], cerium[17], niobium[18], tantalum[19], iron[20], uranium[21], and plutonium[22].

All metal alkoxides that have been investigated thus far are very easily hydrolyzed. In most instances the alkoxides are so sensitive even to small traces of water that special precautions have been adopted to study them[11]. Tin(II)methoxide and tin(II)ethoxide are both very easily hydrolyzed. When no special precautions are taken to exclude water from the reaction, intermediate products, metal oxide alkoxides, $Sn_2O(OR)_2$ are formed. When an excess of water is present, the ultimate product is black tin(II)oxide, obtained under reflux.

Little is known concerning the mechanism of the hydrolysis of metal alkoxides. Bradley[11] feels it is reasonable to assume that the initial step involves the coordination of a water molecule through its oxygen to the metal, equation 11. One of the protons on the water molecule interacts with the oxygen of the alkoxide group through hydrogen bonding and following an electronic rearrangement a molecule of alcohol is expelled, equation 12. The hydroxy-metal alkoxide formed in 12 may further react to form the oxide alkoxide by either 13 or 14.



(11)



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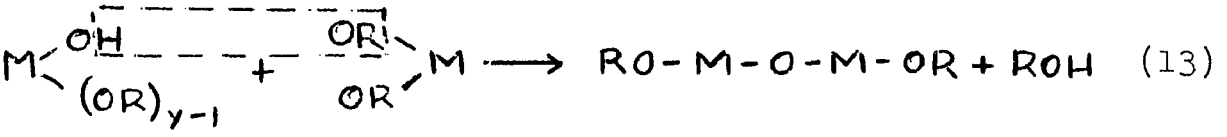

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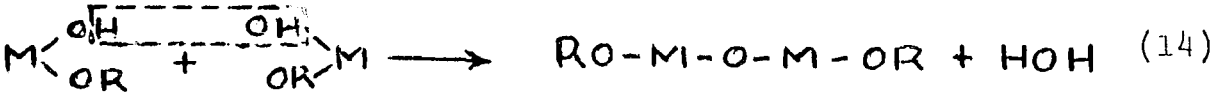
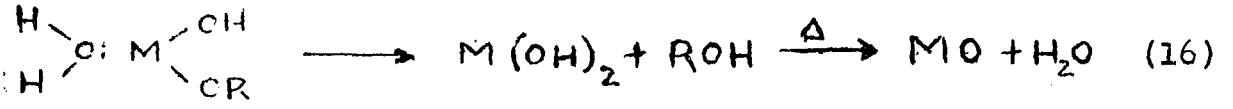


(14)

If a large excess of water is present, the hydroxy-metal alkoxide in 12 reacts with another molecule of water to form the metal oxide, equations 15 and 16.

(15)



(16)

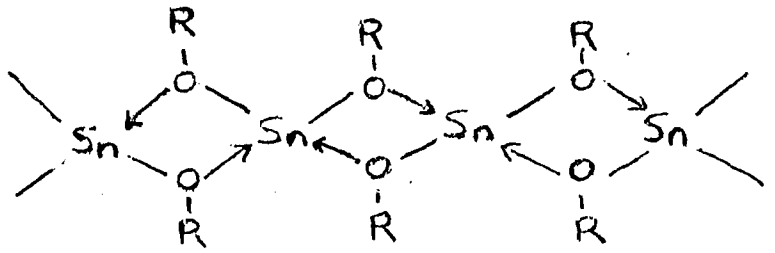
In the tin(II)alkoxides, this scheme accounts for the formation of the intermediate $Sn_2O(OR)_2$ when a limited amount of water is present and the formation of black tin(II)oxide when excess water is in the reaction mixture.

Apart from product analysis, there has been only one report in support of this mechanism[19]. However, several investigators have studied the hydrolysis of titanium(IV) alkoxides and all report the formation of the oxide alkoxide

intermediates[20-22]. There is also some evidence to indicate that as the extent of hydrolysis increases, the ease of hydrolysis of the remaining hydroxyl group(s) decreases. It is felt that this is the case in the tin(II)alkoxides since the alkoxide oxide is formed quite easily while the oxide requires an excess of water present.

One of the more striking characteristics of these alkoxides is rapid polymerization. When freshly prepared, the alkoxides and intermediate products are white. When allowed to stand for any length of time, even in a sealed container in an evacuated desiccator, a pale yellow product is formed. This color change seems to be more rapid at temperatures higher than room temperature. This polymerization causes no significant change in tin content of the compounds.

It is to be expected that this polymerization should occur. Olsen and Rundle[24] have reported that unless sterically hindered, monomeric R_2Sn compounds tend to polymerize quite rapidly. With the possible exception of dicyclohexyltin[25], no monomeric R_2Sn alkyl species have been reported. A few aryl R_2Sn compounds have been reported to be monomeric but only when freshly prepared[26-28]. That polymerization causes a color change from white to yellow has been shown by Kuivila and Beumel[28]. Diphenyltin is known to exist in several modifications which differ in molecular weight, solubility, color, and crystalline form, but have similar tin content[26-29]. It is felt that for the $Sn(OR)_2$ compounds, polymerization occurs as follows:



These alkoxides are insoluble in all common organic solvents and are amorphous by x-ray powder diffraction, supporting this polymerization concept.

The infra-red spectra of the alkoxides and the intermediate products in the 1300cm^{-1} to 400cm^{-1} region are listed in Table I.

TABLE I

Infra-red Spectra of Tin(II)alkoxide Compounds

$Sn(OCH_3)_2$	$Sn_2O(OCH_3)_2$	$Sn(OC_2H_5)_2$	$Sn_2O(OC_2H_5)_2$
1025	1015	1160	1145
570	740	1150	1092
	565	1092	1045
		1048	960
		965	880
		885	740
		578	575
		475	548
			472

Frequency in cm^{-1}

The infra-red spectra of metal alkoxides has been discussed by Barraclough[32]. He suggested that a comparison of the metal alkoxide spectra with the corresponding alcohol would permit one to make tentative assignments to the metal-oxygen and carbon-oxygen stretching frequencies.

The infra-red spectra of methanol and ethanol in the $1100cm^{-1}$ - $400cm^{-1}$ region are shown in Table II.

TABLE II

Infra-red Spectra of Methanol and Ethanol

MeOH	$1030cm^{-1}$					
EtOH	1081	1050	876	802	750-600	425

On this basis, the following metal-oxygen and carbon-oxygen frequencies are tentatively assigned in Table III.

TABLE III

Metal-Oxygen and Carbon-Oxygen Stretching Frequencies

Compound	C-O (cm^{-1})	M-O (cm^{-1})
$Sn(OCH_3)_2$	1025	570
$Sn_2O(OCH_3)_2$	1015	565 (center of broad band)
$Sn(OC_2H_5)_2$	1092, 1048	578
$Sn_2O(OC_2H_5)_2$	1092, 1045	575, 548

The ethoxide C-O and M-O assignments are in good agreement with those of a previous examination of metal ethoxides(32). There appears to have been no previous report on the infra-red spectrum of metal methoxides, but a comparison of the methoxide spectrum with that of methanol makes the assignments seem reasonable. In support, Amberger and co-workers(57) give $1035cm^{-1}$ for the Sn-O-C stretch in $(CH_3)_3Sn(OCH_3)$, and, we have shown in this laboratory that the major absorption for tin(II)oxide appears between $600cm^{-1}$ and $485cm^{-1}$.

Although the dominating characteristic of the metal alkoxides is the ease with which they react with water, it appears that many alkoxides will react with a wide variety of other hydroxyl-containing compounds. Mehrotra and co-workers[23] have shown that aluminum isopropoxide will react with carboxylic acids to form aluminum tri-soaps. Beta-diketones, such as acetyl acetone, will displace two or more alkoxide groups from the metal alkoxides of titanium(IV), zirconium(IV) and tantalum(V)[11].

In this work we have shown that tin(II)methoxide will undergo similar reactions with hydroxyl-containing compounds. The reactions appear to be quite similar to the reaction of the alkoxide with water. With acetic acid, tin(II)acetate is formed. The reaction probably involves the formation of a tin-oxygen bond by coordination through the hydroxyl oxygen and a subsequent elimination of methanol, equation 17.

$$2CH_3COOH + Sn(OCH_3)_2 \longrightarrow Sn(C_2H_3O_2)_2 + 2CH_3OH \qquad (17)$$

The infra-red spectrum of the solid product formed in this reaction is that of the coordinated acetate ion[54-56]. It is given in Table XVI.

A similar reaction undoubtedly occurs when 8-quinolinol or 5,7-dibromo-8-quinolinol is reacted with tin(II)methoxide, equation 18, to give a tin(II) chelate compound.

$$2C_9H_6NOH + Sn(OCH_3)_2 \longrightarrow Sn(C_9H_6NO)_2 + 2CH_3OH \qquad (18)$$

This chelate has been previously reported by Stevens[35].

The same chelate is formed when tin(II)chloride, sodium methoxide, and 8-quinolinol are reacted in methanol solution according to the reaction:

$$SnCl_2 + 2NaOCH_3 + 2C_9H_6NOH \longrightarrow Sn(C_9H_6NO)_2 + 2NaCl + 2CH_3OH \qquad (19)$$

It is not certain how this reaction occurs, but it is felt that it can be explained by either of two mechanisms. Sodium methoxide reacts with 8-quinolinol to form the sodium salt and methanol, equation 20, and the sodium salt reacts with tin(II)chloride forming the chelate and sodium chloride, equation 21.

$$C_9H_6NOH + NaOCH_3 \longrightarrow NaC_9H_6NO + CH_3OH \qquad (20)$$

$$2(NaC_9H_6NO) + SnCl_2 \longrightarrow Sn(C_9H_6NO)_2 + 2NaCl \qquad (21)$$

The other possibility which cannot be excluded is that sodium methoxide reacts with tin(II)chloride forming tin(II)methoxide and sodium chloride, equation 22, and the tin(II)methoxide reacts with 8-quinolinol to form the chelate as before, equation 23.

$$SnCl_2 + 2NaOCH_3 \longrightarrow Sn(OCH_3)_2 + 2NaCl \qquad (22)$$

$$Sn(OCH_3)_2 + 2C_9H_6NOH \longrightarrow Sn(C_9H_6NO)_2 + 2CH_3OH \qquad (23)$$

If the reaction between tin(II)methoxide and 8-quinolinol is carried out in an acetone - glacial acetic acid solvent system instead of methanol, no chelate is formed. Instead, a compound with the empirical formula $Sn(OOCH_3)(C_9H_6NO)$ is precipitated.

It is felt that the reactions which occur here are: tin(II)methoxide reacts with glacial acetic to form tin(II) acetate, equation 17. The tin(II)acetate reacts with 8-quinolinol to form $Sn(OOCH_3)(C_9H_6NO)$, equation 24. Fanning and Jonassen[48] have postulated this sort of mechanism

$$Sn(C_2H_3O_2)_2 + C_9H_6NOH \longrightarrow Sn(C_9H_6NO)(C_2H_3O_2) + CH_3COOH \qquad (24)$$

for the reaction of $Cu(CH_3CO_2)_2$ with 8-quinolinol and we have shown that the reaction between tin(II)chloride and 8-quinolinol gives a product with the empirical formula $Sn(C_9H_6NO)Cl$.

We were not successful in an attempt to replace both acetate ions with $C_9H_6NO^-$ groups by digesting the $Sn(C_9H_6NO)$-$(C_2H_3O_2)$ compound in its own filtrate. Instead, a compound that gave a negative test for stannous tin resulted. Elemental analysis and infra-red spectrum indicated that $Sn(C_9H_6NO)_2$-$(C_2H_3O)_2$ was formed.

It is not presently known how tin(II) can be oxidized to tin(IV) in this solvent system. That an oxidation from

tin(II) to tin(IV) can occur in various solvent systems has been demonstrated by several workers. Wilkinson[7] has shown that the carbonyl - π - cyclopentadienyl complexes of iron, molybdenum, and tungsten contain tin(IV) though tin(II) was the starting material. Muetterties[30] has shown that some SnF_3^- salts can be oxidized to $SnF_6^=$ salts in aqueous hydrofluoric acid solution. Kroenke and Kenney[31] have shown that tin(II)chloride and phthalonitrile react to give dichloro(phthalocyano)tin(IV), $C_{32}H_{16}N_8SnCl_2$. So, even though the mechanism of oxidation in this solvent system is not known, it does not seem unreasonable to assume that prolonged contact of a tin(II) species with warm glacial acetic acid - acetone could result in oxidation to a tin(IV) compound.

Experimental

Detailed preparations of the compounds are as follows:

Tin(II)methoxide - 6 g. (0.032 mole) of tin(II)chloride were dissolved in 200 ml. of absolute methanol. Freshly dried triethylamine was added until a permanent precipitate formed. The white precipitate was filtered, washed with methanol and anhydrous ether. The compound was vacuum dried and analyzed immediately for tin content.

Anal. Calcd. for $Sn(OCH_3)_2$: Sn, 65.68%

Found: Sn, 65.04, 65.57

Triethylammonium chloride was recovered from the filtrate by the addition of a large volume of anhydrous ether. This

compound was dissolved repeatedly in chloroform and reprecipitated with ether before identification.

Bis-[methoxytin(II)] oxide - This compound was formed when a reaction similar to the one above was run except that no special precautions were taken to exclude moisture from the reaction mixture.

Anal. Calcd. for $Sn_2O(OCH_3)_2$: Sn, 75.2

Found: Sn, 76.25, 75.61

Triethylammonium chloride was recovered as above.

The same compound resulted from the reaction of triethylamine with tin(II)bromide in methanol. Tin(II) bromide was prepared by the following method. Twelve g. (0.1 mole) of mossy tin were covered with 100 ml. of methanol. Bromine was added dropwise until all the tin had reacted. The solution was filtered and refluxed for 48-72 hours over mossy tin. The solution was filtered and stored over mossy tin.

Triethylamine was added to 100 ml. of this solution until a permanent precipitate was formed. This precipitate was filtered and washed with methanol and then ether, and dried over calcium chloride in a vacuum desiccator. Tin analysis was done immediately after drying.

Anal. Calcd. for $Sn_2O(OCH_3)_2$: Sn, 75.2

Found: 75.9, 75.9

Triethylammonium bromide was precipitated as above for triethylammonium chloride.

Reaction of $SnBr_2$ with $Na(OCH_3)$ in methanol - To 100 ml. of a tin(II)bromide-methanol solution was added a methanol

solution of sodium methoxide until a permanent white precipitate was formed. The white precipitate was filtered and washed with large volumes of methanol until the filtrate gave no test for bromide ion. The white precipitate gave an infra-red spectrum that was identical to the other methoxide compounds. Qualitative tests showed tin(II) was present. Sodium bromide was recovered from the first filtrate by the addition of ether.

Tin(II)ethoxide - Three g. (0.015 mole) of tin(II) chloride were dissolved in 75 ml. of ethanol. Anhydrous triethylamine was added until a permanent precipitate was formed. The compound was filtered, washed several times with ethanol and then anhydrous ether. The compound was dried with suction and analyzed immediately for tin content.

Anal. Calcd. for $Sn(OC_2H_5)_2$: Sn, 56.87

Found: Sn, 56.29

Triethylammonium chloride was recovered as above.

Bis-[ethoxytin(II)] oxide - This compound precipitates when triethylamine is added to an ethanol solution of tin(II) chloride, (2 g. in 100 ml. of alcohol). No special precautions were taken to exclude moisture from the reaction mixture. The white precipitate was filtered and treated as above.

Anal. Calcd. for $Sn_2O(OC_2H_5)_2$: Sn, 69.13

Found: 68.43. 68.66

A compound with slightly higher tin content is obtained if 95 per cent ethanol is used in the reaction.

Anal. Found % Sn: 71.13, 71.18

Reaction of tin(II)methoxide with acetic acid - Freshly prepared tin(II)methoxide was slurried in dry 2,2'-dimethoxyethane. Glacial acetic acid was added dropwise with stirring. A fluffy white precipitate was filtered and washed with acetic acid and dimethoxyethane. The compound was dried over calcium chloride.

Anal. Calcd. for $Sn(C_2H_3O_2)_2$: Sn, 50.10

Found: Sn, 49.80, 49.70

The x-ray powder pattern of this compound is given in Table XXIV.

Reaction of tin(II)methoxide with 8-quinolinol in methanol - Freshly prepared tin(II)methoxide was slurried in 100 ml. of absolute methanol. An estimated excess of a methanol solution of 8-quinolinol was added slowly with stirring. This reaction mixture was refluxed for 2-3 hours and a bright yellow precipitate formed. This compound was filtered, washed with methanol and dried with ether and suction. Final drying was in a 50°C. oven.

Anal. Calcd. for $Sn(C_9H_6NO)_2$: Sn, 29.18 N, 6.88

Found: Sn, 28.81, 29.07, 28.60; N, 6.93

The x-ray powder pattern of this chelate is given in Table XXV.

Reaction of tin(II)methoxide with 8-quinolinol in acetone - glacial acetic acid - Freshly prepared tin(II) methoxide was slurried in anhydrous acetone and an excess of glacial acetic acid was added dropwise with vigorous stirring. To this solution was added 1.45 g. (0.01 mole) of 8-quinolinol in acetone. A pale yellow precipitate formed, was filtered and washed with acetone, and ether, and dried at 50°C.

Anal. Calcd. for $Sn(C_9H_6NO)(C_2H_3O_2)$: Sn, 36.76; N, 4.33

Found: Sn, 36.54, 36.41, 36.88; N, 4.54

About 1 g. of this solid was returned to the above filtrate and a small amount of 8-quinolinol in acetone was added. This mixture was allowed to digest with occasional mechanical stirring for 48 hours. A yellow precipitate was filtered and treated as above. A qualitative test for tin(II) was negative.

Anal. Calcd. for $Sn(C_9H_6NO)_2(C_2H_3O_2)_2$: Sn, 22.60; N, 5.33

Found: Sn, 21.71, 22.25, 21.97; N, 5.51

Reaction of tin(II)chloride with sodium methoxide and 8-quinolinol in methanol - 1.1 g. (0.02 mole) of sodium methoxide were dissolved in 100 ml. of absolute methanol. To this solution 2.90 g. (0.02 mole) of 8-quinolinol were added. The resulting solution was pale yellow. To this pale yellow solution, 1.89 g. (0.01 mole) of tin(II)chloride in 100 ml. of absolute methanol were added. An immediate, bright yellow precipitate resulted. This precipitate was filtered, washed with several portions of water until the

filtrate gave a negative chloride test, then washed with ether and dried in a 50°C. oven. This compound was identified by its infra-red spectrum and x-ray powder diffraction pattern as $Sn(C_9H_6NO)_2$.

The initial filtrate was evaporated to dryness, the residue dissolved in a small amount of water, filtered and evaporated again to dryness. This final residue was identified as sodium chloride by its x-ray powder diffraction pattern.

Reaction of tin(II)methoxide with 5,7-dibromo-8-quinolinol in methanol - Freshly prepared tin(II)methoxide was slurried in anhydrous methanol. An estimated excess of 5,7-dibromo-8-quinolinol in methanol was added. This mixture was refluxed for four hours. The resulting yellow compound was filtered, washed with methanol and ether, and dried at 50°C.

Anal. Calcd. for $Sn(C_9H_4NOBr_2)_2$: Sn, 16.42

Found: Sn, 16.78, 16.96

The x-ray powder diffraction pattern of this chelate is given in Table XXV.

Reaction of tin(II)methoxide with excess water - Three g. of freshly prepared tin(II)methoxide were refluxed with 100 ml. of distilled water. After about 45 minutes of refluxing, a black suspension appeared. Refluxing was continued for about two hours. The black compound was filtered, dried and identified as tin(II)oxide by its x-ray powder diffraction pattern, given in Table XV.

Reaction of tin(II)ethoxide with excess water - This reaction was run as above using freshly prepared tin(II) ethoxide and 75 ml. of distilled water. Tin(II)oxide was again identified by its x-ray powder diffraction pattern.

CHAPTER II

THE REACTIONS OF TIN(II)CHLORIDE WITH NITROGEN AND OXYGEN-CONTAINING COMPOUNDS

In this work it was found that tin(II)chloride will react with a number of nitrogen and oxygen-containing compounds. Several new compounds were prepared and characterized.

This discussion, like the previous one, is divided into sections. Each section is concerned with a separate phase of the work first is the general method of preparation of the complexes; second is a discussion of the complexes formed and structural studies; and last is the experimental section. Detailed preparations of the complexes are included in this experimental section. The empirical formulae, together with the analytical data and color of the complex compounds are given in Tables VIII, IX, X, and XI.

Preparation of the Complexes

In general, a non-aqueous solution of tin(II)chloride was added to a non-aqueous solution of the complexing compound. In some instances, the method of addition was reversed. Molar ratios of the reactants were varied to see if compounds of different stoichiometry could be prepared with the same complexing compound.

In most cases, immediate precipitation occurred; some of the complexes, however, precipitated only after standing at room temperature, while the sulfoxide complexes

formed only at dry ice temperature. In one instance, the pyridine complex, it was necessary to evaporate most of the solvent before precipitation. In all cases, the precipitates were filtered, washed with the appropriate non-aqueous solvent and anhydrous ether, and finally dried either in a 50°C. oven or in a vacuum desiccator over calcium chloride.

Results and Discussion

Reactions with quarternary ammonium chlorides, $[R_4N]Cl$. When quarternary ammonium chlorides, $[R_4N]Cl$, are reacted with tin(II)chloride, simple salts are formed according to the reaction

$$[R_4N]Cl + SnCl_2 \longrightarrow [R_4N]SnCl_3 \qquad (25)$$

Varying the molar ratios of the reactants had no effect on the product formed. This confirms recent reports that the preferred coordination number for tin(II), in inorganic compounds, is three. The x-ray powder patterns of these compounds are in Table XXVIII.

2,2′-bipyridyl, $C_{10}H_8N_2$. 2,2′-bipyridyl, reacts with a large number of metal salts. A review of these complexes has been given by Brandt(33).

Tin(II)chloride reacts quite readily with 2,2′-bipyridyl to give a bright yellow compound, $SnCl_2 \cdot C_{10}H_8N_2$. Attempts to prepare a hydrated compound, $SnCl_2 \cdot C_{10}H_8N_2 \cdot X(H_2O)$ were not successful. With tin(II)chloride dihydrate as the starting compound, a bright yellow precipitate, identified by its x-ray powder pattern as $SnCl_2 \cdot C_{10}H_8N_2$, was formed. The powder pattern of this compound is given in Table XXX.

Pyridine-N-oxide, C_5H_5NO. The donor properties of pyridine-N-oxide are well known(34-35). This ligand forms two complexes with tin(II)chloride, containing one mole and two moles of ligand, respectively. The 1:1 complex is formed when the reactants are mixed in a 1:1 ratio; the 1:2 complex is formed when the reactants are mixed in a tin(II)chloride to ligand ratio of 1:2. Each of these complex compounds has a distinctive x-ray powder pattern given in Table XXXI.

Pyridine - C_5H_5N. Since pyridine is known to form complexes with a very large number of metal salts(40), it was surprising that a complex with tin(II)chloride was so difficult to prepare. No complex is formed when the reactants are mixed in tetrahydrofuran, dimethoxyethane, methanol, or when excess pyridine is used as the solvent. A compound with the empirical formula $SnCl_2 \cdot C_5H_5N$ was formed when tin(II) chloride was dissolved in excess pyridine, refluxed, evaporated to a very small volume and anhydrous dimethoxyethane added. Great care must be taken to exclude all moisture from the reaction mixture to prevent the formation of a compound containing the pyridinium ion.

The x-ray powder pattern of $SnCl_2 \cdot C_5H_5N$ is given in Table XXIX.

8-quinolinol, C_9H_6NOH. 8-quinolinol was reacted with tin(II)chloride under a variety of conditions in a number of non-aqueous solvents. The nature of the product formed depends on temperature, solvent, concentration, and time.

The compounds formed and the conditions used are given in Table IX.

It was found that tin(II)chloride and 8-quinolinol reacted to form the complex α-$Sn(C_9H_6NO)Cl$ at very low temperature and at room temperature. At refluxing temperature, another form of this complex β-$Sn(C_9H_6NO)Cl$ was formed. The α-form can be converted to the β-form by refluxing the former in acetone. α-$Sn(C_9H_6NO)Cl$ can be converted to the chelate, $Sn(C_9H_6NO)_2$, by the addition of aqueous ammonia in ethanol(35).

If the reaction is carried out at room temperature in a molar ratio of 1:2, (metal halide: ligand), using dimethoxyethane as the solvent, a compound of variable composition precipitates. It is felt that this compound is a mixture of $Sn(C_9H_6NO)Cl$ and $[C_9H_6NHOH]Cl$. Infra-red evidence supports this. This mixture can be separated and one of the products identified as $Sn(C_9H_6NO)Cl$, by washing with anhydrous methanol. The hydrochloride, $[C_9H_6NHOH]Cl$, is soluble in methanol but not in cold dimethoxyethane.

The chelate compound, $Sn(C_9H_6NO)_2$, cannot be converted to $Sn(C_9H_6NO)Cl$ by the addition of hydrochloric acid in tetrahydrofuran. The only identifiable product from this reaction is the hydrochloride, $[C_9H_6NHOH]Cl$.

The α and β forms of $Sn(C_9H_6NO)Cl$ have the same infra-red spectra but very different x-ray powder patterns.

Product analysis indicates that the first reaction is the displacement of one of the chloride anions from the tin(II)chloride because of the reaction of the proton of C_9H_6NOH with the chloride to give HCl, equation 26.

$$SnCl_2 + C_9H_6NOH \longrightarrow Sn(C_9H_6NO)Cl + HCl \qquad (26)$$

If an excess of the ligand is present, the HCl formed reacts further with C_9H_6NOH to form the hydrochloride, $[C_9H_6NHOH]Cl$, equation 27.

$$HCl + C_9H_6NOH \longrightarrow [C_9H_6NHOH]Cl \qquad (27)$$

A reaction of the type in equation 26 has been shown to be present in the formation of the mixed complexes $Cu(C_9H_6NO)Cl$ and $Cu(C_9H_6NO)Br$[36].

On the other hand in basic solution (aqueous NH_3 or $NaOCH_3$), the HCl formed reacts to form NaCl or NH_4Cl, and the chelate, $Sn(C_9H_6NO)_2$ is formed.

Dimethyl- and Diphenyl-sulfoxide. The donor properties of dimethylsulfoxide have been extensively studied since 1960[58-61], and the donor properties of diphenylsulfoxide have been mentioned briefly[59]. Tin(II)chloride in ethanol reacts with these two ligands at dry ice temperature to give a complex containing two moles of ligand per mole of metal halide. Both of these complexes appear to be relatively stable to air oxidation and both are non-hygroscopic. Shifts in the infra-red spectra indicate that coordination is through the oxygen atom. The x-ray powder patterns of these complexes are given in Table XXXIII.

1,4-dioxane, $C_4H_8O_2$. A number of 1,4-dioxane complexes have been made and studied[62-67]. In this work a complex with the empirical formula $SnCl_2 \cdot C_4H_8O_2$ was prepared by two different reactions. The complex was formed by dissolving tin(II)chloride dihydrate in excess 1,4-dioxane, refluxing, and cooling; or by grinding tin(II)chloride dihydrate and 1,4-dioxane in a mortar.

This compound is susceptible to attack by water in the reaction mixture and must be filtered immediately. The x-ray powder pattern is given in Table XXXII. $SnCl_2 \cdot C_4H_8O_2$ has been reported previously[52].

A compound containing strong water bands in the infra-red is obtained if the compound $SnCl_2 \cdot C_4H_8O_2$ is allowed to digest in its own filtrate for 48-72 hours. This compound also gives a qualitative test for tin(II) and chloride ion. The infra-red spectrum also indicates coordinated dioxane is present.

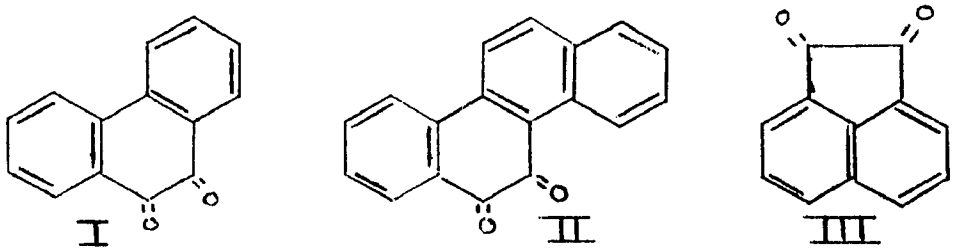
A compound giving a similar strong water absorption in the infra-red is also obtained if anhydrous tin(II)chloride is reacted with excess dioxane and allowed to stand for several hours until a crystallization occurs, no special precautions being taken to exclude moisture from the reaction mixture.

It is felt that these compounds are the result of the attack by water on prolonged standing, of the anhydrous complex.

These compounds were not further investigated.

Acetylacetone. A pale pink compound was isolated from the reaction between acetylacetone and tin(II)chloride by evaporating the excess acetylacetone under vacuum. Qualitative tests showed the presence of tin(II), chloride ion, and the infra-red spectra showed coordinated acetylacetone. Elemental analysis did not establish a definite compound. This compound was not investigated further.

o-Quinones. Crowley and Haendler[67] have prepared a large number of metal halide - o-quinone complexes and have done preliminary characterization. In the present work, the reaction of tin(II)chloride with four o-quinones was investigated. The four o-quinones were 9,10-phenanthrenequinone, (I, phenqu), 1,2-chrysenequinone, (II, chryqu), acenaphthenequinone, (III), and 2-nitrophenanthrenequinone.



I II III

Tin(II)chloride gave evidence of reaction with 9,10-phenanthrenequinone, chrysenequinone, and 2-nitrophenanthrenequinone. When tin(II)chloride in a small amount of methanol was added to a boiling glacial acetic acid solution of the o-quinone, an immediate color change took place. The solution turned black or dark red but no precipitate was formed. Impure solids, which we were not able to purify,

were obtained by evaporation of the solvent. Their colors are listed in Table IV.

TABLE IV

Colors of the Impure Quinone Complexes

Quinone	Solution Color	Solid Color
9,10-phenanqu.	Black	Dark brown
2-nitrophenanqu.	Dark red	Green
Chrysqu.	Black	Green

If dimethoxyethane is used as the solvent, color changes again indicate reaction has occurred. Here, too, we were unable to isolate a pure compound by solvent evaporation.

There was no evidence of reaction with acenaphthenequinone. This is not unexpected since Crowley(67) reported that this quinone showed no evidence of reaction with metal halides in glacial acetic acid. He attributes this to the fact that the coordinating oxygen atoms are either too far apart for complex formation or that they are not co-planar with the rest of the molecule and thus are not in position to coordinate.

Structural Studies

The studies of the structures of the compounds were based on infra-red and conductance measurements. Studies in the infra-red were done to determine the changes in the spectra of the donor molecules on coordination. Using these shifts in infra-red, it was possible to assign Sn-donor atom stretching frequencies in a number of cases.

Conductance measurements were run on a few of the complexes. From these measurements, it was possible to show that the coordinating ligands did not displace chloride ion from the coordination sphere of the tin atom.

Infra-red spectral studies. The infra-red spectra of the complexes were run in the $4000cm^{-1}$ - $400cm^{-1}$ region. Three techniques were used, mull, potassium bromide disc, and solution spectra. The spectra of the compounds are discussed according to the nitrogen or oxygen-containing compound used in the preparation.

Quarternary ammonium halides. The infra-red spectra of these compounds are those of the quarternary ammonium cations, essentially unmodified from that of the parent quarternary ammonium chloride. It has been shown in this laboratory that tin(II)chloride does not absorb in the region $4000cm^{-1}$ - $400cm^{-1}$. The spectrum of one example, tetramethylammonium trichlorostannite(II) is given in Table XVII.

Pyridine complex. The infra-red spectrum of pyridine has been extensively investigated and unequivocal assignments have been made for most of the observed bands(37-39) but the infra-red spectra of pyridine complexes have received little systematic attention. The first such systematic study was made by Gill(40) and co-workers. They compared a large number of pyridine - metal halide complexes and pyridinium salts, with free pyridine. They also report that

infra-red spectrum of coordinated pyridine can be distinguished readily from that of free pyridine by the presence of a weak band between 1250cm^{-1} and 1235cm^{-1}; by a shift in the strong 1578cm^{-1} band to 1600cm^{-1}; and by shifts of the 601cm^{-1} and 403cm^{-1} bands to 625cm^{-1} and 420cm^{-1}, respectively.

The infra-red spectrum of the tin(II)chloride - pyridine compound confirms the presence of coordinated pyridine (Table XX). For purposes of comparison, the spectra of free pyridine is also shown in this table[40].

It was not possible to assign a metal - nitrogen vibration for this complex. Gill[40] feels that this vibration probably occurs below 400cm^{-1} in the pyridine - metal complex system.

The infra-red spectrum of a compound containing 36 per cent (vs. 43 per cent for a 1:1 compound) tin is very different from that of coordinated pyridine. A comparison of this spectrum with that of other pyridinium salts clearly shows that this compound contains the pyridinium ion.

2,2'-bipyridyl. The infra-red spectra of a number of bis- and tris-2,2'-bipyridyl complexes have been studied by several workers[41,42,43]. All bands above 600cm^{-1} can be assigned to the ligand[42]. Below 600cm^{-1}, new bands appear that are not found in the spectra of the pure ligand and these are assigned to metal - nitrogen vibrations. On this basis, the new band appearing at 460cm^{-1} is assigned

the Sn-N stretch in the $SnCl_2 \cdot C_{10}H_8N_2$ complex. It must be emphasized that this assignment is a tentative one and that the spectrum of this complex should be examined very carefully in the $400cm^{-1}$ - $200cm^{-1}$ region. The infra-red spectrum is given in Table XIX.

Pyridine-N-oxide. For this ligand the region of interest in the infra-red is between $1250cm^{-1}$ and $1190cm^{-1}$. The N-O absorption for the free ligand is said to occur at $1243cm^{-1}$(44). If it is assumed that coordination in the complexes is through the oxygen atom(45), it would be expected that the N-O bond would be lengthened and the N-O frequency shifted to lower frequency. In these two complexes, the N-O frequency occurs at $1208cm^{-1}$ and $1200cm^{-1}$ in the bis-complex and at $1195cm^{-1}$ for the 1:1 compound (Table XVIII).

It has been pointed out by Quagliano(34), that the frequencies of the N-O band in a number of divalent metal complexes can be divided into two groups, those appearing at $1220cm^{-1}$, and those appearing at $1205cm^{-1}$. He has shown that in those complexes which have pyridine-N-oxide as the only ligand in the first coordination of the metal ion, i.e., $[Ni(C_5H_5NO)_6]Br_2$, the N-O frequency is observed at $1220cm^{-1}$. When the N-O frequency is observed at $1205cm^{-1}$ the first coordination sphere of the metal ion is made up of pyridine - N-oxide and another ligand (H_2O, halide or nitrate), i.e., $[Zn(C_5H_5NO)_2Cl_2]$.

Using this information, the tin(II)chloride complexes can be formulated as $[Sn(C_5H_5NO)Cl_2]$ and $[Sn(C_5H_5NO)_2Cl_2]$, respectively.

8-hydroxyquinoline and 5,7-dibromo-8-hydroxyquinoline.

Although the infra-red spectra of a large number of metal - C_9H_6NOH and $C_9H_4NOHX_2$ complexes have been studied, only a few of the peaks have been characterized. Phillips and Merritt[46] have made tentative assignments at 3000cm^{-1} - 2900cm^{-1} (C-H), near 1600cm^{-1} (aromatic ring frequencies), and near 1400cm^{-1} (C-O or C-N stretching vibrations) for some of the major bands in the 3000cm^{-1} and 1600cm^{-1} - 1400cm^{-1} regions. The band appearing at 1090cm^{-1} in C_9H_6NOH has been assigned to the aryl-oxygen vibration[48]. Charles and co-workers[47] have measured the infra-red spectra of some 30 metal - C_9H_6NOH complexes and have shown that this band is shifted to higher frequency by chelate formation, and is attributed to the formation of M-O-C$\leqslant$ system.

The infra-red spectra of the complexes of 8-hydroxy-quinoline and its 5,7-dibromo-derivative are listed in Table XXI. All show the characteristic bands of C_9H_6NO- species.

The major differences in the spectra are as follows: C_9H_6NOH has a strong, broad band at 3200cm^{-1} due to OH stretch, no band at 1100cm^{-1} where the Sn-O-C system absorbes, and no band near 510cm^{-1}, the region of SnO absorption. $[C_9H_6NHOH]Cl$ has a strong, broad band near 3000cm^{-1} - 2600cm^{-1} due to a

combination of hydrogen bonded OH^- and NH^+ vibrations, no band at 1100cm^{-1}, and no band near 510cm^{-1}. The compounds $Sn(C_9H_4NOBr_2)_2$, $Sn(C_9H_6NO)_2$, $Sn(C_9H_6NO)Cl$, $Sn(C_9H_6NO)(C_2H_3O_2)$, and $Sn(C_9H_6NO)_2(C_2H_3O_2)_2$ all show a strong absorption near 1100cm^{-1} and a weaker one near 510cm^{-1}. In addition, the latter two compounds show strong absorption at 1592cm^{-1} and 670cm^{-1} for the mono-acetate and 1600cm^{-1}, 681cm^{-1} and 665cm^{-1} for the diacetate. It is felt that these new bands are due to the acetate ion.

α- and β-$Sn(C_9H_6NO)Cl$ have identical infra-red spectra. This is not unexpected since α- and β-$Cu(C_9H_6NO)_2$ have identical spectra(48), but entirely different x-ray powder patterns.

In addition, there are some minor differences in the spectra of the $Sn(C_9H_6NO)Cl$ compounds and the chelate $Sn(C_9H_6NO)_2$, but the spectra are very similar. Again, this is not unexpected since the spectra of $Cu(C_9H_6NO)_2$ and $Cu(C_9H_6NO)Cl$ have only minor differences(48). The infra-red spectra of these compounds are given in Table XXI.

Dimethyl- and diphenylsulfoxide. Cotton(58) has made an extensive study of the infra-red spectra of dimethylsulfoxide complexes and has successfully made assignments for every band appearing in the spectra of both the free ligand and the complexes.

In considering the spectra of the complexes of DMSO, chief interest lies in the behavior of the S-O stretching

frequency. It would be expected that coordination of the oxygen atom in R_2SO complexes would lower the S-O stretching frequency. Prior to Cotton's work, it had been demonstrated by Cotton[68] and Sheldon[69] that in triphenylphosphineoxide complexes, the P-O stretching frequency was lowered by $50cm^{-1}$ when coordinated. It would be expected then that similar shifts should occur in the S-O stretching frequency of the DMSO complexes.

Cotton has also pointed out, however, that there is the possibility that coordination in the DMSO complexes could also occur through the sulfur atom, which has an available lone pair of electrons. Of the more than 30 DMSO complexes which have been prepared, only two, $PdCl_2 \cdot 2DMSO$ and $PtCl_2 \cdot 2DMSO$ appear to be bonded through the sulfur atom.

The infra-red spectrum of $SnCl_2 \cdot 2DMSO$, Table XXII, is very similar to that given for the other DMSO complexes. The very strong band at $1055cm^{-1}$ which Cotton has assigned to the S-O stretch disappears completely and a new, very strong band appears at $920cm^{-1}$. Because of this shift in the S-O stretching frequency, it is concluded that bonding is through the oxygen atom in this complex.

The S-O stretching frequency of all of the oxygen bonded complexes appears between $960cm^{-1}$ and $910cm^{-1}$ while the S-O stretching frequency in the sulfur bonded complexes occurs between $1157cm^{-1}$ and $1116cm^{-1}$. The following Table V lists the S-O stretching frequencies for the $SnCl_2 \cdot 2DMSO$ complex prepared in this work and some of the previously prepared complexes.

TABLE V

Frequencies of S-O Stretching Bands in Various DMSO Complexes

Compound(58)	Frequency cm^{-1}
Sulfur bonded	
$PdCl_2 \cdot 2DMSO$	1116
$PtCl_2 \cdot 2DMSO$	1157,1134
Oxygen bonded	
$SnCl_2 \cdot 2DMSO$	940sh,920
$SnCl_4 \cdot 2DMSO$	915
$MnCl_2 \cdot 3DMSO$	950
$FeI_2 \cdot 4DMSO$	937
$ZnCl_2 \cdot 2DMSO$	952
$CuBr_2 \cdot 2DMSO$	911

A completely analogous situation exists in the infra-red spectrum of the DPSO complex. A comparison of the infra-red spectra of the complex with that of the free ligand allows one to assign an S-O stretching frequency for the complex. Barnard(70) has shown that the S-O stretching frequency in solid DPSO occurs at $1035cm^{-1}$. In the $SnCl_2 \cdot 2DPSO$ complex, there is no band at $1035cm^{-1}$ and two very strong new bands at $975cm^{-1}$ and $950cm^{-1}$. These bands are assigned to the S-O frequency and clearly show that in this complex bonding is also through the oxygen.

The infra-red spectrum in the $1300-400cm^{-1}$ region is given in Table XXII.

1,4-dioxane. A complete analysis of the infra-red spectrum of 1,4-dioxane has not yet been done. It is not possible then, to make assignments for the observed bands in the $SnCl_2 \cdot$ 1,4-dioxane prepared in this work. A comparison of the spectra of the complex with that of the free ligand as given by Shrene and co-workers(72) show only slight differences in all but one band. The band at about 900cm^{-1} is assigned by Shrene to the six-membered heterocyclic oxygen frequency. In the complex, this band is considerably weaker and a strong band appears at 835cm^{-1} which is absent in the free ligand. This new band then could possibly be caused by a shift in the ring-oxygen frequency by coordination through one of the ring oxygens. It must be emphasized that this is only a tentative assignment.

The only other major difference in the spectra of the free ligand and the complex is a shift in the 1122cm^{-1} band to 1100cm^{-1} in the complex. The reason for this shift is not known.

The spectra of the free ligand and the complex in the 1250cm^{-1} - 800cm^{-1} region are given in Table XXIII.

Conductance measurements. Sears and co-workers(49) have measured the conductances of a large number of 1:1 electrolytes in dimethylformamide, DMF. Four of the complexes prepared in this work were chosen for conductance measurements in this solvent. The results are given in Table VI.

TABLE VI

Conductance Measurements of Some Tin(II) Complexes

Compound	Λ_m $ohm^{-1}\,cm^2\,mol^{-1}$	Concn. m.mole
$Sn(C_9H_6NO)_2$	2.2	1.07
$SnCl_2 \cdot C_5H_5NO$	22.2	1.0
$SnCl_2 \cdot 2C_5H_5NO$	18.9	1.02
$[(CH_3)_4N]SnCl_3$	105.0	1.31

Quagliano[34] has pointed out that in DMF at 25°C. 1:1 complexes of pyridine-N-oxide exhibit conductances in the 85 range, those of 2:1 complexes are in the 140-170 range, 3:1 complexes are above 200 and non-conductors below 45. It is obvious from the table that the chelate, $Sn(C_9H_6NO)_2$, and the two pyridine-N-oxide complexes are non-electrolytes.

The value for the quarternary ammonium salt is slightly high for a 1:1 electrolyte but could scarcely be anything but a 1:1 compound. Some of the values for the 1:1 electrolytes given by Sears are in the 90 range.

The conductance measurements for the pyridine-N-oxide complexes substantiate the infra-red studies which indicated that the population of the group surrounding the tin atom consists of pyridine-N-oxide and halide. The proposed formulations $[Sn(C_5H_5NO)Cl_2]$ and $[Sn(C_5H_5NO)_2Cl_2]$ are thus assumed correct.

Proposed formulations. Based on experimental evidence from elemental analysis, infra-red, conductance, and x-ray powder diffraction studies, the following formulations for the O- and N-containing complexes are proposed.

TABLE VII

Suggested Formulations for the Complexes

Formulation	
$[(CH_3)_4N]SnCl_3$	tetramethylammonium trichlorostannite
$[(C_2H_5)_4N]SnCl_3$	tetraethylammonium trichlorostannite
$[C_6H_5(CH_3)_3N]SnCl_3$	phenyltrimethylammonium trichlorostannite
$SnCl_2 \cdot C_5H_5N$	pyridinedichlorotin
$SnCl_2 \cdot C_{10}H_8N_2$	2,2-dipyridyldichlorotin
$SnCl_2 \cdot C_5H_5NO$	pyridine-N-oxidedichlorotin
$SnCl_2 \cdot 2C_5H_5NO$	bis-(pyridine-N-oxide)-dichlorotin
$Sn(C_9H_6NO)_2$	bis-(8-quinolinolato)-tin
$Sn(C_9H_6NO)Cl$	chloro-8-quinolinolatotin
$Sn(C_9H_6NO)(C_2H_3O_2)$	acetato-8-quinolinolatotin
$Sn(C_9H_6NO)_2(C_2H_3O_2)_2$	bis-acetato-bis-8-quinolinolatotin(IV)
$Sn(C_9H_4NOBr_2)_2$	bis-(5,7-dibromo-8-quinolinolato)-tin
$SnCl_2 \cdot 2(CH_3)_2SO$	bis-(dimethylsulfoxide)-dichlorotin
$SnCl_2 \cdot 2(C_6H_5)_2SO$	bis-(diphenylsulfoxide)-dichlorotin
$SnCl_2 \cdot C_4H_8O_2$	1,4-dioxanedichlorotin

Experimental

Detailed preparation of the complexes is as follows:

Tetramethylammonium trichlorostannite - 1.89g. (0.01 mole) of anhydrous tin(II)chloride were dissolved in approximately 25 ml. of absolute methanol. To this was added 1.09 g. (0.01 mole) of tetramethylammonium chloride dissolved in 50 ml. of absolute methanol. The complex salt precipitated after a

brief vigorous stirring. Varying the molar ratio of the reactants had no effect on the product formed. When 2.2 g. (0.02 mole) of the ammonium salt dissolved in methanol were added to 1.89 g. (0.01 mole) of tin(II)chloride in methanol, the same compound is precipitated. Similarly, when 1.09 g. (0.01 mole) of the ammonium salt is added to 3.8 g. (0.02 mole) and 7.6 g. (0.04 mole) of tin(II)chloride, respectively, tetramethylammonium trichlorostannite is precipitated.

Tetraethylammonium trichlorostannite - This white complex salt is prepared by a method similar to the one used for the preceding compound using 1.7 g. (0.01 mole) of ammonium salt and 3.8 g. (0.02 mole) of tin(II)chloride both dissolved in absolute ethanol.

Phenyltrimethylammonium trichlorostannite - This salt was prepared as in the preceding method using 1.7 g. (0.01 mole) of ammonium salt and 3.8 g. (0.02 mole) of tin(II) chloride both dissolved in ethanol.

Pyridinedichlorotin(II) - 1.89 g. (0.01 mole) of anhydrous tin(II)chloride were dissolved in 50 ml. of carefully dried pyridine giving a clear solution. This solution was gently refluxed under nitrogen for about one hour. The solution slowly turned pale yellow but no precipitate was formed on cooling. The pale yellow solution was evaporated in a vacuum desiccator at 50°C. to about one-fourth the

original volume. Dry dimethoxyethane was added and a light tan solid which analyzed for $SnCl_2 \cdot C_5H_5N$ was recovered.

A compound containing less tin than a 1:1 complex and more tin than a 1:2 complex is precipitated if moisture is not rigorously excluded from the above reaction. The infra-red spectrum of this compound clearly shows the presence of pyridinium ion. It was not further investigated.

2,2′-dipyridyldichlorotin(II) - 2.5 g. (0.013 mole) of anhydrous tin(II)chloride and 1.5 g. (0.01 mole) of 2,2′-dipyridyl were each dissolved in 100 ml. of dry tetrahydrofuran. The ligand solution was added slowly to the tin(II)chloride solution. The resulting solution turned yellow but no precipitate was formed. After several minutes, a bright yellow precipitate began to form and in about 30 minutes precipitation seemed to be complete. The yellow compound analyzed for $SnCl_2 \cdot C_{10}H_8N_2$. The same compound is formed if 2.25 g. (0.01 mole) of tin(II)chloride dihydrate is used instead of the anhydrous metal chloride.

Pyridine-N-oxidedichlorotin(II) - 7.6 g. (0.04 mole) of anhydrous tin(II)chloride dissolved in tetrahydrofuran were added to 3.8 g. (0.04 mole) of pyridine-N-oxide in tetrahydrofuran. A white complex, $SnCl_2 \cdot C_5H_5NO$, precipitated immediately. This complex is stable when stored in a sealed vial in a desiccator.

Bis-(pyridine-N-oxide)-dichlorotin(II) - The off-white complex, $SnCl_2 \cdot 2C_5H_5NO$, precipitated immediately when 7.58 g. (0.04 mole) of tin(II)chloride in tetrahydrofuran were added to 7.6 g. (0.08 mole) of the ligand in the same solvent. This compound takes on a pronounced yellow cast in a few days and turns completely brown in several weeks. A distinct pyridine odor can be detected above the complex. This decomposition appears to be caused by light and not by moisture or atmospheric oxygen. Similar observations have been made for other pyridine-N-oxide complexes(45).

α-(chloro-8-quinolinolatotin) - 1.9 g. (0.01 mole) of anhydrous tin(II)chloride dissolved in 50 ml. of dimethoxyethane was cooled to dry ice temperature and 1.45 g. (0.01 mole) of 8-quinolinol, dissolved in dimethoxyethane were added slowly. An immediate pale yellow precipitate, α-$Sn(C_9H_6NO)Cl$, was formed.

The same compound is formed when the above reaction is run at room temperature. If, however, 2.9 g. (0.02 mole) of ligand are used, a compound of variable composition results. Infra-red spectrum indicates the formation of some $[C_9H_6NHOH]Cl$. If this mixture is washed with anhydrous methanol, elemental analysis, infra-red spectrum, and x-ray powder diffraction show that the residue left from the washing is α-$Sn(C_9H_6NO)Cl$. It is concluded then, that the variable composition product is a mixture of $[C_9H_6NHOH]Cl$ and α-$Sn(C_9H_6NO)Cl$. The α- compound is also formed in acetone at room temperature. 1.9 g. (0.01 mole) of tin(II)chloride

in acetone were added to 1.45 g. (0.01 mole) of 8-quinolinol. An immediate pale yellow precipitate was formed and identified by its x-ray powder pattern as α-$Sn(C_9H_6NO)Cl$.

β-(chloro-8-quinolinolatotin) - The β- form of this compound is formed when reactions are carried out under reflux conditions.

In acetone or chloroform, 1.89 g. (0.01 mole) of tin(II)chloride refluxed with 1.45 g. (0.01 mole) of 8-quinolinol gives a pale yellow precipitate of β-$Sn(C_9H_6NO)Cl$. In dimethoxyethane, 1.89 g. (0.01 mole) of tin(II)chloride refluxed with 2.9 g. (0.02 mole) of 8-quinolinol gives the same compound.

Conversion of the α- form to the β- form - 1 g. of α-$Sn(C_9H_6NO)Cl$ was slurried in 50 ml. of dry acetone and refluxed for about four hours. The slurry was filtered while hot, washed with hot acetone and dried in a 50°C. oven. An x-ray powder photograph showed that the α- form had been converted to the β- form.

Reaction of the variable composition with aqueous ammonia - 1 g. of the mixture was slurried in 100 ml. of 95 per cent ethanol and 10 ml. of aqueous ammonia was added. This slurry was refluxed for about one hour. A bright yellow compound was recovered by filtration and identified by its x-ray powder photograph as the chelate $Sn(C_9H_6NO)_2$.

Reaction of bis-(8-quinolinolatotin) with hydrochloric acid - Approximately 1 g. of the chelate was slurried in dry tetrahydrofuran. As hydrochloric acid was added dropwise, the bright yellow chelate precipitate was replaced by a pale yellow compound which contained chloride ion but no tin. An x-ray powder photograph of this compound is identical to the x-ray powder photograph of $[C_9H_6NHOH]Cl$.

Bis-(dimethylsulfoxide)-dichlorotin - 10 g. (0.053 mole) of tin(II)chloride was dissolved in 50 ml. of 100 per cent ethanol. An estimated excess of dimethylsulfoxide was added dropwise. After standing at room temperature for 30 minutes, the solution was only slightly cloudy. The solution was only slightly cloudy after heating gently over an infra-red lamp until the ethanol was boiling. Then it was cooled quickly in a dry ice - acetone slush bath. A large volume of white precipitate settled out immediately. The precipitate and solution were allowed to come slowly to room temperature before filtering.

Bis-(diphenylsulfoxide)-dichlorotin - This compound was formed when a reaction similar to the preceding one was run using 4 g. (0.02 mole) of tin(II)chloride and 4.2 g. (0.02 mole) of diphenylsulfoxide.

1,4-dioxane-dichlorotin - Five g. (0.022 mole) of tin(II)chloride dihydrate was dissolved in a small amount of 1,4-dioxane. After a vigorous, exothermic reaction, a

white precipitate formed which dissolved when a small amount of ligand was added to the reaction mixture. This solution was refluxed for three hours and cooled in an ice bath. A white compound, $SnCl_2 \cdot C_4H_8O_2$, separated out on cooling.

The same compound is formed when 10 g. (0.044 mole) of tin(II)chloride dihydrate is covered with a little 1,4-dioxane and ground with a mortar and pestle.

Reaction with acetylacetone - Two g. (0.011 mole) of tin(II)chloride was dissolved in a large excess of acetylacetone. This clear solution turned yellow after 24 hours but no precipitate was formed. The yellow solution was evaporated at 50°C. in a vacuum desiccator until very pale pink crystals were deposited. An elemental analysis of this compound approximates that required for $SnCl_2 \cdot 2AcAc$. Attempts to prepare an analytically pure sample were not successful.

Reaction with o-quinones - 1.89 g. (0.01 mole) of tin(II)chloride dissolved in 5 ml. of methanol were added to 0.01 mole of the quinone dissolved in 75 ml. of boiling glacial acetic acid. As indicated in Table IV, an immediate darkening of the solution occurred. The solutions were boiled for several minutes and then evaporated to a small volume in a vacuum desiccator at 60°C. until precipitation occurred. All attempts to isolate pure compounds, by adding ligroin, dimethoxyethane or tetrahydrofuran to the colored solution were not successful.

CHAPTER III

EXPERIMENTAL

Chemicals - Reagent grade chemicals were used without further purification except as noted below.

Methyl alcohol - Fisher Certified Reagent (0.01% H_2O) was refluxed with magnesium turnings and distilled immediately prior to use if the solvent had been open for some time. Alternately, a freshly opened can of the same grade was used without further drying.

Triethylamine - Eastman triethylamine was dried for several days over barium oxide and fractionally distilled from fresh barium oxide.

Anhydrous tin(II)chloride - Reagent grade tin(II) chloride dihydrate was dehydrated according to the method of Stephen(53). One mole, 226 g. of tin(II)chloride dehydrate was covered with two moles, 190 ml., of acetic anhydride. After a short time a vigorous, exothermic reaction resulted and the anhydrous salt separated out. The anhydrous tin(II)chloride was filtered, washed many times with anhydrous ether until the filtrate had no odor of acetic acid, dried by suction, and stored in a vacuum desiccator in a sealed container over calcium chloride. As long as all moisture and air are excluded from the desiccator, tin(II)chloride can be stored for several weeks.

Pyridine - Reagent grade pyridine was dried several days over barium oxide, distilled, and stored over fresh barium oxide.

Pyridine-N-oxide - Practical grade pyridine-N-oxide was vacuum distilled and the fraction distilling between 125 and 130°C. at 8mm pressure was used.

N,N-dimethylformamide - Reagent grade DMF was vigorously shaken over barium oxide for 20 hours, decanted, and distilled under reduced pressure. That fraction that distilled at 41°C. at 10mm Hg. was used. The specific conductance of the purified solvent was 2×10^{-7} mho-cm^{-1}.

Analytical - Carbon and hydrogen analysis were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Nitrogen was determined with the Coleman Model 29 Nitrogen Analyzer. Tin was determined as the oxide by careful evaporation with concentrated sulfuric acid and subsequent ignition at 800°C. Chloride was determined either gravimetrically as silver chloride or volumetrically by the Volhard Method, ferric ammonium sulfate being used as the indicator.

X-ray diffraction data - Powder patterns were obtained for all crystalline complexes prepared in this study. The samples were finely ground and mounted in 0.3mm capillaries.

The patterns were taken with the 57.3mm Phillips camera using copper and iron radiation (1.5418 Å and 1.9373 Å, respectively). The inter-planar spacings, d values, were obtained in either of two ways; directly from a Nies Chart, or by determining the angle of diffraction, θ, with a film reader and from θ, the appropriate d value.

Infra-red spectra - The infra-red spectra of all substances were taken with a Perkin-Elmer Model 21 Spectrophotometer or a Perkin-Elmer Model 337 Spectrophotometer. Sodium chloride optics were used with both instruments in the 4000cm^{-1} - 600cm^{-1} and potassium bromide optics in the 600-400cm^{-1} region using the Model 337. Mull spectra were obtained using Nujol and Halocarbon mulls. A few of the spectra were obtained by means of the potassium bromide disk technique or in solution. Both the mull and disk techniques were used on some of the complexes and in every case agreement was excellent.

Conductance measurements - Conductance measurements were made in N,N-dimethylformamide solution. Those compounds chosen for conductance studies were sufficiently soluble, without decomposition, in DMF to give approximately M/1000 solutions.

Table VIII

Reaction of Tin(II)chloride with Quarternary Ammonium Chlorides

R_4NX	Solvent	Ratio $R_4NX:SnCl_2$	Product	Analysis Theory % Sn	Theory % Cl	Found % Sn	Found % Cl
$(CH_3)_4NCl$	MeOH	1:1	$[(CH_3)_4N]SnCl_3$	39.65	35.58	39.63	35.29
$(CH_3)_4NCl$	MeOH	2:1	$[(CH_3)_4N]SnCl_3$	(*)			
$(CH_3)_4NCl$	MeOH	1:2	$[(CH_3)_4N]SnCl_3$	(*)			
$(CH_3)_4NCl$	MeOH	1:4	$[(CH_3)_4N]SnCl_3$	39.65	-	39.57 39.81	-
$(C_2H_5)_4NCl$	EtOH	1:2	$[(C_2H_5)_4N]SnCl_3$	33.39	29.96	33.57 33.51	29.97 29.91
$\phi(CH_3)_3NCl$	EtOH	1:2	$[\phi(CH_3)_3N]SnCl_3$	32.83	29.47	32.84	29.45 29.25

*Identified by x-ray powder pattern

Me_3 complex, silver-grey; others are white

Table IX

Reactions of Tin(II) Salts with 8-quinolinol

Temp.	Solvent	Ratio of $SnCl_2$: L	Product	Analysis							
				Theory %				Found %			
				Sn	C	H	Cl	Sn	C	H	Cl
-78	DME	1:1	α-SnOxCl	39.79	-	-	11.90	39.58	-	-	11.64 11.70
Room	DME	1:1	Same	--	-	-	--	39.17 39.23	-	-	11.88
Room	DME	1:2	Mixture	(identified by infrared spectrum)							
Room	DME/MeOH	1:2	α-SnOxCl	39.79	36.20	2.01	11.90	38.98	36.29	2.24	11.74
Room	Aq. NH_3-EtOH	-	$Sn(Ox)_2$	(identified by x-ray powder pattern)							
Room	Me_2CO	1:1	α-SnOxCl	(identified by x-ray powder pattern)							
Reflux	Me_2CO	-form	β-SnOxCl	(identified by x-ray powder pattern)							
Reflux	CH_3Cl	1:1	β-SnOxCl	39.79	36.20	2.01	11.90	39.61	36.51	2.33	11.86
Reflux	Me_2CO	1:1	β-SnOxCl	(identified by x-ray powder pattern)							
Reflux	DME	1:2	β-SnOxCl	(identified by x-ray powder pattern)							

DME = dimethoxyethane Ox = $C_9H_6NO^-$ ion All complexes are yellow.

Table X

Tin(II)chloride Complexes with Pyridine and Derivatives

Compound	C %		H %		N %		Sn %		Cl %	
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found
$SnCl_2 \cdot Py$	22.32	21.64	1.86	2.11	5.21	4.90	44.17	43.62 43.54	--	--
$SnCl_2 \cdot PyNO$	21.07	20.70	1.75	1.92	--	--	41.69	41.62	24.91	24.37
$SnCl_2 \cdot 2PyNO$	31.60	31.01	2.26	2.91	--	--	31.24	31.29	--	--
$SnCl_2 \cdot DiPy$	--	--	--	--	--	--	34.31	34.45 34.04	20.51	19.89

Py complex, light tan PyNO complex, white 2PyNO complex, white DiPy complex, yellow

Table XI

Reactions of Tin(II)chloride with Oxygen Donors

Donor	Solvent	Product	Analysis					
			Theory %				Found %	
			Sn	Cl	C	H	Sn	Cl
DMSO	EtOH	$SnCl_2 \cdot 2DMSO$	34.31	20.06	--	--	33.96	19.87
DPSO	EtOH	$SnCl_2 \cdot 2DPSO$	19.97	11.94	--	--	20.24	11.15 11.39
Diox	Diox	$SnCl_2 \cdot Diox$	42.71	25.55	--	--	42.48 42.71	25.74
AcAc	AcAc	Unknown	--	--	30.00	3.56	29.40 29.78 30.74	--
Phenq	HOAc	Unknown	--	--	53.34	3.14	19.05 19.17	12.20
Chrysqu	HOAc	Unknown	--	--	--	--	22.73 22.44	

APPENDIX

(1) Tables of data

(2) The reactions of tin(IV) compounds with 9,10-phenanthrenequinone

(3) The preparation and properties of ammonium hexafluorostannate

Table XII

Infrared Spectra of Triethylammonium Halides

$(C_2H_5)_3NHCl$	$(C_2H_5)_3NHBr$
2900	2910
2700	2710
2500	2620
1460	2480
1400	1460
1375	1425
1170	1375
1064	1165
1030	1065
860	1035
810	845
	800

Frequency given in cm^{-1}.

Table XIII

X-ray Powder Diffraction Data for Triethylammonium Halides

$(C_2H_5)_3NHCl$		$(C_2H_5)_3NHBr$	
d_{obs}	d_{lit}	d_{obs}	d_{lit}
7.3	7.25	7.3	7.3
5.1	5.07	5.1	5.18
4.2	4.18	4.2	4.23
3.6	3.64	3.6	3.69
3.5	3.54	3.2	3.65
3.25	3.22	2.7	3.28
2.70	2.70	2.6	2.78
2.55	2.54	2.4	2.59
2.40	2.41	2.3	2.44
2.15	2.17	2.2	2.39
2.09	2.00	2.1	2.21
2.00		2.0	2.11
1.99		1.95	2.04
1.78		1.83	2.03
		1.79	1.96
			1.84
			1.83
			1.79
			1.78

Table XIV

X-ray Powder Data for Sodium Halides

NaBr		NaCl	
d_{obs}	d_{lit}	d_{obs}	d_{lit}
3.4	3.44	3.3	3.2
2.9	2.98	2.85	2.82
2.1	2.11	2.00	1.99
1.8	1.80	1.70	1.70
1.7	1.72	1.64	1.62
1.5	1.49	1.42	1.41
1.3	1.37	1.30	1.29
1.22	1.22	1.20	1.20
1.13	1.15	1.10	1.15
1.03	1.05	1.09	1.08
1.00	1.01		

Table XV

X-ray Powder Data for Tin(II)oxide

d_{obs}	d_{lit}
4.8	4.85
2.9	2.98
2.65	2.68
2.40	2.41
2.0	2.039
1.90	1.901
1.79	1.797
1.60	1.604
1.49*	1.494
1.38	1.484
1.34	1.382
1.22	1.344
1.21*	1.225
1.17	1.209
1.16	1.202
1.15	1.174
1.10	1.169
1.07	1.152
	1.102
	1.076

*Very broad line

Table XVI

Infrared Spectrum of Tin(II)acetate

Frequency	Intensity
3000	w
2950	
2410	w
1750	w
1715	w
1625	vs
1600	
1540	vs
1410	vs
1380	vs
1345	vs
1327	vs
1160	w
1140	
1020	m
930	w
670	m
660	m

Frequency given in cm^{-1}

w weak
m medium
vs very strong

Table XVII

Infrared Spectrum of Tetramethylammoniumtrichlorostannite(II)

Frequency*	Intensity
3000	w
1500	s
1420	w
1280	w
960	vs

Table XVIII

Infrared Spectra of Pyridine-N-Oxide Complexes

$SnCl_2 \cdot C_5H_5NO$	$SnCl_2 \cdot 2C_5H_5NO$
1235 w	1245 w
1195 s	1205 s
1185 s	1210 s
1170 s	1170 s
1160 sh	1160 sh
1090 w	1090 w
1070 w	1068 m
1020 m	1020 s
920 w	900 w
825 s	830 s
815 vs	820 s
765 vs	765 vs
670 s	670 s

*Frequency in both tables given in cm^{-1}.

Table XIX

Infrared Spectra of Bipyridyl and Tin(II) Complex in the 1600 - 600 cm^{-1} Region

$C_{10}H_8N_2$*	$SnCl_2 \cdot C_{10}H_8N_2$
1583	1605
1560	1565
1421	1500
1252	1495
1140	1440
1090	1320
1085	1243
1041	1210
992	1175
892	1105
755	1057
739	1040
652	1015
	1007
	910
	880
	778
	765
	732
	649

*Reference 42

Table XX

Infrared Spectra of Pyridine and $SnCl_2 \cdot C_5H_5N$ in the 1600 - 1400cm^{-1} Region

Pyridine	$SnCl_2 \cdot C_5H_5N$
1627	1610
1593	
1578	
1570	1480
1478	1450
1436	
1372	
1350	1248
1217	1220
1145	1150
1067	1070
1031	1040
991	1020
942	1015
747	760
700	680
650	640
601	430
403	

Table XXI

Infrared Spectra of 8-quinolinol and the 8-quinolinol Complexes

Compound	Region (cm^{-1})						
	3200		3000	1700-1550	1100	675	510
C_9H_6NOH	3195	to	3000 (br)	1580	1090	--	--
$[C_9H_6NHOH]Cl$	3100	to	2500 (v br)	1610,1580	1090	--	--
$Sn(C_9H_6NO)_2$	--		3050	1600,1572	1100	--	510
α,β-$Sn(C_9H_6NO)Cl$	--		3050,3020	1600,1580	1109	--	510
$Sn(C_9H_6NO)(C_2H_3O_2)$	--		3000,2910	1610,1592,1570	1100	670	515
$Sn(C_9H_6NO)_2(C_2H_3O_2)_2$	--		3000,2900	1660,1610,1580	1110	681,665	*

*run with sodium chloride windows

Table XXII

Infrared Spectra of the Sulfoxide Complexes

$SnCl_2 \cdot 2DMSO$	$SnCl_2 \cdot 2DPSO$
1315 w	1310 w
1295 w	1165 w
1030 s	1155 w
995 s br	1085 s
940 sh	1020 w
920 vs br	970 vs
715 m	950 vs
678 w	840 w
	755 sh
	748 vs
	740 sh
	695 sh
	685 vs

Frequency in cm^{-1}

Table XXIII

Infrared Spectra of 1,4-Dioxane and 1,4-Dioxane Complex

1,4-Dioxane	$SnCl_2 \cdot C_4H_8O_2$
1257 vs	1250 s
1142 vs	
1122 vs	1100 s
1048 s	1060 s
1017 s	1030 m
887 vs	890 m
874 vs	
870 vs	
	335 vs

Frequency in cm^{-1}

Table XXIV

X-ray Powder Data for Tin(II)acetate

d	I
8.5	m
7.1	vvs
6.6	
6.4	m
5.5	w
4.6	w
4.1	m
3.8	w
3.6	vs
3.5	w
3.4	w
3.3	s
3.0	s
2.85	w
2.70	w
2.64	w
2.55	w
2.38	w
2.28	w
2.20	w
2.08	w
2.02	w
1.97	vw
1.92	m
1.78	w
1.72	w

Table XXV

X-ray Powder Data for Chelate Compounds

$Sn(C_9H_6NO)$		C_9H_6NOH		$Sn(C_9H_4NOBr_2)_2$		$C_9H_4NOHBr_2$	
d	I	d	I	d	I	d	I
*	vw	9.7	s	7.7	w	14.0	s
9.1	w	7.3		7.2	w	8.11	
7.5	m	6.3	s	6.5	s	7.3	
6.5	vs	5.8		5.7	vw	6.9	s
5.9	m	3.8	s	5.0	w	4.6	
5.5	w	3.5	s	4.5	m	4.4	
4.8	m	3.3		4.4	m	4.2	
4.4	m	3.1	s	4.2	vw	4.0	s
4.3	m	3.0		4.0	s	3.8	
3.9	vs	2.91		3.8	s	3.76	s
3.85	vs	2.80		3.7	s	3.6	
3.6	vvw	2.46		3.6	s	3.5	
3.29	w	2.39		3.45	w	3.49	
2.9	vw	1.92		3.3	m	3.45	
2.85	w	1.79		3.2	w	3.33	
2.75	m			3.1	w	3.18	
2.65	w			2.9	w	3.08	s
2.52	w			2.85	w	2.99	
2.40	w			2.70	s		
				2.50	w		
				2.48	w		
				2.29	m		
				2.15	m		
				2.08	vw		
				2.00	m		

*line cut by punch

Table XXVI

X-ray Powder Date for $Sn(C_2H_3O_2)(C_9H_6NO)$ and $Sn(C_2H_3O_2)_2(C_9H_6NO)_2$

$Sn(C_2H_3O_2)(C_9H_6NO)$		$Sn(C_2H_3O_2)_2(C_9H_6NO)_2$	
d	I	d	I
8.0	m	9.4	m
7.5	m	7.5	s
6.3	s	6.5	m
5.8	s	6.0	s
5.3	w	5.9	s
4.0	s	4.8	s
3.7	vvw	4.2	m
3.5	vs	3.9	w
3.4		3.7	vs
3.2	w	3.6	vs
3.1	w	3.3	w
2.9	vvw	3.1	vw
2.8	m	2.9	w
2.55	m	2.8	w
2.48	s	2.55	w
2.23	m	2.45	m
2.10	w	2.30	m
2.00	vvw	2.15	m
1.97	vvw	2.05	m
1.95	vvw		

Table XXVII

X-ray Powder Data for α- and β- $Sn(C_9H_6NO)Cl$

α-$Sn(C_9H_6NO)Cl$		β-$Sn(C_9H_6NO)Cl$	
d	I	d	I
9.8	vs	7.5	m
8.5	s	6.6	s
7.0	m	5.8	w
6.0	m	5.6	w
5.0	w	5.2	w
4.6	m	4.9	vs
4.4		4.4	m
4.3	s	4.2	m-s
4.1		3.9	vw
3.8	s	3.8	w
3.6		3.6	w
3.3	s	3.4	w
3.2	vs	3.1	m
3.0	w	2.98	w
2.9	vw	2.89	w
2.75	w-m	2.68	w
2.65	m	2.60	m
2.48	m	2.55	w
2.34	m	2.45	w
2.19	w	2.40	m
2.10		2.28	vw
2.09	w	2.20	w
2.00		2.15	w
1.92	w	2.10	vw
1.87	w	2.00	w
		1.97	w

Table XXVIII

X-ray Powder Data for Quarternary Ammonium Compounds

$[(CH_3)_4N]SnCl_3$		$[(C_2H_5)_4N]SnCl_3$		$[\phi(CH_3)_3N]SnCl_3$	
d	I	d	I	d	I
6.5	s	8.3	m	8.4	s
5.3	w	7.9	m	7.4	s
4.5	vs	6.3	vw	6.0	w
3.2	w	5.8	m	5.7	vw
3.18	m	5.3	s	5.2	s
2.85	m	4.7	vs	4.7	vvw
2.60	w	4.2	w	4.5	vs
2.27	m	3.9	vw	4.2	w
2.15	w	3.7	m	4.0	w
2.05	m	3.6	vw	3.8	m
2.01	m	3.35	w	3.6	m
1.92	vvw	3.2	s	3.4	s
1.75	vw	3.1	s	3.15	m
		2.9	m	3.05	m
		2.68	m	2.98	w
		2.55	m	2.81	m
		2.35	w	2.61	w
		2.24	w	2.50	m
		2.08	w	2.35	w
		1.95	vvw	2.15	w
		1.85	vw	2.10	m
		1.83	vw	2.05	vw
		1.74	w		
		1.71	vw		

Table XXIX

X-ray Powder Data for $SnCl_2 \cdot C_5H_5N$

d	I
6.4	vs
6.0	s
5.2	m
4.2	w
3.9	w
3.7	w
3.15	m
2.8	w
2.58	m
2.51	m
2.45	w
2.35	m
2.20	vw
2.11	vw
2.05	vw
1.95	
1.87	w
1.78	vw

Table XXX

X-ray Powder Data for $SnCl_2 \cdot C_{10}H_8N_2$

d	I
7.8	s
7.0	vs
6.2	s
5.3	w
4.8	w
4.6	w
4.2	m
4.1	m
3.9	m
3.4	m
3.3	w
3.2	vs
3.1	vw
2.9	w
2.8	w
2.62	s
2.38	s
2.24	m
2.10	w
2.08	vw
2.05	vw
1.98	vw
1.88	vvw
1.84	vvw
1.75	vvw

Table XXXI

X-ray Powder Data for Pyridine-N-Oxide Complexes

$SnCl_2 \cdot C_5H_5NO$		$SnCl_2 \cdot 2C_5H_5NO$	
d	I	d	I
7.0	vs	8.5	s
5.7	s	7.5	s
4.8	s	6.5	m
4.5	s	5.5	vs
3.8	w	4.7	s
3.7	m	4.6	s
3.5	s	4.5	vs
3.3	w	4.4	s
3.1	m	4.2	s
2.9	m	4.0	s
2.8	m	3.8	w
2.7	vw	3.5	w
2.65	m	3.4	vw
2.60	vw	3.2	m
2.45	m	3.0	s
2.29	w	2.9	vw
2.20	vw	2.75	w
2.10	w	2.70	w
2.05	w	2.65	w
1.97	w	2.55	m
1.95	m	2.49	w
1.90	s	2.41	vw
1.88	w	2.35	w
1.76	m	2.30	w
1.72	m	2.25	w

Table XXXII

X-ray Powder Data for $SnCl_2 \cdot 1,4$-Dioxane

d	I
6.4	s
5.7	s
4.8	m
4.5	m
3.95	m
3.5	s
3.18	w
2.80	m
2.75	w
2.65	m
2.49	m
2.42	m
2.31	m
2.25	w
2.20	w
2.11	w
2.05	w
2.00	w
1.97	w
1.95	w
1.90	w
1.84	m
1.77	w
1.72	m
1.65	w
1.62	m
1.57	w
1.55	w
1.52	w
1.50	w

Table XXXIII

X-ray Powder for Sulfoxide Complexes

$SnCl_2 \cdot 2DMSO$		$SnCl_2 \cdot 2DPSO$	
d	I	d	I
*	w	10	w
7.8	w	9.5	w
6.5	s	8.5	m
5.5	s	6.3	s
5.0	m	5.5	m
4.4	m	5.0	s
4.1	s	4.6	w
3.9	s	4.4	w
3.5	w	4.2	m
3.3	w	4.0	w
3.1	vvw	3.8	w
3.0	s	3.6	w
**		3.3	m
2.2	m	3.2	m
2.1	m	3.0	m
2.05	w	2.9	w
1.95	vvw	2.75	w
		2.65	w
		2.50	m
		2.32	m

* line cut by punch
** several very weak lines in this region

SURVEY OF THE REACTIONS OF ORGANO-TIN COMPOUNDS WITH o-QUINONES

Introduction. Haendler and Crowley[67] have shown that tin(IV)bromide forms complexes with 9,10-phenanthrene-quinone and chrysenequinone. It was decided to make a brief, preliminary survey to see if other tin(IV) compounds would react with one of these quinones. Table XXXIV gives the results of this survey. X-ray powder patterns for the isolated compounds are given in Table XXXV.

Experimental. 0.01 mole of tin compound was dissolved in a minimum amount of methanol and added to 0.01 mole of the quinone in 75 ml. of hot glacial acetic acid. The solution was evaporated until crystallization occurred, filtered while hot and washed with ligroin. Tin was determined as the oxide as before. X-ray techniques were previously described. Further work is being done in this laboratory on these compounds.

Table XXXIV

Reactions of Tin(IV) Compounds with 9,10-Phenanthrenequinone

Tin Compound	Product	Color	Elemental Analysis %Sn	
			Theory	Found
SnI_4	$SnI_4 \cdot Phq$	Brown	14.22	14.67 14.48
$BuSnCl_3$	$BuSnCl_3 \cdot 2Phq$	Green	16.97	
Bu_2SnCl_2	$Bu_2SnCl_2 \cdot 2Phq$	Black	16.48	16.04 16.02
$\phi SnCl_3$	$\phi SnCl_3 \cdot Phq$	Black	23.25	22.91 22.53
$SnCl_4$	Reaction	Brown		
$Bu_2Sn(OCH_3)_2$	No evidence of reaction			
$(CH_3)_2SnCl_2$	No evidence of reaction			
ϕ_2SnCl_2	No evidence of reaction			

Table XXXV

X-ray Data for Tin(IV) Quinone Complexes

$SnI_4 \cdot Pq$		$Bu_2SnCl_2 \cdot 2Pq$		$BuSnCl_3 \cdot 2Pq$	
d	I	d	I	d	I
8.5	m	9.0	vw	8.0	m
7.2	s	7.0	m	7.5	s
6.3	m	6.4	w	6.4	s
6.0	s	5.3	w	6.2	s
5.5	vvw	4.6	w	5.8	w
5.0	m	4.2	m	5.5	w
4.7	m	3.6	s	4.8	s
4.2	m	3.2	s	4.6	s
4.0	m	2.8	w	4.4	w
3.8	m	2.5	vw	4.1	m
3.7	m			3.9	m
3.5	vvw			3.6	m
3.3	vs			3.3	vs
3.2	vw			3.1	vs
3.1	vw			2.9	w
2.95	w			2.8	w
2.79	w				
2.70	m				
2.60	m				
2.45	m				
2.35	m				

THE PREPARATION AND PROPERTIES OF AMMONIUM HEXAFLUOROSTANNATE

Introduction. Several ammonium fluorometallates of the transition and post-transition metals have been prepared in this laboratory by the reaction of ammonium fluoride in methanol with a metal bromide in the same solvent(73-75). Ammonium hexafluorostannate, $(NH_4)_2SnF_6$, was prepared using this method.

This complex fluoride has been known for some time. Prior to 1900, J.C.G. de Marignac(76) had prepared it by treating ammonium stannate with hydrofluoric acid. Mellor(77) prepared it by the action of ammonium fluoride or sulfate on silver or lead fluorostannate. Recently Kriegsman and Kessler(78-79-80) have studied the infra-red spectra of a number of complex fluorostannates, including $(NH_4)_2SnF_6$.

It has also been shown in this laboratory(81-82) that anhydrous metal fluorides can be prepared from ammonium fluorometallates by thermal decomposition according to the reaction

$$(NH_4)_xMF_y \xrightarrow{\Delta} x(NH_4F) + MF_{(y-x)}$$

Our interest in $(NH_4)_2SnF_6$ was stimulated by the possibility of using it as the starting compound in the preparation of anhydrous tin(IV)fluoride by thermal decomposition and also by the lack of any recent data on the structure of this compound.

The Preparation of Ammonium Hexafluorostannate

The complex was prepared using the method of Johnson and Haendler[74]. The purity was verified by elemental analysis and by x-ray powder diffraction.

TABLE XXXVI

Elemental Analysis

	Calcd.	Found
Per cent Sn	44.16	43.86, 44.68
" " F	42.43	42.68, 42.75
" " NH_4	13.41	13.28, 13.18

Structural Studies

X-ray powder diffraction. X-ray powder diffraction data are listed in Table XXXVII. The powder data were successfully indexed on the basis of a hexagonal unit cell, with parameters a_o and c_o equal to 5.980 Å and 4.789 Å, respectively. $(NH_4)_2SnF_6$ is probably isomorphous with its rubidium analog, Rb_2SnF_6, which has been shown by Muetterties[83] to be hexagonal, with a_o and c_o equal to 6.038 and 4.824, respectively.

Infra-red spectrum. The infra-red spectrum of $(NH_4)_2SnF_6$ is relatively simple. The major bands are given in Table XXXVIII. The bands in the region above 600cm^{-1}

are due to the NH_4^+ ion; those below 600cm^{-1} are due to Sn-F bond(79). The infra-red spectrum indicated no hydrogen bonding is present in the complex. The x-ray powder diffraction data substantiate this.

Waddington(88) has suggested the use of infra-red spectra in conjunction with x-ray powder data to show the presence or absence of hydrogen bonding in ammonium compounds. Cox and Sharpe(89) have used this technique to show the absence of hydrogen bonding in ammonium hexafluoroferrate (III). Crocket(82) also used it in discussing hydrogen bonding and isomorphism in the ammonium, potassium, and rubidium fluorometallates of copper(II) and Baker(84) in discussing the ammonium and potassium fluorometallates of uranium and the Group V metals. The criterion used is the free rotation of the ammonium ion which would not be possible if the ion were hydrogen bonded. If the ammonium compound is isomorphous with the corresponding potassium and rubidium compounds, as shown from x-ray powder patterns, the ammonium ion would be free to rotate and thus there could be no hydrogen bonding. As was previously stated, $(NH_4)_2SnF_6$ is probably isomorphous with Rb_2SnF_6. Potassium hexafluorostannate has been prepared by Hoppe(90), but no powder data are available for comparison.

It has also been shown by Baker(84), that in hydrogen bonded ammonium fluorometallate complexes, the infra-red spectrum shows strong splitting in the 3000cm^{-1} and 1400cm^{-1} regions and a band at 1700cm^{-1}. The infra-red spectrum of $(NH_4)_2SnF_6$ shows none of these characteristics.

Table XXXVII

X-ray Powder Data for Ammonium Hexafluorostannate

$a = 5.980$ Å $c = 4.789$ Å

hkl	I	d_{obs}	d_{calc}	Q_{obs}	Q_{calc}
100	100	5.179	5.245	0.0373	0.0363
001	25	4.789	4.841	.0437	.0426
101	100	3.535	3.557	.0800	.0790
110	30	3.011	3.028	.1102	.1091
111	35	2.559	2.567	.1527	.1518
201	90	2.298	2.305	.1892	.1881
102	30	2.194	2.197	.2075	.2070
210	10	1.979	1.982	.2549	.2545
112	40	1.888	1.890	.2804	.2797
211	80	1.832	1.834	.2976	.2972
202	85	1.777	1.778	.3164	.3160
300	10	1.748	1.748	.3270	.3272
301	15	1.643	1.644	.3700	.3699
003	1	1.609	1.613	.3846	.3839
103	10	1.541	1.542	.4201	.4204
212	50	1.534	1.533	.4247	.4252
220	30	1.513	1.514	.4356	.4363
310	10	1.456	1.454	.4717	.4726
221	5	1.445	1.444	.4783	.4789
113	5	1.425	1.424	.4920	.4930
302	5	1.418	1.417	.4974	.4978

TABLE XXXVIII

Infra-red Spectrum of Ammonium Hexafluorostannate

Frequency(cm^{-1})	Intensity	Assignment
3270	VS	NH_4^+
1430	VS(Broad)	NH_4^+
565	VS(Broad)	Sn-F

The fluorine atoms are undoubtedly in an octahedral arrangement around the tin atom since the Sn-F absorption is in the region for octahedral Sn-F absorption(78-85).

Thermal analysis. Two techniques were employed in in the thermal analysis of $(NH_4)_2SnF_6$, thermogravimetric analysis, TGA, and differential thermal analysis, DTA.

Thermogravimetric analysis. Thermogravimetric analysis was carried out on a balance constructed by Kingston(86). The thermograph showed a weight loss which began at 250°C. and continued until the loss in weight corresponded to one mole of ammonium fluoride at 325°C. At this temperature there was a slight pause in weight loss, then an extremely rapid weight loss that continued to approximately 500°C. It is felt that this rapid weight loss is due to a general decomposition of the product remaining after the loss of one mole of NH_4F. The sample continued to lose weight after the total calculated weight loss for two moles of ammonium fluoride had been reached. The final product was a black, crusty fluoride containing solid that we were not able to identify.

The decomposition after 325°C. is often violent; on several occasions most of the sample was blown out of the sample holder. On one occasion we were able to remove the sample after a weight loss ocrresponding to approximately one mole of ammonium fluoride. The x-ray powder pattern of the material is given in Table XXXIX. The appearance of a new phase is indicated by a large number of lines that are not in the pattern of $(NH_4)_2SnF_6$.

Differential thermal analysis. Differential thermal analysis was carried out on an apparatus described by Shinn[87] using a slight suction to remove the volatile products. The results are shown in Figure 1. The curve shows a small transformation beginning at 300°C. At 330°C. the differential temperature rises sharply to 390°C. and then falls off quite rapidly. During the sharp temperature rise the evolving gasses become quite dense and large amounts of sample are blown out of the sample holder. The final product is a hard, black, unidentifiable solid, very similar in appearance to the final product of the TGA.

Both TGA and DTA results indicate that the thermal decomposition of $(NH_4)_2SnF_6$ goes according to the reaction:

$$(NH_4)_2SnF_6 \xrightarrow[300^\circ C\ DTA]{250^\circ C\ TGA} \left[(NH_4)_2SnF_5\right]x \xrightarrow[\text{violent decomposition}]{\Delta} \text{Unknown Product}$$

Further work on this decomposition is now being carried out in this laboratory.

Experimental

Preparation of the $SnBr_4$-methanol solution. 12 g. (0.1 mole) of finely divided tin was covered with 100 ml. of absolute methanol (0.01 per cent water). A slight excess of bromine was added dropwise. It was necessary to warm the solution to initiate the reaction, but once started, the reaction is exothermic and vigorous. When all the metal appeared to have reacted, the solution was filtered and stored until needed.

Preparation of the complex. The filtered methanol solution of the metal bromide was added slowly to a rapidly stirred saturated solution of ammonium fluoride in methanol. The product was filtered, washed several times with dilute ammonium fluoride in methanol, then pure methanol until the filtrate gave a negative test for bromide ion, and finally with anhydrous ether. The complex was oven dried at 110°C. Regrinding of the complex and digestion in a dilute alcohol solution of ammonium fluoride improved the elemental analysis and the quality of the x-ray powder pattern.

Analytical. Fluorine was determined by distillation of fluorosilicic acid from sulfuric acid solution and then titration with thorium nitrate using the method of Grant and Haendler(93).

Ammonia(90) was determined by distillation from strongly alkaline solution into cold 2% boric acid solution

followed by titration with standard hydrochloric acid, using methyl purple indicator.

Tin was determined gravimetrically as the oxide by slow evaporation to dryness with concentrated nitric acid in platinum crucibles and igniting at 800°C.

X-ray powder diffraction studies. The samples were mounted in 0.3mm glass capillaries. Powder diffraction patterns were taken using the 57.3mm and 114.56mm Phillips cameras. The powder patterns from the latter were used for accurate structural determinations. Iron radiation with a wave length of 1.9373Å was used. Intensities for the lines were estimated visually.

The diffraction angle of each line on the powder pattern was read and the interplanar spacings of the sets of planes responsible for the observed lines were thus obtained. Using these observed values, values for Q obs., $(\frac{\sin^2\theta obs}{\lambda})4$, were obtained for each d value.

Using the method of Henry, Lipson and Wooster(91) preliminary values were obtained for the lattice parameters a and c. From these parameters, values for Q calc., $\sin^2\theta$ calc., and d calc. were calculated using a program developed for the IBM 1620 computer by Haendler and Cooney(92). The calculated values were compared with the observed values, and, a and c were adjusted and the calculations repeated until the best agreement between the observed and calculated values were obtained. In this way all the lines in the pattern were successfully indexed.

Infra-red spectrum. The infra-red spectrum in the $4000cm^{-1}$ to $600cm^{-1}$ region was run with a Perkin-Elmer 21 using NaCl optics, and in the $600cm^{-1}$ to $400cm^{-1}$ region with a Perkin-Elmer 337 using KBr optics. Halocarbon and Nujol mulls were employed.

Thermal decomposition. Thermogravimetric analysis was carried out on an apparatus described and constructed by Kingston(86). The decompositions were performed with the generous help of Kingston. Differential thermal analysis was carried out on an apparatus described by Shinn(87).

Acknowledgement. The author wishes to thank Miss Sandra Roscoe and Miss Blanca Haendler for their assistance in programming the data for the IBM 1620 Computer calculations.

Table XXXIX

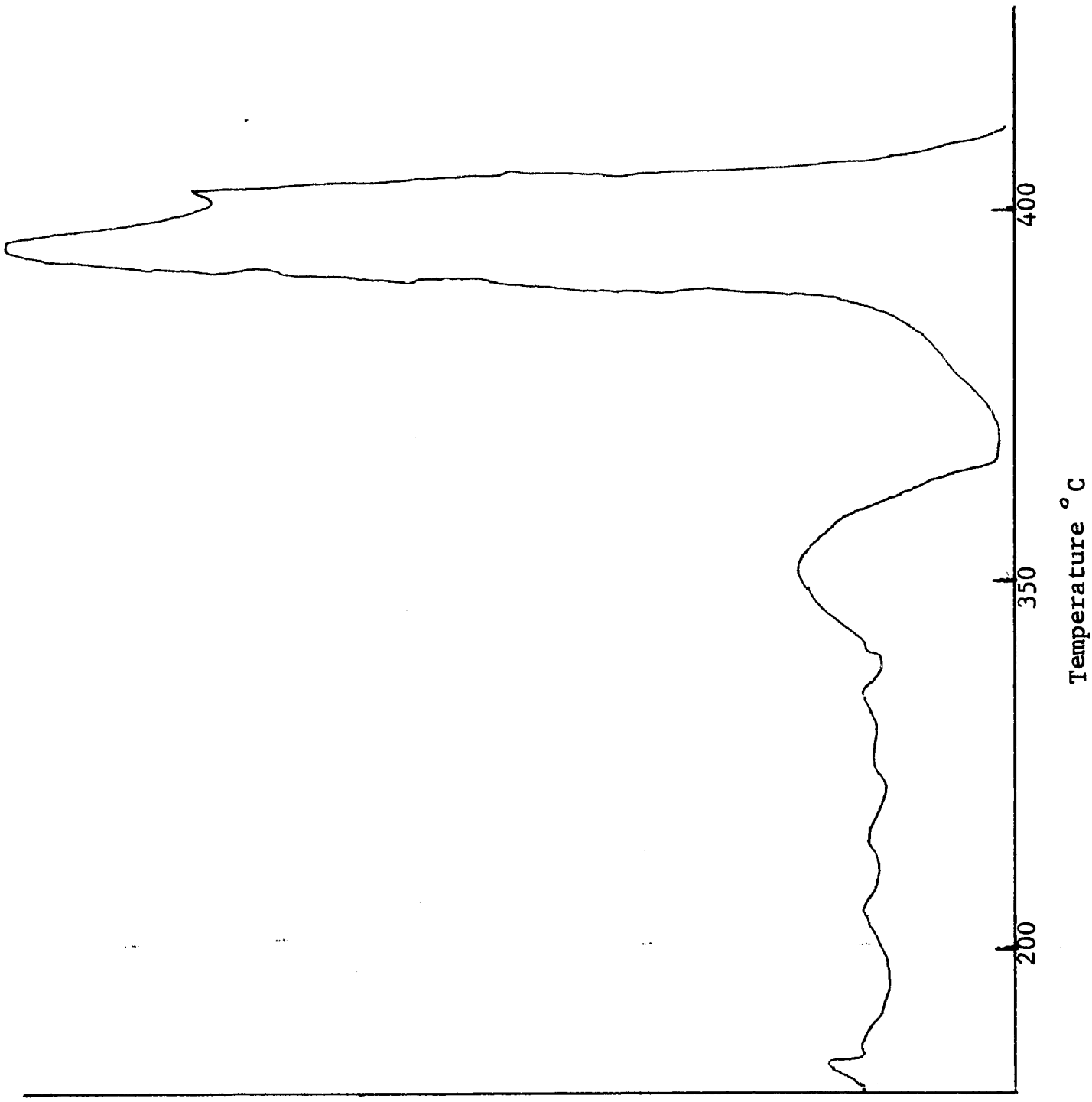
First Decomposition Product of $(NH_4)_2SnF_6$

d	I
6.91	w
6.51	w
5.59	m
5.40	s
5.18	s
4.84	m
3.93	w
3.61	s
3.53	s
3.40	vw
3.23	w
3.00	m
2.84	vw
2.56	s
2.30	s
2.20	s
2.03	vw
1.97	m
1.89	m
1.83	s
1.77	m
1.69	w
1.64	m
1.54	s
1.51	w
1.46	m
1.43	m
1.41	m
1.37	vw

Figure 1

Differential Thermal Analysis

$(NH_4)_2SnF_6$



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