ACCEPTOR PROPERTIES OF HALIDES OF ELEMENTS

OF GROUPS IV AND V

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2,2'-Bipyridyl forms equimolar complexes, $MX_3\text{·bipy}$, with the trihalides of arsenic, antimony and bismuth, and also with the mono-organosubstituted halides of these elements, $R\text{MX}_2\text{·bipy}$. Most of the crystalline compounds are covalent, but are partially ionised in nitrobenzene solution as $(\text{MX}_2\text{·bipy})^+X^-$. Ionisation increases from chlorides to iodides, but decreases from arsenic to bismuth. The first trend can be correlated with decreasing strength of the metal-halogen bond, and the second with an increasing preference for higher coordination numbers down the Group.

Diphenylgermanium halides do not react with 2,2'-bipyridyl, but germanium tetraiodide forms the adduct $\text{GeI}_4\text{·2bipy}$. With various organotin halides and the diphenyl-lead halides, 2,2'-bipyridyl forms six-coordinate complexes, $R\text{SnX}_4\text{·bipy}$ and $\text{Ph}_2\text{PbX}_2\text{·bipy}$. These are non-electrolytes in nitrobenzene, although slight ionisation is apparent among the tin complexes.

2,2'2''-Terpyridyl does not react with germanium tetra-chloride, but forms a 1:1 adduct with germanium tetraiodide, $\text{GeI}_4\text{·terpy}$. This tridentate ligand also reacts with two molecules of dimethyltin and diphenyltin chlorides and bromides to form compounds containing six-coordinate tin
cations, \( (R_2SnX_{\text{terpy}})^+ \), and unusual five-coordinate tin anions, \( R_2SnX_{3}^- \). No corresponding complex anion is formed with dimethyltin diiodide. The diphenyl-lead halides all coordinate one molecule of \( 2,2',2''\text{-terpyridyl} \) to form complexes \( \text{Ph}_2\text{PbX}_2\text{-terpy} \), which show only a slight tendency to ionise in nitrobenzene, and are presumably seven-coordinate. Differences in the acceptor behaviour of Group IV halides can again be related to preference for higher coordination numbers at the bottom of the Group.
2. INTRODUCTION

There is considerable evidence that the tetrahalides of silicon, germanium, tin and lead in Group IV and the trihalides of phosphorus, arsenic, antimony and bismuth in Group V all form addition compounds with donor molecules, particularly nitrogen bases. In both groups it is apparent that the heavier elements form the greatest number of complexes and the acceptor properties of silicon and of phosphorus are rather weak. The non-occurrence of complex anions of the type $PX_4^-$, in the case of phosphorus, and the fact that related anions are restricted to complex fluorides in the case of silicon, illustrate this point.

Where organohalides are accessible it is known that these also form addition compounds, but little is known of the ability of Group V organohalides to coordinate donor molecules. It is clear that as halogens are replaced by organic groups the acceptor properties of the resulting halide are much reduced and this effect is most marked for the lighter elements. The silicon halides, $R_2SiX_2$, for example, form acetylacetonates with non-chelated structures while the tin halides, $R_2SnX_2$, form a variety of addition products and also complex anions of the type $R_2SnX_4^{2-}$.

Chelate complexes are known for several of the Group IV
halides. Silicon$^3$, germanium$^4$, and tin$^5$, tetrachlorides all coordinate 2,2'-bipyridyl and germanium tetrachloride and tetraphenylborate have been reported to coordinate 1,10-phenanthroline$^6$. These chelate complexes are more stable and more resistant to hydrolysis than corresponding complexes with monodentate amines.

Comparatively little is known about the constitution and stereochemistry of these addition compounds. Table I is a list of adducts formed by the Group IV halides selected to illustrate the range of compositions which occur.

**TABLE I**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
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<tbody>
<tr>
<td>SiCl$_4$·2py (a)</td>
<td>SiBr$_4$·2py</td>
</tr>
<tr>
<td>SiCl$_4$·bipy (b)</td>
<td>SiBr$_4$·bipy</td>
</tr>
<tr>
<td>SiCl$_4$·3Me$_3$</td>
<td>SiCl$_4$·2Me$_3$</td>
</tr>
<tr>
<td>SiCl$_4$·2Me$_3$</td>
<td>GeBr$_4$·2py</td>
</tr>
<tr>
<td>GeCl$_4$·bipy</td>
<td>GeBr$_4$·bipy</td>
</tr>
<tr>
<td>SnCl$_4$·2py</td>
<td>SnBr$_4$·bipy</td>
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<tr>
<td>SnCl$_4$·bipy</td>
<td>SnBr$_4$·bipy</td>
</tr>
<tr>
<td>Me$_2$SnCl$_2$·2py</td>
<td>Me$_2$SnBr$_2$·2py</td>
</tr>
<tr>
<td>Me$_3$SnCl$_3$·py</td>
<td>Ph$_2$PbCl$_2$·bipy</td>
</tr>
<tr>
<td>Ph$_2$PbCl$_2$·bipy</td>
<td>Ph$_2$PbBr$_2$·bipy</td>
</tr>
</tbody>
</table>

(a) py = pyridine
(b) bipy = 2,2'-bipyridyl
The majority of the adducts are of the form $M_4L_2$ (where $L$ represents one electron pair donor) and undoubtedly have the metal in octahedral coordination. A structural study of $CeI_4.2py$ by x-ray methods\(^6\) has shown this to be so for this complex at least. The two pyridine nitrogen atoms occupy trans positions.

However, the nature of the compounds having compositions $MX_4L$ and $MX_4.4L$ is less certain. In the compound $SiI_4.py$ some of the silicon-iodine bonds must be broken and a structure such as $[SiI_2.py]^{2+} 2I^- \text{ is likely}^7$. The lead complexes $Pb_2FbX_2.py$ may contain eight-coordinate lead. For the 1:1 adducts ionic, covalent, or polymeric formulations are possible. The low volatility of the silyl iodide-trimethylamine adduct together with its high conductivity in acetonitrile solution indicate that it should be formulated $\left[SiH_3,Me_3\right]^+$ $8^-$. On the other hand the complex $Me_3SnCl.py$ is low melting, very soluble in non-polar solvents, and has a very low conductivity in nitrobenzene. A recent x-ray study has shown that it is truly covalent based on a trigonal bipyramid with the chlorine and nitrogen atoms in polar positions\(^9\).

Table II is a representative list of the nitrogen base adducts which have been reported for the Group V trihalides. A diversity of combining ratios is apparent. Nothing is known of the structure of these compounds. The 1:1 adducts
are probably simple molecular addition compounds but it is possible that some ionisation of metal halogen bonds has taken place in those adducts with more than one mole of base coordinating.

<p>| | |</p>
<table>
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<tbody>
<tr>
<td>PCl₃·NMe₃</td>
<td>PBr₃·NMe₃</td>
</tr>
<tr>
<td>AsCl₃·py</td>
<td>AsBr₃·py</td>
</tr>
<tr>
<td>AsCl₃·2py</td>
<td>AsBr₃·2py</td>
</tr>
<tr>
<td>SbCl₃·py</td>
<td>SbCl₃·NMe₃</td>
</tr>
<tr>
<td>BiCl₃·2py</td>
<td>BiBr₃·2py</td>
</tr>
</tbody>
</table>

(a) py = pyridine

Walden when examining the properties of arsenic trichloride as an ionising solvent observed that pyridine gave rise to a conducting solution. Apparently ionisation of arsenic-chlorine bonds had occurred as a result of the coordination of the pyridine, and it seemed likely that ionisation of most of the trihalides of this group would occur under the influence of electron donor molecules.

No systematic study has been made of these Group IV and Group V adducts with the intention of comparing and contrasting the behaviour of the coordinating elements. It
was decided to study the 2,2'-bipyridyl complexes of the Group V trihalides especially from the point of view of any possible ionisation. Greater stability was expected to be associated with chelate complexes and with this ligand if 1:1 adducts were to be formed these would have the somewhat uncommon coordination number of five so that ionisation would reflect coordination preferences, at least in part.

Because there are no stable lead tetrahalides, the Group IV organohalides were selected for study, so including all the elements of the group for comparison. Adducts of organohalides frequently have greater solubility in organic solvents than the adducts of simple halides so that measurement of conductivities was facilitated by working with organohalides.

In view of the evident reluctance of organotin halides to form cations even when a base is coordinated to the tin as in Me₃SnCl.py, it was of interest to examine the coordination behaviour of these halides towards a tridentate chelating ligand. Such a ligand is 2,2',2''-terpyridyl and in the one structural study made of a complex of this molecule it remained planar and filled three coordination positions⁴. It has been shown previously that this ligand does not react with silicon tetrachloride⁵ - a surprising result since octahedral cations of silicon are known, e.g., Si(acac)₃⁺. However, the possibility remained that it would react with
the halides of the heavier elements of Group IV. The reactions of both $2,2'$-bipyridyl and $2,2',2''$-terpyridyl with the Group IV organohalides were studied.

Fluorides were not included in these comparisons since the organofluorides of tin and lead are insoluble in organic solvents as also is bismuth trifluoride.

It was thought that an investigation of the series of complexes outlined above would permit an assessment of the acceptor behaviour of the Group IV and Group V halides to be made, especially with regard to preferred coordination numbers and also the extent of ionisation of the various adducts.

The complex chemistry of the Group IV and Group V halides will be reviewed before discussing the results of the present work.
3. COMPLEX CHEMISTRY OF THE GROUP IV HALIDES

The complex chemistry of these halides falls into two main categories.

(1) Addition compounds formed by electron donor molecules with the halides acting as electron acceptors.

(2) Complex halide anions.

In discussing addition compounds this review will be concerned primarily with those formed by nitrogen bases. With silicon and germanium halides ammonolysis occurs readily and completely and it is only with tertiary amines that complex formation can take place. Resistance to ammonolysis becomes apparent in the organogermanium and organotin halides and addition products with ammonia, primary amines, and secondary amines are possible. No ammonolysis occurs with lead tetrachloride or the organolead halides.

The majority of the complexes of this group have the element in octahedral coordination. In the case of tin a coordination number of five is well established, but no other element of the group shares this feature except silicon in an unusual complex with triethanolamine. It is quite possible that lead has coordination numbers as high as eight in some of its complexes.

The following review will cover the detailed complex
chemistry of each element individually.

A. Silicon Halides

The first addition compound of a silicon halide, SiCl$_4$.2py, was correctly identified by Hardin$^{12}$. Similar 2:1 complexes are formed between trimethylamine and silicon tetrafluoride$^{13}$ and between pyridine and silicon tetrafluoride$^{14}$ and tetrabromide$^{15}$. All these complexes almost certainly contain six-coordinate silicon. However, the reaction between pyridine and silicon tetraiodide produced a compound of different composition. Wannagat et al.$^{16}$ and Muettterties$^7$ both report an adduct with four moles of pyridine, SiI$_4$.4py. Muettterties suggests the formulation (SiI$_2$.py)$_2$ and the presence of iodide ions is indicated by the ability of the compound to absorb iodine, presumably to form polyiodide ions.

A series of 1:1 adducts with nitrogen donors is also known. Trimethylamine reacts with silicon tetrafluoride$^{15}$, tetrachloride$^{15}$, and the silyl halides$^{16}$ to form the compounds SiF$_4$.3Me$_3$, SiCl$_4$.3Me$_3$, SiH$_2$.3Me$_3$. Most of these adducts appear to be best described as six-coordinate halogen-bridged structures$^{15}$, but the trimethylamine-silyl iodide adduct has low volatility and gives a conducting solution in acetonitrile$^8$, which indicates that it is probably a salt, (SiH$_3$.3Me$_3$)$^+$.I$^-$. 
The only complex anion known is the familiar hexafluorosilicate, SiF$_6^{2-}$, in which the fluorine atoms are arranged octahedrally about the silicon$^{17}$.

B. Germanium IV Halides

Germanium tetrachloride is completely ammonolysed in liquid ammonia solution$^{18,19}$, to germanium imide, Ge(NH)$_2$, and ammonium chloride. That primary and secondary amines similarly cause ammonolysis was shown by Thomas and Southwood$^{20}$, but with a tertiary amine, diethylaniline, these workers observed no interaction with germanium tetrachloride. Johnson and Sidwell$^{21}$ later showed that germanium tetraiodide was also ammonolysed by primary and secondary amines, but with triethylamine they isolated an addition compound of the iodide with five moles of amine, GeI$_4$·5NET$_3$. This same complex has also been reported by Karantassis and Capatos$^{22}$, while with germanium tetrachloride Trost$^{23}$ reported an adduct with four moles of triethylamine GeCl$_4$·4NET$_3$. High amine : halide ratios are more likely to occur with the iodide than the chloride since the germanium-iodine bond is weaker and more readily broken.

Diphenylgermanium dichloride is not ammonolysed by ethylamine but neither does it form a definite addition compound with this amine$^{24}$.

More recently Abel$^{25}$, and Tronev and Lebedev$^{26}$ have
prepared the di-pyridine adduct of germanium tetrachloride, GeCl$_4$.2py, similar to the related di-pyridine adducts of silicon and tin tetrachlorides. This complex was expected to have an octahedral arrangement of ligands about the germanium atom and such an arrangement has been confirmed by the X-ray structure determination made by Hulme, Leigh and Beattie. The coordinated pyridines occupy trans positions.

Various other six-coordinate complexes are known. Ferguson et al. have prepared germanium tetrafluoride and tetrachloride adducts with two moles of trimethylamine and a chelate complex with tetramethylethylenediamine. Germanium tetrafluoride adducts with two moles of pyridine, dimethyl-aniline, ammonia, pyrrolidine, and piperidine, have also been reported. Lebedev and Tronev have prepared stable chelate complexes of germanium tetrachloride and tetrabromide with the ligands 2,2'-bipyridyl and 1,10-phenanthroline. These have monomeric molecular weights in boiling benzene and are therefore six-coordinate.

A number of 1:1 adducts are also known. Both germanium tetrafluoride and tetrachloride form 1:1 compounds with trimethylamine. It is suggested that these have polymeric halogen-bridged structures which retain the octahedral configuration about the germanium atom. However, the stable 1:1 adduct of ammonia with monofluorogermane is thought to have an ionic structure, (GeH$_3$,F$_3$)$_4^+$,F$^-$.
Hexafluorogermanates are well known, occurring with most monovalent cations. They are generally isomorphous with the corresponding fluoro- silicates.

Complex chloride anions are also known for germanium. Everest and Harrison\textsuperscript{30} studied the adsorption of anions from a germanium tetrachloride-hydrochloric acid solution, on an ion-exchange resin and interpreted their results as indicating the existence of both GeCl\textsubscript{5}\textsuperscript{\textminus} and GeCl\textsubscript{6}\textsuperscript{2\textminus} ions as well as complex hydroxy-chloro-anions, Ge(\textit{OH})\textsubscript{x}Cl\textsubscript{5\textminus-x}. Hexachlorogermanates can be prepared as stable solids, only with large symmetrical cations. Laubengayer et al.\textsuperscript{31} prepared caesium hexachlorogermanate and more recently Udovenko and Fialkov\textsuperscript{32} have prepared hexachlorogermanates with caesium, rubidium, and tetramethylammonium ions but no salts were formed with lithium, potassium, sodium, or ammonium ions.

The very low solubility of germanium tetrabromide in hydrobromic acid\textsuperscript{30} indicates that no bromogermanates exist.

\section*{C. Tin IV Halides}

Like the tetrahalides of silicon and germanium, the tetrahalides of tin are ammonolysed by liquid ammonia and by primary and secondary amines. This ammonolysis, however, is not complete and even after prolonged washing with ammonia the last tin-halogen bond remains intact, the
composition of the final product being $\text{SnX}_4(\text{NR}_3)_2$\[33,34]. With tertiary amines addition reactions invariably take place. Trimethylamine forms diamines, $\text{SnX}_4.2\text{NH}_3$, with the chloride\[35,15], bromide\[36], and iodide\[36]. However, with trimethylamine Böhme and Boll\[37] report a tetraminate, $\text{SnBr}_4.4\text{NR}_3$, which they formulate, $(\text{Sn}\text{NR}_3)_4\text{Br}^-$. Octahedral coordination about the tin as in $(\text{SnBr}_2.4\text{NR}_3)_2\text{Br}^-$ is perhaps more likely. This adduct is soluble in water and silver nitrate precipitates all the bromine as silver bromide. After removal of the silver bromide and concentration of the resulting solution, Böhme and Boll obtained $(\text{Sn}\text{NR}_3)_6\text{H}_2\text{NO}_3^-$. Pfeiffer et al.\[38] prepared the pyridine adducts of the tetrahalides and found them all to be of the form $\text{SnX}_4.2\text{py}$. Cooper and Wardlaw\[39] analyzed the pyridine and quinoline adducts of tin tetraiodide as $\text{SnI}_4.2.5\text{py}$, and $\text{SnI}_4.2.5\text{quinol}$. Chelate complexes with 2,2'-bipyridyl were prepared by Allison and Mann\[5]. All the adducts were of 1:1 composition and were more resistant to hydrolysis than the corresponding pyridine adducts. They were quite insoluble in organic solvents and had high melting points.

Organotin halides also react with amines to form addition compounds. Some unusual compositions have been reported. Methyltin trichloride and tribromide both coordinate two moles of pyridine to form the expected six-coordinated complexes $\text{SnCl}_3.2\text{py}$\[40,38]. With methyltin triiodide Pfeiffer
et al. \(^{38}\) reported an adduct with four moles of pyridine, MeSn\(_3\)py. Recently Beattie and McQuillan\(^{41}\) have reinvestigated this reaction and they could prepare only the di-pyridine adduct, MeSn\(_3\)2py. Phenanthroline similarly formed a 1:1 adduct, MeSn\(_3\)phenan\(^{41}\). Dimethyltin dibromides all form 2:1 adducts with pyridine, Me\(_2\)SnX\(_2\)py\(^{38,40}\). Ammoniates of these halides are reported with four moles of ammonia, Me\(_2\)SnX\(_2\)NH\(_3\)\(^{42}\). Among the diethyltin halides a variety of ammoniates occur, Et\(_2\)SnCl\(_2\)NH\(_3\)\(^{43}\), Et\(_2\)SnCl\(_2\)NH\(_3\)\(^{42}\), Et\(_2\)SnBr\(_2\)NH\(_3\)\(^{42}\), Et\(_2\)SnI\(_2\)NH\(_3\)\(^{42}\), and Et\(_2\)SnI\(_2\)NH\(_3\)\(^{42}\). The di-organotin halides form chelate complexes with bipyridyl, R\(_2\)SnX\(_2\)bipy\(^{44,45}\), phenanthroline, R\(_2\)SnX\(_2\)phenan\(^{44,45}\), and 8-hydroxy quinoline R\(_2\)Sn(oxine)\(_2\)\(^{46}\).

In the trimethyltin halide series acceptor properties are becoming weaker and fewer addition compounds exist. Kraus and Green\(^{47}\) prepared mono- and di-ammoniates of trimethyltin chloride, Me\(_3\)SnCl,NH\(_3\) and Me\(_3\)SnCl,2NH\(_3\), and a di-pyridine adduct of trimethyltin iodide, Me\(_3\)SnI,2py. Pyridine with trimethyltin chloride formed only a 1:1 adduct, Me\(_3\)SnCl,py. Early workers considered this to be an ionic compound based on quaternised nitrogen (Me\(_3\)Sn,py\(^+\)Cl\(^-\)). On the basis of infra-red evidence, which showed a planar Me\(_3\)Sn group to be present in the molecule, Beattie\(^{41}\) suggested that the compound contained five coordinate tin, the structure being based on
a trigonal bipyramid. An X-ray crystallographic study\textsuperscript{18,9} has verified this structure.

Further evidence of the acceptor properties of the tin atom in triorganotin compounds, \( \text{R}_3\text{SnX} \), is provided by the unusual structures of those compounds in which the radical \( X \), itself contains a donor atom. Such a compound is trimethyltin fluoride which has long been considered\textsuperscript{19} an ionic solid because of its high melting point and low solubility in organic solvents. Beattie and Gilson\textsuperscript{50} suggested that a polymeric structure involving fluorine-bridging was also compatible with its physical and chemical properties. An X-ray study by Clark, O'Brien and Trotter\textsuperscript{51} has confirmed this polymeric structure. The tin atom is five-coordinate but its stereochemistry is not simple. Similarly, triorganotin acetates and imidazoles\textsuperscript{52} are polymeric with bridging groups, and not ionic as once supposed\textsuperscript{53}. The infra-red spectrum of trimethyltin perchlorate\textsuperscript{54} suggests that it is composed of planar trimethyltin groups bridged by partially covalent perchlorate groups to form chains. The structures of trimethyltin nitrate\textsuperscript{54}, tetrafluoroborate\textsuperscript{55}, hexafluorocarsenate\textsuperscript{56}, and hexafluoroantimonate\textsuperscript{56} are apparently similar.

Both trimethyltin perchlorate and trimethyltin nitrate form di-ammonia adducts\textsuperscript{54}. Since the infra-red spectra of these compounds have absorption bands typical of ionic
perchlorate and ionic nitrate groups respectively, it is considered that these adducts both contain the complex tin cation, $\text{Me}_3\text{Sn(\text{NH}_3)_2}^+$. This is the only example of an organotin cation which exists in the solid state.

Although the organotin halides are not ionised in a polar solvent, the coordination of an amine or donor molecule does promote slight ionisation. Kraus and Greer$^{57}$ showed that the conductivity of trimethyltin chloride in nitrobenzene was increased by the addition of pyridine. A similar but slightly greater effect was noticed on the addition of pyridine to dimethyltrifluoromethyltin chloride$^{58}$. Prince$^{59}$ represented the ionisation of a triorganotin chloride in an ionising solvent in the presence of an electron pair donor (L) by an equilibrium of the type

$$
\text{L}^+ + \text{R}_3\text{SnCl} \rightleftharpoons \text{L:SnR}_3^+ + \text{Cl}^-
$$

Thomas and Rochow$^{60}$ studied the di-pyridine adduct of dimethyltin dichloride, $\text{Me}_2\text{SnCl}_2\cdot2\text{py}$, and found it to be a weak electrolyte in acetonitrile. The nature of the ions was not determined. In aqueous solutions ionisation takes place readily. Triethyltin chloride is a typical 1:1 electrolyte in water$^{61}$. For dimethyltin dichloride in water Rochow and Seyferth$^{62}$ write equilibria of the type

$$
\text{Me}_2\text{SnCl}_2 + n\text{H}_2\text{O} \rightleftharpoons \text{Me}_2\text{Sn(\text{H}_2\text{O})}_n^{2+} + 2\text{Cl}^-
$$

$$
\text{Me}_2\text{Sn(\text{H}_2\text{O})}_n^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Me}_2\text{Sn(\text{H}_2\text{O})}_{n-1}^{4+} + \text{H}_3\text{O}^+
$$
It is clear that in non-aqueous solvents, including those of high dielectric constant such as dimethylformamide, only slight ionisation of these halides takes place even in the presence of a coordinating amine.

Many complex halide anions are known for tin, and are much more stable than those of silicon, germanium or lead. Hexahalogenostannates are known with fluorine, chlorine, bromine, and iodine. From Everest and Harrison's study of the anions present in hydrochloric acid solutions of tin tetrachloride it is clear that singly charged, five-coordinate ions, \( \text{SnCl}_5^- \), also exist. These ions are present in the triphenylmethyl salt, \( \text{Ph}_3\text{C}^+\text{SnCl}_5^- \).

A wide range of complex organotin anions has been reported, always in combination with large cations such as pyridinium or diazonium. Pfeiffer et al. prepared pyridinium salts of the following anions: \( \text{MeSnCl}_5^2^- \), \( \text{MeSnBr}_5^2^- \), \( \text{Me}_2\text{SnCl}_4^2^- \), \( \text{Me}_2\text{SnBr}_4^2^- \). Reutov et al. described diazonium salts of \( \text{EtSnCl}_5^2^- \) and \( \text{Et}_2\text{SnCl}_4^2^- \). With tri organosubstituted halides the only anions which could be isolated in stable salts were those containing three phenyl groups, \( (\text{pyH})_2\text{Ph}_3\text{SnCl}_3 \) and \( (\text{pyH})_2\text{Ph}_3\text{SnBr}_3 \).

It is noticeable that not one of the reported complex anions of the organotin halides contains iodine and it may be supposed that such anions would be unstable.

A very unusual anion has been reported by Grigor and
Seyferth. The nucleophilic displacement of bromine from trimethyltin bromide by triphenylphosphine-methylene produced a compound containing a complex tin anion \( \text{Ph}_2\text{PCH}_2\text{SnMe}_3^+ \text{Me}_3\text{SnBr}_2^- \). They also prepared the tetraethylammonium salt of this anion, \((\text{Et}_4\text{N})^+\text{Me}_3\text{SnBr}_2^-\) by evaporating an aqueous solution containing tetraethylammonium bromide with a five molar excess of trimethyltin bromide. On the grounds that all the other reported anions of organotin halides contain six-coordinate tin these authors postulated a dimeric structure for this ion involving halogen-bridging. However, in view of the considerable evidence now in favour of five-coordinate tin, it seems likely that this is yet a further example.

D. Lead IV Halides

The complex chemistry of the lead halides is very limited because of the instability of tetravalent lead. The tetrachloride is the only tetrahalide which exists and is itself not very stable. However, it is reported not to undergo ammonolysis\(^{74,75}\), but forms an addition compound with four moles of ammonia, PbCl\(_4\)·4NH\(_3\)\(_2\). Mathews\(^{76}\) also reports adducts with three moles of aniline, PbCl\(_4\)·3C\(_6\)H\(_5\)NH\(_2\), and two moles of pyridine or quinoline, PbCl\(_4\)·2py. Organo-lead halides are more stable, especially the diphenyl-lead series, and even diphenyl-lead diiodide is known as a stable
yellow solid. Pfeiffer, Truskier and Disselkamp\textsuperscript{77} report adducts of diphenyl-lead dichloride and dibromide with four moles of ammonia and four moles of pyridine, $\text{Ph}_2\text{PbX}_2 \cdot 4 \text{NH}_3$ and $\text{Ph}_2\text{PbX}_2 \cdot 4 \text{py}$. These compounds are unstable and lose ammonia or pyridine in the air.

Among the anion complexes, both fluorides and chlorides are known. Brauner\textsuperscript{78} obtained a salt of composition $K_3[\text{PbF}_8]$ by the action of hydrogen fluoride on lead tetraacetate. Dove\textsuperscript{79} showed that this is more correctly formulated $K_3(\text{HF}_2)(\text{PbF}_6)$, the lead atom being six-coordinate rather than eight-coordinate. Chloroplumbates are well known especially ammonium chloroplumbate which is stable up to 225$^\circ$. Complex salts of alkyl-lead trichlorides with pyridinium or quinolinium cations have been obtained\textsuperscript{80} $(\text{pyH})_2(\text{AlkPbCl}_5)$.
As in Group IV, the complex chemistry of these halides may be divided into two main categories.

(1) Addition compounds formed between the halides acting as electron acceptors, and electron donor molecules.

(2) Complex halide anions resulting from the coordination of one or more halide ions by the trihalides.

The trihalides of Group V also have the ability to act as electron-pair donors. This ability is shown by the weak complexes formed between phosphorus trichloride and the halides of boron, aluminium, and gallium. They also form complexes with transition metals which utilise both their donor and acceptor properties, e.g., \( \text{Ni(PF}_3\text{)}_4 \), \( \text{Ni(CO)}_5(\text{PH}_3)_3 \) and \( (\text{PF}_3)_2\text{PtCl}_2 \).

Because of the lone pair of electrons present in these halides there is opportunity for the sigma bond formed by the coordination of an electron donor, to be reinforced by a certain degree of pi-bonding, providing that the donor atom is capable of accepting electrons. Such complexes are formed with phosphines, arsines, sulphides and amines. Complexes with aromatic amines will also have some opportunity for this back coordination by resonance within the heterocyclic ring.
The case of ammonolysis follows the same order as in Group IV. Bismuth tribalides do not undergo ammonolysis and simple ammonia adducts are known.

The complex halide anions of this group cover a wide range of compositions and although few structure determinations have been made several unusual structures have emerged. In the case of antimony complexes, where evidence is available, the lone pair of electrons appears always to be stereochemically active. One class of complex anions which contain an organic radical is known, RSbCl$_3$. This is the only evidence for the existence of acceptor properties among the organoantimony III halides.

The following discussion treats the complex chemistry of each element individually.

A. Phosphorus III Halides

That phosphorus trifluoride and trimethylamine react together in a 1:1 ratio was reported by Parry and Bissett, and the existence of an unstable adduct of these components, which was solid at -78°C, was described by Griffiths and Burg. The phosphorus trifluoride-trimethylamine system was more carefully examined by Holmes and Wagner, and they confirmed the existence of a 1:1 adduct. Holmes also demonstrated that trimethylamine interacts with phosphorus trichloride, phosphorus tribromide, and methyldichloro-
phosphine. That electron transfer from nitrogen to phosphorus is involved in these complexes was shown by the fact that increasing the electron density at the phosphorus atom, as in trimethylphosphine, prevented complex formation. With these same complexes Holmes derived the energy of complexing of the components in solution, which is equivalent to the phosphorus-nitrogen bond energy. The figures for this P-N bond energy in the trimethylamine complexes of phosphorus trichloride, tribromide, and methylidichlorophosphine are 6.4, 3.1 and 2.9 Kcal/mole respectively. From these figures it can be seen that the interaction is rather weak, and that it falls off with decreasing electronegativity of the halogens bound to phosphorus, and also as halogens are replaced by organic groups.

With pyridine, which is a weaker base than trimethylamine, Meister et al. observed no interaction with phosphorus trifluoride at room temperature. A liquid mixture of phosphorus trifluoride and pyridine had a $^{19}\text{F}$ n.m.r. spectrum characteristic of the trifluoride itself, and there was no perturbation of the $^{31}\text{P} - ^{19}\text{F}$ coupling constant. Dimethylsulphoxide was also without interaction.

The crystal structure of the cyclic compound $(\text{CF}_3\text{P})_5$ is unusual in that there is a very close approach of one fluorine atom and one phosphorus atom across the ring. It has been suggested that this is due to complex formation,
the phosphorus acting as an acceptor.

A number of complexes have been reported with phosphine and arsine ligands. Trimethylarsine forms a 1:1 adduct with phosphorus trichloride, $\text{PCl}_3\cdot\text{AsMe}_3$ and trimethylphosphine forms a 2:1 adduct $\text{PCl}_3\cdot2\text{PH}_3$. The chelating ligand, o-phenylenebisdimethylarsine, also coordinates to the phosphorus trihalides$^9$ to form compounds which may be five-coordinate in the solid state, but which show a definite tendency to ionise in nitrobenzene as $(\text{PX}_2\text{D})^+\text{X}^-$. Both conductivity and molecular weight measurements support this ionisation.

All evidence points to the non-existence of complex anions of the type $\text{PX}_4^-$. Woolf$^{9}$ showed that phosphorus trifluoride did not combine with potassium fluoride during three months at room temperature. Neither did it combine with potassium fluoride heated to $240^\circ$ in a vacuum. Muetterties et al.$^{91}$ confirmed these observations.

B. Arsenic III Halides

Walden's study of the electrolytic conductance of pyridine and quinoline in arsenic trichloride solution suggested the existence of a 1:1 adduct of arsenic trichloride and pyridine. Such a compound, $\text{AsCl}_3\cdot\text{py}$, was prepared by Gibson, Johnson and Vining$^{97}$ by bringing together the components in 1:1 proportions in chlorobenzene.
solution. However, Shirey \(^{98}\), by dissolving arsenic trichloride in an excess of pyridine obtained crystals of an adduct with two moles of pyridine, AsCl\(_3\)-2py. Both these compounds were crystalline, and readily hydrolysed to pyridinium chloride and arsenic III oxide. Holmes and Bertaut \(^{94}\) prepared a compound of arsenic trichloride with one mole of trimethylamine, AsCl\(_3\).tNMMe\(_3\).

With arsenic tribromide, Dafert and Melinski \(^{99}\), reported an adduct with two moles of pyridine, AsBr\(_3\)-2py, and with arsenic triiodide an adduct with three moles of pyridine, AsI\(_3\)-3py. It is significant that the greatest number of pyridine molecules is coordinated by the triiodide, since all the arsenic-halogen bonds, that with iodine is the most readily broken. Muetterties has observed \(^{7}\) that while pyridine forms 1:1 molecular compounds with boron trichloride and tribromide, pyridine reacts with boron triiodide to form a 2:1 ionic compound, (Bl\(_2\)-2py)\(^{1+}\).-1.

Several complexes with phosphines and arsines are known. Arsenic trichloride coordinates two moles of trimethylphosphine, AsCl\(_3\).2PMe\(_3\), \(^{94}\) and Burrows and Turner \(^{100}\) reported a crystalline adduct of arsenic triiodide with phenylidimethylyarsine, AsI\(_3\).AsPhMe\(_2\). Chelate complexes of o-phenylcyclohexidimethylarsine with all three halides were prepared by Sutton \(^{95}\). They were all of 1:1 composition AsX\(_3\)-P. The trichloride and tribromide adducts were effectively non-
electrolytes in nitrobenzene and had normal molecular weights in this solvent. In contrast with this the triiodide adduct had a molar conductivity of 10.4 ohm$^{-1}$cm$^2$mole$^{-1}$ in nitrobenzene and a reduced molecular weight. This suggested ionisation as (AsI$_2$.D)$^+$I$^-$, and Sutton confirmed this by treating the adduct, dissolved in acetone, with perchloric acid when the corresponding perchlorate was formed, (AsI$_2$.D)ClO$_4$. This compound had a normal conductivity of 25 ohm$^{-1}$cm$^2$mole$^{-1}$ in nitrobenzene.

Further evidence of the readiness of an arsenic-halogen bond to ionise as a result of the coordination of an electron donor is provided by the salts formed between dimethylhalogencarboxylates and tertiary phosphines$^{101,102}$. Braddock and Coates$^{102}$ prepared a series of these compounds, finding that the salts of greatest stability were formed between triethylphosphine and iodoarsines. Triphenylphosphine did not react. Conductivity data given only for the iodides indicate that they are strong electrolytes in nitrobenzene, e.g., (Me$_2$As.PEt$_3$)$^+$I$^-$: A very unstable complex was also formed between dimethyliodoarsine and pyridine, (Me$_2$As.py)$^+$I$^-$. The existence of cations of the type AsX$_2^+$ is further suggested by the self-ionisation of arsenic trifluoride and by the complexes (AsF$_2$)(SbF$_6$)$^{103}$ and (AsCl$_2$)(SbCl$_6$)$^{104}$. A number of complex arsenic anions occur in combination
with organic cations. Petzold\textsuperscript{105}, has prepared the following salts, \(\text{Me}_2\text{NH}_2(\text{AsCl}_4)\), \(\text{Et}_2\text{NH}_2(\text{AsBr}_4)\), and \((\text{EtNH}_3)_2(\text{AsBr}_5)\). The quinolinium salt of the tetrachloroarsenite ion, \(\text{QuinH}(\text{AsCl}_4)\), was prepared by Dehn\textsuperscript{106}. It is not known whether the stereochemistry of these anions is influenced by the presence of the lone pair of electrons. The tetrachloroarsenite ion could have a simple tetrahedral structure. The caesium salt, \(\text{Cs}_3\text{As}_2\text{Cl}_9\), has been shown by an x-ray structure determination not to contain the \(\text{As}_2\text{Cl}_9^3\) \textsuperscript{-} unit\textsuperscript{107}. The structure is best described as consisting of discrete, pyramidal, arsenic trichloride molecules and caesium and chloride ions\textsuperscript{108}. 

C. Antimony III Halides

Most of the nitrogen base addition compounds of antimony have been reported with the trichloride. Pfeiffer and Schneider\textsuperscript{109} found that pyridine reacted with antimony trichloride in other solution to give initially \(2\text{SbCl}_3\cdot\text{py}\), which lost pyridine to form \(\text{SbCl}_3\cdot\text{py}\). This same 1:1 adduct has also been reported by Das and Pani\textsuperscript{110}, and by Watarai and Kinomi\textsuperscript{111}. Trimethylamine similarly forms a 1:1 adduct with antimony trichloride, \(\text{SbCl}_3\cdot3\text{NMMe}_3\), but with triethylamine a 1:2 adduct, \((\text{SbCl}_3)_2\cdot3\text{Et}_3\cdot2\text{H}\) resulted. A chelate complex of \(\beta\)-hydroxy-quinoline with antimony trichloride has been prepared by Patanaik and Pani\textsuperscript{112}, \(\text{SbCl}_2\cdot\text{oxine}\).
According to Watari and Kinumaki\textsuperscript{111}, the interaction of antimony tribromide and antimony triiodide with pyridine resulted in the compounds, $4\text{SbBr}_3\cdot7\text{py}$ and $2\text{SbI}_3\cdot3\text{py}$. These may be mixtures or impure samples of the di-pyridine adducts. The organoantimony compound, tristrifluoromethyl-antimony coordinates one mole of pyridine, $\text{Sb(CF}_3)_3\cdot\text{py}\textsuperscript{113}$. 

Among pi-bonding ligands complexes are known with phosphines, arsines, sulphides and triphenylarsine oxide. From the sealed tube reaction of antimony trichloride and dialkyl sulphides, Ray et al.\textsuperscript{114} obtained the 1:1 compounds $\text{SbCl}_3\cdot\text{Me}_2\text{S}$ and $\text{SbCl}_3\cdot\text{Et}_2\text{S}$. With Diarsine, Sutton prepared the 1:1 compounds $\text{SbX}_3\cdot\text{D}_2$\textsuperscript{95}, analogous to the corresponding phosphorus and arsenic complexes. These were non-electrolytes and had monomeric molecular weights in nitrobenzene and must therefore be five-coordinate. The iodide showed some slight ionisation, having a molar conductivity of 1 ohm$^{-1}$cm$^2$mole$^{-1}$ in nitrobenzene. Phillips and Tyree\textsuperscript{115} prepared a compound of antimony trichloride with two moles of triphenylarsine oxide, $\text{SbCl}_3\cdot2\text{Ph}_3\text{AsO}$. This likewise ionised in nitrobenzene, having a molar conductivity of 10.4 ohm$^{-1}$cm$^2$mole$^{-1}$. The higher conductivity can be attributed to the greater donor power of the arsine oxide. 

Ions of the type $\text{SbX}_2^+$ are suggested to be present in fused antimony trihalides and the compound $\text{SbCl}_4^+\text{ClO}_4^-$ is thought to be present when silver perchlorate is dissolved.
in molten antimony trichloride\textsuperscript{116}.

A large number of complex anions containing antimony is known. The type SbX\textsubscript{4}\textsuperscript{−} occurs with all four halogens\textsuperscript{117,95,123}. In the case of sodium\textsuperscript{118} and potassium\textsuperscript{117} tetrafluoroantimonites, crystallographic studies have shown that the structures are complicated. Potassium tetrafluoroantimonite actually contains the ion (SbF\textsubscript{4}\textsuperscript{−})\textsubscript{4}, in which a five-coordinate antimony atom is present (derived from an octahedron with a lone pair occupying one position). Two fluorines in each SbF\textsubscript{5} polyhedron are shared with other SbF\textsubscript{5} groups. In the two salts \(\text{K}_2\text{SbF}_5\)\textsuperscript{119} and \((\text{NH}_4)_2\text{SbCl}_5\)\textsuperscript{120}, five-coordinate antimony is again encountered with the same square pyramidal geometry. Five appears to be a preferred coordination number for antimony since Shealy and Yeakley\textsuperscript{121} found that fifteen different amine hydrobromides, when reacted with antimony tribromide, yielded salts containing the SbBr\textsubscript{5}\textsuperscript{2−} ion. A number of hexahalogenoantimonites is also known. Lamchen et al.\textsuperscript{122} prepared \((\text{Me}_2\text{NH})_3\text{SbBr}_6\) and \((\text{Bu}_2\text{NH})_3\text{SbBr}_6\). The stereochemistry of these anions is unknown.
D. Bismuth III Halides

No ammonolysis occurs with the bismuth trihalides\(^{124}\) and various ammoniates have been reported. Muir\(^{125}\) found adducts of bismuth tribromide with two and three moles of ammonia, BiBr\(_3\).2NH\(_3\), and BiBr\(_3\).3NH\(_3\), and a brick-red triammoniate of bismuth triiodide was prepared by Franklin and Kraus\(^{126}\). A similar addition compound of bismuth trichloride with diphenylamine, BiCl\(_3\).NHPh\(_2\), was reported by Vanino and Hartl\(^{127}\).

As with antimony, five-coordination appears to be favoured by bismuth since Watari and Kimmaki\(^{111}\) report adducts of both bismuth trichloride and tribromide with two moles of pyridine, BiCl\(_3\).2py and BiBr\(_3\).2py, and the Diarsine complexes, BiX\(_3\).D\(^{129}\), are also five-coordinate non-electrolytes.

From aqueous solution it is possible to prepare six-coordinate complex cations of bismuth with three moles of phenanthroline, Bi(phenan)\(_3\)(ClO\(_4\))\(_3\)\(^{128}\).

Complex halide salts of the types \(M(BiX_3)\), \(M_2(BiX_5)\) and \(M_3(BiX_6)\) are all known. Sutton\(^{129}\) prepared bipyridinium and phenanthroline salts of BiCl\(_3\), BiBr\(_3\), and BiI\(_3\); and Lamchen et al.\(^{122}\) prepared \((Me_2NH)_3BiBr_6\), \((Bu_2NH)_3BiCl_6\), and \((Bu_2NH)_3BiBr_6\). There is no reason to believe that the lone pair is not stereochemically active in these complex halides, as it is in the corresponding antimony compounds,
but no structural studies have been made.

2. Group Trends

It is clear that while only weak and easily dissociable adducts are formed between phosphorus trihalides and donor molecules, the complexes of the heavier elements are more stable and greater in number. Higher coordination numbers also occur more frequently with antimony and bismuth than with other members of the group. A coordination number of five is particularly favoured by antimony and bismuth.

There is good evidence that in some arsenic trihalide addition compounds one of the arsenic-halogen bonds is broken to give an ionic adduct, and there is some evidence for simple cations of the type $\text{AsX}^+$. At the bottom of the group, bismuth shows no tendency to form similar ions, either in simple halides or in complexes.
5. 2,2'-BIPYRIDYL COMPLEXES OF THE GROUP V TRIHALIDES

I. RESULTS AND DISCUSSION

2,2'-Bipyridyl forms stable, equimolecular adducts, $\text{MX}_3\cdot\text{bipy}$, with the trihalides of arsenic, antimony and bismuth, but not with the trihalides of phosphorus. It also forms similar complexes with the mono-organosubstituted halides, $\text{RMX}_2\cdot\text{bipy}$. This series of halides reacts also with halide ions to form complex anions, $\text{RMX}_3^-$, of which the type $\text{RbCl}_3^-$ was known. However, neither solid bipyridyl complexes, nor anion complexes, could be prepared from the di-organosubstituted halides.

The complexes are precipitated on mixing solutions of the halide and bipyridyl in an inert solvent, in any proportions, under anhydrous conditions. Their solubilities in most solvents are very low, but they dissolve sufficiently in nitrobenzene for measurement of molar conductivities at $10^{-3}/$. The adducts from organo-substituted halides have higher solubility and enable conductivities to be measured over a slightly greater concentration range.

All the adducts, with the exception of that from arsenic trichloride, were stable towards atmospheric moisture, but as a precaution both the arsenic and antimony complexes
were prepared and handled in a dry box.

Table I lists the molar conductivities of the trihalide complexes in nitrobenzene. Conductivities of the bismuth complexes were also measured in dimethylformamide in which their solubility was greater than in nitrobenzene.

**TABLE I**

Molar Conductivities (ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\)) of MX, bipy Complexes in nitrobenzene at 10\(^{-3}\) M (25\(^\circ\)C)

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<tr>
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<tr>
<td>Bi</td>
<td>2.5</td>
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(a) BiBr\(_3\) bipy is insoluble.
(b) at 0.5 \(10^{-3}\) M

Molar Conductivities (ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\)) of BiX, bipy Complexes in dimethylformamide at 10\(^{-3}\) M (25\(^\circ\)C)

<p>| | | | |</p>
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<thead>
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<tr>
<td>Bi</td>
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For comparison, the molar conductivities of the bipyridyl adducts from methylidiodoaarsine, phenyldiiodostibine and phenyldibromobismuthine are 21.2, 8.2, and 1.5 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\), respectively, all at 10\(^{-3}\) M in nitrobenzene. The triiiodides (Sbi\(_2\), bipy)I\(_3\) and (PhSbi, bipy)I\(_3\) obtained by iodination of the corresponding iodides give respective values 33.6 and 30.6 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) at 10\(^{-3}\) M.
Ionisation trends as inferred from these molar conductivities decrease progressively from arsenic to bismuth, but increase from chlorides to iodides. The possibility that these variations arise from reversibility of the equilibrium

$$\text{Bipy} + \text{MX}_3 \rightleftharpoons \text{MX}_3 \cdot \text{bipy} \quad \rightarrow \text{ionisation}$$

is excluded because atomic sizes and bond polarities would require that the equilibrium lie furthest to the right with bismuth trichloride and least with arsenic triiodide, and so give the reverse order.

The approach towards conductivities characteristic of 1:1 electrolytes is compatible with an ionisation

$$\text{MX}_3 \cdot \text{bipy} \rightleftharpoons (\text{MX}_2 \cdot \text{bipy})^+ + \text{X}^-$$

rather than a more complicated type leading to the formation of a complex halide anion such as,

$$(\text{MX}_3 \cdot \text{bipy})_2 \rightleftharpoons (\text{MX}_2 \cdot (\text{bipy})_2)^+ + \text{MX}_3^-$$

Anions, $\text{MX}_3^-$, are known for arsenic, antimony and bismuth. Molecular weight measurements, which would have been useful in deciding the mode of ionisation were not possible because of the low solubility of the complexes in any suitable solvents.

For the bipyridyl adduct of phenyldiiodostibine conductivities were measured from $1 \times 10^{-3} \text{M}$ to $2 \times 10^{-2} \text{M}$. Over this limited concentration range the molar conductivity showed a linear dependence on the square root of the
concentration, obeying the relationship $\Lambda_m = 10.8 - 83 \sqrt{c}$. (Fig. 1). This argues that only one, simple mode of ionization was occurring in this compound since it is usual, when several ionisation schemes are involved, for the conductivity to show an irregular dependence on square root of concentration. Furthermore, the absorption spectrum of this compound in methylene chloride does not show the peak at $360 \mu$, which was found to be characteristic of the anion, $\text{PhSbI}_3^-$, in the salt $(\text{BipyH})^+\text{PhSbI}_3^-$. 

In accordance with the availability of a halide ion, the iodide complexes of antimony react with iodine to produce the corresponding triiodide, viz.,

$$(\text{SbI}_2\cdot\text{bipy})^+\text{I}^- + \text{I}_2 \rightarrow (\text{SbI}_2\cdot\text{bipy})^+\text{I}_3^-$$

These reactions were followed by conductimetric titration (Fig. 2), since the triiodides are more highly dissociated due to the greater solvation energy of the triiodide than the iodide ion. This is a consequence of the triiodide being more polarisable than the simple iodide. Harris followed the formation of triphenylarsenic dibromide and triphenylarsenic tetrabromide, in acetonitrile, in the same manner. While the simple bromide, $(\text{Ph}_3\text{AsBr})\text{Br}$, had a conductivity $\Lambda_m = 12.7 \text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$, the tribromide, $(\text{Ph}_3\text{AsBr})\text{Br}_3$, had a conductivity $\Lambda_m = 104.2 \text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$. For the triiodide derived from $\text{PhSbI}_2\cdot\text{bipy}$, the presence of the $\text{I}_3^-$ absorption bands (at 362 and 292 $\mu$) super-
FIG. 1. \( \Lambda_m \) VERSUS \( \sqrt{c} \) for PhSbI\(_2\)_bipy.
### DATA FOR FIG. 2.

#### Upper Curve.

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FIG. 2.

$\Lambda_m$ VERSUS MOLE RATIO OF $I_2$: $SbI_3$:bipy (upper curve) AND bipy:$AsCl_3$ (lower curve)
imposed upon the otherwise unchanged spectrum of the parent iodide, confirmed the dissolved compound to be constituted, (PhSbI₃,bipy)⁺I₃⁻. It is clear that, in the case of the iodide complexes at least, ionisation takes place by splitting off a simple halide ion, leaving a four-coordinate cation, (MI₂,bipy)⁺. In view of the regular trends in the conductivity figures and the equimolar composition of all the adducts, it is most likely that the chloride and bromide complexes ionise similarly.

Sutton⁹⁵ prepared and studied the Diarsine (o-phenylenediaminomethylarsine) complexes of the Group V trihalides and found them to form a series of equimolar composition, MX₃·Diarsine. Favourable solubility of these compounds in nitrobenzene enabled conductivity data to be supplemented by molecular weight measurements. By this means, and also by the isolation of (AsI₂·Diarsine)⁺ClO₄⁻, Sutton was able to show unambiguously that ionisation in the Diarsine series occurred according to the equation -

\[ \text{MX}_3 \cdot \text{Diarsine} \rightarrow (\text{MX}_2 \cdot \text{Diarsine})^+ + X^- \]

Phillips and Tyree⁴¹⁵ prepared trichloro-bis(triphenylarsineoxide)antimony III, SbCl₃(Ph₃AsO)₂, and found its conductivity in nitrobenzene to be 10.4 cm² mole⁻¹ cm⁻¹. Partial ionisation as (SbCl₂(Ph₃AsO)₂)⁺ + Cl⁻ was suggested to explain the conductivity.

The variation as between solutions of chlorides, bromides
and iodides in the formation of kinetically free ions can be linked with several inter-related properties. Table II lists "ionic bond energy" (which is the energy required for the process $M-X \rightarrow M^+X^-$, i.e., ionisation potential of the metal and electron affinity of the halogen, added, with regard to sign, to the ordinary bond energy) for the arsenic-halogen and antimony-halogen bonds. No bond energies are available for the bismuth-halogen bonds.$^{134}$

**TABLE II**

<table>
<thead>
<tr>
<th>Ionic Bond Energies (k.cal/mole)</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>229</td>
<td>216</td>
<td>209</td>
</tr>
<tr>
<td>Sb</td>
<td>184</td>
<td>173</td>
<td>165</td>
</tr>
</tbody>
</table>

The progressive fall from chlorides to iodides parallels the observed increase in conductivity. Solvation energies of the halide ions in aprotic solvents$^{135}$, increasing from chloride to iodide, would enhance the trend as would also the lower electronegativity of the halogen atoms within the cation. Both horizontal and vertical ionisation trends accord with those to be anticipated on purely steric grounds. However, the variation down the group is the reverse of that expected from the ionisation potentials of arsenic, antimony and bismuth, from the derived ionic bond energies, from the polarities of the
halogen bonds (deduced from the dipole moments of the halides)\(^\text{136}\), and from the probable degree of charge transfer from nitrogen to the coordination centre. The order also runs counter to that expected from the aqueous chemistry of the elements, but direct comparison with aqueous systems is not justifiable since the behaviour of the halides in protic solvents is complicated by solvolysis.

The decreasing ionisation down the group is part of a more general effect common to several series of compounds. Diarsine complexes of the trihalides\(^\text{95}\), in which there can be little or no resultant charge transfer to the coordinated centre, are less strongly ionised than the bipyridyl compounds, but the ionisation trends are entirely similar, and continue to the phosphorus halides. (Table III)

<table>
<thead>
<tr>
<th></th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>--</td>
<td>2.3</td>
<td>17.9</td>
</tr>
<tr>
<td>As</td>
<td>1.0</td>
<td>2.0</td>
<td>10.4</td>
</tr>
<tr>
<td>Sb</td>
<td>0.5</td>
<td>1.00</td>
<td>3.9</td>
</tr>
<tr>
<td>Bi</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Ionisation is therefore facilitated by electron accession from a coordinating base, but is not conditional
upon it. The same ionisation order appears with oxidation state V compounds without the stimulus of complex formation. A study\(^{137}\) of the vibrational spectra of trimethylphosphine dihalides suggests that in the solid state these have the ionic structure, \(\text{Me}_3\text{PX}^+\text{X}^-\). Triphenylphosphine dihalides and triphenylarsenic dihalides ionise in acetonitrile\(^{131}\). On the other hand, trimethylantimony dihalides are poorly conducting in ionising solvents\(^{138}\) and covalent in the solid state with a trigonal bipyramidal structure\(^{139}\). The antimony-halogen bonds are a little longer than expected for completely covalent bonds. Chemical properties and solubility characteristics of triphenylbismuth dihalides, \(\text{Ph}_3\text{BiX}_2\)\(^{130}\), point to a covalent constitution. Likewise phosphorus pentachloride has an ionic crystal lattice, but antimony pentachloride a covalent lattice\(^{141}\). Irrespective of the oxidation state the ionisation trend can be correlated with the preference of the lighter elements for covalency numbers less than five and the increasing tolerance of the heavier elements towards higher coordination numbers. In accord with this generalisation the additional covalent bonds arising from bipyridyl coordination promote greatest ionisation at the top of the group. Table IV, a list of the complex halide anions occurring in Group V, indicates how the higher anions are restricted to the heavier elements. Antimony assumes five-fold coordination in \((\text{SbP}^\text{V}_4)_4\) even when the stoichiometry does not demand it\(^{149}\).
TABLE IV

Halide Ions of Trivalent Arsenic, Antimony and Bismuth

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AsF$_4^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsCl$_4^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsBr$_4^-$</td>
<td>AsBr$_2^-$</td>
<td></td>
</tr>
<tr>
<td>SbF$_5^-$</td>
<td>SbF$_2^-$</td>
<td></td>
</tr>
<tr>
<td>SbCl$_5^-$</td>
<td>SbCl$_2^-$</td>
<td>SbCl$_3^-$</td>
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<tr>
<td>BiF$_5^-$</td>
<td>BiF$_2^-$</td>
<td>BiF$_3^-$</td>
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<tr>
<td>BiCl$_5^-$</td>
<td>BiCl$_2^-$</td>
<td>BiCl$_3^-$</td>
</tr>
<tr>
<td>BiBr$_5^-$</td>
<td>BiBr$_2^-$</td>
<td>BiBr$_3^-$</td>
</tr>
</tbody>
</table>

The inability of the phosphorus trihalides to form bipyridyl complexes when they yield (unstable) trimethylamine derivatives$^{89,90}$ can be ascribed to the low acceptor properties of these halides together with the preference of the lighter elements for lower coordination numbers.

Introduction of organic substituents into halides reduces their acceptor properties and underlies the inability of di-organosubstituted halides to form complexes. It would also account for the lower conductivities of RMX$_2$.bipy adducts than the corresponding MX$_3$.bipy compounds. Ionisation in the RMX$_2$.bipy series, nevertheless, follows the same order and bears the same relationship to the coordination preference of the central atom.
Being a closely related series of complexes, it was anticipated that some structural similarities may exist among the solid compounds. X-ray powder data for all the complexes are tabulated on pages 44, 45, 46. From the close similarity of the powder patterns of the adducts from antimony and bismuth tribromide, and also from antimony and bismuth triiodide, it is concluded that these two pairs of compounds are isomorphous. The conductivities of solutions of the bismuth halide complexes in both nitrobenzene and dimethylformamide are so low as to exclude the possibility of their being ionised in the solid state. The isomorphous derivatives from the antimony halides must also be covalent in the solid.

The structure of a number of five-coordinate antimony III compounds have been examined\textsuperscript{142}, and in all cases the lone pair of electrons is stereochemically active, the geometrical arrangement about the antimony being a square pyramid with the antimony slightly displaced below the basal plane. This displacement is attributed to lone pair-bond pair repulsions. It is very probable that the bipyridyl complexes of the antimony and bismuth trihalides adopt a similar configuration.
### d Values and Intensities (a)

of X-ray Powder Lines from HCl$_3$·bipy Complex

<table>
<thead>
<tr>
<th></th>
<th>AsCl$_3$·bipy</th>
<th>SbCl$_3$·bipy</th>
<th>BiCl$_3$·bipy</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.99 (s)</td>
<td>9.56 (m)</td>
<td>8.42 (s)</td>
<td></td>
</tr>
<tr>
<td>6.83 (w)</td>
<td>7.83 (s)</td>
<td>7.73 (s)</td>
<td></td>
</tr>
<tr>
<td>5.84 (s)</td>
<td>6.71 (m)</td>
<td>6.28 (w)</td>
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</tr>
<tr>
<td>4.95 (m)</td>
<td>6.11 (w)</td>
<td>5.88 (m)</td>
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<td>3.80 (m)</td>
<td>5.59 (w)</td>
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<td>5.04 (m)</td>
<td>4.55 (s)</td>
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</tr>
<tr>
<td>3.06 (w)</td>
<td>4.70 (w)</td>
<td>4.15 (m)</td>
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</tr>
<tr>
<td>2.78 (m)</td>
<td>4.15 (m)</td>
<td>3.89 (m)</td>
<td></td>
</tr>
<tr>
<td>2.65 (w)</td>
<td>3.91 (m)</td>
<td>3.13 (w)</td>
<td></td>
</tr>
<tr>
<td>2.23 (m)</td>
<td>3.70 (m)</td>
<td>2.94 (w)</td>
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</tbody>
</table>

(a) s, strong
m, medium
w, weak
### d Values and Intensities (a)

**of X-ray Powder Lines from MBr₃-bipy Complex**

<table>
<thead>
<tr>
<th></th>
<th>AsBr₃-bipy</th>
<th>SbBr₃-bipy</th>
<th>BiBr₃-bipy</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.40 (s)</td>
<td>8.02 (s)</td>
<td>8.24 (s)</td>
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<td>8.07 (m)</td>
<td>7.05 (m)</td>
<td>7.05 (m)</td>
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<td>6.09 (m)</td>
<td>6.09 (m)</td>
<td></td>
</tr>
<tr>
<td>7.35 (m)</td>
<td>5.06 (w)</td>
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<tr>
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<td>3.61 (m)</td>
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<tr>
<td>4.53 (w)</td>
<td>3.04 (s)</td>
<td>3.09 (s)</td>
<td></td>
</tr>
<tr>
<td>4.01 (m)</td>
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<td>3.47 (m)</td>
<td>2.12 (w)</td>
<td>2.40 (w)</td>
<td></td>
</tr>
<tr>
<td>3.14 (m)</td>
<td>2.16 (w)</td>
<td>2.15 (w)</td>
<td></td>
</tr>
</tbody>
</table>

(a) s, strong
m, medium
w, weak
d Values and Intensities (a)
of X-ray Powder Lines from ML₃bipy Complex

<table>
<thead>
<tr>
<th></th>
<th>AsL₃bipy</th>
<th>ShL₃bipy</th>
<th>BiL₃bipy</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.71 (m)</td>
<td>8.26 (s)</td>
<td>8.51 (s)</td>
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</tr>
<tr>
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<td>5.09 (m)</td>
<td>5.44 (s)</td>
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<td>4.85 (s)</td>
<td>3.93 (m)</td>
<td>3.96 (m)</td>
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<tr>
<td>4.34 (s)</td>
<td>3.72 (m)</td>
<td>3.77 (m)</td>
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</tr>
<tr>
<td>3.83 (s)</td>
<td>3.21 (s)</td>
<td>3.29 (s)</td>
<td></td>
</tr>
<tr>
<td>3.56 (w)</td>
<td>2.93 (m)</td>
<td>2.94 (m)</td>
<td></td>
</tr>
<tr>
<td>3.40 (m)</td>
<td>2.78 (w)</td>
<td>2.78 (w)</td>
<td></td>
</tr>
<tr>
<td>3.19 (m)</td>
<td>2.23 (m)</td>
<td>2.23 (m)</td>
<td></td>
</tr>
</tbody>
</table>

(a) s, strong
m, medium
w, weak
II EXPERIMENTAL

Arsenic Trihalide Complexes

The preparation and all handling of these complexes was carried out in a dry-box. Complexes were prepared by mixing solutions of 2,2'-bipyridyl and the halide, in approximately equimolar proportions, in an anhydrous hydrocarbon solvent. After collection on a filter and washing with more of the solvent, the compounds were pumped dry in a high vacuum.

Trichloro-bipyridyl-arsenicIII. Reaction between freshly distilled arsenic trichloride and bipyridyl in sodium-dried benzene gave the adduct as a pale yellow powder. This was hydrolysed rapidly to arsenicIII oxide even under dry-box conditions. (The arsenicIII oxide was identified by its powder photograph.) Owing to its extreme moisture sensitivity combustion analysis was not practicable. Conductometric titration of bipyridyl against arsenic trichloride in nitrobenzene solution indicated a 1:1 interaction in solution. (Fig. 2)

Analysis: Calculated for \( \text{C}_{40}\text{H}_{8}\text{N}_{2}\text{AsCl}_{3} \): Cl, 34.6%. Found: Cl, 32.5%.

Tribromo-bipyridyl-arsenicIII. From benzene solution this adduct was precipitated as a bright yellow powder. It was much more resistant to hydrolysis than the chloride complex
and was unchanged on exposure to the air.

Analysis: Calculated for $\text{C}_{10}\text{H}_{8}\text{N}_{2}\text{AsBr}_3$: C, 25.5; H, 1.7; N, 6.0; Br, 50.9%

Found: C, 25.8; H, 1.9; N, 5.2; Br, 50.6%

**Triiodo-bipyridyl-arsenic(III).** This complex precipitated as an orange-brown microcrystalline powder from toluene solutions of its components. Like the bromide, this complex was stable towards atmospheric moisture.

Analysis: Calculated for $\text{C}_{10}\text{H}_{8}\text{N}_{2}\text{AsI}_3$: C, 19.6; H, 1.3; N, 4.6%

Found: C, 18.9; H, 1.9; N, 4.6%

**Antimony Tribalide Complexes**

These were prepared and handled in a dry-box. The preparative procedure was the same as described for the arsenic complexes.

**Trichloro-bipyridyl-antimony(III).** This was precipitated as a cream powder from benzene.

Analysis: Calculated for $\text{C}_{10}\text{H}_{8}\text{N}_{2}\text{SbCl}_3$: C, 31.2; H, 2.4; N, 7.3; Cl, 27.7%

Found: C, 29.3; H, 2.2; N, 7.2; Cl, 27.7%

**Tribromo-bipyridyl-antimony(III).** Freshly distilled antimony tribromide in toluene reacted with bipyridyl in the same solvent to produce the adduct as a bright yellow powder.
Analysis: Calculated for $C_{10}H_8N_2SbBr_3$: $C$, 23.2; $N$, 1.6; 
$N$, 5.4; Br, 46.3%.

Found: $C$, 23.0; $N$, 1.7; $N$, 4.5; Br, 45.9%.

Triodo-bipyridyl-antimonyIII. From toluene solution this adduct precipitated as a dark red powder. Conductimetric titration of this adduct in nitrobenzene with iodine indicated a 1:1 interaction, (Fig. 2), confirming the stoichiometry of the reaction leading to the triiodide, ($Sb\_2bipy$)$_3$I$^-$. 

Analysis: Calculated for $C_{10}H_8N_2SbI_3$: $C$, 48.2; $N$, 1.2; 
$I$, 57.8%.

Found: $C$, 47.7; $N$, 1.0; $I$, 57.3%.

Bismuth Tribromide Complexes

These complexes showed no tendency to hydrolyse in the air and dry-box techniques were not necessary for their preparation and manipulation.

Trichloro-bipyridyl-bismuthIII. Bismuth trichloride dissolved in hot benzene reacted with bipyridyl in the same solvent to give a white powder.

Analysis: Calculated for $C_{10}H_8N_2BiCl_3$: $C$, 25.5; $N$, 1.7; 
$N$, 5.9; Cl, 22.6%.

Found: $C$, 25.7; $N$, 1.9; $N$, 5.5; Cl, 22.6%.

Tribromo-bipyridyl-bismuthIII. Because of the low solubility of bismuth tribromide in hydrocarbon solvents this complex was prepared from acetone solutions of its components as
small cream coloured crystals.

Analysis: Calculated for C_{10}H_{8}N_{2}Br_{3}: C, 19.9; H, 1.3; N, 4.6%;
Found: C, 20.3; H, 1.6; N, 4.6%.

Triiodo-bipyridyl-bismuthIII. This was likewise prepared from acetone as bright red crystals.

Analysis: Calculated for C_{10}H_{8}N_{2}BiI_{3}: C, 16.1; H, 1.1; N, 3.8%;
Found: C, 16.1; H, 1.3; N, 3.2%.

Complexes from Organosubstituted Halides

(1) Bipyridyl Complexes

Methylidiodo-bipyridyl-arsenicIII. This adduct formed as golden yellow needles when methylidiodoarsine and bipyridyl were brought together in benzene, m.p. 120° (with decomposition). Like the parent iodide the adduct was stable toward atmospheric moisture.

Analysis: Calculated for C_{11}H_{14}N_{2}AsI_{3}: I, 50.8%
Found: I, 50.8%.

Phenylidiodo-bipyridyl-antimonyIII. Reaction between phenylidiodostibine and bipyridyl in any anhydrous hydrocarbon solvent produced the adduct as a red solid, but from methylene chloride, in which the adduct is appreciably soluble, small red needles were obtained. In nitrobenzene
or methylene chloride solution this compound reacts with iodine to form the triiodide, \((\text{PhSbI}_3\text{bipy})\)\(\text{I}_3\). The absorption spectrum of this triiodide in methylene chloride solution has an \(\varepsilon_{\text{max}}\) at 362 nm (\(\varepsilon = 24,000\)).

**Analysis:** Calculated for \(\text{C}_{16}\text{H}_{15}\text{N}_2\text{SbI}_2\): C, 31.4; H, 2.1; N, 4.7%.

**Found:** C, 30.6; H, 2.6; N, 4.7%.

**Phenylidibromo-bipyridyl-bismuthIII.** From warm benzene this complex separated as small cream needles.

**Analysis:** Calculated for \(\text{C}_{16}\text{H}_{15}\text{BiBr}_2\): C, 31.9; H, 2.2; N, 4.7%; Br, 26.6%.

**Found:** C, 33.0; H, 2.6; N, 4.2; Br, 26.4%.

Under the conditions detailed above diphenylchlorostibine and diphenylchlorobismuthine did not react with bipyridyl.

(2) Anion Complexes

**Bipyridinium Phenyltriiodoantimonite.** The bipyridinium salt of phenyltriiodoantimonite separated as orange-red needles upon addition of 0.16 g of bipyridyl to 0.5 g of phenylidiodostibine in 25 ml of ethanol and 6 ml of hydroiodic acid. A solution of \(0.8 \times 10^{-3}\) M, in nitrobenzene had a molar conductivity at 25° of \(17.5 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}\). In methylene chloride solution the salt showed an absorption maximum at
characteristic of the anion.

Analysis: Calculated for C$_{16}$$\text{H}_{14}$$\text{N}_2$$\text{Sb}_3$: C, 26.1; H, 1.9; N, 3.8%.
Found: C, 25.7; H, 2.2; N, 3.7%.

Bipyridinium Phenyltribromobismuthite. This salt was obtained similarly from phenyltribromobismuthine. 0.16 g of bipyridyl was added to 0.4 g of phenyltribromobismuthine dissolved in 30 ml of ethanol and 5 ml of conc. hydrobromic acid when cream needles of the salt separated out. A solution 0.8 x 10$^{-3}$ M in nitrobenzene had a molar conductivity of 23.0 ohm$^{-1}$ cm$^2$ mole$^{-1}$ at 25$^\circ$.

Analysis: Calculated for C$_{16}$$\text{H}_{14}$$\text{N}_2$$\text{Br}_3$: C, 26.1; H, 2.1; N, 4.1; Br, 35.1%.
Found: C, 27.0; H, 2.2; N, 4.3; Br, 35.9%.

No salts of related complex anions could be obtained from diphenylchlorostibine and diphenylchlorobismuthine.

**Behaviour of the Phosphorus Trisalides towards Bipyridyl**

The behaviour of phosphorus trichloride was examined in a vacuum line. Carefully purified phosphorus trichloride was distilled on to a sample of bipyridyl in a little benzene as solvent. No reaction was observed.
The behaviour of the less volatile phosphorus tribromide was examined in a dry-box. Freshly distilled phosphorus tribromide, b.p. 174°C, was added to bipyridyl in benzene solution. No reaction occurred.

Phosphorus triiodide was also handled in the dry-box. A freshly prepared sample and bipyridyl in benzene produced a brown precipitate in low yield. The X-ray powder pattern of this precipitate was identical with that of a sample of bipyridinium triiodide prepared from bipyridinium iodide and iodine. Repeated experiments with rigorously purified and dried reactants and solvent always produced a small yield of this product.

Analysis: Calculated for C$_{10}$H$_9$N$_2$I$_3$: C, 22.3; H, 1.7; N, 5.2%. Found: C, 22.7; H, 2.0; N, 4.8%.
The Group V organochalides were prepared by the following routes.

\[
\begin{align*}
\text{MeAsI}_2 & \quad \text{AsO}_3^3^- + \text{MeI} \rightarrow \text{MeAsO}_2^2^- + \text{I}^- \\
& \quad \text{SO}_2 \text{ reduction} \\
& \quad \text{and NaI} \rightarrow \text{MeAsI}_2 \\
\text{PhSbl}_2 & \quad \text{PhSbO}_2\text{H}_2 \quad \text{addition of NaI} \rightarrow \text{PhSbl}_2 \\
& \quad \text{from Scheller reaction} \\
\text{Ph}_2\text{SbCl} & \quad \text{SbCl}_3 \quad \text{dil. HCl} \\
& \quad \text{CuCl}_2 \quad \text{Ph}_2\text{SbO}_2\text{H} \quad \text{Ph}_2\text{SbCl}_3 \\
& \quad \text{phenylhydrazine} \quad \text{reduction} \\
& \quad \text{Ph}_2\text{SbCl} \\
\text{PhBiBr}_2 & \quad \text{Ph}_3\text{Bi+2BiBr}_3 \quad \rightarrow \text{3PhBiBr}_2 \\
\text{Ph}_2\text{BiCl} & \quad 2\text{Ph}_3\text{Bi+BiCl}_3 \quad \rightarrow \text{3Ph}_2\text{BiCl}
\end{align*}
\]

**Methyldiiodocarsine, MeAsI**

This was prepared by a small scale adoption of the procedure described in Inorganic Syntheses. To a stirred solution of 36 g of arsenicIII oxide and 64 g of sodium hydroxide in 100 ml of water contained in a 1 litre flask, was added 76 g of methyl iodide in 500 ml of alcohol. After 20 hours' stirring the solution was evaporated to dryness under reduced pressure and the residue dissolved in about 100 ml of water. 40 ml of conc. hydrochloric acid was added and a steady stream of SO₂ passed into the
stirred mixture for 45 minutes. During this $\text{SO}_2$ reduction 70 g of sodium iodide in 60 ml of water was slowly added to the mixture. Solid material was then removed by filtration and the arsine extracted with ether. Removal of solvent gave the product as small yellow crystals, m.p. 27-28° (lit. 29°).

**Phenylatibonic Acid, PhSbO$_2$**

This was prepared by the Scheller reaction as modified by Doak and Steinman. 18.6 g of aniline was dissolved in 500 ml of ethanol in a 3 litre beaker, which was cooled with an ice-bath and equipped with a stirrer. 20 g of sulphuric acid and 55.6 g of antimony trichloride were added, and when these had completely dissolved diazotization was effected with 1.4 g of sodium nitrite in 20 ml of water. After stirring for thirty minutes, 4 g of cuprous bromide was added and the cooling bath removed. Nitrogen evolution began and the mixture was left overnight, by which time the gas evolution was complete. After steam distillation to remove alcohol, the crude acid was filtered off and pressed dry. It was then dissolved in a conc. hydrochloric acid-ethanol mixture (1:1) and 100 ml of pyridine reagent added (80 ml of conc. hydrochloric acid diluted to 100 ml with pyridine). After cooling, the precipitated pyridinium salt was collected on a sintered glass filter and washed with conc. hydrochloric acid. It was then
dissolved in 6 litres of 1% sodium carbonate solution and stirred with 5 g of activated charcoal. After filtration a very bulky precipitate of the pure acid was obtained by dropwise addition of dil. hydrochloric acid. The acid was collected on a large Buchner funnel, and washed with very dilute acid and finally air-dried.

**Diphenylstibinic Acid, Ph₂SbO₂H**

This was prepared by the method described by Sergeev and Bruker\(^{1h5}\). 27 g of phenylhydrazine was added to a solution of 57 g of antimony trichloride and 42.5 g of cupric chloride in 100 ml of conc. hydrochloric acid and 200 ml of water. This mixture was vigorously stirred for five hours in a 1 litre beaker. The flocculent precipitate which formed was filtered off and washed with dilute hydrochloric acid. It was then extracted with acetone, and the acetone extract, after dilution with water, yielded diphenylstibinic acid as a white solid which was filtered and air-dried.

**Phenyldiodostibine, PhSbI₂**

This was prepared following the method of Schmidt\(^{1h6}\). 10 g of phenylstibonic acid was dissolved in 40 ml of conc. hydrochloric acid and the whole cooled in ice. 10 g of stannous chloride in 50 ml of conc. hydrochloric acid was added. Addition of a saturated solution of sodium iodide
was then continued until precipitation of the yellow solid was complete. This was removed by filtration through a sintered glass filter and pressed dry. Recrystallisation from acetic acid gave the iodide as yellow needles, m.p. 69° (lit. 146 69°).

**Diphenylchlorostibine, Ph₂SbCl**

On cooling the solution obtained by dissolving diphenylstibinic acid in the minimum quantity of hot dilute hydrochloric acid, long colourless needles of diphenylantimony trichloride were obtained, m.p. 176°. When a solution of this chloride in dilute acid was cooled in ice and stannous chloride in conc. hydrochloric acid added, crystals of diphenylchlorostibine settled out. These were filtered off, washed and dried in a desiccator, m.p. 68° (lit. 147 68°).

**Triphenylbismuthine, Ph₃Bi**

This was prepared as described by Blicke et al. 147. Phenylmagnesium bromide was prepared in the usual way from 80 g of bromobenzene, 12 g of magnesium and 300 ml of diethyl ether. 200 ml of dry benzene was then added, followed by 41 g of solid bismuth trichloride in 5 portions over 30 minutes. The mixture was heated on a steam bath and stirred for a further 4 hours. After decomposition with ice and ammonium chloride the ether was separated out.
and dried with sodium sulphate. Removal of the solvent gave crystalline triphenylbismuthine, m.p. 76-77° (lit. 147 77°).

**Phenyl dibromobismuthine, PhBiBr₂**

3 g of bismuth tribromide in ether added to 1.5 g of triphenylbismuthine in ether produced yellow crystals of phenyl dibromobismuthine. After recrystallisation from benzene these had m.p. 202° (lit. 148 202°).

**Diphenylchlorobismuthine, Ph₂BiCl**

4 g of triphenylbismuthine in ether added to 1.5 g of bismuth trichloride in ether slowly deposited colourless crystals of diphenylchlorobismuthine, m.p. 185° (lit. 148 184-185°).
6. 2,2'-BIPYRIDYL AND 2,2'2''-TERPYRIDYL COMPLEXES
OF THE GROUP IV HALIDES

I. RESULTS AND DISCUSSION

(1) 2,2'-Bipyridyl Complexes

Table I summarises the behaviour of bipyridyl towards certain halides and organohalides of Group IV. Molar conductivities of the individual compounds in nitrobenzene are also included in the table.

**TABLE I**

Bipyridyl Complexes of Group IV Halides and Organohalides and their Molar Conductivities in Nitrobenzene at 10⁻³ M (25º)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeCl₂·bipy</td>
<td>0.3</td>
</tr>
<tr>
<td>GeBr₂·bipy</td>
<td>0.1</td>
</tr>
<tr>
<td>GeI₂·2bipy</td>
<td>2.8</td>
</tr>
<tr>
<td>Ph₂GeCl₂</td>
<td>no reaction</td>
</tr>
<tr>
<td>SnCl₂·bipy</td>
<td>0.5</td>
</tr>
<tr>
<td>SnBr₂·bipy</td>
<td>0.1</td>
</tr>
<tr>
<td>SnI₂·bipy</td>
<td>1.2</td>
</tr>
<tr>
<td>Me₂SnCl₂·bipy</td>
<td>0.3</td>
</tr>
<tr>
<td>Me₂SnBr₂·bipy</td>
<td>0.1</td>
</tr>
<tr>
<td>Me₂SnI₂·bipy</td>
<td>2.4</td>
</tr>
<tr>
<td>Ph₂PbCl₂·bipy</td>
<td>0.3</td>
</tr>
<tr>
<td>Ph₂PbBr₂·bipy</td>
<td>0.9</td>
</tr>
<tr>
<td>Ph₂PbI₂·bipy</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Although germanium tetrachloride and tetrabromide are known to form 1:1, six-coordinate complexes with bipyridyl\(^1\), germanium tetraiodide was found to coordinate two moles of this base to form a brick-red, readily hydrolysed solid, GeI\(_4\)·2bipy. This had a molar conductivity of 42.8 cm\(^2\)mole\(^{-1}\) cm\(^2\)mole\(^{-1}\) in nitrobenzene, and is therefore formulated as a 2:1 electrolyte, (GeI\(_2\)·2bipy\(_{2+}\)I\(^{-}\)). This behaviour parallels that of silicon tetraiodide which coordinates four moles of pyridine\(^7,14\). The diphenylgermanium halides do not react with bipyridyl to form solid compounds. In this respect germanium more closely resembles silicon than tin, since the organo-tin halides have well-developed acceptor properties.

Trimethyltin bromide, dimethyltin dichloride and diiodide, and methyltin triiodide all form 1:1 adducts with bipyridyl. These compounds are high-melting (with the exception of Me\(_3\)SnBr·bipy), and stable towards atmospheric moisture, as are the parent halides.

Diphenyl-lead halides similarly form 1:1 adducts with bipyridyl, Ph\(_2\)PbX\(_2\)·bipy, which are also high-melting, but unlike the tin complexes, have low solubility in most organic solvents. Although diphenyl-lead dichloride and dibromide have been reported\(^7\) to form addition compounds with four moles of pyridine, treatment of these halides with an excess of bipyridyl always resulted in the 1:1 compounds. The steric demands of the planar bipyridyl molecule, where
the pyridine rings are rigidly orientated, may be such that it is impossible for more than one ligand molecule to coordinate.

All these complexes must contain six-coordinate tin or lead in the solid state. Electron transfer from nitrogen to the metal, and the resulting charge redistribution will make the metal-halogen bonds more polar and more susceptible to ionisation in polar solvents. Coordination of pyridine to trimethyltin chloride lengthens the tin-chlorine bond, in the crystalline adduct by about 0.05 Å. Kraus and Greer studied the slight conductivity of trimethyltin chloride in the presence of pyridine, while Thomas and Kochow observed that the bis-pyridine adduct of dimethyltin dichloride ionised slightly in acetonitrile. Accordingly, it was of interest to measure the conductivity of these chelate complexes of tin and lead.

From the conductivity figures in Table I it can be seen that none of the adducts ionise to any sensible degree except Me₂SnL₂·bipy and MeSnL₂·bipy. As in Group V it is apparent that the complexes with metal-iodine bonds ionise to a greater extent than those with metal-chlorine bonds. The nature of the ions is uncertain, but five-coordinate species such as (Me₂SnL·bipy)⁺ and (MeSnL₂·bipy)⁺ are likely since one other five-coordinate ion is known, (Me₃Sn₂₂M₂)⁺.
It is evident from the low measured conductivities of all these bipyridyl complexes that when organotin and organolead halides can adopt the coordination number of six in a neutral complex they are reluctant to ionise in a non-aqueous solvent. Similarly with the monodentate ligand, pyridine, tin can adopt the coordination number of five, as in Me₃SnCl·py or six, as in Me₂SnCl₂·2py, and only slight ionisation results. It was for these reasons that the behaviour of the organotin and organolead halides towards 2,2',2''-terpyridyl, a tridentate ligand, was examined. The increased electron accession from three-coordinated nitrogen atoms, and the unfavourable coordination number this would impose upon the metal, should promote ionisation.

(2) Coordination Behaviour of 2,2',2''-Terpyridyl

Morgan and Burstall\textsuperscript{149} first showed that terpyridyl coordinated strongly with transition metals. With platinum and palladium, complexes of the type (PtCl\textsubscript{3}.terpy)Cl and (PdCl\textsubscript{2}.terpy)Cl were formed\textsuperscript{150}, and Morgan and Burstall used these compounds as an argument for square-planar coordination in platinum and palladium complexes\textsuperscript{151}. IronII, cobaltII, nickelII, and other transition metal ions coordinated two moles of the base to form six-coordinate cations in which the ligands must be arranged in two equatorial planes at right angles. Cupric chloride, zinc chloride and
cadmium chloride coordinate only one mole of terpyridyl, and the structure of these compounds was uncertain until an X-ray crystallographic study was made of ZnCl₂.terpy by Corbridge and Cox\(^1^1\). These authors found the configuration around the zinc atom to be that of a distorted trigonal bipyramid, with the three nitrogen atoms of the planar terpyridyl molecule all coordinated to the zinc. Because of the distortion of the terpyridyl skeleton which is necessary to permit coordination of the three nitrogens, and the resulting strain involved, terpyridyl complexes are not so stable as might otherwise have been expected for a tridentate chelate molecule\(^1^7^4\). In ZnCl₂.terpy, the mean zinc-nitrogen distance was 2.2\(\text{\AA}\). The sum of the covalent radii of tin and nitrogen (2.1\(\text{\AA}\)) and the tin-nitrogen bond distance found in Me₃SnCl.py\(^9\) (2.26±0.1\(\text{\AA}\)) both suggest that the tin atom would be a very suitable size to coordinate terpyridyl.

Beattie and Leigh\(^3\) found that while bipyridyl forms a stable chelate complex with silicon tetrachloride, SiCl₄.bipy, there was no interaction between terpyridyl and silicon tetrachloride. This suggests that if terpyridyl cannot coordinate all three of its nitrogen atoms, the third uncoordinated pyridine ring prevents the ligand from functioning as a bidentate by exerting a strong steric effect. In other words, terpyridyl must coordinate in three positions or not at all.
(3) 2,2',3''-Terpyridyl Complexes

The reactions of terpyridyl with Group IV halides and organohalides are summarised in Table II. Molar conductivity figures for the complexes in nitrobenzene are also included in the table.

**TABLE II**

Terpyridyl Complexes of Group IV Halides and Organohalides and their Molar Conductivities in Nitrobenzene at 10^{-3} M

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conductivity (M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl₄</td>
<td>no reaction</td>
</tr>
<tr>
<td>GeCl₄</td>
<td>no reaction</td>
</tr>
<tr>
<td>Ph₂GeCl₂</td>
<td>no reaction</td>
</tr>
<tr>
<td>SiCl₄·terpy</td>
<td>GeCl₄·terpy</td>
</tr>
<tr>
<td></td>
<td>24.2</td>
</tr>
<tr>
<td>SiCl₄·terpy</td>
<td>GeCl₄·terpy</td>
</tr>
<tr>
<td></td>
<td>23.2</td>
</tr>
<tr>
<td>(Me₂SnCl₂)₂·terpy</td>
<td>(Me₂SnBr₂)₂·terpy</td>
</tr>
<tr>
<td></td>
<td>13.8</td>
</tr>
<tr>
<td>(Ph₂SnCl₂)₂·terpy</td>
<td>(Ph₂SnBr₂)₂·terpy</td>
</tr>
<tr>
<td></td>
<td>14.1</td>
</tr>
<tr>
<td>(Ph₂SnCl₂)₂·terpy</td>
<td>(Ph₂SnBr₂)₂·terpy</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
</tr>
<tr>
<td>Ph₂PbCl₂·terpy</td>
<td>Ph₂PbBr₂·terpy</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>Ph₂PbCl₂·terpy</td>
<td>Ph₂PbBr₂·terpy</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>Ph₂PbI₂·terpy</td>
<td>Ph₂PbI₂·terpy</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
</tr>
</tbody>
</table>

(a) Ph₂SnI₂ is very unstable

No solid compound was obtained from germanium tetra-
chloride and terpyridyl, but germanium tetraiodide formed
the 1:1 adduct GeI₄.terpy. This difference in behavior must be related to the comparative ease with which the germanium-iodine bond is broken. For the same reason, bipyridyl forms the adduct GeI₄.2bipy, and triethylamine the adduct GeI₄.5NET₃.²¹,²²

Reaction of terpyridyl with dimethyltin and diphenyltin dichloride and dibromide produced solid compounds which have two moles of halide combined with one mole of terpyridyl, \((R₂SnX₂)₂.\text{terpy}\). Tin tetraiodide and dimethyltin diiodide formed 1:1 adducts SnI₄.terpy and Me₂SnI₂.terpy. These compounds are insoluble in petroleum ether or benzene, but quite soluble in more polar solvents such as alcohol and nitrobenzene. In nitrobenzene they have molar conductivities approaching typical values for 1:1 electrolytes, and are therefore formulated as \((R₂SnX.\text{terpy})^+R₂SnX₃^-\) in the case of the chlorides and bromides, and as \((Me₂SnI.\text{terpy})^+I^-\) and \((SnI₃.\text{terpy})^+I^-\) in the case of the iodides. In confirmation of these formulations the terpyridyl adducts of diphenyltin dichloride and dibromide reacted with sodium tetraphenylborate in alcohol when the compounds \((\text{Ph₂SnCl.terpy})\text{BPh₄}^+\) and \((\text{Ph₂SnBr.terpy})\text{BPh₄}^+\) separated as pale yellow crystals. These two complexes have molar conductivities of 17.9 and 18.3 \(\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}\), respectively in nitrobenzene.

Conductimetric titration of terpyridyl against dimethyltin dichloride and dimethyltin diiodide in nitrobenzene
<table>
<thead>
<tr>
<th>Mole ratio</th>
<th>Specific conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.3</td>
</tr>
<tr>
<td>0.04</td>
<td>1.5</td>
</tr>
<tr>
<td>0.08</td>
<td>2.9</td>
</tr>
<tr>
<td>0.13</td>
<td>4.2</td>
</tr>
<tr>
<td>0.17</td>
<td>5.4</td>
</tr>
<tr>
<td>0.22</td>
<td>6.6</td>
</tr>
<tr>
<td>0.26</td>
<td>7.8</td>
</tr>
<tr>
<td>0.30</td>
<td>8.6</td>
</tr>
<tr>
<td>0.35</td>
<td>9.5</td>
</tr>
<tr>
<td>0.39</td>
<td>10.4</td>
</tr>
<tr>
<td>0.43</td>
<td>11.0</td>
</tr>
<tr>
<td>0.46</td>
<td>11.5</td>
</tr>
<tr>
<td>0.52</td>
<td>11.8</td>
</tr>
<tr>
<td>0.56</td>
<td>12.0</td>
</tr>
<tr>
<td>0.51</td>
<td>12.3</td>
</tr>
<tr>
<td>0.65</td>
<td>12.4</td>
</tr>
<tr>
<td>0.70</td>
<td>12.5</td>
</tr>
<tr>
<td>0.74</td>
<td>12.7</td>
</tr>
<tr>
<td>0.78</td>
<td>12.8</td>
</tr>
<tr>
<td>0.83</td>
<td>12.9</td>
</tr>
<tr>
<td>0.87</td>
<td>13.0</td>
</tr>
</tbody>
</table>
FIG. 3. $\lambda_m$ (arbitrary units)

VERSUS MOLE RATIO Terpy:Me$_2$SnCl$_2$
### DATA FOR FIG. 4.

<table>
<thead>
<tr>
<th>Mole ratio</th>
<th>Specific Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.4</td>
</tr>
<tr>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>0.13</td>
<td>2.2</td>
</tr>
<tr>
<td>0.20</td>
<td>3.2</td>
</tr>
<tr>
<td>0.27</td>
<td>4.1</td>
</tr>
<tr>
<td>0.33</td>
<td>5.1</td>
</tr>
<tr>
<td>0.40</td>
<td>6.1</td>
</tr>
<tr>
<td>0.47</td>
<td>7.0</td>
</tr>
<tr>
<td>0.53</td>
<td>7.8</td>
</tr>
<tr>
<td>0.60</td>
<td>8.5</td>
</tr>
<tr>
<td>0.67</td>
<td>9.2</td>
</tr>
<tr>
<td>0.73</td>
<td>9.7</td>
</tr>
<tr>
<td>0.80</td>
<td>10.3</td>
</tr>
<tr>
<td>0.87</td>
<td>10.7</td>
</tr>
<tr>
<td>0.93</td>
<td>11.2</td>
</tr>
<tr>
<td>1.00</td>
<td>11.5</td>
</tr>
<tr>
<td>1.07</td>
<td>11.7</td>
</tr>
<tr>
<td>1.13</td>
<td>11.9</td>
</tr>
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<td>1.20</td>
<td>12.1</td>
</tr>
<tr>
<td>1.27</td>
<td>12.2</td>
</tr>
<tr>
<td>1.33</td>
<td>12.3</td>
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<tr>
<td>1.40</td>
<td>12.4</td>
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<tr>
<td>1.47</td>
<td>12.5</td>
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<tr>
<td>1.53</td>
<td>12.6</td>
</tr>
<tr>
<td>1.60</td>
<td>12.6</td>
</tr>
<tr>
<td>1.67</td>
<td>12.7</td>
</tr>
</tbody>
</table>
FIG. 4. $\Lambda_m$ (arbitrary units)

VERSUS MOLE RATIO terpy:Me$_2$SnI$_2$
(Figs. 3 and 4) clearly indicate that in solution one mole of terpyridyl interacts with two moles of dimethyltin dichloride, but with only one mole of dimethyltin diiodide. The shape of these curves also reveals that some non-ionic dissociation occurs in nitrobenzene since the conductivity is increased by further addition of terpyridyl.

\[ 2\text{Me}_2\text{SnCl}_2 + \text{terpy} \rightleftharpoons (\text{Me}_2\text{SnCl}_2\text{terpy})^+ + \text{Me}_2\text{SnCl}_3^- \]

and

\[ \text{Me}_2\text{SnI}_2 + \text{terpy} \rightleftharpoons (\text{Me}_2\text{SnI}_2\text{terpy})^+ + \text{I}^- \]

This explains why the molar conductivities are lower than those normally associated with 1-1 electrolytes.

The complex tin anions, \( R_2\text{SnX}_3^- \), which must occur in these compounds are of a type not previously reported, although there is other evidence for five-coordinate tin (page 16). Anions, \( R_2\text{SnX}_4^- \), are well known, and like the anion \( R_2\text{SnX}_3^- \) found in the terpyridyl complexes, occur only when \( X \) is chloride or bromide. A closely related ion, \( \text{Me}_2\text{SnBr}_2^- \), occurred in the compound resulting from the reaction of triphenylphosphinomethylenec with trimethyltin bromide, \( (\text{Ph}_3\text{PCH}_2\text{SnMe}_3)^+\text{Me}_2\text{SnBr}_2^- \), but the reaction with dimethyltin dibromide produced a normal six-coordinate anion \( (\text{Ph}_3\text{PCH}_2\text{SnMe}_2\text{CH}_2\text{PPPh}_3)^2\text{Me}_2\text{SnBr}_4^{-2} \). Seyferth and Grim \(^{73}\) postulate \( \text{Me}_2\text{SnBr}_2^- \) to be a six-coordinate tin anion, \( \text{Me}_6\text{SnBr}_2^- \), by halogen-bridging, but this postulate seems unnecessary, and five-coordinate tin is more likely. It
would seem that singly charged ions of the type $\text{R}_3\text{SnX}_2^-$, $\text{R}_2\text{SnX}_3^-$, and possibly $\text{RSnX}_4^-$, are of wide occurrence provided halide ions are not present in excess, as in acid solution, when the more usual six-coordinate ions $\text{R}_2\text{SnX}_3^{2-}$, $\text{R}_2\text{SnX}_4^{2-}$, and $\text{RSnX}_5^{2-}$ will predominate.

Terpyridyl reacts with diphenyl-lead dichloride, dibromide, and diiodide to form a series of 1:1 adducts $\text{Ph}_2\text{PbX}_2$-terpy. The chloride and bromide are colourless crystalline solids, but the iodide is yellow. They are sufficiently soluble in nitrobenzene for conductivity measurement, but are only weakly conducting in this solvent. The low molar conductivities (Table II) suggest that the solid compounds are covalent, with the lead atoms probably seven-coordinate.

The marked difference in behaviour between terpyridyl complexes of organotin and organolead halides indicates that tin-halogen bonds are more readily ionised than lead-halogen bonds. Unfortunately, this comparison cannot be extended to germanium since germanium tetrachloride and the diphenylgermanium halides do not react with terpyridyl. However, the behaviour of germanium halides in other circumstances does suggest that the trend towards increasing ease of ionisation continues from tin to germanium. Examples are provided by the bipyridyl derivatives of germanium and tin tetraiodides. In the germanium adduct germanium-iodine bonds are broken to permit the coordination of two moles of
bipyridyl, GeI₄·2bipy, while tin tetraiodide forms a six-coordinate covalent adduct, SnI₄·bipy⁵. Methyltin triiodide and dimethyltin diiodide form similar covalent adducts, MeSnI₃·bipy and Me₂I₂·bipy. The ionic adducts (GeI₃·Me₃)⁺I⁻⁹, (SiH₃·Me₃)⁺I⁻⁸, and the covalent compound, Me₃SnCl·py⁴¹ are also in accord with this same trend.

Table III lists the available bond energy data. No figure is available for the tin-iodine bond energy in tin tetraiodide, but it will doubtless follow tin tetrachloride and tin tetrabromide in being less than the corresponding germanium-halogen bond energies.

### TABLE III

**Bond Energies for M-X bonds in Group IV**¹³⁴ (k. cal/mole)

<table>
<thead>
<tr>
<th>M</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>94</td>
<td>74</td>
<td>56</td>
</tr>
<tr>
<td>Ge</td>
<td>81</td>
<td>66</td>
<td>51</td>
</tr>
<tr>
<td>Sn</td>
<td>76</td>
<td>65</td>
<td>--</td>
</tr>
</tbody>
</table>

The dipole moments of a number of Group IV organo-halides are tabulated in Table IV¹⁵²,¹⁷⁵.

### TABLE IV

**Dipole Moments of Group IV Organohalides**

<table>
<thead>
<tr>
<th>SiH₃Cl</th>
<th>1.28</th>
<th>SiH₂Cl₂</th>
<th>1.17</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH₃Cl</td>
<td>2.03</td>
<td>Ph₃GeBr</td>
<td>2.5</td>
</tr>
<tr>
<td>Et₃SnCl</td>
<td>3.44</td>
<td>Ph₃SnCl</td>
<td>3.30</td>
</tr>
<tr>
<td>Et₃PbCl</td>
<td>4.39</td>
<td>Ph₃PbCl</td>
<td>4.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Et₂SnCl₂</td>
<td>3.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Et₂PbCl₂</td>
<td>4.70</td>
</tr>
</tbody>
</table>
From the extreme polarity of the lead-halogen bonds, indicated by the high dipole moments, it might have been expected that ionisation would occur readily in complexes of these halides. The differences between the tin and lead terpyridyl complexes must be connected with the ability of the lead atom to adopt coordination numbers higher than six. The pyridine adducts of diphenyl-lead dihalides, \( \text{Pb}_2\text{PbX}_2 \cdot 2\text{py} \), possibly contain eight-coordinate lead, as also does lead tetra-acetate. This compound is non-conducting in acetic acid, and also non-associated in this solvent\(^{153}\). However, interchange of radioactive and inactive lead atoms occurs between plumbous and lead tetra-acetate when they are dissolved in acetic acid\(^{154}\). A structure in which the acetate groups are chelating is suggested to explain these facts\(^{153}\). A coordination number of seven has been found for lead\( \text{II} \) in the bis-thiourea complex of lead dichloride, \( \text{PbCl}_2 \cdot 2\text{thiourea} \), and is also possible in the aniline complex of lead tetrachloride, \( \text{PbCl}_4 \cdot \text{C}_6\text{H}_5\text{N} \), \(^{74}\).

The increasing ease of ionisation on passing from lead to tin is clearly established, but the sharply reduced acceptor properties of germanium prevented the formation of a uniform series of terpyridyl adducts which would have made possible direct comparison between germanium, tin and lead. However, other evidence suggests that the trend continues from tin to germanium. As in Group \( V \), this
ionisation order is not that expected from the metal-halogen bond energies, the bond polarities, and examples from aqueous chemistry. The observed order must be explained by the fact that higher covalencies become increasingly favourable with respect to energy as the Group is descended.
II EXPERIMENTAL

Complexes of Tin Halides

(a) Bipyridyl Complexes

These were all prepared by the general procedure of mixing approximately equimolar proportions of halide and ligand in a dry hydrocarbon solvent. The complexes separated as crystals and were removed on a sintered glass filter, washed with solvent, and dried in a high vacuum. A dry-box was not used for these preparations, but long exposure to the air was avoided.

Dimethyldichloro-bipyridyl-tinIV

2 ml of dimethyltin dichloride was mixed with 2 ml of bipyridyl in 25 ml of benzene solution when a white micro-crystalline solid was precipitated, m.p. 238-239\(^0\) (lit.\(^1\) 240\(^0\)).

Analysis: Calculated for \(\text{C}_{12}\text{H}_{14}\text{N}_2\text{SnCl}_2\): C, 38.4; H, 3.7; N, 7.4%.

Found: C, 38.5; H, 3.9; N, 7.0%.

Dimethyldiiodo-bipyridyl-tinIV

Using dimethyltin diiodide in the above preparation colourless crystals of the addition compound were deposited, m.p. 244\(^0\).
Analysis: Calculated for \( \text{C}_{12}\text{H}_{14}\text{N}_2\text{SnI}_2 \): \( \text{C}, 25.8\%; \text{H}, 2.5\%; \text{N}, 5.0\% \).

Found: \( \text{C}, 26.1\%; \text{H}, 2.7\%; \text{N}, 4.6\% \).

**Methyltriiodo-bipyridyl-tinIV**

Yellow needles of this complex were deposited when solutions of methyltin triiodide and bipyridyl in benzene were mixed, m.p. 260° (with decomposition).

Analysis: Calculated for \( \text{C}_{14}\text{H}_{14}\text{N}_2\text{SnI}_3 \): \( \text{C}, 19.7\%; \text{H}, 1.9\%; \text{N}, 4.2\% \).

Found: \( \text{C}, 20.0\%; \text{H}, 1.9\%; \text{N}, 3.7\% \).

**Trimethylbromo-bipyridyl-tinIV**

This complex was very soluble in organic solvents and was best prepared from petroleum ether (50-70°) as long colourless needles, m.p. 65°.

Analysis: Calculated for \( \text{C}_{15}\text{H}_{17}\text{N}_2\text{SnBr} \): \( \text{C}, 39.0\%; \text{H}, 4.3\%; \text{N}, 7.0\% \).

Found: \( \text{C}, 37.6\%; \text{H}, 4.6\%; \text{N}, 6.6\% \).

**(b) Terepyridyl Complexes**

These were prepared in the same manner as the bipyridyl derivatives except that petroleum ether was used exclusively as the solvent since these complexes proved to be quite insoluble in this solvent, and high yields were obtained by using it. All the complexes were quite soluble in ethanol, acetone, and nitrobenzene. They could be recrystallised from ethanol.
2,2',2''-Terpyridyl

Material obtained from G. F. Smith Chemical Co., Columbus, Ohio, was recrystallised from petroleum ether (50-70°) as very pale yellow crystals, m.p. 88-89°.

Diphenylchloro-terpyridyl-tinIV, Diphenyltrichlorostannate

Precipitated as a white solid on mixing 1 mM of halide with approximately 0.5 mM of terpyridyl in 25 ml of petroleum ether, m.p. 104°.

Analysis: Calculated for C_{30}H_{31}N_{5}Sn_{2}Cl_{4}: C, 50.8; H, 3.4; N, 4.6%.

Found: C, 51.0; H, 3.5; N, 4.4%.

Diphenylbromo-terpyridyl-tinIV, Diphenyltribromostannate

In the above preparation using diphenyltin dibromide a cream coloured solid was precipitated, m.p. 120°.

Analysis: Calculated for C_{39}H_{34}N_{5}Sn_{2}Br_{4}: C, 42.7, H, 2.8; N, 3.6; Br, 29.1%.

Found: C, 42.8; H, 3.1; N, 3.7; Br, 29.3%.

Dimethylchloro-terpyridyl-tinIV, Dimethyltrichlorostannate

1 mM of dimethyltin dichloride and 0.5 mM of terpyridyl in petroleum ether precipitated a white microcrystalline powder, m.p. 182-186°. Conductimetric titration of terpyridyl versus dimethyltin dichloride in nitrobenzene indicated a 2:1 interaction of halide and ligand in solution (Fig.3).
Analysis:  Calculated for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{Sn}_2\text{Cl}_4$: C, 34.0; H, 3.4; N, 6.2%.

Found:   C, 34.7; H, 3.8; N, 5.5%.

**Dimethylbromo-terpyridyl-tinIV. Dimethyltribromostannate**

In the above preparation, using dimethyltin dibromide, a
cream coloured solid was obtained, m.p. 178-180°.

Analysis:  Calculated for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{Sn}_2\text{Br}_4$: C, 26.8; H, 2.7; N, 5.0; Br, 37.5%.

Found:   C, 27.2; H, 2.9; N, 4.6; Br, 36.8%.

**Dimethylido-terpyridyl-tinIV. Iodide**

Dimethyltin diiodide and terpyridyl mixed in any proportion in petroleum ether precipitated the 1:1 adduct as a yellow powder, m.p. 202° (with decomposition). Conductimetric titration of terpyridyl versus dimethyltin diiodide in nitrobenzene indicated a 1:1 interaction of halide and ligand in solution (Fig. 4).

Analysis:  Calculated for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{SnI}_2$: C, 32.0; H, 2.7; N, 6.6; I, 39.8%.

Found:   C, 31.9; H, 3.2; N, 5.9; I, 39.8%.

**Triiodo-terpyridyl-tinIV. Iodide**

Tin tetraiodide and terpyridyl mixed in any proportions in petroleum ether precipitated the 1:1 adduct as a dark red powder.
Analysis: Calculated for $C_{15}H_{41}N_3SnI_4$: $C$, 21.0; $H$, 1.3; $N$, 4.9%.

Found: $C$, 21.3; $H$, 1.5; $N$, 4.3%.

Trimethyltin bromide, in petroleum ether solution, did not react with terpyridyl to produce a solid adduct.

(c) Tetraphenylborate derivatives of the complex tin cations

Reaction between sodium tetraphenylborate and diphenylchloro-terpyridyl-tinIV diphenyltrichlorostannate and diphenylbromo-terpyridyl-tinIV diphenyltribromostannate produced the tetraphenylborates of the complex tin cations ($Ph_2SnXterpy$).

Diphenylchloro-terpyridyl-tinIV Tetraphenylborate

Approximately 0.3 g of the terpyridyl adduct was dissolved in 30 ml of warm ethanol and 0.1 g of sodium tetraphenylborate in 5 ml of ethanol added. There was immediate formation of very pale yellow crystals. These were filtered off and pumped dry, m.p. 182°.

Analysis: Calculated for $C_{51}H_{41}N_3SnBCl$: $C$, 71.1; $H$, 4.8; $N$, 4.9%.

Found: $C$, 70.7; $H$, 5.3; $N$, 4.6%.

Diphenylbromo-terpyridyl-tinIV Tetraphenylborate

This was prepared in exactly the same way as the chloro-complex described above. It formed pale yellow crystals, m.p. 185°. This compound exploded on combustion in oxygen, and the analysis figures quoted were obtained by combustion in
Analysis: Calculated for $\text{C}_{51}\text{H}_{14}\text{N}_{3}\text{SnBr}_4$: $C$, 67.7; $H$, 4.5; $N$, 4.6%.
Found: $C$, 66.4; $H$, 4.7; $N$, 4.3%.

Complexes of the Lead Halides

(a) Bipyridyl Complexes

Because of the low solubility of the diphenyl-lead dihalides in hydrocarbon solvents, acetone was used for the preparation of the bipyridyl complexes. The halide was mixed with a three or four molar excess of bipyridyl in acetone when a crystalline deposit of the 1:1 adduct was obtained. This was filtered off, washed with acetone and pumped dry.

Diphenyl dichloro-bipyridyl-leadIV

Formed small white crystals from acetone, m.p. over 300$^\circ$.

Analysis: Calculated for $\text{C}_{22}\text{H}_{18}\text{PbCl}_2$: $C$, 44.9; $H$, 3.0; $N$, 4.8%.
Found: $C$, 45.0; $H$, 3.6; $N$, 4.4%.

Diphenyl dibromo-bipyridyl-leadIV

Formed small white crystals from acetone, m.p. 250$^\circ$ (with decomposition).

Analysis: Calculated for $\text{C}_{22}\text{H}_{18}\text{PbBr}_2$: $C$, 39.0; $H$, 2.7; $N$, 4.1; Br, 23.6%.
Found: $C$, 39.5; $H$, 3.1; $H$, 3.7; Br, 23.2%.
Diphenylidiodo-bipyridyl-lead IV

Formed pale yellow crystals from acetone, m.p. 180°; (with decomposition).

Analysis: Calculated for \( \text{C}_{22}\text{H}_{18}\text{PbI}_2 \): \( \text{C}, 34.2; \text{H}, 2.3; \text{Pb}, 3.6\% \).
Found: \( \text{C}, 34.0; \text{H}, 2.6; \text{Pb}, 3.2\% \).

(b) Terpyridyl Complexes

These were readily prepared by mixing equimolar proportions of halide and terpyridyl in ethanol. They were noticeably more soluble than corresponding bipyridyl complexes in organic solvents.

Diphenylidichloro-terpyridyl-lead IV

This complex separated slowly from ethanol as colourless needles, m.p. 253-255°.

Analysis: Calculated for \( \text{C}_{27}\text{H}_{21}\text{PbCl}_2 \): \( \text{C}, 48.6; \text{H}, 3.2; \text{Pb}, 6.3\% \).
Found: \( \text{C}, 48.4; \text{H}, 3.6; \text{Pb}, 5.9\% \).

Diphenylidibromo-terpyridyl-lead IV

This complex separated slowly from ethanol as colourless needles, m.p. 233-234°.

Analysis: Calculated for \( \text{C}_{27}\text{H}_{21}\text{PbBr}_2 \): \( \text{C}, 43.0; \text{H}, 2.8; \text{Pb}, 5.6; \text{Br}, 21.2\% \).
Found: \( \text{C}, 43.4; \text{H}, 3.2; \text{Pb}, 5.3; \text{Br}, 21.9\% \).
Diphenyldiido-terpyridyl-leadIV

On standing this complex separated from ethanol as yellow needles, m.p. 150°.

Analysis: Calculated for C_{27}H_{24}N_{3}PbI_{2}: C, 38.2; H, 2.5; N, 5.0%. Found: C, 37.7; H, 2.9; N, 4.6%.

Complexes of the Germanium Halides

(a) Diphenylgermanium Dihalides

No solid compounds were formed between diphenylgermanium dichloride and diiodide with either bipyridyl or terpyridyl under the same reaction conditions as produce complexes with organotin and organolead halides.

(b) Bipyridyl Complex of Germanium Tetraiodide

The interaction between germanium tetraiodide and bipyridyl was examined in a dry-box. A three molar excess of bipyridyl in sodium-dried benzene was added to germanium tetraiodide in the same solvent. The resulting red-brown solid was filtered off and washed with benzene. This compound was completely hydrolysed to germaniumIV oxide in several minutes when exposed to the air.

Analysis: Calculated for C_{20}H_{16}GeI_{4}: I, 57.0%. Found: I, 57.3%.
(c) Reaction of Terpyridyl with Germanium Tetrachloride and Germanium Tetraiodide

These reactions were carried out in the dry-box. A sample of germanium tetrachloride, which had been distilled in the vacuum-line, was dissolved in toluene and treated with a solution of terpyridyl in toluene. No reaction was observed.

Mixing equimolar quantities of germanium tetraiodide and terpyridyl, both in toluene solution, produced a red-brown solid which was filtered off and washed with toluene. It was freed from solvent under vacuum. On exposure to the air the red solid was rapidly hydrolysed to germaniumIV oxide. This compound was not prepared in analytical purity, but iodine analyses were close to those calculated for the 1:1 adduct.

Analysis: Calculated for $\text{C}_{15}^\text{H}_{11}^\text{N}_{3}^\text{GeI}_4$: 1,62.4%.
Found: 1,60.1, 59.9%.
The Group IV organohalides were prepared by the following routes.

\[
\begin{align*}
\text{Ph}_2\text{GeX}_2 & \quad \text{Br}_2 \quad \text{HX} \\
\text{Ph}_4\text{Ge} & \quad \rightarrow \quad \text{Ph}_2\text{GeO} & \quad \rightarrow \quad \text{Ph}_2\text{GeX}_2 \\
\text{Me}_2\text{SnBr} & \quad \text{Me}_4\text{Sn} + \text{SnBr}_4 & \quad \rightarrow \quad 2\text{Me}_2\text{SnX}_2 \\
\text{Me}_2\text{SnX}_2 & \quad \text{Me}_4\text{Sn} + \text{SnCl}_4 & \quad \rightarrow \quad \text{Me}_2\text{SnCl}_2 & \quad \text{OH}^- \\
\text{Me}_2\text{SnBr} & \quad \text{Me}_4\text{Sn} + \text{SnBr}_4 & \quad \rightarrow \quad \text{Me}_2\text{SnBr} \\
\text{Me}_2\text{SnCl}_2 & \quad \text{Me}_4\text{Sn} + \text{SnBr}_4 & \quad \rightarrow \quad \text{Me}_2\text{SnCl}_2 & \quad \text{OH}^- \\
\text{Me}_2\text{SnO} & \quad \text{HX} & \quad \rightarrow \quad \text{Me}_2\text{SnX}_2 \\
\text{Me}_2\text{SnI}_3 & \quad \text{SnO}_2^2- + \text{MeI} & \quad \rightarrow \quad \text{MeSnO}_2\text{H} & \quad \text{HI} & \quad \rightarrow \quad \text{MeSnI}_3 \\
\text{Ph}_2\text{PbX}_2 & \quad \text{Ph}_4\text{Pb} & \quad \text{HNO}_3 & \quad \text{HX} & \quad \rightarrow \quad \text{Ph}_2\text{Pb(NO}_3)^2_2 & \quad \rightarrow \quad \text{Ph}_2\text{PbX}_2 \\
\end{align*}
\]

**Tetraphenylgermane, Ph₄Ge**

This was prepared by the reaction between phenylmagnesium bromide and germanium tetrachloride in either toluene or tetrahydrofuran. The preparation in tetrahydrofuran, which required separation of the Grignard solution from any unreacted magnesium did not appear to offer any advantages over the simpler preparation in toluene. The tetraphenylgermane was recrystallised from toluene, m.p. 230° (lit. 237°).
Diphenylgermanium oxide, Ph₂GeO

Cleavage of tetraphenylgermane with bromine in a high boiling solvent such as dibromoethane produced diphenyldibromogermane which was hydrolysed without separation, and the resulting oxide was obtained in reasonable purity when volatile material had been removed by steam distillation. The method of Metlesics and Zeiss\textsuperscript{158} was followed in detail, using 10 g samples of tetraphenylgermane. The oxide so obtained was dissolved in boiling acetic acid and any insoluble coloured impurities removed by filtration through a plug of glass wool. Cooling and dilution of the acetic acid solution produced a white oxide which was filtered off and air-dried.

Diphenyldichlorogermane, Ph₂GeCl₂

Diphenyldichlorogermane was prepared by treating diphenylgermanium oxide with hydrochloric acid. 6 g of the oxide was warmed with 30 ml of conc. hydrochloric acid. The oily chloride so produced was twice extracted with benzene, and the benzene solution dried over calcium chloride. Removal of the solvent left the chloride which was distilled under high vacuum, yielding a clear liquid.

Diphenyldiiodogermane, Ph₂GeI₂

Treatment of diphenylgermanium oxide with colourless, constant boiling hydriodic acid gave diphenyldiiodogermane.
2 g samples of the oxide were covered with hydriodic acid (which had been freshly distilled off red phosphorus) and warmed on a water bath until all the oxide had reacted. On cooling, the iodide solidified and was freed from adhering acid by pressing between filter papers. Recrystallisation from nitromethane\(^{159}\) yielded colourless crystals, m.p. 70\(^\circ\) C, (lit.\(^{159}\) 70-71\(^\circ\) C).

**Germanium Dioxide, GeO\(_2\)**

Hydrolysis of germanium tetrachloride with a hot solution of ammonium hydroxide produced a white precipitate of hydrated germanium dioxide. This was filtered off, washed several times with water, and air-dried.

**Germanium Tetraiodide, GeI\(_4\)**

Hydriodic acid converts germanium dioxide to germanium tetraiodide. The method described by Foster and Williston\(^{160}\) was followed, but using only 2 g of oxide and 12 ml of freshly distilled hydriodic acid. The tetraiodide was filtered off on a sintered glass crucible and pressed as dry as possible. Recrystallisation from chloroform gave orange-red crystals which were freed from chloroform in a vacuum desiccator, m.p. 146\(^\circ\) C (lit.\(^{160}\) 146\(^\circ\) C).

**Diphenyltin Dichloride, Ph\(_2\)SnCl\(_2\)**

The redistribution reaction between tin tetrachloride and tetraphenyltin gives the dichloride in high yield.
20 g of tetraphenylnitin (L. Light and Co.) was dissolved in 12.2 g of tin tetrachloride, and the mixture slowly warmed to over 200°. After two hours at this temperature the mixture was allowed to cool, and it eventually solidified. Repeated recrystallisations from petroleum ether (50-70°) gave pure white crystals of diphenyltin dichloride, m.p. 42° (lit.161 42°).

Diphenyltin dibromide, PhSnBr₂

A similar redistribution reaction between tin tetra-
bromide and tetraphenylnitin gave the dibromide. 23.5 g of
tetraphenylnitin and 24.1 g of the bromide were treated in
exactly the same manner as in the chloride preparation
described above. Recrystallisation of the solid reaction
product from petroleum ether (50-70°) gave the pure dibromide.
This solidified with difficulty, but after standing for some
time crystals with m.p. 37° were obtained, (lit.162 38°).

Tetramethyltin, Me₄Sn

This was prepared from the reaction between methyl-
magnesium iodide and tin tetrachloride, the solvent being di-
n-butyl ether as recommended by Edgell and Ward163. The
solvent was dried over calcium chloride and distilled before
use, the fraction b.p. 140-142° being used. The Grignard
reagent was prepared in the usual manner from 50 g of mag-
nesium turnings and 225 g of methyl iodide in 600 ml of di-
n-butyl ether. About three hours were required for its
formation. After cooling to room temperature, 75 g of tin tetrachloride was added at a rate sufficient to cause gentle refluxing of the mixture, and following the completion of this step, the mixture was heated under reflux for a further hour. The crude product was then distilled from the reaction mixture. A mixture of tetramethyltin and di-n-butyl ether distilling at 85-120° was taken. Edgell and Ward state that the bulk of the tetramethyltin-di-n-butyl ether mixture distils at 85-95°, but in fact, little material came over in this boiling range. Pure tetramethyltin was obtained by careful fractionation of this mixture, using a 60 cm column packed with single-turn helices. 40 g of tetramethyltin distilling at 76.0° (761 mm) was obtained.

**Dimethyltin dichloride, Me₂SnCl₂**

A mixture of 11.8 g of tetramethyltin and 17.2 g of tin tetrachloride was heated in an oil-bath at 210° for a period of three hours. On cooling the reaction product solidified. Several recrystallisations from petroleum ether (50-70°) yielded pure white crystals of dimethyltin dichloride, m.p. 106°, (lit. 164 106°).

**Dimethyltin oxide, Me₂SnO**

Dimethyltin dichloride in aqueous ethanol solution was treated with just sufficient dilute potassium hydroxide solution to precipitate completely the polymeric dimethyltin
oxide. This was collected on a filter, washed with water and ethanol and air-dried.

**Dimethylditin dibromide, Me₂SnBr₂**

Dimethylditin oxide was covered with conc. hydrobromic acid in a porcelain crucible and warmed on a water bath until all the oxide had been converted to an oily layer of molten dimethylditin dibromide. This layer solidified on cooling, and was freed from hydrobromic acid by pressing between filter papers. Recrystallisation from petroleum ether (50-70°) gave small white crystals, m.p. 75-76°, (lit. 165 75-77°).

**Dimethylditin diiodide, Me₂SnI₂**

This was prepared by treating dimethylditin oxide with freshly distilled, constant boiling hydriodic acid in the manner described for the preparation of dimethylditin dibromide. Two recrystallisations from petroleum ether (50-70°) gave the iodide as flaky white crystals, m.p. 42° (lit. 166 42°).

**Trimethylditin bromide, Me₃SnBr**

This was prepared by the redistribution reaction between tetramethylditin and tin tetrabromide as described by Clark and Willis 167. 19.4 g of tin tetrabromide was slowly added to 23.7 g of tetramethylditin, and the mixture warmed to 150°, and kept at that temperature for about four hours. Distillation through a short Vigreux column gave trimethylditin bromide, b.p. 160-165°, as a clear liquid. On standing at
room temperature this eventually solidified.

**Methylin triiodide, MeSnI₃**

Methylstannonic acid, MeSnOH was prepared from potassium stannite and methyl iodide. 20 g of stannous chloride was dissolved in sufficient concentrated potassium hydroxide solution. 15 g of methyl iodide in 100 ml of alcohol was then added, and the mixture stirred vigorously for 30 hours. After removal of the alcohol on a water bath, neutralisation with dilute hydrochloric acid produced a gelatinous precipitate of the acid which was filtered off with suction and washed several times with water, and air-dried. After warming this acid with hydriodic acid for some time on a water bath, the white methylstannonic acid was replaced by a yellow solid. Recrystallisation of this solid from petroleum ether (50-70°C) gave long yellow needles of methylin triiodide, m.p. 85-86°C (lit.¹⁶⁵ 84-85°C).

**Tetraphenyl-lead, Ph₄Pb**

Reaction between phenylmagnesium bromide and finely ground solid leadII chloride in toluene produces both tetraphenyl lead and free lead. The preparation described by Setzer, Leeper and Gilman¹⁶⁹ was followed in detail. The Grignard reagent was prepared from 36 g of magnesium and 234 g of bromobenzene in 500 ml of diethyl ether. When this reaction was complete, 500 ml of toluene was added, followed
by 181 g of very finely ground lead II chloride in three portions at five minute intervals. The mixture was refluxed for five hours longer and hydrolyzed by pouring upon crushed ice and ammonium chloride. The ether-toluene layer was decanted, and the solid filtered from the aqueous layer and air-dried. This mixture of tetraphenyl lead and metallic lead was extracted with 400 ml of chloroform in a Soxhlet extractor to yield pure crystalline tetraphenyl lead, m.p. 228° (lit. 169 225-226°).

Diphenyl-lead dinitrate, \( \text{Ph}_2\text{Pb(NO}_3\text{)}_2 \)

Polis170 described the cleavage of two phenyl groups from tetraphenyl-lead with nitric acid. 10 g samples of tetraphenyl-lead were added slowly to 50 ml of boiling concentrated nitric acid. After cooling, the resultant diphenyl-lead dinitrate was filtered off through a sintered glass crucible and washed with a little water. This nitrate was used for the preparation of the diphenyl-lead dihalides.

Diphenyl-lead dichloride, \( \text{Ph}_2\text{PbCl}_2 \)

Diphenyl-lead dinitrate was dissolved in boiling water, acidified with a few drops of nitric acid. Addition of dilute hydrochloric acid precipitated diphenyl-lead dichloride as a fine white solid. This was collected on a filter, washed with water, and dried in vacuo over \( \text{P}_2\text{O}_5 \) at 80°.
Diphenyl-lead dibromide, $Ph_2PbBr_2$

This was prepared in exactly the same manner as the chloride, but using an aqueous sodium bromide solution instead of hydrochloric acid. The white solid was separated and dried in the same way.

Diphenyl-lead diiodide, $Ph_2PbI_2$

In the chloride preparation above, hydrochloric acid was replaced by an aqueous solution of sodium iodide. A yellow solid was precipitated. This was filtered off, washed, and pressed as dry as possible. Recrystallisation from chloroform gave small yellow crystals, m.p. 104° (lit. 170 102°).
(a) Conductivity Measurements

Conductivity measurements were made in this work to determine the extent of ionisation of certain bipyridyl and terpyridyl complexes. Molar conductivities were used for the purpose of comparing one compound with another. Molar conductivity, $\Lambda_m$, is given by the relationship $\Lambda_m = \frac{1000K}{c}$, where $K$ is the specific conductivity (ohm$^{-1}$ cm$^{-1}$) of a solution of concentration $c$, (g.mole litre$^{-1}$). The specific conductivity $K = \frac{\text{cell constant}}{\text{resistance of solution}}$. The cell constant is dependent upon the dimensions of the electrodes and their distance apart. The conductivity cell, (depicted in Fig. 5), had shiny platinum electrodes and was calibrated with a 10$^{-3}$M solution of potassium chloride. Such a solution of potassium chloride has a specific conductivity of 14.088x10$^{-4}$ ohm$^{-1}$ cm$^{-1}$ at 25$^\circ$C$^{171}$. All measurements were made at 25.0±0.1$^\circ$ using a Philips type GPh249 conductivity bridge and the cell constant was 0.331. The cell was recalibrated at various intervals, but the constant was not found to alter.

Nitrobenzene was the main solvent used since it is unreactive, and also does not solvate strongly. It has a relatively high dielectric constant (36.1 at 20$^\circ$C$^{172}$, and
the limiting molar conductivity of a large number of 1-1 electrolytes has been recorded in this solvent\textsuperscript{173}. Conductivity measurements on the bismuth halide complexes, whose solubilities in nitrobenzene were very low, were also made in dimethylformamide, but all other measurements were made in nitrobenzene. Limiting molar conductivities of strong 1-1 electrolytes usually fall within the range $\Lambda_0=25-35$ in nitrobenzene\textsuperscript{173}, and $\Lambda_0=60-80$ in dimethylformamide\textsuperscript{145}.

Solutions of germanium, arsenic and antimony complexes were made up in the dry-box. The conductivity cell was dried in an oven and allowed to cool in the dry-box. The molar conductivities quoted are those measured after attainment of thermal equilibrium with the thermostat bath at $25^\circ$. These showed no tendency to drift, and measurements were reproducible on different preparations of the complexes and using different samples of nitrobenzene.

Normal precautions were taken to prevent access of moisture in measurements on the tin, lead and bismuth complexes, but the dry-box was not necessary.

Conductimetric titrations were made in the titration cell depicted in Fig. 5. The interaction of bipyridyl and a Group V halide or terpyridyl and a Group IV halide was followed by measuring the change of conductivity produced. A solution of the ligand at least ten times as concentrated as the solution of halide, was run in from a microburette
FIG. 5. CONDUCTIVITY AND TITRATION CELLS
which was attached to the cell by means of a ground glass joint. The measured specific conductivity was corrected for dilution by multiplying by the factor $\frac{V_1V}{V}$, (where $V$ is the original volume of solution, and $v$ the volume of solution added), and plotted against the mole ratio of the reactants. The break in the resulting curve indicates the equivalence point. The cell constant of the titration cell was 0.595.

(b) Purification and Drying of Conductivity Solvents

(1) Nitrobenzene.

Nitrobenzene was purified by the method of Witschenke and Kraus. 'Analar' grade nitrobenzene (Hopkin and Williams) was dried over calcium chloride or calcium sulphate. It was then distilled under reduced pressure, care being taken that the temperature of the vapour did not rise above 50°. The middle fraction was collected. This nitrobenzene had a specific conductivity of about $10^{-7}\text{ohm}^{-1}\text{cm}^{-1}$, but after standing over Linde molecular sieve pellets (Type 4A) this was further reduced to less than $10^{-8}\text{ohm}^{-1}\text{cm}^{-1}$.

(2) $N,N'$-Dimethylformamide.

Dimethylformamide was purified by the method of Prue and Sherrington. It was first mixed with approximately 10% by volume of A.R. sodium-dried benzene and the azetropes distilled off at atmospheric pressure. This removed the bulk of the water. The undistilled dimethylformamide was
then shaken repeatedly with phosphorus pentoxide, decanted, and distilled under reduced pressure. This dimethylformamide had a specific conductivity of $1 \times 10^{-6} \text{ohm}^{-1} \text{cm}^{-1}$ when first distilled, but this rapidly increased to $3 \times 10^{-6} \text{ohm}^{-1} \text{cm}^{-1}$.

(c) Analyses

Carbon, hydrogen and nitrogen determinations were carried out at the Microanalytical Laboratory of the University of Otago by Dr. A. D. Campbell. Nitrogen determinations were not always very satisfactory. Both the Dumas and Kjeldahl methods were tried and the Dumas method found to be the most reliable. The difficulty of determining heterocyclic nitrogen has been mentioned by other workers\textsuperscript{95}.

Halogen analyses were made by hydrolysing weighed samples of the complexes with water or dilute sodium hydroxide solution, and then acidifying with $6\text{M}$ nitric acid. This acid solution was titrated with standard silver nitrate solution using the Volhard procedure. The silver nitrate was standardised against A.R. potassium chloride. In the case of chloride determinations, the solubility of the silver chloride precipitate was reduced by shaking with nitrobenzene as recommended by Vogel\textsuperscript{178}, before titration with thiocyanate. Analyses were made on approximately 0.2 g samples of bipyridyl complexes and 0.05-0.10 g samples of terpyridyl complexes.
(d) Ultra-violet Spectra

These were recorded in methylene chloride solution using a Beckman DK2A recording spectrophotometer. The methylene chloride was dried over calcium chloride.

(e) X-ray Powder Photographs

X-ray powder photographs were obtained using a Philips 11,48 cm diameter camera with copper Kα radiation filtered through a nickel filter. Ilford X-ray films of grade 'C' were used for all photographs and exposures varied between four and twelve hours. Samples to be photographed were finely ground, inserted into Lindemann tubes, and packed with the aid of small glass fibres of suitable size. The arsenic and antimony halide complexes were handled in the dry-box.

In examining for isomorphism, photographs were compared visually, and by measuring individual d-values and relative intensities.

(f) Vacuum Line

A conventional Stock-type vacuum line was used for examining the reactions of phosphorus trichloride and for purifying volatile halides by distillation through a series of removable traps.

A small vacuum line, comprising only an oil pump,
diffusion pump, McLeod gauge, and liquid-air trap was used for pumping complexes free of solvents.

(g) Dry-Box

Before using, the dry-box was conditioned over-night with fresh phosphorus pentoxide.
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