

University of St Andrews



Full metadata for this thesis is available in
St Andrews Research Repository
at:

<http://research-repository.st-andrews.ac.uk/>

This thesis is protected by original copyright

Dedicated with love and gratitude to
my Mother and Father

INVESTIGATIONS INTO THE
STRUCTURE OF
CO-ORDINATION COMPOUNDS

being a Thesis

presented by

MICHAEL JOSEPH DEVENEY, B.Sc., M.Sc.

to the

University of St. Andrews

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

September, 1968

United College of St. Salvator
and St. Leonard, St. Andrews.



I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a higher degree.

The thesis describes results of research carried out in the Chemistry Department of the United College of St. Salvator and St. Leonard, University of St. Andrews, since 1st January, 1966, under the supervision of Dr. M. Webster.

I hereby certify that Michael Joseph Deveney has spent eleven terms at research work under my supervision, has fulfilled the conditions of Resolution of the University Court, 1967, No.I (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research

ACKNOWLEDGEMENTS

The author wishes to thank Dr. M. Webster for suggesting this topic of research, and for his ready guidance, constant enthusiasm and encouragement during the period in which this work was carried out.

Thanks are also due to many members of the Chemistry Department, for the time they have given to discussion of the problems which arose; particularly Dr. G.S. Harris who "adopted" me during the last year; and to Dr. R.S.Killean of the Physics Department for providing the use of both his expert crystallographic knowledge and equipment; and to Professor I.R. Beattie of Southampton University, for the use of Raman facilities.

I wish to express my gratitude to Professor J.I.G. Cadogan, in whose department this work was carried out; to Mrs Reid, and to all members of the technical staff, particularly Mr. D. McGee, whose glass-blowing skill was a great source of help.

The many friends I have made during the last three years, and my introduction to the ancient and noble pastime of St. Andrews, have helped make the last three years very pleasant ones.

Finally, and most important, I wish to express my deep gratitude and affection to Mary, for typing this thesis, and for translating it into English; and also for her encouragement and understanding at all times.

The receipt of financial support from the University of St. Andrews, during the tenure of this work is gratefully acknowledged.

Abbreviations used:

phen = 1,10-phenanthroline
bipy = 2,2'-bipyridyl
diamine = o-phenylenebisdimethylamine
diars = o-phenylenebisdimethylarsine
Py = pyridine

Spectroscopic

s = strong
m = medium
w = weak
v = very
br = broad

CONTENTS

<u>Section</u>	<u>Chapter</u>	<u>Title</u>	<u>Page</u>
		Summary	
	I	Introduction	1
I	2	Survey of addition compounds of pentahalides of group V.	7
	3	Addition compounds of phen and bipy with group VB pentachlorides.	42
	4	Reactions of diamine and diars with phosphorus and antimony pentachloride.	70
II	5	A study of the solid systems PCl_5-SnCl_4 .	97
III	6	Survey of addition compounds of the trichlorides of group VB.	124
	7	Some addition compounds of arsenic trichloride and tribromide.	157
IV	8	Experimental.	199
		Appendices I - IV.	235
		References	

SUMMARY

SUMMARY

The recent literature relating to complex formation by the pentahalides of group VA and VB, is reviewed, together with a survey of complex formation by the trihalides of phosphorus, arsenic, antimony and bismuth.

Adduct formation by the bidentate chelating ligands, 1,10-phenanthroline, 2,2'-bipyridyl, o-phenylenebisdimethylarsine (I) and o-phenylenebisdimethylamine (II), with phosphorus and antimony pentahalides has been investigated, and structures for the hitherto unknown compounds suggested on the basis of infrared and Raman spectroscopy. An oxidation/reduction reaction is postulated for the reaction of (I) and (II) with antimony pentachloride, to rationalize the experimental observations.

The trihalides of group VB with the same ligands have been found to give adducts of the type $MHal_3, \text{ligand}$ and $2MHal_3, \text{ligand}$. Infrared and Raman spectra of these compounds and $PyHMCl_4$ ($M = \text{As or Sb}$, $Py = \text{pyridine}$) are reported and discussed. In addition to spectral measurements, cryoscopic and conductometric techniques for solution studies have been undertaken.

The compound $AsCl_5, SbCl_5, AsCl_3$ has been prepared and characterized, and is formulated in the solid state as $(AsCl_4)^+(SbCl_6)^-AsCl_3$. Removal of the solvated $AsCl_3$ gives $AsCl_5, SbCl_5$, which has been shown to be $(AsCl_4)^+(SbCl_6)^-$.

The compounds $\text{PCl}_5, \text{SnCl}_4$ and $2\text{PCl}_5, \text{SnCl}_4$ have been studied spectroscopically, and have been found to exist in the solid state as $\text{PCl}_4^+ \text{SnCl}_5^-$ and $\text{PCl}_4^+ \text{SnCl}_6^{2-}$, respectively. A third compound, of stoichiometry $3\text{PCl}_5, 2\text{SnCl}_4$ was also isolated, and it is suggested that this may contain the ion $\text{Sn}_2\text{Cl}_{11}^{3-}$. Infrared studies indicate that complex formation takes place between PBr_5 and SnBr_4 in nitromethane, but solid complexes could not be isolated, nor could the nature of the species present in solution be established.

CHAPTER I

INTRODUCTION

I N T R O D U C T I O N

Infrared and Raman spectroscopy are well established techniques for the study of molecular vibrations. These two techniques are complementary, and the vibrational spectrum of a molecule is a combination of its infrared and Raman spectra. Of all vibrations only those which involve a change of dipole moment of the bond are infrared active. Raman activity requires a change in polarisability during the vibration. In a polyatomic molecule, having a centre of symmetry, only those vibrations which are symmetric with respect to the centre of symmetry (g vibrations) involve a change in the polarisability and are, therefore, Raman active. These symmetric vibrations are infrared inactive. Conversely, asymmetric vibrations (u, ungerade vibrations) are infrared active and Raman inactive. Thus, in an octahedral molecule of O_h symmetry such as $SbCl_6^-$, we have six fundamental frequencies. Three of these, V_1, V_2, V_5 are Raman active, whereas two, V_3 , and V_4 , are infrared active. The sixth is inactive. The combined use of these two techniques is, therefore, invaluable in the study of ions or molecules of this type.

Nearly all metal halogen vibrations occur below 700cm^{-1} , and many much lower than this. It is only as a result of instrumental developments, and the ready availability in recent years of commercial instruments which extend to 200cm^{-1} and even lower, that the study of metal halides and their complexes, by

infrared spectroscopy, has been possible.

In Raman spectroscopy it is a shift from the frequency of the exciting radiation which is being measured. Therefore, it has always been possible to obtain information about a lower wavelength region than was possible by infrared techniques. Experimental difficulties had, until recently, confined this technique to the hands of a few experts. The introduction of laser sources has revolutionized Raman spectroscopy. This new source, and the simplification in experimental techniques which it has introduced, is the subject of a recent paper³⁵⁷.

The study of metal halides and their complexes has been carried out by a number of workers, notably Beattie, Clark and Fowles in Britain, Christie in the United States and Dehnicke in Germany. These, and other workers, have successfully studied the structure and stereochemistry of a number of metal halide adducts. Beattie^{233,358} has shown that it is possible to identify cis and trans isomers of the type MX_4L_2 (fig.2, page 4). He has also indicated the value of elementary vibrational analysis in helping to make assignments of an observed spectrum.

One of the objects of the work carried out in this thesis was to investigate the structures of compounds formed between phosphorus pentachloride and stannic chloride, by means of vibrational spectroscopy. It was intended to determine the structure of the compounds reported in the literature^{256,259}, and also to investigate the stereochemistry involved. It was further intended to investigate the reported reaction²⁶², in solution, between phosphorus

pentabromide and stannic bromide, by these same techniques.

In a recent literature survey, Webster²³⁰ has shown that the pentahalides of group V form numerous adducts with a large variety of organic and inorganic molecules. Several different types of reaction can be noted in the formation of these complexes. The pentahalide can accept a halide ion forming MX_6^- . This type of reaction is particularly noted with antimony pentachloride; the chloride accepting ability of which is well known. This type of reaction has been identified by X-ray crystallography, for example $MeCO^+ SbCl_6^-$ ¹⁵². The pentahalide can act as a chloride ion donor. This is well established with phosphorus pentachloride. The PCl_4^+ ion has been identified in a number of compounds by a variety of techniques (table 7, chapter 2). Many of the organic molecules act as monodentate ligands giving rise to six-fold co-ordination around the metal atom (fig. 1, page 4). Several cases of autoionisation have been proposed, giving rise to structures of the type shown in fig. 2, page 4. This question is discussed in chapter 2. Recent work has shown that this concept is limited. With transition metal halides in dimethylformamide, Katzin¹⁶¹ has shown that autoionisation can occur. He predicts that solvents of low base strength, but a high dielectric constant, should, in general, favour autoionisation, or as he calls it, co-ordination disproportionation, of metal halides. Libus and Puchalska¹⁶² have recently demonstrated the same effect in the system $AlCl_3$, MeCN. In the examples discussed by these two authors^{161,162} it was found that both tetrahedral and octahedral species were present in the complex. Libus discusses the basic

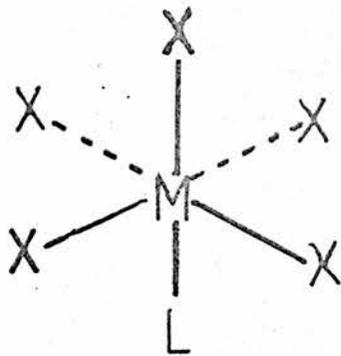


FIG. 1

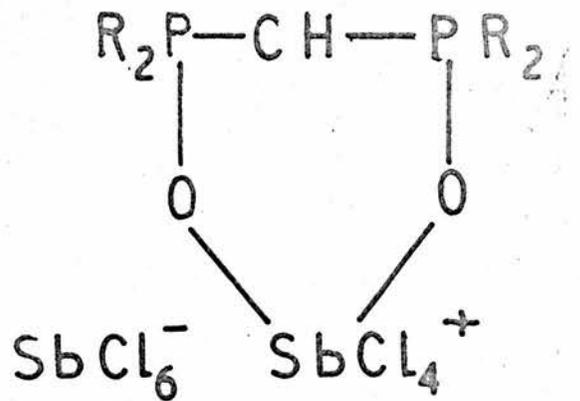


FIG. 3

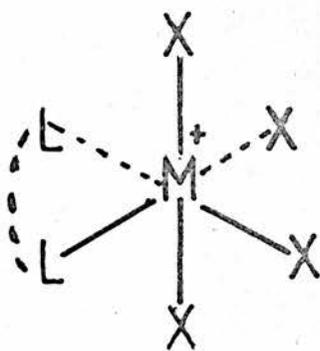


FIG. 2

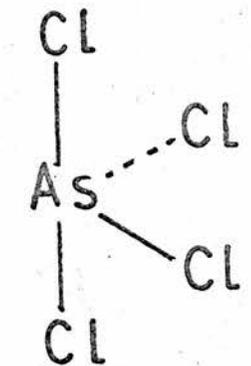
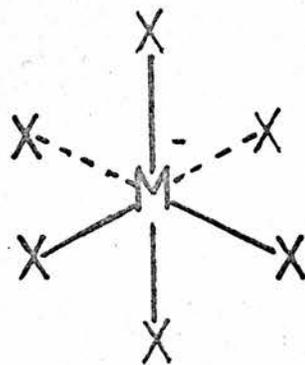


FIG. 4A

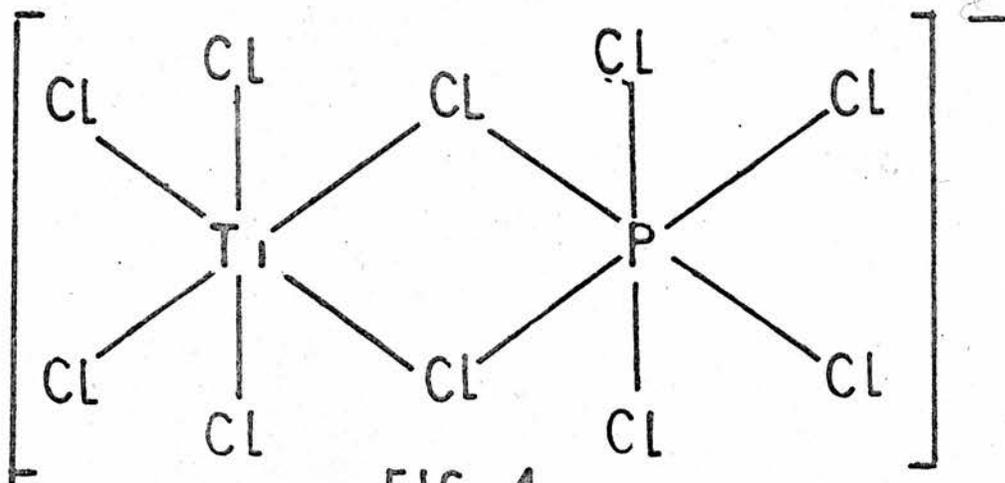


FIG. 4

relationship between the different configurations present, and concludes that it is unlikely that co-ordination disproportionation should, to any measurable extent, occur in systems in which complexes of only one configuration, either octahedral or tetrahedral, are formed. The configurations which have been proposed for the autoionisation of the group V pentahalides contain only octahedral species, which disagrees with this observation.

There have been no systematic studies using bidentate chelating ligands with any pentahalide of group VB. Walmsley and Tyree³⁵⁹ have reported the compound $R_2P(O)CH_2P(O)R_2 \cdot 2SbCl_5$ which is ionic, and this, together with the infrared spectrum of the P - O region, indicates the structure shown in fig. 3, page 4. A similar type of compound has been reported by Lindqvist³⁶⁰. Webster¹⁷ has reported the compound $(PCl_4^{phen})^+ SbCl_6^-$. The PCl_4^+ and $AsCl_4^+$ ions are well established, both by x-ray crystallography and by vibrational spectroscopy. The ion $SbCl_4^+$ has been reported in the compound $SbCl_4F$, but recent x-ray data²⁵² shows that it has a polymeric structure. These ions are isoelectronic with MCl_4 molecules, (M = Si, Ge, Sn), which all form octahedral compounds with bidentate chelating ligands. It therefore seems possible that MCl_4^+ ions might form stable ions with similar ligands. Thus it was of interest to investigate reactions of some bidentate ligands with group VB pentachlorides, and to determine the stereochemistry of the products by vibrational analysis. Besides the formation of ionic species there are other possibilities which must be considered, for example,

seven co-ordinate species might be formed, as with the compound NbCl_5 , diars⁷⁷, or an oxidation-reduction reaction between the ligand and the metal halide may occur.²⁰³ Section 1 of this thesis reports a spectroscopic study of the compounds formed between PCl_5 , SbCl_5 and AsCl_5 , SbCl_5 with bidentate ligands. Cryoscopic molecular weight and conductance measurements, in nitrobenzene, are also reported for these compounds.

The addition compounds of group VB pentahalides have been investigated structurally by a number of techniques²³⁰. In contrast, very little structural work has been reported on the trihalide adducts of the same group, although a large number of addition compounds have been reported in the literature. In section 3 of this thesis the literature is comprehensively surveyed from 1917 to June 1968, for addition compounds of group VB trihalides, and is briefly reviewed. A spectroscopic study is reported on a number of compounds of arsenic trichloride and tribromide, with bidentate chelating ligands. Cryoscopic molecular weight and conductance measurements are also reported in support of the stereochemistry suggested.

SECTION I

CHAPTER 2

Survey of addition compounds of
pentahalides of group V.

INTRODUCTION

In recent years several excellent reviews on the pentahalides of group V have appeared in the literature. George²²⁹ has reviewed the pentahalides and oxyhalides of group VB and VIB. Payne³¹⁸ has reviewed the halides of group VB. He discusses the trihalides and pentahalides, both with respect to their chemistry and the addition complexes they form. The latter forms the basis of a review by Webster²³⁰, who exhaustively surveyed the literature on addition complexes of group V pentahalides. More recently Kolditz²³¹ has discussed the halides of arsenic and antimony. Webster's literature survey is complete to December 1964. The following survey is intended to bring this review up to date, and it is intended that the literature should be complete up to, and including, June 1968.

This survey covers molecular addition compounds formed between group V pentahalides and any other molecule. It is generally agreed that the group V pentahalides act as acceptor molecules, and have well established Lewis acid behaviour. However, phosphorus pentachloride is a well established chloride ion donor. It is ionic in many of its complexes, where the PCl_4^+ ion has been shown unambiguously to be present²³⁰. It could be argued that phosphorus pentachloride acts as a donor in these circumstances, in fact it certainly donates a chloride ion.

Compounds are reported in which the participating molecules have no stable existence. For example, a number of addition

complexes of AsCl_5 are reported, even though AsCl_5 itself has been shown conclusively to be non-existent²³¹. Another example is $\text{NF}_5, \text{AsF}_5$ which was prepared by the reaction of nitrogen trifluoride, fluorine and arsenic pentafluoride in a glow discharge vessel at -78°C ¹³⁰.

The data is presented in tabular form, and the "other" molecule is listed under its chemical formula. In the "comments" column the proposed structure is given, although in many cases no structure has been proposed. Where necessary the chemical name of the molecule is also included. A brief discussion is given on each group of compounds with particular reference to stoichiometry, stereochemistry and structure, and to the state, solution or solid, to which the proposed structure refers. Care must be taken not to extrapolate a proposed structure from one state to another, for example, single crystal X-ray analysis shows the compound 2,2'-bipyridyl- AsCl_3 to be molecular in the solid state, with a dimeric chlorine bridged structure, in which each arsenic atom is six co-ordinate³²⁰; whereas in nitrobenzene it behaves as a 1:1 electrolyte.

The Pentafluorides of Group V

Most of the reported adducts of the pentafluorides have a 1:1 stoichiometry. In most cases where other stoichiometries have been reported no structure has been determined or even postulated. In some cases fluorine bridged structures may be involved. A recent X-ray study by Edwards³¹⁶ has shown the existence of the ion $\text{Nb}_2\text{F}_{11}^-$,

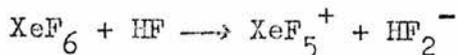
in which each niobium atom is surrounded by a sextet of fluorine atoms in a regular octahedron, with one bridging fluorine atom. He considers this to be a fragment of the NbF_5 tetramer. The ion $\text{Sb}_2\text{F}_{11}^-$ seems to be reasonably well established by i.r. and n.m.r. techniques^{59,60,67}. Gillespie and Moss⁶⁰, from n.m.r. studies, propose the following equilibria



Weidlein and Dehnicke¹⁰¹, on the basis of infrared studies, propose that the ions $\text{Sb}_2\text{F}_{11}^-$ and $\text{Sb}_3\text{F}_{16}^-$ are present in the compounds $\text{VO}_2\text{F} \cdot 2\text{SbF}_5$ and $\text{VO}_2\text{F} \cdot 3\text{SbF}_5$.

The recently discovered inert gas fluorides form a number of interesting addition compounds with the pentafluorides of group V. Gard and Cady² report the crystalline solids $\text{XeF}_6 \cdot 2\text{SbF}_5$, $\text{XeF}_6 \cdot \text{SbF}_5$ and $2\text{XeF}_6 \cdot \text{SbF}_5$. Malm¹⁵⁰ has prepared the compound $\text{XeF}_6 \cdot \text{AsF}_5$, whereas Pullen and Cady⁸⁶ found the compounds $2\text{XeF}_6 \cdot \text{AsF}_5$. With PF_5 they only found the 2:1 adduct.

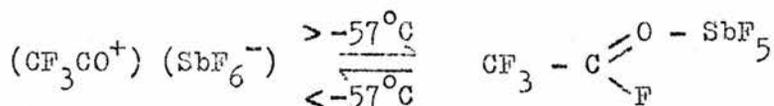
Xenon difluoride and krypton difluoride form a number of compounds of varying stoichiometry with the group V pentafluorides. Cohen and Peacock¹⁰³, on the basis of ^{19}F n.m.r. spectroscopy, propose the structure $\text{F}_5\text{SbFXeF} \cdot \text{SbF}_5$ and this is the only structural work appearing on these compounds to date. Xenon hexafluoride is highly conducting in anhydrous HF, and this has been explained on the basis of the following ionisation reaction :



The XeF_5^+ ion has also been found in the compound $\text{XeF}_5^+ \cdot \text{BF}_4^-$, using

infrared and Raman techniques²²⁷. It seems possible that the structures of the above reported adducts will be ionic, and may well contain fluorine bridged ions. However, further work, such as conductivity measurements and structural determinations, is certainly required to resolve this problem. In this respect, recent work by Martin³¹¹ has shown that in bromine trifluoride the adducts XeF_2, MF_5 ($M = P, As, Sb$) are ionic. No structure has been postulated, nor is there any evidence to indicate that interaction with the solvent is not involved.

Many of the reported adducts are with fluorine containing donors. The structures of these adducts are, in most cases, ionic containing the MF_6^- ion. Thus they exhibit the well established fluoride ion accepting ability of the MF_5 molecules. It is interesting in this respect to note the temperature dependence of the system:



as postulated by Lindner³¹⁰. Edwards and Jones⁹² determined the crystal structure of BrF_3, SbF_5 . They found it to contain some covalent character. This gives rise to square planar BrF_4 units which are linked through cis bridging fluorine atoms to the octahedral SbF_6^- ion. They point out that this fluorine bridging is comparatively weak. The same authors³¹⁶ have recently determined the structure of the complex $SeF_4, 2NbF_5$, by the same technique.

This structure is ionic, $SeF_3^+ Nb_2F_{11}^-$, and once again contains some

degree of covalent character. Copeland et. al.³³ have published X-ray data on $\text{PyH}^+ \text{MF}_6^-$ (Py = pyridine, M = P, As, Sb). X-ray work has also been used to establish the structures of $\text{NF}_4^+ \text{AsF}_6^-$ ⁽⁸⁸⁾, $\text{CH}_3\text{CO}^+ \text{SbF}_6^-$ ⁽³⁴⁾, $(\text{CH}_3)_2\text{CHCO}^+ \text{SbF}_6^-$ ⁽¹²¹⁾ and $\text{SbF}_5 \cdot \text{SO}_2$ ⁽³¹²⁾

Infrared and Raman spectroscopy are well established tools in structural determinations. This method is well illustrated in the text by Nakamoto²³². Pitts et.al.⁴¹ have shown that the complex $\text{IO}_2\text{F} \cdot \text{AsF}_5$ is $\text{IO}_2^+ \text{AsF}_6^-$ by infrared methods, and not the previously reported $\text{IO}_2\text{F}_2^- \text{AsF}_4^+$. Christie and his co-workers^{42,44,54,314} have made use of the same technique to determine the structures $\text{ClF}_2^+ \text{PF}_6^-$, $\text{ClF}_2^+ \text{AsF}_6^-$, $\text{NF}_4^+ \text{AsF}_6^-$ and $\text{IF}_6^+ \text{AsF}_6^-$.

Another tool which has proved to be of great value in structural determinations of these pentafluorides is ^{19}F . n.m.r. spectroscopy. In the 1:1 addition complexes of PF_5 and HCONMe_2 ⁽⁶⁾ and dimethyl formamide (D.M.F.) it has been used to show that bonding takes place through the carbonyl oxygen. Hatton¹² studied solutions of NbF_5 and TaF_5 in Et_2O and EtOH by this method, and suggests that ionic complexes such as $\text{NbF}_4(\text{EtOH})_2^+ \text{NbF}_6^-$, exist in solution.

The pentafluorides of phosphorus, arsenic and antimony all form 1:1 addition complexes with methyl cyanide. There seems to be considerable controversy in the literature concerning the nature of these adducts, both in solution and in the solid state. Muettterties and his co-workers^{90,226}, using ^{19}F . n.m.r. spectroscopy, could find no evidence for the MF_6^- ion, and proposed a molecular structure based on an octahedral central atom. Kolditz³¹, on the other hand,

found the 1:1 addition complexes to be good conductors in acetonitrile and on this basis and hydrolysis experiments, proposed the equilibrium $2MF_5 \cdot CH_3CN \rightleftharpoons MF_4(CH_3CN)_2^+ + MF_6^-$. In the case of $M = Sb$ the equilibrium is shifted to the molecular side. Kolditz¹²⁵ reinvestigated the problem using ^{31}P . n.m.r. He suggests that the coupling constant found; +146ppm. (with 85% H_3PO_4 as reference) indicates the presence of PF_6^- . However, he goes on to say that the sextet observed (with intensities 1:5:10:10:5:1) show the presence, not of six but five fluorine atoms around the phosphorus. He points out that the equilibrium proposed has now shifted to the molecular side because of the high concentration (18%) used in n.m.r. measurements. The n.m.r. technique is not sufficiently sensitive to detect small amounts of PF_6^- ion which would be expected due to the above equilibrium. In this work attempts were made to react PF_5 with bidentate chelating ligands (phen., diamine.), but no compounds could be obtained. It was felt that if such autoionisation did take place then PF_5 should readily react with these donor molecules.

Conductivity measurements are made in very dilute solutions, and great care must be taken to exclude water. The adduct $SbCl_5 \cdot CH_3CN$, on the basis of conductivity measurements was suggested to exist in solution as $SbCl_4(CH_3CN)_2^+ SbCl_6^-$ ^{247,248}. Recent X-ray work¹¹³ has shown the solid to be molecular, and this is supported by N.Q.R. studies¹³⁷. A reinvestigation of the conductivity carried out in a vacuum line under strictly anhydrous conditions, showed that $SbCl_5$ is a very weak electrolyte in

acetonitrile³⁴⁶. A value $\Lambda_{.01} = 23 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ was found. It may well be that future investigations will show that even this value is too high. The possibility of both impurities interfering, and hydrolysis taking place, in this type of work, cannot be overstressed.

The whole question of autoionisation of the pentafluorides, and their addition complexes, in solution, is still unsolved. Muetterties²²⁸ carried out a molecular weight determination in acetonitrile (ebulliometric), of the complex $\text{PF}_5 \cdot \text{N}(\text{CH}_3)_3$, and found it to be monomeric; whereas Kolditz and Rehak³¹ found it gave conducting solutions in acetonitrile ($\Lambda_{0.01\text{m}} = 53 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$). Further structural studies on these compounds, both in solution and in the solid state, are obviously required to solve this problem.

Phosphorus Pentachloride and Bromide

It is well established that phosphorus pentachloride exists, both in a molecular and ionic form. Several studies of the vibrational spectrum of both these forms have recently been reported^{233,234,235}. It is interesting to note that most of the reported adducts of PCl_5 are ionic. PCl_5 appears to lose a chloride ion easily, and many of the formulated ionic species contain the PCl_4^+ ion. It appears that the PCl_4^+ ion is more stable to hydrolysis than the PCl_6^- ion, which is only formed in the presence of strong chloride donors. Beattie²³³ has shown that the adduct $\text{PCl}_5 \cdot \text{AsCl}_5$ exists as $\text{PCl}_4^+ \text{AsCl}_6^-$, and not the previously reported

$\text{AsCl}_4^+ \text{PCl}_6^-$ ²⁴⁰. This is confirmed by the work of Wicker and Grimmer¹⁵⁷, who proposed the same structure on the results of ³¹P. n.m.r. studies. These authors claim that PCl_6^- is formed photo-chemically in a Raman beam, according to the equation:



Beattie experienced considerable difficulty in preparing this compound, and wrote it as $\text{PCl}_4^+ x\text{AsCl}_6^-, (1+x)\text{PCl}_6^-$. The peak he observed at 392cm^{-1} in the Raman may well be due to AsCl_3 as outlined above. Wicker and Grimmer have also studied the compounds $\text{TiCl}_4, \text{PCl}_5$ and $\text{TiCl}_4 \cdot 2\text{PCl}_5$. On the basis of ³¹P. n.m.r. results, they postulate the former as $\text{PCl}_4^+ \text{TiCl}_5^-$. In the n.m.r. spectrum of the latter compound, they observed two phosphorus signals of equal intensity, one due to PCl_4^+ , and the other with a chemical shift (relative to 85% H_3PO_4) very similar to that of PCl_6^- . They, therefore, postulate the structure as $\text{PCl}_4^+ \text{TiPCl}_{10}^-$, see fig.4, page 4. This is in contrast to the structure, $2\text{PCl}_4^+ \text{TiCl}_6^{2-}$, proposed by Slawish⁷². The same authors³¹³ have also investigated the system $\text{PCl}_5\text{-SnCl}_4$. The 2:1 compound they report as $2\text{PCl}_4^+ \text{SnCl}_6^{2-}$, but they were unable to decide the structure of the 1:1 complex. A study of this same system has been reported in this work. Vibrational spectroscopy indicates the structure of these two compounds to be: (1:1), $\text{PCl}_4^+ \text{SnCl}_5^-$; and (2:1), $2\text{PCl}_4^+ \text{SnCl}_6^{2-}$. Gerding¹⁴¹ has studied a number of addition compounds of PCl_5 with MCl_n ($n = 3, 4, 5$). Using infrared and Raman spectroscopy, he established the structures to be of the type $\text{PCl}_4^+ \text{MCl}_{n+1}^-$.

A vibrational study of the complex $\text{ClN}(\text{PCl}_3)_2 \cdot \text{PCl}_5$ established the presence of the hexaphosphorus (V) chloride ion⁷³, whilst nuclear quadrupole resonance studies⁶⁸, and vibrational analysis, showed the complex $\text{Et}_4\text{NCl} \cdot \text{PCl}_5$, to have the structure $\text{Et}_4\text{N}^+\text{PCl}_6^-$.

In this work it has been shown that PCl_5 reacts with the bidentate ligands 1,10-phenanthroline, 2,2'-bipyridyl and *o*-phenylenebisdimethylamine (L), to give 1:1 adducts which are formulated as $\text{LPCl}_4^+\text{Cl}^-$, whilst with *o*-phenylenebisdimethylarsine reduction to PCl_3 takes place. This last reaction confirms the work of Sutton²⁰³.

The only addition compound of phosphorus pentabromide to appear recently in the literature is $\text{PBr}_5 \cdot \text{Br}_2$. Both X-ray crystal structure⁸⁵ and conductivity combined with freezing point data in nitrobenzene⁹⁸ show the compound to be ionic $\text{PBr}_4^+\text{Br}_3^-$.

Arsenic Pentachloride

Whereas PCl_5 and SbCl_5 are stable, arsenic (V) chloride has never been isolated. Many efforts have been made to isolate this compound without success. Beattie²³³ has calculated the fundamental vibrational spectrum of this hypothetical molecule, and suggests that a small quantity, in equilibrium with its dissociation products, may be detected in the future. However, the system $\text{AsCl}_3 \cdot \text{Cl}_2$ has a simple eutectic which does not give any indication of compound formation²³⁹. Careful vapour pressure measurements²⁴¹ on the same

system, and negligible chloride exchange between radioactive chlorine and arsenic trichloride²⁴², confirm this finding. Various explanations have been proposed for the non existence of AsCl_5 . The large energy differences between the 4s - 4p and 4d orbitals in arsenic have been put forward as a possible explanation³¹⁸. Drago³¹⁷, on the other hand, gives a thermodynamic discussion of this problem.

Although AsCl_5 is non existent, the ion AsCl_4^+ is well known, and more recently, the ion AsCl_6^- has been identified. The ion AsCl_4^+ is tetrahedral (T_d) and its fundamental vibrational spectrum has been reported by Dehnicke²³⁸, and confirmed by Beattie²³³. Beattie also reports the fundamental frequencies of the ion AsCl_6^- , observed in the compound $\text{Et}_4\text{NAsCl}_6$, which was prepared by Schmulbach¹⁶.

Schmulbach has pointed out that there are three ways of stabilising arsenic (V) chloride by complexation. They are:

1. $\text{AsCl}_3 + \text{Cl}_2 + \text{MCl}_n = (\text{AsCl}_4^+)(\text{MCl}_{n+1}^-)$
2. $\text{AsCl}_3 + \text{Cl}_2 + (\text{Q}^+)(\text{Cl}^-) = \text{Q}^+ \text{AsCl}_6^-$
3. $\text{AsCl}_3 \text{xD} + \text{Cl}_2 = \text{AsCl}_5 \text{yD} + (\text{x-y})\text{D}$

Q is any bulky cation, whilst D is a neutral ligand.

Nearly all of the early work on stabilising AsCl_5 was by method 1.²³⁰, which may well account for the large number of compounds containing AsCl_4^+ compared to the number containing AsCl_6^- . It seems to be well established that the PCl_4^+ ion is more stable than PCl_6^- , whereas the opposite appears to apply in the case of the antimony analogues, if indeed, any SbCl_4^+ compounds are known.

Antimony Pentachloride

Because of its powerful acceptor properties, adducts of antimony pentachloride have been far more widely investigated than any other group V pentahalides. Adducts with more than three hundred molecules have appeared in the literature. Because of this large number it is convenient to classify the compounds into groups, depending on the type of donor molecule. The following classification has been used:

1. Solvates, i.e. the donor molecule, usually a Lewis base, is a standard solvent.

2. Lewis Bases. This group is, by far, the largest in the present classification, with co-ordination from nitrogen or oxygen atoms. Co-ordination from phosphorus, arsenic and sulphur atoms have also been reported ²³⁰.

3. Chloride Ion Donors. This may be sub-divided into (a) inorganic chloride ion donors, (b) organic chloride ion donors.

4. Bidentate ligands.

5. Stabilisation of an organic cation or radical with SbCl_6^- .

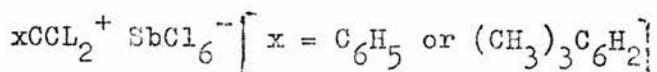
It must be pointed out that this classification is arbitrary. With the possible exception of section five, nearly all the compounds formed show Lewis acid-base behaviour.

The solvates, in most cases, appear to be straightforward Lewis bases donating through oxygen or nitrogen. However, Paul²⁴ reports adducts with acetamide with the stoichiometries 1:2 and 1:5. He reports that they are ionic, but makes no attempt to rationalize the unusual stoichiometry. The same author²⁴⁴ reports a 1:1 adduct with HOAc which is also ionic. Again he makes no attempt to propose a structure. Jain¹⁵ reports a number of 2:1 complexes of SbCl_5 . In an earlier paper he suggests a species containing 7 co-ordinate antimony, but later, on the basis of molecular weight measurements, he suggests that they are 1:1 adducts with a second donor molecule loosely held.

Gutmann^{47,48} and Kazitsyna^{99,219,220} have reported a number of adducts with organic azo groups. Infrared studies indicate that bonding takes place through the azo group.

Thayer and West⁴ report the interesting series $(\text{CH}_3)_3\text{MN}_3, \text{SbCl}_5$ (M= Si, Ge, Sn). They show that coordination takes place through the α nitrogen atom. The series of hydrazides reported by Paul¹⁰² are of interest in that they act as bidentate ligands, but each carbonyl oxygen donates to a different antimony pentachloride molecule.

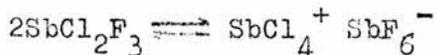
Volz^{61,62} has made some interesting studies on mono substituted carbon tetrachloride. Carbon tetrachloride is unaffected by antimony pentachloride but substitution of one of the chlorine atoms by a phenyl or mesityl group makes the removal of a chloride ion possible, forming:



Gutmann²⁰ and Masaguer²⁶ have produced a number of compounds of transition metal ions. Antimony pentachloride reacts with the metal halide to produce M^{n+} which is then stabilised by 6 methyl cyanide (solvent) molecules presumably in an octahedral disposition.

With the characterization of $SbCl_5, MeCN$ as molecular, rather than ionic species, it now seems doubtful if any monodentate ligand does, in fact, cause autoionisation, giving rise to structures of the type $MX_4 2L^+ MX_6^-$. Bidentate ligands, however, seem capable of producing species of the type $LSbCl_4^+ SbCl_6^-$. Webster²³⁷ has reported the 2:1 adduct between $SbCl_5$ and 1,10-phenanthroline. Infrared and Raman data indicate a structure of the type outlined above. Bott^{3,64} has indicated similar structures with bidentate ligands.

Although PCl_4^+ and $AsCl_4^+$ ions are well known there is very little evidence to support the existence of the anion $SbCl_4^+$. Conductivity measurements in SO_2 suggest the equilibrium:



This equilibrium, however, lies to the left, indicating mainly a molecular compound. Dehnicke and Weidlein²⁵⁰, on the basis of a spectroscopic investigation, indicate that the molecular form is present in the crystalline substance. More recently, the same authors²⁵¹ proposed an ionic structure for $SbCl_4F$, namely $SbCl_4^+ F^-$. Preiss²⁵², however, undertook an X-ray crystal structure and found it to be a polymeric fluorine bridged structure, isomorphous with the tetramer $TaCl_4F$ ²⁵³.

The Pentachlorides and Pentabromides of Niobium and Tantalum

Adduct formation is observed through a variety of donors in these pentahalides. Oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic, antimony and bismuth all appear capable of donating an electron pair to the above mentioned halides.

Fowles^{224,225} has carried out some very interesting work on the acceptor properties of these pentahalides. It was originally suggested²⁴⁶ that vanadium, niobium and tantalum belong to class A. acceptors, i.e. they fall into the 'hard' category in the 'soft hard acid base concept' (SHAB). Thus they should combine most readily with donors of the first row of the periodic table. Fowles and his co-workers have prepared adducts of these pentahalides with dioxan, thioxan, selenoxan, pentamethylenesulphide, pentamethyleneoxide and tetrahydrothiophen. Infrared and n.m.r. indicate that bonding takes place through the sulphur or selenium rather than through the oxygen. Thus, when combined with chlorides and bromides, these metals behave as 'soft' (B) acids.

Desnoyers⁷⁸ has prepared a series of complexes $(C_6H_5)_3M$ where (M = N, P, As, Sb, Bi). They form 1:1 and 1:2 complexes with $NbCl_5$. The 1:1 adducts are possibly based on six co-ordinate niobium, but no rationalisation of either type has been proposed.

Nyholm⁷⁷ has prepared and characterised the very interesting 1:1 adducts between NbX_5 (X = Cl, Br) and o-phenylenobisdimethylarsine. These compounds appear to be monomeric seven co-ordinate species. This is the only case of a group V pentahalide forming a molecular compound with a bidentate chelating ligand.

TABLE 1: Addition Compounds of PF₅

Other Molecules (L)	Ratios PF ₅ :L	Reference	Comments
HCONMe ₂	1:1	6	n.m.r. in solution shows bonding through the oxygen
CH ₃ PF ₄	1:1	7	
(CH ₃) ₂ PF ₃	1:1	7	
CH ₃ CN	1:1	31,139 90,125	Conductivity measurements suggest PF ₄ ^{2L+} PF ₆ ⁻
N(CH ₃) ₃	1:1	31,228 35	(PF ₄ ^{2L}) ⁺ PF ₆ ⁻
C ₅ H ₆ NF	1:1	33	PyH ⁺ PF ₆ ⁻ , X-ray structure
R ₂ O	1:1	35,36 37,38,68	R=CH ₃ , C ₂ H ₅ , n-C ₃ H ₇ , i-C ₃ H ₇ n-C ₄ H ₉
R ₂ S	1:1	35 38	R=CH ₃ , C ₂ H ₅ R=CH ₃
(CH ₃) ₃ SF	1:1	38	(CH ₃) ₃ S ⁺ PF ₆ ⁻
Me ₂ Se	1:1	35	
NEt ₃	1:1	35	
ClF ₃	1:1	44	ClF ₂ ⁺ PF ₆ ⁻ . I.R.
NO ₂ F	1:1	82	NO ₂ ⁺ PF ₆ ⁻
NOF	1:1	82 134	NO ⁺ PF ₆ ⁻
XeF ₆	1:2	86	
VF ₄	1:1	117	VF ₃ ⁺ PF ₆ ⁻
(D.M.F.)C ₃ H ₇ NO	1:1	140	n.m.r. shows bonding through carbonyl oxygen
CH ₃ COF	1:1	310	

TABLE 1: Continued

Other Molecules (L)	Ratios PF ₅ :L	Reference	Comments
PCl ₄ F	1:1	142	PCl ₄ ⁺ PF ₆ ⁻
Et ₃ PClF	1:1	142	Et ₃ PCl ⁺ PF ₆ ⁻
XeF ₂	1:1 1:2	311	Electrolytes in BrF ₃

TABLE 2: Addition Compounds of AsF₅

Other Molecules (L)	Ratios AsF ₅ :L	Reference	Comments
HCONMe ₂	1:1	6,140	n.m.r.
MeCN	1:1	31 90	AsF ₄ 2L ⁺ AsF ₆ ⁻ molecular
NMe ₃	1:1	31	AsF ₄ 2L ⁺ AsF ₆ ⁻
SO ₂	1:1	31	2AsF ₅ L ⇌ AsF ₄ 2L ⁺ AsF ₆ ⁻
XeOF ₄	unstable adduct	32 150	
PyHF	1:1	33	PyH ⁺ AsF ₆ ⁻ crystal structure
IO ₂ F	1:1	41	IO ₂ ⁺ AsF ₆ ⁻ by infrared
ClF ₃	1:1	42,44	ClF ₂ ⁺ AsF ₆ ⁻ by infrared
IF ₃	1:1	45	IF ₂ ⁺ AsF ₆ ⁻ proposed
NF ₅	1:1	53,130 88,126	NF ₄ ⁺ AsF ₆ ⁻
F ₃ NO	1:1	55	F ₂ NO ⁺ AsF ₆ ⁻ ¹⁹ F.n.m.r.

TABLE 2: Continued

Other Molecule (L)	Ratio AsF ₅ :L	Reference	Comments
NO ₂ F	1:1	82	NO ₂ ⁺ AsF ₆ ⁻
NOF	1:1	82	NO ⁺ AsF ₆ ⁻
XeF ₆	1:2	86 87,150	
XeF ₂	1:1	311	Electrolyte in BrF ₃
N ₂ F ₄	2:1 1:1	89	N ₂ F ₃ ⁺ AsF ₆ ⁻
SCl ₃ F	1:1	91	SCl ₃ ⁺ AsF ₆ ⁻ by infrared and Raman
SeCl ₃ F	1:1	91	SeCl ₃ ⁺ AsF ₆ ⁻
TeCl ₃ F	1:1	91	TeCl ₃ ⁺ AsF ₆ ⁻
BrF ₃	1:1	92	BrF ₂ ⁺ AsF ₆ ⁻ crystal structure
AsCl ₄ F	1:1	109	AsCl ₄ ⁺ AsF ₆ ⁻
VF ₄	1:1	117	VF ₃ ⁺ AsF ₆ ⁻
IF ₇	1:1	314	IF ₆ ⁺ AsF ₆ ⁻ by infrared and Raman
CsF	1:1	435	Infrared and Raman of AsF ₆ ⁻
NO ₂	No reaction	151	

TABLE 3: Addition Compounds of SbF₅

Other Molecule (L)	Ratio SbF ₅ :L	Reference	Comments
XeF ₆	1:1 1:2 2:1	2	
XeF ₂	1:1 3:2 2:1 6:1	103,136,311 136 136 136	Study of the binary system
KrF ₂	1:1 2:1	150	
Me ₂ PF ₃	1:1	7	
EtPF ₄	1:1	7	
MePF ₄	1:1	7	
HCONMe ₂ (D.M.F.)	1:1	140,6	n.m.r. shows that bonding is through the carbonyl oxygen
Et ₃ N	1:1	12	
N ₂ F ₄	2:1 3:2	13,59	N ₂ F ₃ ⁺ Sb ₂ F ₁₁ ⁻
N ₂ F ₂	2:1	59,149 67	N ₂ F ⁺ Sb ₂ F ₁₁ ⁻
NF ₃	1:1	53	NF ₂ ⁺ SbF ₆ ⁻
NF ₅	1:1	53	NF ₄ ⁺ SbF ₆ ⁻
ClF ₃	1:1	44	ClF ₂ ⁺ SbF ₆ ⁻
BrF ₃	1:1	92	crystal structure
IF ₃	1:1	45	IF ₂ ⁺ SbF ₆ ⁻
S ₄ N ₄	1:1 4:1	104,21 21	

TABLE 3: Continued

Other Molecule (L)	Ratio SbF ₅ :L	Reference	Comments
CH ₃ CN	1:1	31 90	Ionic SbF ₄ ^{2L+} SbF ₆ ⁻ molecular
C ₄ H ₈ O ₂	1:1	31	
C ₅ H ₅ N	1:1	31	
BiF ₅	2:1	31	
XeOF ₄	2:1	32,150	
PyFH	1:1	33	PyH ⁺ SbF ₆ ⁻ , crystal structure
CH ₃ COF	1:1	34	CH ₃ CO ⁺ SbF ₆ ⁻ , crystal structure
HF	1:1 1:2	12 60	Ionic H ₂ F ⁺ SbF ₆ ⁻
F ₃ NO	1:1	55	F ₂ NO ⁺ SbF ₆ ⁻
(CH ₂) _n (COF) ₂	2:1	56	SbF ₆ ⁻ CC(CH ₂) _n CO ⁺ SbF ₆ ⁻ n=0-7 by I.R. and n.m.r.
(CH ₂) _n CHCOF	1:1	58	(CH ₂) _n CHCO ⁺ SbF ₆ ⁻ . n=2-10
SbF ₆ ⁻	1:n	149,60	(Sb _{n+1} F _{5n+1}) ⁻
NO ₂ F	1:1	82	NO ₂ ⁺ SbF ₆ ⁻
NOF	1:1	82	NO ⁺ SbF ₆ ⁻
VO ₂ F	1:1	101	VO ₂ ⁺ SbF ₆ ⁻
	3:1	101	VO ₂ ⁺ Sb ₃ F ₁₆ ⁻
	2:1	101	VO ₂ ⁺ Sb ₂ F ₁₁ ⁻
TiOF ₂	2:1	101	TiO ²⁺ 2SbF ₆ ⁻
RR'C:CR''COF	1:1	107	RR':CR''CO ⁺ SbF ₆ ⁻
VF ₄	1:1	117	VF ₃ ⁺ SbF ₆ ⁻

TABLE 3: Continued

Other Molecule (L)	Ratio SbF ₅ :L	Reference	Comments
HSO ₃ F	1:2	245	H ₂ SO ₃ F ⁺ (SbF ₅ SO ₃ F) ⁻
CH ₃ COF	1:1	310	CF ₃ -C≡O ⁺ SbF ₆ ⁻
C ₂ H ₅ COF	1:1	310	
CF ₃ COF	1:1	310	
C ₂ F ₅ COF	1:1	310	
SO ₂	1:1	312	X-ray structure
SF ₄	1:1	423	SF ₃ ⁺ SbF ₆ ⁻ Raman spectroscopy
SeF ₄	1:1		SeF ₃ ⁺ SbF ₆ ⁻
TeF ₄	1:1		possibly molecular
LiF	1:1	435	I.R. and Raman of SbF ₆ ⁻

TABLE 4. Addition Compounds of NbF₅

Other Molecules (L)	Ratio NbF ₅ :L	Reference	Comments
Et ₂ O	1:1	12,94	n.m.r. solution
EtOH	1:1	12	n.m.r. NbF ₄ (EtOH) ₂ ⁺ NbF ₆ ⁻
NEt ₃	1:1	12	
Me ₂ O	1:1 1:2	94	Indicated by V.P. studies
Me ₂ S	1:1 1:2	94	
Et ₂ S	1:1	94,80	
T.H.F.	1:2	94	
Me ₂ SO	1:2	79	M.pt. 44°C. Liquid has a high conductance.
SeF ₄	1:1 2:1	316 316	SeF ₃ ⁺ NbF ₆ ⁻ . X-ray structure SeF ₃ ⁺ Nb ₂ F ₁₁ ⁻
SeOF ₂	1:1	316	
EtNH ₂	1:1	319	
Et ₂ NH	1:1	319	
Et ₃ N	1:1	319	

TABLE 5: Addition Compounds of TaF₅

Other Molecules (L)	Ratio TaF ₅ :L	Reference	Comments
Et ₂ O	1:1	12,94.	n.m.r. solution
Me ₂ O	1:1	94	1:2 indicated only by vapour pressure measurements
	1:2		
Me ₂ S	1:1	94	
	1:2	94	
Et ₂ S	1:1	94	
T.H.F.	1:2	94	
XeF ₂	2:1	81	
NaF	1:1	315	Na ⁺ TaF ₆ ⁻
	1:2		2Na ⁺ TaF ₇ ²⁻
	1:3		3Na ⁺ TaF ₈ ³⁻
EtNH ₂	1:1	319	
Et ₂ NH	1:1	319	
Et ₃ N	1:1	319	

TABLE 6: Addition Compounds of VF₅

(L)	VF ₅ :L	115
XeF ₆	1:2	115
XeOF ₅	1:2	115

TABLE 7: Addition Compounds of PCl_5

Other Molecule (L)	Ratio $\text{PCl}_5:\text{L}$	Reference	Comments
SbCl_5	1:1	17,141	$\text{PCl}_4^+ \text{SbCl}_6^-$
$\text{SbCl}_5:\text{phen}$	1:1:1	17	$\text{LPCl}_4^+ \text{SbCl}_6^-$
T.H.F. SbCl_5	1:2:1	17	$(\text{PCl}_4^+)_2 \text{SbCl}_6^-$ in solution
Py, SbCl_5	1:2:1	17	
T.H.T. SbCl_5	1:2:1	17	In soln. a trans. adduct
Phen.	1:1	18	$\text{LPCl}_4^+ \text{Cl}^-$
$\text{Me}(\text{CH}_2)_n \text{CH}_2 \text{C}:\text{CH}$	2:1	39	$[\text{Me}(\text{CH}_2)_n \text{CH}:\text{CClCH}_2 \text{PCl}_3]^+ \text{PCl}_6^-$
$\text{C}_{15}\text{H}_{10}\text{O}$	1:1	40	
EtOAc	..	69	
$(\phi_3\text{O})_3\text{PCl}_2$	1:1	70	$(\phi_3\text{O})_3\text{PCl}^+ \text{PCl}_6^-$
TiCl_4	1:1	313	$\text{PCl}_4^+ \text{TiCl}_5^-$ n.m.r.
	2:1	72,313	$(\text{PCl}_4^+)_2 \text{TiCl}_6^{2-}$
$\text{ClN}(\text{PCl}_3)_2$	1:1	73	$\text{N}(\text{PCl}_3)_2^+ \text{PCl}_6^-$
$(\text{C}_2\text{H}_5)_4\text{NCl}$	1:1	68	$\text{Et}_4\text{N}^+ \text{PCl}_6^-$ from N.Q.R.
TeCl_4	1:1	83	$\text{PCl}_4^+ \text{TeCl}_5^-$
$\text{C}_5\text{H}_5\text{N}$	1:1	125	^{31}P .n.m.r. study
BCl_3	1:1	137,141	X-ray powder data
AlCl_3	1:1	141	Vibrational spectra used
SeCl_4	1:1	141	to determine structures.
TeCl_4	1:1	141	All are: $\text{PCl}_4^+ \text{MCl}_{n+1}^-$
GaCl_3	1:1	141	

TABLE 7: Continued

Other Molecules (L)	Ratio PCl ₅ :L	Reference	Comments
Crystal Violet	1:1	143	
TaCl ₅	1:1	156	PCl ₄ ⁺ TaCl ₆ ⁻ i.r. and R.
AsCl ₅	1:1	157,233	PCl ₄ ⁺ AsCl ₆ ⁻ ³¹ P. n.m.r.
SnCl ₄	1:1	This work, 313	PCl ₄ ⁺ SnCl ₅ ⁻ i.r. and R
	2:1		2PCl ₄ ⁺ SnCl ₆ ²⁻

TABLE 8: Addition Compounds of PBr₅

(L)	PBr ₅ :L		
Br ₂	1:1	85	PBr ₄ ⁺ Br ₃ ⁻ crystal structure
		98	PBr ₄ ⁺ Br ₃ ⁻ in ϕ NO ₂

TABLE 9: Addition Compounds of AsCl₅

(L)	AsCl ₅ :L		
(C ₆ H ₅) ₃ PO	1:2	16	(AsCl ₄ 2L) ⁺ Cl ⁻
Et ₄ NCl	1:1	16,91,233	Et ₄ N ⁺ AsCl ₆ ⁻
SbCl ₅	1:1	18,233,237	AsCl ₄ ⁺ SbCl ₆ ⁻ i.r. and R.
SbCl ₅ AsCl ₃	1:1:1	156,18,237	AsCl ₄ ⁺ SbCl ₆ ⁻ AsCl ₃
SbCl ₅ ,phen	1:1:1	18	Ionic LAsCl ₄ ⁺ SbCl ₆ ⁻
AlCl ₃	1:1	68	N.Q.R. AsCl ₄ ⁺ AlCl ₄ ⁻

TABLE 9: Continued

Other Molecule (L)	Ratio AsCl ₅ :L	Reference	Comments
AsF ₅	1:1	93,238	AsCl ₄ ⁺ AsF ₆ ⁻
PCl ₅	1:1	157,233	PCl ₄ ⁺ AsCl ₆ ⁻ ³¹ P. n.m.r.

TABLE 10: Addition Compounds of SbCl₅

Other Molecule (L)	Ratio SbCl ₅ :L	Reference	Comments
MeCOEt	1:1	1	N.M.R. study on coupling const. in the ketone
HCONMe ₂	1:1	6,108,227*	Solution n.m.r. *crystal structure
Ac ₂ O	1:1	9	
CH ₃ OH	1:1	15	
CH ₃ CN	1:1	15,113*,137	*crystal structure
C ₆ H ₅ NO ₂	1:1 2:3 1:2	15	
CH ₃ NO ₂	1:1	22,132	
HSO ₃ F	1:1	22	
HCO ₂ H	1:1	22	
CH ₃ CO ₂ H	1:1	22	
ACNH ₂	1:2 1:5	24	Forms two ionic solvates
POCl ₃	1:1	25,137	

TABLE 10: Continued

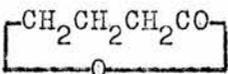
Other Molecule (L)	Ratio SbCl ₅ :L	Reference	Comments
HOAc	1:1	244	Ionic
C ₆ H ₇ NO	1:1	8	i.r. spectral study L = 1-methyl-2-pyridone
C ₁₀ H ₉ NO	1:1	8	L = 1-methyl-2-quinolone
Me ₃ MN ₃ M=Si, Ge, Sn.	1:1	4,10	Bonding takes place through the α nitrogen
C ₆ H ₅ CHO	1:1	15,137	
C ₆ H ₅ CO ₂ H	1:1	15	
CH ₃ COC ₆ H ₅	1:2	15	
Ph.N: N. Ph	1:1	129 47,48,99	
<u>p</u> -HN:NPh, H ₂ O	1:1:1	219	
<u>p</u> -Cl C ₆ H ₄ N:NC ₆ H ₅	1:1	47,48	
<u>p</u> -O ₂ C ₆ H ₄ N:NC ₆ H ₅	1:1	47,48	
MeN ₃	1:1	50	
ClC ₂ H ₄ Cl		52	
Benzolaniline	1:1	57	Complexes are formed by co-ordination through nitrogen
<u>p</u> -dimethylamine- benzolaniline	1:1	57	
Benzol- <u>p</u> -dimethyl- aminoaniline	1:1	57	
C ₂ H ₅ O(R)CO	1:1	95	Measurement of enthalpies of formation: R=H, CH ₃ , C ₂ H ₅
CH ₃ O(CH ₃)CO	1:1	95	
	1:1	95	

TABLE 10: Continued

Other Molecules (L)	Ratio SbCl ₅ :L	Reference	Comments
p-Me ₂ NC ₆ H ₄ N:NPh	1:1 1:2	99 219	Bonded to antimony through the azo group
p-EtOC ₆ H ₄ N:NPh	1:1	99	
p-EtOC ₆ H ₄ N:NPh, H ₂ C	1:1:2	220	
p-H ₂ NC ₆ H ₄ N:NPh	1:1	99	
p-PhN:NC ₆ H ₄ NH ₂ , H ₂ O	1:1	220	
C ₄ H ₃ SCOCH:CH ₂ C ₆ H ₄ X	1:1	100,122	U.V. study, X = Cl, H, C ₆ H ₅ , Me, OMe, NO ₂
C ₄ H ₃ CH:CHCOC ₆ H ₄ R	1:1	100,122	R = Cl, H, Ph, Me, OEt, OMe
Me ₂ (CN)CN:NC(CN)Me ₂	3:1	236	L = azobisisobutyronitrile
(H ₂ N) ₂ CO	1:1	93	Bonding through carbonyl oxygen
C ₂ H ₆ N ₂ O	1:1	102	L = Acetyl hydrazide
C ₄ H ₈ N ₂ O ₂	2:1	102	L = Diacetyl hydrazide
C ₃ H ₅ N ₃ O	1:1	102	L = Cyanoacetylhydrazide
(ϕ ₂ CO) ₂ N ₂ H ₂	2:1	102	L = dibenzoylhydrazide
C ₆ H ₁₂ NOCl	1:1	105	L = acetylmorpholine
C ₆ H ₅ COCl	1:1	106	Crystal structure shows co-ordination is through oxygen of the benzoyl group
C ₂ H ₅ COCl	1:1	110	
C ₂ H ₅ COCl	1:1	110	
SeOCl ₂	1:1	111	Crystal structure shows bonding is through oxygen

TABLE 10: Continued

Other Molecule (L)	Ratio SbCl ₅ :L	Reference	Comments
C ₁₄ H ₁₀ O	1:1	112	Bonding is through oxygen L = anthrone
C ₁₄ H ₁₀ NO ₃	1:1	112	L = 10-nitroanthrone
C ₁₇ H ₁₀ O	1:1	112,243	L = benzanthrone
C ₉ H ₈ NO	1:1	116,118	Bonding is through oxygen L = oxine
C ₃ H ₇ NO	1:1	140	n.m.r. indicates bonding is through carbonyl oxygen. L = N.N. dimethylformamide.
Me ₂ N(Me)CO	1:1	148	Measurement of heat of formation
(Me ₂ N) ₂ CO	1:1	148	
Me ₂ N(CF ₃)CO	1:1	148	
Me ₂ NC1CO	1:1	148	
Me ₂ N(C ₆ H ₅ O)CO	1:1	148	
OEt ₂	1:1	132	
CH ₃ CONH ₂	1:2	146	
C ₆ H ₅ NHCOCH ₃	1:2 1:3	146	
C ₆ H ₅ CONH ₂	1:1 1:2	146	
C ₆ H ₅ NHCOC ₆ H ₅	1:2	146	
C ₆ H ₈ O ₂	1:1	160	L = 3-hydroxy-2,4-dimethyl- cyclobutanone. Co-ordination through the carbonyl oxygen.
C ₆ H ₇ O ₂ Cl	1:1	160	L = 2-chloro-3-hydroxy-2,4- dimethylcyclobutanone.

TABLE 10: Continued

Other Molecule (L)	Ratio SbCl ₅ :L	Reference	Comments
$\phi_3\text{CCl}$	1:1	27,29 49	$\phi_3\text{C}^+ \text{SbCl}_6^-$
$\phi_3\text{COH}$	1:1	27,29	$\phi_3\text{C}^+ \text{SbCl}_5\text{OH}^-$
HCN, HCl	1:2:3	28	$\text{C}_2\text{N}_2\text{H}_5\text{Cl}_2^+ \text{SbCl}_6^-$
$\text{CH}_3\text{CN}, \text{HCl}$	1:1:2	51	$\text{CH}_3\text{C}(\text{Cl})\text{:NH}_2^+ \text{SbCl}_6^-$
$(\text{CH}_2)_n\text{CHCOCl}$	1:1	58	$(\text{CH}_2)_n\text{CHCO}^+ \text{SbCl}_6^-$. n=2-10
2,4,6-Me ₃ C ₆ H ₂ CCl ₃	1:1	61,62	$\text{Me}_3\text{C}_6\text{H}_2\text{CCl}_2^+ \text{SbCl}_6^-$
2,4,6-Me ₃ C ₆ H ₂ COCl	1:1	61,62	$\text{Me}_3\text{C}_6\text{H}_2\text{CO}^+ \text{SbCl}_6^-$
$\text{C}_6\text{H}_5\text{CCl}_3$	1:1	61,62	$\text{C}_6\text{H}_5\text{CCl}_2^+ \text{SbCl}_6^-$
C_3Cl_4	1:1	65	$\text{C}_3\text{Cl}_3^+ \text{SbCl}_6^-$ L = tetrachlorocyclopropane
$\phi_2\text{Cl}_4\text{C}_5\text{O}$	1:1	66	
MeCOCl	1:1	152	$\text{MeCO}^+ \text{SbCl}_6^-$. Crystal structure
$\text{O-ClC}_6\text{H}_4\text{N}_2\text{Cl}$	1:1	158	$\text{O-ClC}_6\text{H}_4\text{N}_2^+ \text{SbCl}_6^-$. Crystal structure
$\text{C}_4\text{H}_2\text{N}_3\text{Cl}$	1:1	159	$(\text{CN})_2\text{C:C}^+\text{NH}_2 \text{SbCl}_6^-$
$\text{Ph}_2\text{C}_3\text{Cl}_2$	1:1	145	$\text{Ph}_2\text{C}_3\text{Cl}^+ \text{SbCl}_6^-$ L = diphenyldichlorocyclopropane
Me_2CHCOCl	1:1	121	$\text{Me}_2\text{CHCO}^+ \text{SbCl}_6^-$
SCl_2	1:1	11	$\text{SCl}^+ \text{SbCl}_6^-$
S_2Cl_2	1:1	19	$\text{S}_2\text{Cl}^+ \text{SbCl}_6^-$
PCl_5	1:1	17,68	$\text{PCl}_4^+ \text{SbCl}_6^-$. i.r., R., N.Q.R.
VNCl_4	1:1	23	$\text{VNCl}_3^+ \text{SbCl}_6^-$

TABLE 10: Continued

Other Molecule (L)	Ratio SbCl ₅ :L	Reference	Comments
MCl ₄	1:1	83	MCl ₃ ⁺ SbCl ₆ ⁻ . M = Si, Se, Te.
NOCl	1:1	68	NO ⁺ SbCl ₆ ⁻ . N.Q.R.
COCl	No inter- action	123	
AsCl ₅	1:1	18,233 156,240	AsCl ₄ ⁺ SbCl ₆ ⁻
AsCl ₅ , AsCl ₃	1:1:1	18,156	AsCl ₄ ⁺ SbCl ₆ ⁻ AsCl ₃
Me ₂ SbCl ₂	1:1	144	Me ₂ SbCl ⁺ SbCl ₆ ⁻
VCl ₃	1:1	20	VCl ₂ ⁺ SbCl ₆ ⁻
VCl ₃ , MeCN	3:1:8	20,113A	V ³⁺ (SbCl ₆ ⁻) ₃ MeCN ₈
CrCl ₃ , MeCN	3:1:6	20	Cr ³⁺ MeCN ₆ (SbCl ₆ ⁻) ₃
	1:1:4	20	CrCl ₂ ⁺ SbCl ₆ ⁻ MeCN ₄
	2:1:5	26	CrCl ₂ ²⁺ SbCl ₆ ⁻ MeCN ₅
CoCl ₂ , MeCN	2:1:6	26	Co ²⁺ (MeCN ₆) (SbCl ₆ ⁻) ₂
CuCl ₂ , MeCN	2:1:6		
NiCl ₂ , MeCN	2:1:6		
TiCl ₄ , POCl ₃	1:1:3	25	Found as a phase in the ternary system.
Et ₄ NCl	1:1	68	Et ₄ N ⁺ SbCl ₆ ⁻ . By N.Q.R. studies
NH ₄ Cl	1:1	128	NH ₄ ⁺ SbCl ₆ ⁻
MeNH ₃ Cl	1:1	128	MeNH ₃ ⁺ SbCl ₆ ⁻
(PCl ₃) ₂ NCl	1:1	128	(PCl ₃) ₂ N ⁺ SbCl ₆ ⁻
Me ₂ NPCl ₄	1:1	128	Me ₂ NPCl ₃ ⁺ SbCl ₆ ⁻
MePCl ₄	1:1	96	MePCl ₃ ⁺ SbCl ₆ ⁻

TABLE 10: Continued

Other Molecule (L)	Ratio SbCl ₅ :L	Reference	Comments
$\phi_3\text{PCl}_2$	1:1	124	$\phi_3\text{PCl}^+ \text{SbCl}_6^-$
$(\text{n-C}_4\text{H}_9)_3\text{PCl}_2$	1:1	124	$(\text{C}_4\text{H}_9)_3\text{PCl}^+ \text{SbCl}_6^-$
$\phi_n\text{PCl}_{5-n}$	1:1	192	$\phi_n\text{PCl}_{4-n} \text{SbCl}_6^-$ n = 0,1,2,3
H ₂ O	1:1	153	Measures enthalpy of formation
HCl	1:1	135	i.r. of SbCl ₆ ⁻ ion
MCl ₂ , $\phi_2\text{SO}$	2:1:6	119	M(DPSO) ²⁺ (SbCl ₆ ⁻) ₂ M = Co(II), Ni(II).
N ₂ C(CO ₂ Et) ₃	2:1	3	L SbCl ₄ ⁺ SbCl ₆ ⁻
C ₁₂ H ₈ N ₂	2:1	18	L SbCl ₄ ⁺ SbCl ₆ ⁻ L = 1,10-phenanthroline
Diazomalonic ester	2:1	3,64	L SbCl ₄ ⁺ SbCl ₆ ⁻
C ₁₀ H ₈ N ₂	2:1	this work	L SbCl ₄ ⁺ SbCl ₆ ⁻ L = 2,2'-bipyridyl
BzCN ₂ CO ₂ Et, HCl	1:1:1	3	LH ⁺ SbCl ₆ ⁻
1,2,4,5, (Me ₂ S) ₄ C ₆ H ₂	1:1	5	Formation of cation radical
C ₁₂ H ₉ N	1:2	30	Formation charge transfer complex
C ₁₀ H ₈ N ₂ O ₃ , HCl	1:1:1	46	LH ⁺ SbCl ₆ ⁻
RR'N ₂ C ₂ O ₂ , HCl	1:1:1	64	LH ⁺ SbCl ₆ ⁻ R = C ₆ H ₅ , R' = OCH ₃ , CH ₃
C ₂₈ H ₃₁ N ₂ O ₃ HCl ₂	1:1	133	RhH ⁺ SbCl ₆ ⁻ L = rhodamine B hydrochloride

TABLE 11: Addition Compounds of SbBr₅

Other Molecule (L)	Ratio SbBr ₅ :L	Reference	Comments
C ₁₇ H ₁₀ O	1:1	112	Monomeric non electrolyte L = benzanthrone

TABLE 12: Addition Compounds of NbCl₅

Other Molecule (L)	Ratio NbCl ₅ :L	Reference	Comments
POCl ₃	1:1	74	
φ ₃ PO	1:1	75,126	
φ ₃ AsO	1:1	75	
MeCN	1:1	76	non electrolyte
C ₁₀ H ₁₆ As ₂	1:1	77	L = Diars. 7 co-ord. niobium
φ ₃ N	1:1 2:1	78	Only prep. and analytical data given.
φ ₃ P	1:1 2:1	78	1:1 prep. in CCl ₄ , <u>n</u> -hexane and cyclohexane. ⁴
φ ₃ As	1:1 2:1	78	2:1 prep. in benzene
φ ₃ Sb	1:1 2:1	78	
φ ₃ Bi	1:1 2:1	78	
Pr ₂ S	1:1	80	
Pr ₂ O	1:1	80	
NOCl	1:1	114	

TABLE 12: Continued

Other Molecule (L)	Ratio NbCl ₅ :L	Reference	Comments
AlCl ₃ , POCl ₃	1:1:3	130	X-ray powder photograph.
WOCl ₄	1:1	147	Eutectic system studied by thermal analysis.
TlCl	1:1	154	
C ₄ H ₈ OSe	1:1	224	L = selenoxan
C ₄ H ₈ OS	1:1	224, 225	L = 1,4-thioxan
C ₄ H ₈ O ₂	1:1	225	L = dioxan
C ₅ H ₁₀ O	1:1	225	L = pentamethylene oxide
C ₅ H ₁₀ S	1:1	225	L = pentamethylene sulphide
C ₄ H ₈ S	1:1	225	L = tetrahydrothiophen
(C ₆ H ₅) ₃ PO	1:1	223	
C ₆ H ₅ ·CH ₂ (C ₆ H ₅) ₂ PO	1:1	223	
(NMe ₂) ₃ PO	1:1	223	

TABLE 13: Addition Compounds of NbBr₅

Other Molecules (L)	Ratio NbBr ₅ :L	Reference	Comments
C ₁₀ H ₁₆ As ₂	1:1	77	7 co-ord. species
C ₄ H ₈ O ₂	1:1	225	i.r. and n.m.r. study
C ₄ H ₈ OS	1:1	225	
C ₅ H ₁₀ S	1:1	225	
C ₄ H ₈ S	1:1	225	

TABLE 14: Addition Compounds of TaCl₅

Other Molecule (L)	Ratio TaCl ₅ :L	Reference	Comments
AlCl ₃ , POCl ₃	1:1:3	74, 130	Thermal analysis of the triple system AlCl ₃ -TaCl ₅ -POCl ₃
φ ₃ PO	1:1	75	
φ ₃ AsO	1:1	75	
Me ₂ O	1:1	80	
Et ₂ O	1:1	80	
NOCl	1:1	114	
NOCl ₄	1:1	147	Eutectic systems studied by thermal analysis
TlCl	1:1	154	
OxH	1:5	155	
C ₄ H ₈ O ₂	1:1	225	i.r. and n.m.r. study

TABLE 14: Continued

Other Molecule (L)	Ratio TaCl ₅	Reference	Comments
C ₄ H ₈ OS	1:1	225	
C ₅ H ₁₀ O	1:1	225	
C ₅ H ₁₀ S	1:1	225	
C ₄ H ₈ S	1:1	225	
(C ₆ H ₅) ₃ PO	1:1	223	
C ₆ H ₅ CH ₂ ·(C ₆ H ₅) ₂ PO	1:1	223	

TABLE 15: Addition Compounds of TaBr₅

Other Molecule (L)	Ratio TaBr ₅ :L	Reference	Comments
C ₄ H ₈ O ₂	1:1	225	i.r. and n.m.r. study
C ₄ H ₈ OS	1:1	225	
C ₅ H ₁₀ O	1:1	225	
C ₅ H ₁₀ S	1:1	225	

CHAPTER 3

Addition compounds of phen and
bipy with group VB pentachlorides.

Reactions of the bidentate ligands 2,2'-bipyridyl (bipy) and o-phenanthroline (phen), with any of the group VB pentahalides have not, so far, been reported. Beattie and Webster¹⁷ have reported the reaction of phen with the compound $\text{PCl}_4^+ \text{SbCl}_6^-$, and report the formation of the adduct $(\text{PCl}_4, \text{phen})^+ \text{SbCl}_6^-$. With group VA pentahalides such as NbCl_5 , reaction, rather than adduct formation, takes place²³⁰. These ligands form 1:1 addition complexes with many of the group IVB tetrahalides. Infrared spectra of the 1:1 adducts of GeCl_4 and SnCl_4 have been reported⁴¹². These adducts give three strong bands in the M-Cl stretching region, as expected for a cis adduct of C_{2v} symmetry. Recently, Clees and Huber⁴¹³ have reported 1:1 adducts of these ligands with PbCl_4 .

There are two approaches to an infrared study of the type of complexes reported above. Schilt and Taylor⁴¹⁴ have studied changes in the spectra of these ligands, on complexing with metal salts. They observed changes in the region $700 - 900\text{cm}^{-1}$, and also a general shift of ring vibrations in the region $1400 - 1600\text{cm}^{-1}$. However, the gross features of the spectra of various complexes were very similar, and no correlation of the changes in the spectra with physical properties was found. Instead of attempting to examine the stereochemistry of complexes from observations of the relatively small changes in the infrared spectrum of the ligand on coordination, the grossly altered acceptor skeleton may be studied. This technique has been used by Beattie and his co-workers for a number of metal halide complexes. It has been pointed out on a number of occasions that this approach, which depends on the number of metal-halogen

vibrations observed, must be used with caution. Fermi resonance may make a combination band intense enough to be accepted as a fundamental. Alternatively, certain fundamentals may be very weak and not observed. Accidental degeneracies may occur, or bands may be unresolved, lattice vibrations may appear or, finally, in the solid state, crystal field effects may resolve degeneracies. Thus one triply degenerate f_{1u} fundamental of symmetrical SiF_6^{2-} is resolved into two peaks in the crystalline compound BaSiF_6 . This is probably caused by an elongation of the octahedron along the three fold axis, causing a lowering of symmetry from O_h to D_{3d} , so that $f_{1u} \rightarrow a_{2u} + e_u$ ⁴¹².

The addition compounds of PCl_5 and SbCl_5 with phen and bipy were prepared by adding a solution of the ligand to the halide, in the same solvent, different solvents were used for each preparation. In the case of SbCl_5 -bipy the halide, in carbon disulphide, was added slowly to the ligand in the same solvent. In every case immediate precipitation occurred. The composition of the products obtained was independent of the relative amounts of starting materials, and also of the order in which they were mixed. The stoichiometry of the products was determined by analysis for chloride and ligand. PCl_5 formed 1:1 adducts with both these ligands, whereas SbCl_5 formed 2:1 adducts ($2\text{SbCl}_5\text{L}$).

Schmulbach¹⁶ has investigated the $\text{AsCl}_3 - \text{Cl}_2$ -phen system, but found the products too unstable to be characterised. The ion $(\text{AsCl}_4, \text{phen})^+$ is isoelectronic with the stable (in the absence of moisture) $\text{GeCl}_4, \text{phen}$. Therefore, it was felt that the arsenic ion

should be isolable in association with a suitable anion. Gutmann has reported the compound $\text{AsCl}_5, \text{SbCl}_5^{240}$. We prepared this compound and also isolated a crystalline material with one molecule of AsCl_3 in the crystal lattice, i.e. $\text{AsCl}_5, \text{SbCl}_5, \text{AsCl}_3$. This compound is discussed later in this chapter. Treatment of this crystalline material with phen, using methyl cyanide as a solvent gave a yellow precipitate, and analysis established its stoichiometry as $\text{AsCl}_5, \text{SbCl}_5, \text{phen}$. A similar reaction with bipy yielded the complex $\text{AsCl}_3, \text{bipy}$. Attempts were made to react PF_5 with the adduct phen in the solid state and in solution. No reaction was observed between PF_5 and phen (solid). In benzene solution a solid compound was isolated which contained the PF_6^- ion, but no other P - F bonds. This was almost certainly due to hydrolysis of the PF_5 by traces of water in the solvent.

The infrared spectra of these compounds, as mulls, were recorded in the range $2000 - 200\text{cm}^{-1}$, and the Raman spectra from $100 - 600\text{cm}^{-1}$. For convenience these are tabulated in two groups; the infrared spectra, over the range $2000 - 600\text{cm}^{-1}$, are given in table 17, page 51. The vibrational spectra (i.r. and R.), from 600cm^{-1} (or Δcm^{-1}) are given in tables 18, 19, pages 56, 58; The spectra (i.r. and R.) are reproduced in figs. 6,7,8, pages 55, 57 and 59. Molecular weight and conductivity measurements in nitrobenzene, were also measured, and the results are presented in table 16, page 47.

Discussion of Results and Conclusions

A. Conductivity and Molecular Weight Measurements.

The results of conductivity and cryoscopic molecular weight measurements, in nitrobenzene solution, are reported in table 16. A plot of Λ_m versus \sqrt{c} for the compounds $\text{PCl}_5, \text{phen}$ and $2\text{SbCl}_5, \text{phen}$ are given in fig. 5. Both the slope of the line and the Λ_0 values obtained indicate that these compounds are 1:1 electrolytes. In nitrobenzene solution, Λ_{001m} values between 20 and 40 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ have been reported as being indicative of a 1:1 electrolyte⁴¹⁵.

The results of these measurements indicate that in solution these compounds are 1:1 electrolytes, and for 1:1 compounds the structure must be $\text{MCl}_4 \text{L}^+ \text{Cl}^-$, whereas the 2:1 compounds have the structure $\text{M}' \text{Cl}_4 \text{L}^+ \text{MCl}_6^-$.

B. Infrared Study in the range 2000. - 650 cm^{-1}

The infrared spectra of both the ligands and the complexes over the range 2000 - 650 cm^{-1} are reported in table 17. These infrared spectra show reasonable agreement with those reported previously^{414,416}, however, some displacement of the peaks is observed. The strong band reported at 1505 cm^{-1} is found at 1495 cm^{-1} . This band was found to shift on compound formation, being found at 1530 cm^{-1} in $\text{PCl}_5, \text{phen}$. In the compound $\text{AsCl}_5, \text{SbCl}_5, \text{phen}$ it is found at 1515 cm^{-1} . whereas in $2\text{SbCl}_5, \text{phen}$ it occurs at 1555 cm^{-1} . These shifts are indicative of complex formation⁴¹⁴ as are the changes in the band pattern in the 700 - 900 cm^{-1} region. Bellamy⁴²¹ has shown that strong bands in

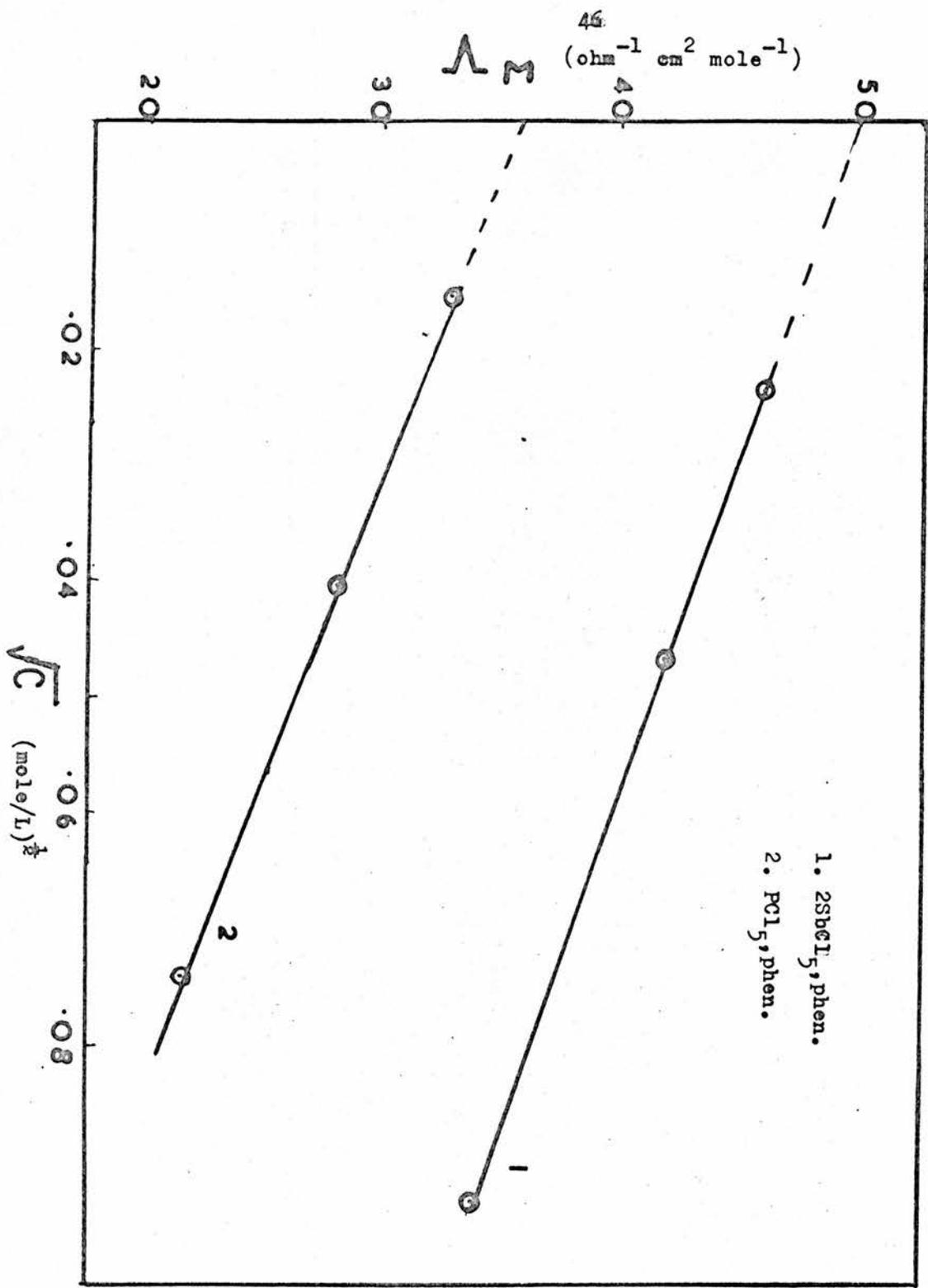


FIGURE 5

TABLE 16: Molecular Weight and Conductivity Measurements.A. Conductivity.

Compound	Molar Conc. mole litre ⁻¹ (x10 ³)	Resistance Ohms (x10 ³)	Molar Cond. Mho cm ² mole ⁻¹
PCl ₅ , phen	1.58	12.2	28.47
	5.28	4.90	21.69
	0.40	42.2	32.93
2SbCl ₅ , phen	8.58	1.9	33.8
	2.14	6.1	42.04
	0.54	22.0	46.63
AsCl ₅ , SbCl ₅ , phen	4.61	4.05	29.46
2SbCl ₅ , bipy	2.36	7.5	31.2
PCl ₅ , bipy	3.68	7.4	20.3

B. Molecular Weight.

Compound	Conc. %w/w.	M. found	Mo(calc.)	M/Mo
PCl ₅ , phen	0.16	160	388.4	0.412
		179.5		0.462
	0.30	207.8		0.534
2SbCl ₅ , phen	0.21	362	778.2	0.466
	0.36	377		0.485
AsCl ₅ , SbCl ₅ , phen	0.49	350	731.4	0.480
2SbCl ₅ , bipy	0.44	385	754	0.510
	0.84	372		0.494
PCl ₅ , bipy			572.6	

this region, in spectra of aromatic hydrocarbons, have been identified with motions of ring hydrogen atoms, moving in phase, out of the plane of the ring. He has also shown that the frequencies of these bands depend on the number of adjacent hydrogen atoms, and the positions and patterns of these bands have been used to determine substitution patterns. In phenanthroline, and in its complexes, two strong bands appear in the regions 725cm^{-1} and 850cm^{-1} . Schilt and Taylor⁴¹⁴ point out that the band at 725cm^{-1} is associated with out of plane motion of the hydrogen atoms in the terminal positions 2, 3, 4 and 7, 8, 9, and the band at 850cm^{-1} with the hydrogen atoms in positions 5 and 6. The infrared spectrum of 2,2'-bipyridyl recorded shows reasonable agreement with published spectra^{414,416}. However, the ring vibrations reported at 1580cm^{-1} and 1560cm^{-1} are found at 1560cm^{-1} and 1544cm^{-1} respectively. These are found to shift on complex formation, and in PCl_5 , bipy give rise to a multiplet of peaks around 1600cm^{-1} . Changes in the band at 751cm^{-1} , due to out of plane deformation of ring hydrogen atoms, is also observed.

C. Ligand Vibrations in the region 650cm^{-1} - 200cm^{-1}

The infrared spectra of both free and coordinated phen and bipy in the $450 - 200\text{cm}^{-1}$ region have been reported^{416,417}. In the case of bipy the strong band at 399cm^{-1} has been assigned to an out of plane ring vibration⁴¹⁸. This band is raised by as much as 20cm^{-1} on coordination, whereas the weak band at 427cm^{-1} is virtually unchanged. In PCl_5 -bipy these bands are completely obscured by the strong P-Cl band at 439cm^{-1} . In 2SbCl_5 , bipy bands are observed at 410cm^{-1} and

440 cm^{-1} . However these two bands are almost of equal intensity, whereas one would expect the higher frequency band to be much weaker. In fact one of these bands may be due to a metal-halogen vibration. Clark⁴¹⁸ has observed a weak band in the region 350 cm^{-1} in a number of bipy adducts. He suggests that this band, which is too weak to be seen in the free ligand, gains in intensity on coordination. In PCl_5 , bipy a weak band is observed at 331 cm^{-1} but in the SbCl_5 complex this region is completely obscured by the metal-halogen vibrations.

Phenanthroline is reported to have bands at 431w, 408m, 259m and 241s cm^{-1} , 416, 417. A weak band was observed at 252 cm^{-1} by us, but no strong band was observed at lower frequencies. The band at 402 cm^{-1} in the free ligand, shifts on complex formation, appearing at 409 cm^{-1} in the SbCl_5 complex, at 435 cm^{-1} in the AsCl_5 , SbCl_5 , phen complex.

The Raman spectra of the ligands have not been reported previously in the literature. They are given in tables 18 and 19. Besides a number of weak bands in the range 550 - 400 Δcm^{-1} , phen shows two strong bands at 245 Δcm^{-1} and 409 Δcm^{-1} . It was impossible to definitely assign these bands in the complexes, but the medium band at 243 Δcm^{-1} (PCl_5 , phen) or 235 Δcm^{-1} (AsCl_5 , SbCl_5 , phen) may well be associated with the band at 245 Δcm^{-1} in the free ligand. The 409 Δcm^{-1} peak does not appear to be present in the complexes, although a shift to higher frequencies and a decrease in intensity could well account for this. A weak band in the region 435 - 440 Δcm^{-1} appears in all of the complexes. Bipy has two strong bands at 80 and 105 Δcm^{-1} , below the range covered for the complexes. The two weak bands

1030 w	1036 M-w	1059	1031 m.	1027 m.	1029 m.
988 M	999 s.	1029 m.	983 m.br.	962 w.br.	1018 m.
970 w	975 sh.	999 s.	934 br.m.	970 br.w	
960 w.	946 m.	975 sh.			
	940 w.	934 br.m.			
	916 m.w.				
850 sh.m.	839 s.	857 s.	885 m.	870 m.	915 m.
839 s.	812 sh.	847			
810 w.	812 sh.	809 w.			
780 w.	786 m.	770 s.	780 sh.	781 sh.	782 sh.
	769 m.	748 s.			
761 m.w.	745 s.		751br.v.s.	761 s.	761 s.
730 s.	729 w.	717 w.		720 m.	732 sh.
720 w.sh.	716 sh.	709 m.	710 sh.	705 m.	719 m.
	712 m-s.				706 w.
702 m-w.	692 m.	695 s.			
	685 s.	672 w.		661 w.	670 m-w.
	670 m.	662 w.		651	
	651 w.	617 w.	616 m.		618 w.
618 m.	613 m.				

TABLE 17: Infrared Spectra of the Adducts of 1,10-phenanthroline and 2,2'-bipyridyl with MCl_5 in the range $2000 \text{ cm}^{-1} - 600 \text{ cm}^{-1}$. (all spectra recorded as nujol mulls).

phen	PCl_5 , phen	AsCl_5 , SbCl_5 , phen.	2SbCl_5 , phen.	bipy.	2SbCl_5 , bipy.	PCl_5
1601 M	1605 M	1631 1615 M	1680 1619 S 1610 M			
1582 S	1588 S 1575 sh	1583 S 1573 sh	1558 S	1560 sh. S	1595 w.	1615 w. 1600
1540 Br. M				1542 s.	1582 m-s.	1590 m. 1575
1495 S	1532 S 1510 w	1514 S	1539 M 1515 M		1510 w	1518 w 1505
	1490 w	1493 w 1325 w	1490 sh			
	1308 sh 1272 M		1308 sh			
1210 w	1228 M 1202 sh	1231 sh. w. 1215 M	1240 w 1216 M 1206 M	1238 m 1200	1245 m	1241 w. 1232
1132 M	1150 sh 1142 M	1156 M 1149 sh.	1152 w 1142 m.	1127 w.	1161 m.	1161 m. 1149
1083 m-s	1096 Br. w.	1100 M 1094 sh.	1090 M	1078 m.		1678 m.
1070 M sh.			1073 w.	1056 w,	1062	

in the free ligand were not observed in the compounds which have been reported.

D. Metal-Halogen Vibrations (Infrared and Raman)

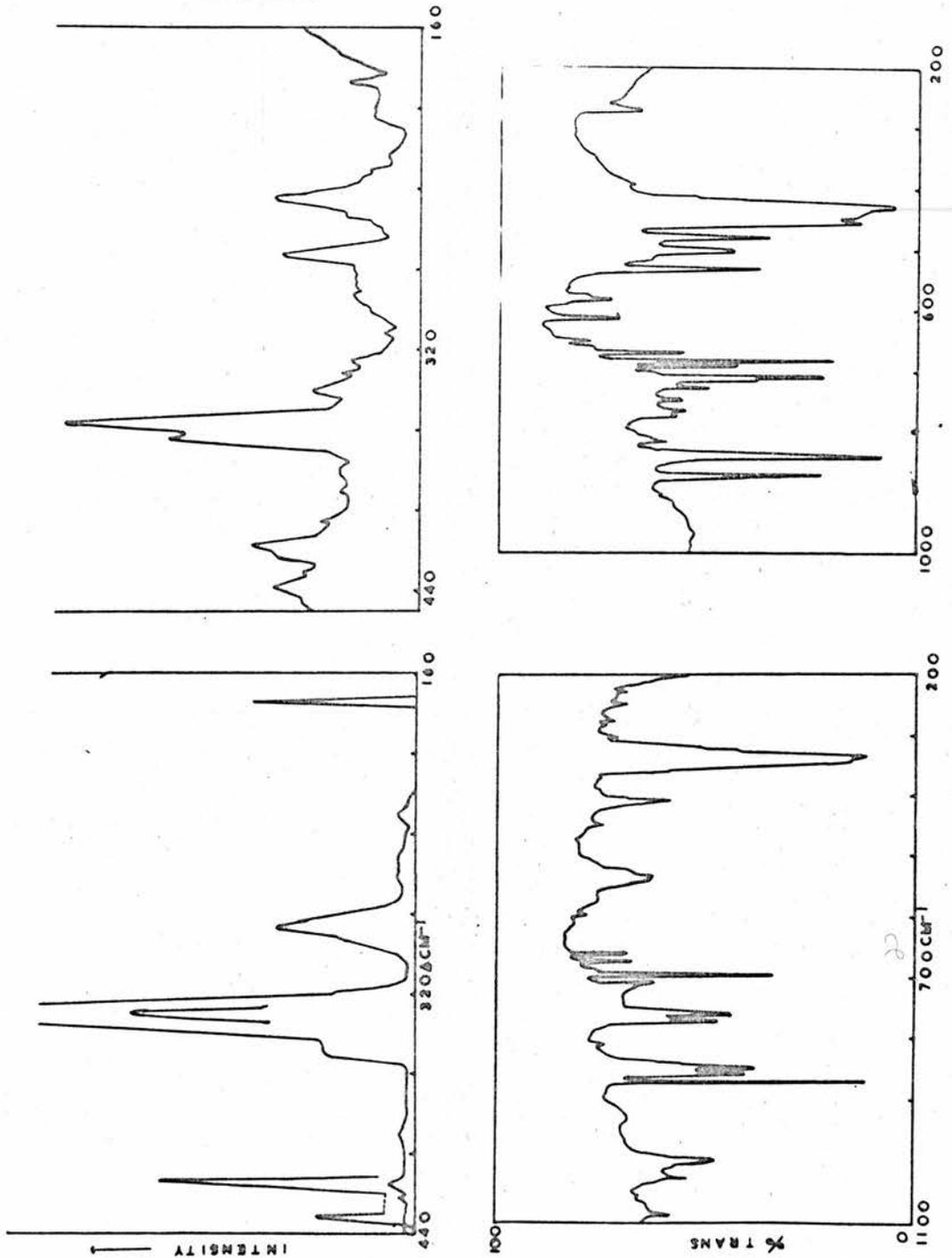
It has already been pointed out that an ion such as $\text{PCl}_4, \text{phen}^+$ belongs to the point group C_{2v} . Group theoretical arguments predict that such an ion (molecule) should have four metal-halogen stretching frequencies; $2A_2 + B_1 + B_2$. All are infrared and Raman active. Beattie³⁵⁸ has shown that three of these bands should occur, as a group, at a higher frequency than the fourth. This can be explained by considering the metal-halogen part of the ion separately. Thus we have a tetrahedral ion distorted to a structure of the type shown in fig. 4a, page 4 for the AsCl_4^- ion. The symmetry changes from $T_d \rightarrow C_{2v}$ resulting in $A_1 \rightarrow A_1$ and $F_2 \rightarrow A_1 + B_1 + B_2$ ⁴¹⁹. All C_{2v} species are infrared active, and all except A_2 are Raman active. If the distortion is small the effect would be, essentially, a resolution of the F_2 mode to give a closely spaced triplet plus a weak vibration near the Raman active A_1 mode of the original (T_d) tetrachloride. However, as a general rule the frequency of metal halogen stretching bands, for a particular metal-halogen, depends on the coordination number of the metal, assuming that the metal remains in the same oxidation state. Thus for the series $\text{PCl}_4^+, \text{PCl}_5, \text{PCl}_6^-$ the asymmetric P-Cl stretch occurs at 658cm^{-1} , 448 and 444cm^{-1} respectively. Therefore, in the case of $\text{PCl}_4, \text{phen}^+$, allowing for the weakening of the P-Cl bond on coordination of the bidentate ligand, we might expect three vibrations around 500cm^{-1}

and one about 350cm^{-1} . Examination of the spectra (i.r. and R.) of PCl_5 , phen, shows three bands at 439 v.s. 450 sh. 460 s. cm^{-1} in the infrared, whereas the Raman spectrum has a strong band at $356\Delta\text{cm}^{-1}$. A weak band at $437\Delta\text{cm}^{-1}$ is also observed in the Raman spectrum. A number of other medium - weak bands appear, but no attempt has been made to assign them. The possibility of phosphorus - nitrogen vibrations, for these ligands, occurring above 200cm^{-1} has been dismissed by Clark⁴¹⁸, neither does it seem likely that they are ligand vibrations, but it is possible that they are P-Cl bending vibrations. The fact that only one strong band, rather than the predicted pattern, is observed in the Raman spectrum has been noted by other workers¹⁷. It has been suggested⁴²² that B type stretching modes may be particularly weak in the Raman effect. The intensity of a Raman line is related to $(\partial\alpha/\partial Q)$, which is the rate of change of polarisability (α), with the change in the normal coordinates²³². It has been observed that this is greatest for the "linear" Cl-P-Cl stretching mode where the light phosphorus atom has little movement. This stretching mode can be reasonably assigned to the strong Raman band at $356\Delta\text{cm}^{-1}$. The B type modes, the asymmetric stretching, will presumably involve movement of the phosphorus atom, and may well be far less intense in the Raman effect than the symmetric modes. On this basis the band at 356 (R) is assigned to the $\nu_1 A_1$ mode, and the band at 439 (i.r. and R.) is assigned to $\nu_2 A_1$ mode. No attempt has been made to assign the other two stretching modes. Clark⁴¹⁷ has suggested that in the infrared the asymmetric "B" modes will be more intense than the symmetric "A" type modes.

The infrared and Raman spectra of $\text{PCl}_5, \text{bipy}$ are similar to $\text{PCl}_5, \text{phen}$; two strong bands are observed in the infrared, a very intense band at 438cm^{-1} , a strong band at 510cm^{-1} and two weak bands at 346 and 330cm^{-1} . One of these weak bands may be associated with the symmetric A_1 vibration and the other a ligand vibration unobserved in the free ligand⁴¹⁸. The Raman spectrum has one strong band at $356\Delta\text{cm}^{-1}$ and two medium intensity bands at 242 and $277\Delta\text{cm}^{-1}$.

The vibrational spectra of the compounds $2\text{SbCl}_5, \text{phen}$, $2\text{SbCl}_5, \text{bipy}$ and $\text{AsCl}_5, \text{SbCl}_5, \text{phen}$ all show bands due to SbCl_6^- ion²³³. The first two mentioned compounds have several bands of medium intensity, $350 - 530\text{cm}^{-1}$ which should be associated with Sb-Cl stretching modes in the cation. The Raman spectrum shows only strong bands associated with the anion. However, a broad shoulder at $360\Delta\text{cm}^{-1}$ in the Raman spectrum of $2\text{SbCl}_5, \text{bipy}$ may well be associated with the A_1 symmetric stretching of the cation. In $\text{AsCl}_5, \text{SbCl}_5, \text{phen}$ a strong band at 368cm^{-1} and a shoulder at 378cm^{-1} are presumably metal-halogen vibrations of the cation. Weak bands at 275cm^{-1} and 251cm^{-1} can be assigned to ligand vibrations⁴¹⁷. The medium band at 229cm^{-1} (i.r.) 235cm^{-1} (R) must be associated with the anion, also the strong band at $320\Delta\text{cm}^{-1}$ (R), 312cm^{-1} (i.r.). However the complexity of the spectra and the presence of the anion SbCl_6^- makes it impossible to assign these vibrations with any degree of accuracy. It is felt, however, that these spectra confirm the presence of a cation of type MCl_4L^+ of C_{2v} symmetry.

Figure 6: i.r. and R.



Raman

A. Phen, 2SbCl_5 B. Phen, PCl_5

Infrared

C. Phen, PCl_5 D. Phen, SbCl_5

TABLE 18: Vibrational Spectra of the Solid Phen ComplexesRaman 100 - 500 cm^{-1} (6328A). Infrared 600 - 200 cm^{-1}

Phen		$\text{PCl}_5, \text{phen}$		$2\text{SbCl}_5, \text{phen}$		$\text{AsCl}_5, \text{SbCl}_5, \text{phen}$	
I.R.	R.	I.R.	R.	I.R.	R.	I.R.	R.
	142 m.s		183 w.		171m ^a		178s ^a
							201m.w.
225				237w.		226m.	209w.
251v.w.	245s.		243m.			249w.	235m
287			273m.		290m ^a		287m ^a
							320s.
			340w.	336v.s. ^a	334v.s. ^a	331v.s. ^a	332v.s. ^a
			356s.		353w.	368m.s.	
		390v.w.	363sh.	392br.w.		372sh.	380m.
402m.	409v.s.		417m.	409m.	419w.		
428w.	432w.	439v.s.	437w.		435w.		
		450sh.		449m.		432m.	
452w.	463sh.	460sh.		459w.		448w.	440w.br.
		480m.					
	513w.	503m.		491w.		501w.	
		532m.		532s.			
	553m.			572sh.m.			586m.

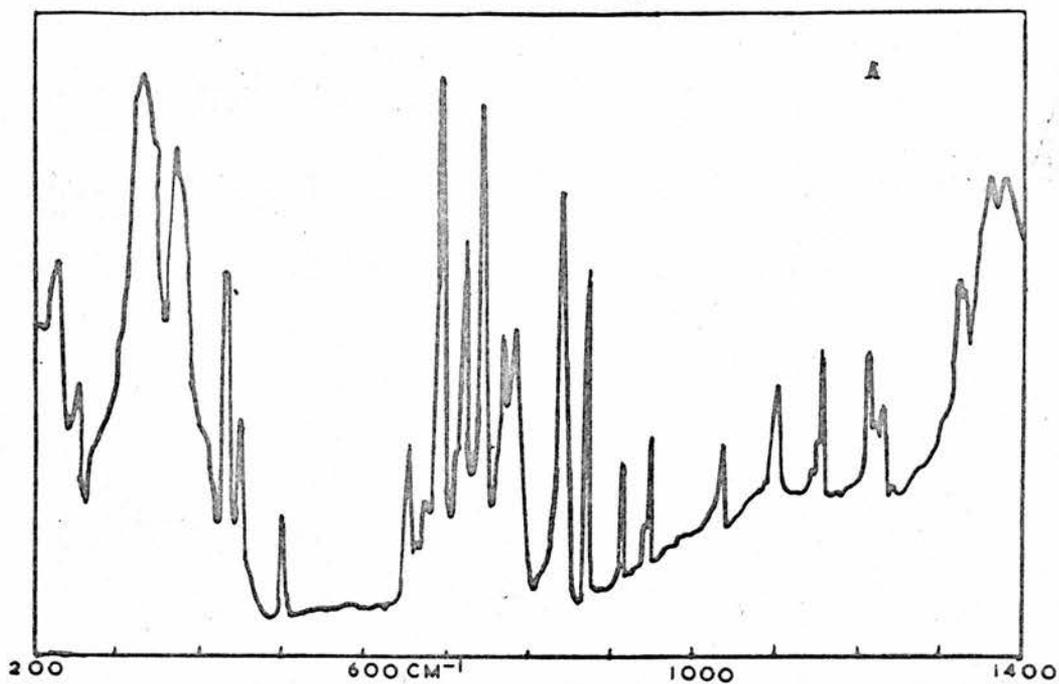


FIGURE 7A ($\text{AsCl}_5, \text{SbCl}_5, \text{phen}$)

A. Infrared

B. Raman

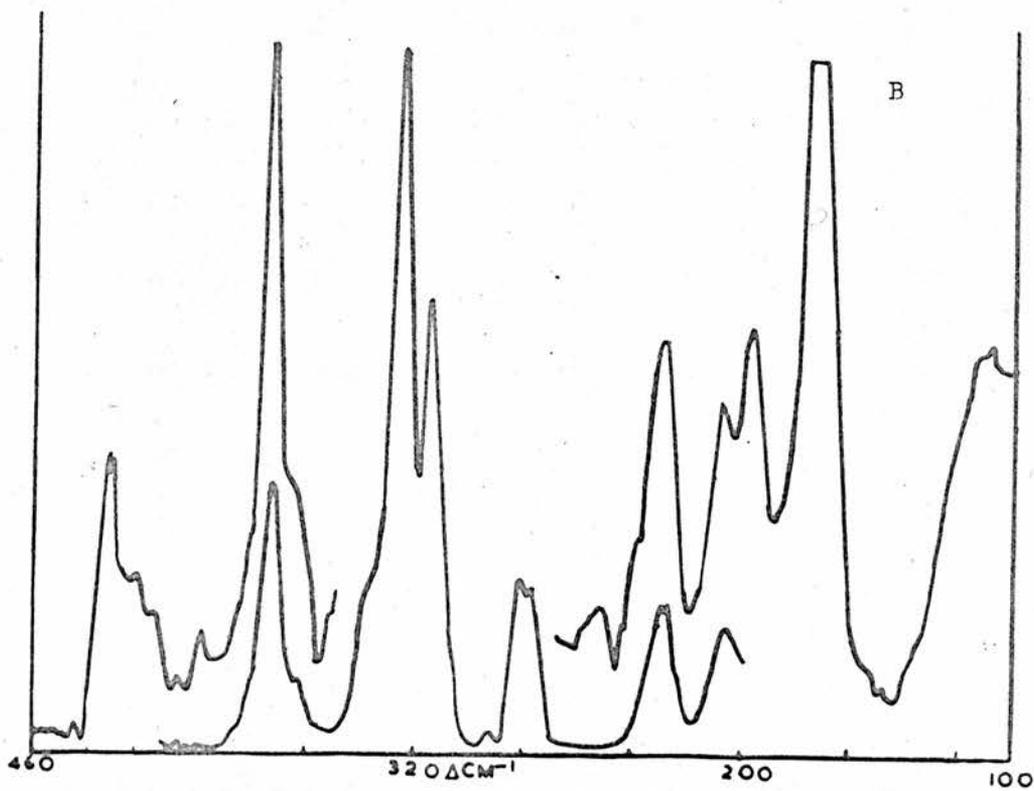


FIGURE 7

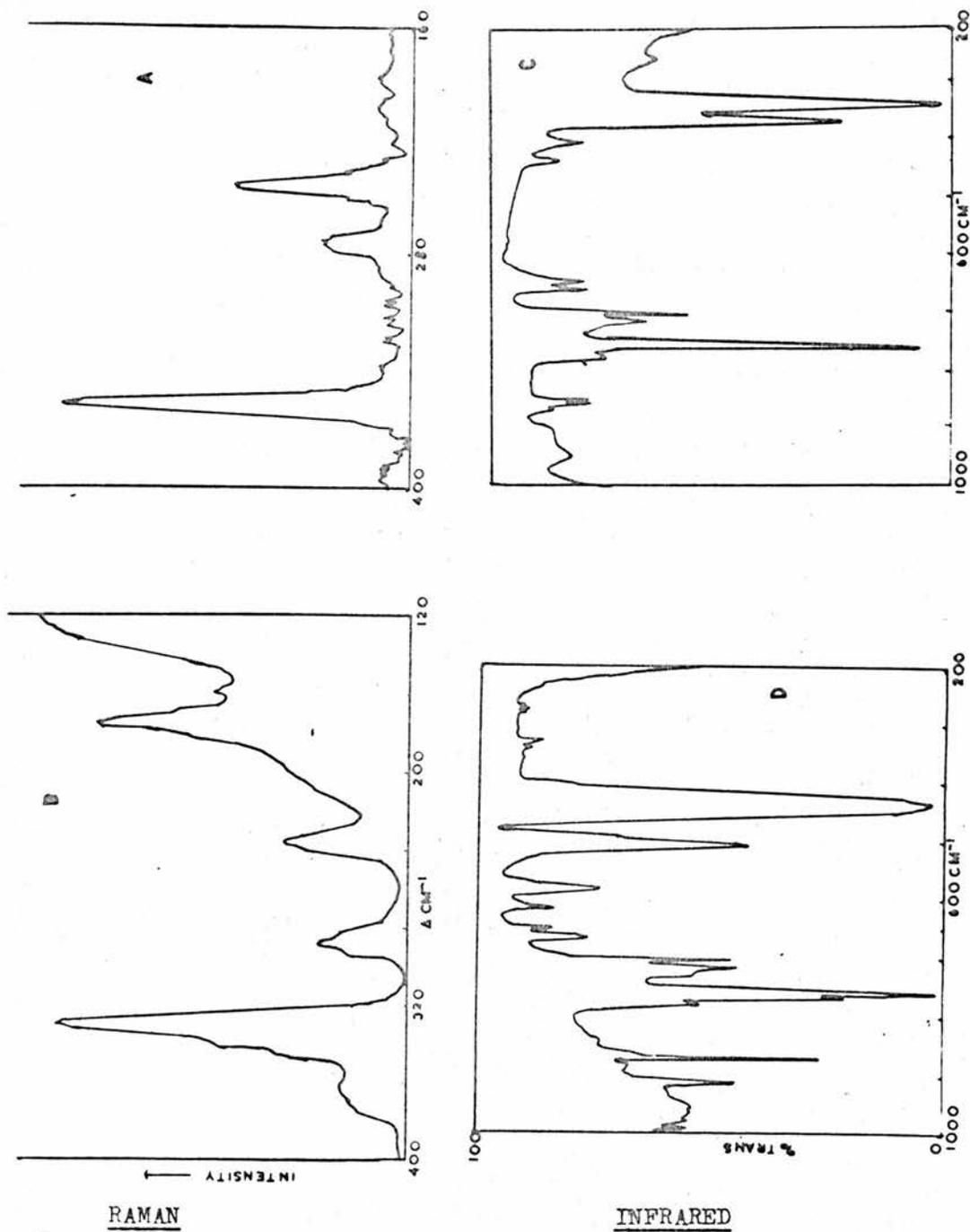
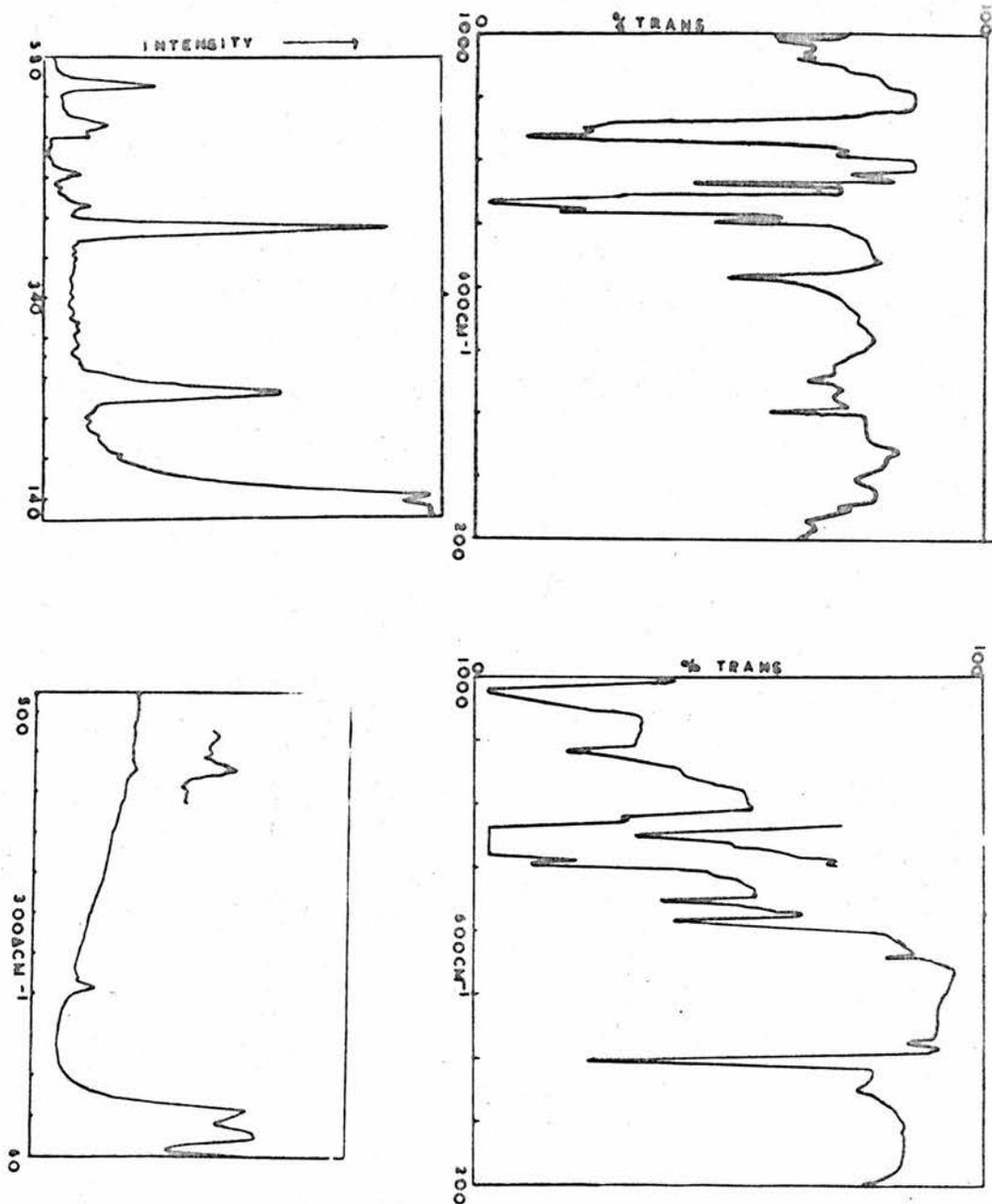


TABLE 19: Vibrational Spectra of the Solid Bipy Complexes

bipy		PCl ₅ , bipy		2SbCl ₅ , bipy	
I.R.	R.	I.R.	R.	I.R.	R.
	80br.s.				
	105br.s.				
	226w.				177s. ^a
			242m.		
			271m.		287m. ^a
				339v.s. ^a	331v.s. ^a
		330v.w.			
350w.br.		347v.w.	356s.	370s.	363w.sh.
399m-s.				410w.	
427v.w.	442v.w.	439v.s.		440w.	
		510s.			

Figure 8: i.r. and R. Spectra of Phen and Bipy.



Raman

A. Bipy.

B. Phen.

Infrared

C. Phen.

D. Bipy.

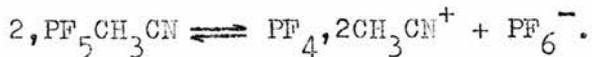
Reaction of Phosphorus Pentafluoride with 1,10-phenanthroline

When PF_5 (gas) was bubbled through a solution of phen in benzene, a pale, brown precipitate slowly appeared. The yield was only about 5%, calculated on the weight of phen used. Chemical tests and the infrared spectrum indicated the presence of the PF_6^- anion. Moreover, ^{19}F . n.m.r. spectroscopy gave resonances only for the PF_6^- ion, indicating that no other P - F bonds existed in the compound. A simple calculation indicated that 10p.p.m. of water in the solution would be sufficient to hydrolyse the PF_5 used. Thus it is almost certain that the material obtained was a hydrolysis product and not an addition compound.

No reaction took place between solid phen and gaseous PF_5 in an all glass vacuum system. Repeatedly condensing the PF_5 onto the ligand and allowing the system to warm to room temperature, gave no pressure change, and infrared studies showed no change in the composition of the vapour. Heating the ligand to its melting point in contact with PF_5 produced some decomposition, and the presence of a deep red-brown solid. Insignificant quantities of PF_5 were consumed during the decomposition, and chemical tests showed the complete absence of PF_6^- ion in this solid.

It has already been pointed out that there is considerable disagreement in the literature concerning the autoionisation of PF_5 according to the equation $2\text{PF}_5 \rightleftharpoons \text{PF}_4^+ + \text{PF}_6^-$. Kolditz¹²⁵ suggests that ionisation of $\text{PF}_5, \text{CH}_3\text{CN}$ may be concentration dependent, giving a molecular form in concentrated solutions, as has been observed by ^{19}F . and ^{31}P .n.m.r.^{90,125}; whereas in dilute solutions

the ionic species are predominant, as inferred by conductivity measurements.³¹ The equilibrium suggested is:



If such autoionisation does occur it is difficult to understand why PF_5 does not react with a bidentate chelating ligand, such as phen (L) to give $\text{PCl}_4 \text{L}^+ \text{PCl}_6^-$.

The System $\text{AsCl}_3 - \text{Cl}_2 - \text{SbCl}_5$

On passing chlorine into a solution of SbCl_5 in AsCl_3 an exothermic reaction takes place, and a white crystalline material precipitates out. Removing the solvent and pumping under high vacuum ($< 10^{-4}$ mm Hg) gives a white amorphous material $\text{AsCl}_5, \text{SbCl}_5$, which was first described by Gutmann²⁴⁰. The crystalline material was isolated by washing it free of AsCl_3 with carbon tetrachloride. It was impossible to obtain a pure, dry sample of this crystalline material for analysis. Instead, a sample, still wet with solvent (CCl_4), was taken and hydrolysed with distilled water in a sealed tube. This solution was transferred quantitatively to a 500 ml volumetric flask, and made up to the mark. The ratio of arsenic to chlorine was determined by analysis for both of these elements. The conditions used for hydrolysis precluded the estimation of any chlorine from the solvent, carbon tetrachloride. The ratio found: $\text{As}:\text{Cl} = 1:6.95$, agrees well with that expected for the compound: $\text{AsCl}_5, \text{SbCl}_5, \text{AsCl}_3$; $\text{As}:\text{Cl} = 1:6.5$. ($\text{AsCl}_5, \text{SbCl}_5$ requires $\text{As}:\text{Cl} = 1:10$.) Qualitative tests indicated the presence of As(III) in a hydrolysed sample of the crystalline material, whereas only a faint trace of As(III) was

detected in a similarly treated sample of $\text{AsCl}_5, \text{SbCl}_5$.

A single crystal X-ray study was made on the crystal. Rotation photographs were used to align a real crystal axis along the camera axis, and from the final photograph it was possible to calculate the spacing along this axis, arbitrarily designated the C axis. This is given by:

$$C = \frac{n \lambda}{\sin [\tan^{-1}(2y/D)]}$$

λ is the wavelength of the radiation $\text{MoK}\alpha = 0.7107$. D is the camera diameter in mm. $D = 57.3$. y is the measured distance from the zero order line to the nth order. The readings taken are given in table 20. This rotation photograph showed symmetry across the zero level, which suggests two 90° angles.

Weissenberg for, zero, first and second layers about C were recorded. The films were indexed with a standard net for a camera of diameter 57.3 mm with 2° rotation per mm travelled. The zero layer photograph, taken along the C axis, was measured along the a^* and b^* axis. The distance between two equivalent spots, n to -n, was measured, corrected to allow for the slope of the line with respect to the axis of rotation, and used to find the value of ϕ , the angle between the crystal and the reflected beam. From these values it was possible to calculate values for a^* and b^* . The lateral distance between the reciprocal axes gave a value for γ^* , the angle between them. This angle is 90° so that $a = 1/a^*$ and $b = 1/b^*$. The cell is therefore, orthorhombic, and the values of the cell parameters are: $a = 11.63 \pm 0.20$; $b = 16.10 \pm 0.05$; $c = 10.16 \pm 0.02$. Å

The crystal was then transferred to a precession camera. Since the crystal is orthorhombic, \bar{C} and \bar{C}^* are coincident, and no adjustment to the goniometer arc was required, as a reciprocal axis was already aligned along the goniometer axis, as required. The photograph taken gave the a^* and c^* axes. The crystal was next rotated through 90° to include the b^* axis. These photographs immediately confirmed that the crystal was orthorhombic, because the angle between the a^* and b^* axes on the film is the real angle between them in the crystal. The usual measurements were made, see table 20, and from the equation: $\frac{1}{d^*} = \frac{60\lambda n}{y}$ the values of a^* , c^* and b^* were calculated and found to agree with the values obtained from rotation and Weissenberg photographs. In the above equation 60 = distance from camera to crystal in mm., and y = distance in mm. between two spots n layers apart.

From the unit cell dimensions the volume of the unit cell was calculated, and from the equation $nM = W \rho V \times 10^{-24}$, the value of W , the mass of the unit cell was calculated. In the above equation, V is the volume of the cell in \AA^3 , ρ = density in gm/cc., and A is Avogadro's number. M is the molecular weight, and n is the number of molecules in the unit cell. Since n must be a small whole number, this gives a value of the molecular weight which depends on the accuracy with which the density was measured. The only molecular weight for this crystal that gives a reasonable value of n is that of the compound $\text{AsCl}_5, \text{SbCl}_5, \text{AsCl}_3$. The value of n was found to be 4, and from this the density was calculated and found to be 2.56 gm/cc., which agrees well with the experimental value of $2.55 \pm .02 \text{ gm/cc.}$

TABLE 20: Measurements from X-ray Photographs of AsCl_5 , SbCl_5 , AsCl_3 .A. Measurements from Weissenberg photographs.

1. Measurement along the reciprocal a axis.

n	X	θ	$\sin \theta$	a^*	a
4	16.00	$7^\circ 9'$.1245	.08756	11.42
6	23.35	$10^\circ 26.5'$.1812	.08496	11.77
8	31.45	$14^\circ 3.6'$.2429	.08547	<u>11.70</u>
				<u>Mean</u>	11.63 \pm 0.2

2. Measurement along the reciprocal b axis.

n	X	θ	$\sin \theta$	a^*	a
7	20.25	$9^\circ 3'$.1573	.06211	16.1
12	34.20	$15^\circ 18'$.2649	.06173	<u>16.2</u>
				<u>Mean</u>	16.15 \pm 0.05

B. Measurements from Rotation photographs.

n	X	$2x/D$	$\theta = \tan^{-1}(2x/D)$	$\sin \theta$	c
4	8.35	.2914	$16^\circ 14'$.2796	10.17
8	19.35	.6754	$34^\circ 02'$.5596	<u>10.16</u>
				<u>Mean</u>	10.16 \pm .005

C. Measurements from Precession photographs.

axis	n	y	d
c^*	16	67.3	10.14
a^*	16	58.0	11.76
b^*	24	63.5	16.10

TABLE 20: ContinuedD. Calculation of Mass of unit cell (W) and Density (ρ).

$$1. W = V \times \rho \times A \times 10^{-24}$$

$$V = 10.14 \times 11.76 \times 16.10 = 1902.39$$

$$A = 6.023 \times 10^{23}$$

$$\rho = 2.55 \pm .02 \text{ gm/c.c.}$$

$$\therefore W = \underline{2921.6}$$

Molecular weight of $\text{AsCl}_5, \text{SbCl}_5, \text{AsCl}_3 = 732.49$

$$n = W/M = \frac{2921.6}{732.49} = 3.99 \therefore n = 4$$

$$2. \rho = \frac{M \times n}{V \times A} = 2.56 \text{ gm/litre.}$$

From the Weissenberg and precession photographs taken, another worker (see footnote) noted the conditions limiting the possible reflections, and with the notation of axis chosen, assigned the space group Ama2(No.40).

It was found impossible to get an infrared spectrum of either of these substances. They reacted with nujol, polythene and both CsI and CsBr plates. However, Raman spectra of both were obtained; these are recorded in table 21, page 69, and figure 9, page 68.

The fundamentals of AsCl_4^+ ion have been reported by Dehnicke²³⁸. This ion is a regular tetrahedron of symmetry (T_d), and has four fundamental vibrations: $V_1(A_1)$, $V_2(E)$, $V_3(F_2)$ and $V_4(F_2)$. These are all Raman active, but only V_3 and V_4 are infrared active. The fundamentals reported by Dehnicke are given in table 21, page 69.

The SbCl_6^- ion has a regular octahedral arrangement of six chlorine atoms around the central antimony, and belongs to the space group O_h . For such a molecule (or ion) there are 15 normal modes which, from symmetry, can be divided into the classes :

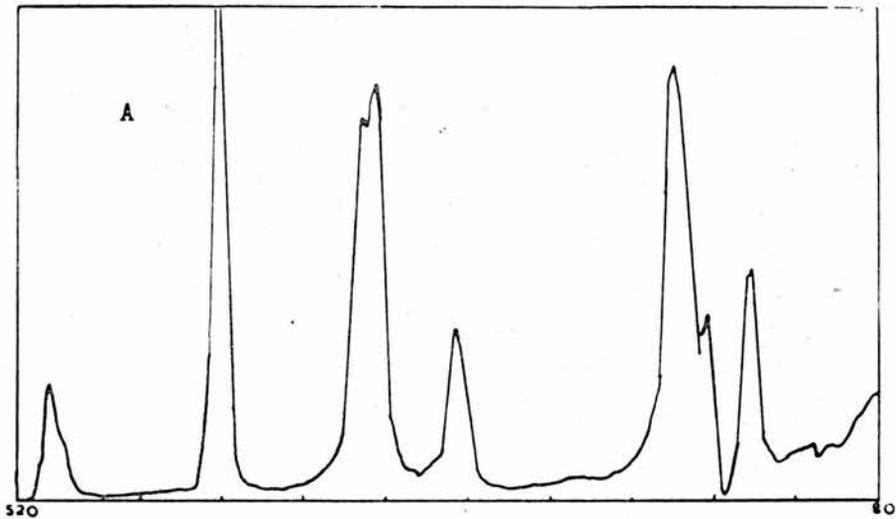
$V_1(A_{1g})$, $V_2(E_g)$, $V_3(F_{1u})$, $V_4(F_{1u})$, $V_5(F_{2g})$, $V_6(F_{2u})$. V_3 and V_4 are infrared active, V_1 , V_2 and V_5 are Raman active, and V_6 is inactive. The Raman spectrum of SbCl_6^- has been published by a number of authors^{232,233}, and is given in table 21, page 69.

The molecule AsCl_3 has a pyramidal structure belonging to the point group C_{3v} which has four fundamental vibrations: $V_1(A_1)$, $V_2(A_1)$, $V_{3a}(E)$ and $V_{4a}(E)$. All four vibrations are infrared and Raman active.

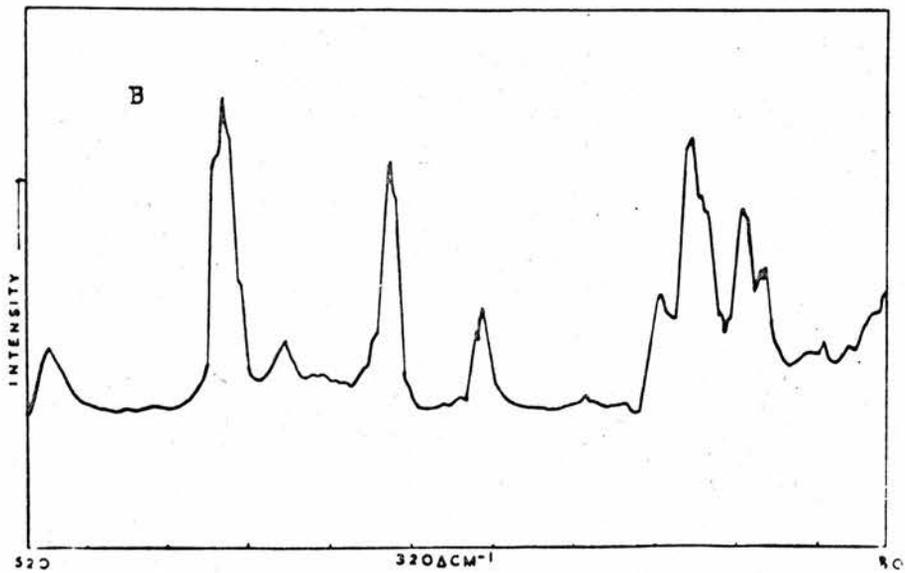
Thanks are due to Dr. M. Webster for noting the conditions and assigning the space group.

The vibrational spectrum of AsCl_3 is reported in Nakamoto's text²³², but $V_3(E)$ has been incorrectly reported to occur at $307 \Delta \text{cm}^{-1}$, rather than $370 \Delta \text{cm}^{-1}$,²⁰⁴. The literature values for the fundamental frequencies are given in table 21, page 69. In this table is reported the Raman data for the compounds $\text{AsCl}_5, \text{SbCl}_5$ (A) and $\text{AsCl}_5, \text{SbCl}_5, \text{AsCl}_3$ (B). The spectra of A and B are very similar and by comparison with the published spectra it can be seen that the ions AsCl_4^+ and SbCl_6^- are present in both compounds. The spectrum of B shows several weak bands which can be assigned to AsCl_3 . Unfortunately the most intense AsCl_3 Raman band V_1 at $410 \Delta \text{cm}^{-1}$, lies under the $V_1(\text{AsCl}_4^+)$ band at $413 \Delta \text{cm}^{-1}$. Since the completion of this work Raman spectra of $\text{AsCl}_5, \text{SbCl}_5$ ²³³ and of $\text{AsCl}_5, \text{SbCl}_5, \text{AsCl}_3$ ⁴²⁰ have been reported in the literature. In both cases the reported spectra and assignments agree well with ours.

Figure 9: Raman Spectra ($80 - 520 \text{ cm}^{-1}$)



A. $\text{AsCl}_5, \text{SbCl}_5$



B. $\text{AsCl}_5, \text{SbCl}_5, \text{AsCl}_3$

TABLE 21: The Raman Spectra of the $\text{AsCl}_5, \text{SbCl}_5, \text{AsCl}_3$ System (6328Å)

AsCl_3 ²⁰⁴	AsCl_4 ⁺²³⁸	$\text{PyH}^+\text{SbCl}_6^-$	$\text{AsCl}_5, \text{SbCl}_5$	$\text{AsCl}_5, \text{SbCl}_5, \text{Assignment}$ AsCl_3	
				59w.	?
		83w.		76w.	?
				122w	?
		156m	151	146w	$V_2(\text{E})\text{AsCl}_4^+$
155				157w	$V_4(\text{E})\text{AsCl}_3$
		180m	174w	177sh	$V_5(\text{F}_{2g})\text{SbCl}_6^-$
	187		186s	185s	$V_4(\text{F}_2)\text{AsCl}_4^+$
194				197w	$V_2(\text{A}_1)\text{AsCl}_3$
		289m-w	284m	284w	$V_2(\text{E}_g)\text{SbCl}_6^-$
		334vs	333vs	330s	$V_1(\text{A}_{1g})\text{SbCl}_6^-$
			339sh		?
				359	**
370				380	$V_3(\text{E})\text{AsCl}_3$
	422		410	413	$V_1(\text{A}_1)\text{AsCl}_4^+$
412					$V_1(\text{A}_1)\text{AsCl}_3$
	500		494	495	$V_3(\text{F}_2)\text{AsCl}_4^+$

** Impurity probably due to free SbCl_5 which has its most intense Raman band at 357cm^{-1} . (436)

CHAPTER 4

Reactions of diamine and diars with
phosphorus and antimony pentachloride.

Introduction

Chatt and Mann⁴³¹ described the preparation of the compound o-phenylenebisdimethylarsine (diars), and since then numerous workers have demonstrated its chelating action with a large number of transition metals. Clark and Nyholm have used this ligand to stabilize eight co-ordination in group IVA metals⁴²⁵, and have also produced the compounds $NbX_5, diars$ and $TaX_5, diars$ ⁷⁷, (X = Cl, Br.), which are monomeric non electrolytes in nitrobenzene, and hence the metal is, presumably, seven co-ordinate. In a sealed tube, $NbCl_5$ reacts with the ligand to give $Nb^{IV}Cl_4, 2diars$. The compound $TiCl_4, 2diars$ has been examined by X-ray diffraction methods⁴²⁵ which show that the co-ordination polyhedron around the titanium atom is a dodecahedron with eight vertices, consisting of four equivalent arsenic atoms and four equivalent chlorine atoms. These authors suggest that when complex formation takes place between this ligand and a transition metal containing d-electrons, the metal-arsenic bond has both σ and π character, the latter arising from back donation of the "non bonding" d-electrons of the metal to the empty d-orbitals of the arsenic atoms. The reaction of diars with group IVA(d^0) and group VA(d^1) has been investigated by Clark and Nyholm⁴²⁵ and by Sutton⁴³. The latter prepared the compounds $TiX_3, diars, H_2O$ and $TiX_4, diars$ (X = Cl, Br.). He suggests that the bonding consists of a σ bond between the "lone pair" on the arsenic and a vacant 3d titanium orbital, and also that the titanium feeds its 3p electrons into a vacant 4d orbital of the arsenic, forming a $p_{\pi} - d_{\pi}$ bond. The same author²⁰³ has prepared a series of compounds of $MX_3, diars$.

(M = P, As, Sb, Br. X = Cl, Br, I.). He suggests that the paired ns-electrons may be partly fed back into the d-orbitals of the arsenic atoms, reinforcing the σ bonding by a certain degree of π bonding. He argues that the apparent lack of reactivity of the ligand phen, towards members of group VB, where π bonding can only be accomplished by resonance in the heterocyclic ring, supports this argument. However, in this thesis a number of adducts of AsX_3 (X = Cl, Br) with the ligands phen and bipy are reported, and a crystal structure of the compound $AsCl_3 \cdot bipy$, reported herein, shows that the compound is a dimer with chlorine bridging, and the 4s electrons are not stereochemically active, although no evidence for π bond formation was available. Other workers^{16,440} have suggested that both phen and bipy can withdraw electrons from the metal into anti-bonding π orbitals on the ligand. Sutton's inability to prepare complexes in which phen was bonded to the metal is probably due to the fact that he carried out his reactions in a hydrohalic acid medium, which must, invariably, lead to products of the type $phenH^+ MX_4^-$.

In 1956 Ahrland, Chatt and Davies²⁴⁶ classified the elements on the basis of their acceptor properties for different types of ligands. In this there are basically two classes of acceptor. a) those which form their most stable complexes with the first ligand of each group, i.e. with N.O. and F., and b) those which form the most stable complexes with the second or subsequent ligand atom. In the table drawn up by Chatt and his co-workers²⁴⁶ the group VB elements are classified as type "a" acceptors, and consequently they

should form far more stable complexes with nitrogen than with phosphorus or arsenic donors. In tables 1 - 11, chapter 2, it can be seen that the majority of donors, in fact, donate through nitrogen or oxygen. It must not be overlooked that ligands containing these donor atoms are far more readily available, and the predominance of compounds with oxygen and nitrogen donors may be, to some extent, a reflection of this fact. Recently Fowles has reported that niobium and tantalum pentachlorides react preferentially with sulphur and selenium rather than oxygen, in the ligands thioxan and selenoxan^{224,225}, although both these metals are classified as "a" type acceptors. Fairbrother⁹⁴ has shown that the pentafluorides of these metals do, in fact, show "a" type behaviour.

Phosphorus and antimony both fall into the "a" category in Chatt's classification, but in view of the work of Fowles and Sutton it was interesting to compare the reactions of PCl_5 and SbCl_5 with nitrogen and arsenic donors, and because of its well established chelating properties, the ligand diars was used. Its nitrogen analogue o-phenylenebisdimethylamine (diamine) was also used. These ligands are not readily available, but their preparation has been described in the literature, and a brief discussion on the preparation of diars is given here.

Preparation of the Ligand o-phenylenebisdimethylarsine.

The reaction scheme used for the preparation of this ligand is outlined on the opposite page, figure 10. This compound was first prepared by Chatt⁴³¹ who converted the oxychloride (VII) by the

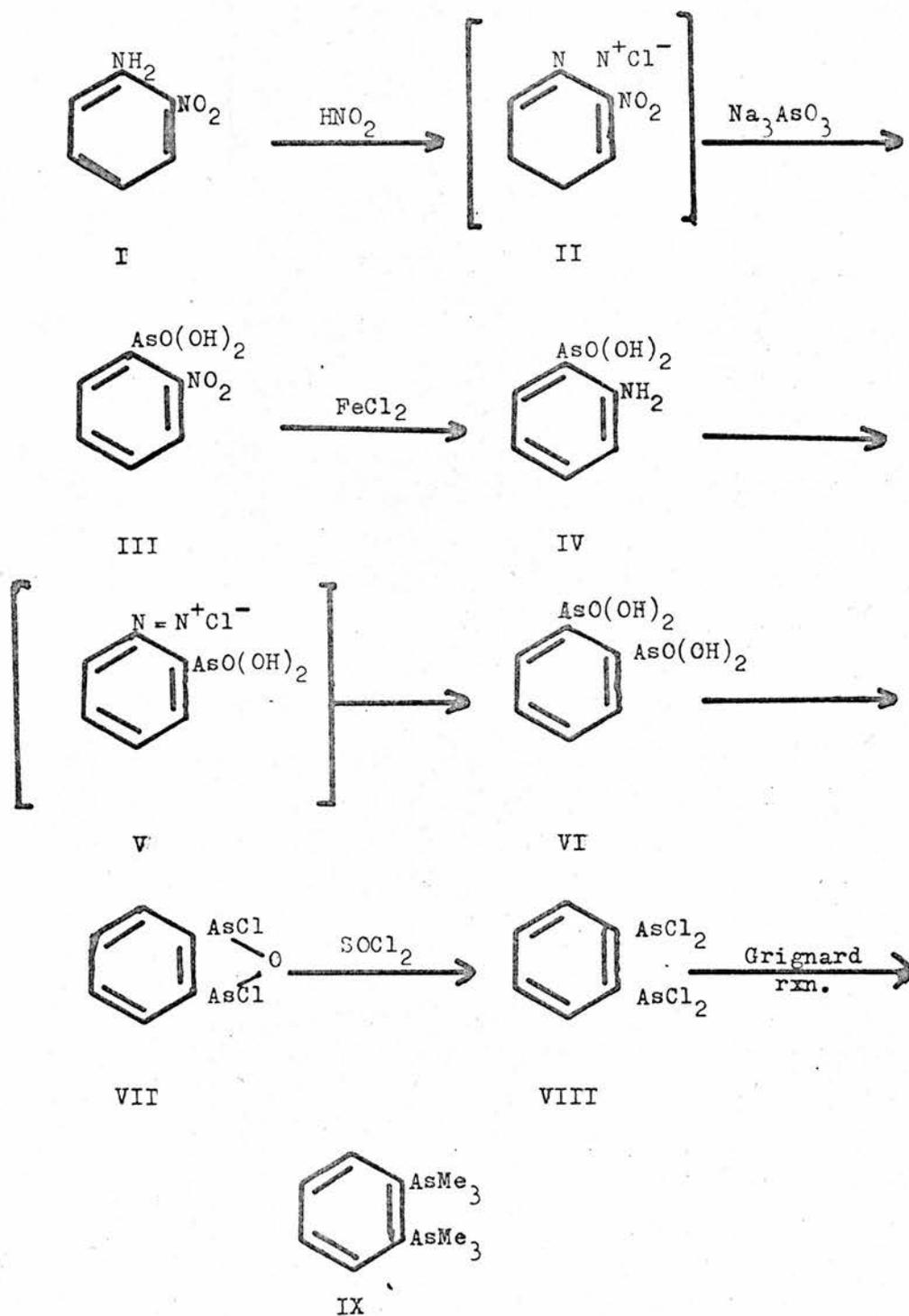


FIGURE 10

action of warm thionyl chloride to the tetrachloride (Vlll), which on treatment with an excess of Grignard reagent, yielded the ditertiary arsine (lX). Although Eberly and Smith⁴³² have reported the preparation of the tetrachloride (Vlll) from the diarsonic acid (VI) by a one step reaction, in our hands the oxychloride (Vll) was isolated.

Numerous methods have appeared in the literature describing each of the earlier stages. The following procedure was found to be most convenient. The preparation of o-nitrophenyl arsonic acid (lll) by the Bart reaction, and reduction of this to the amino compound (IV) was carried out by the method of Jacobs⁴²⁹. A second Bart reaction produced the diarsonic acid (VI)⁴³⁰, and this was converted to the dimethylarsine by the method of Chatt⁴³¹. The compound was identified by analysis, infrared, Raman and 'H. n.m.r. spectroscopy, and was adjudged pure by thin layer chromatography. The infrared and Raman spectra are reported in tables 23, 26, 27, pages 85 and 92.

A recent two step reaction has been published⁴⁷⁰ which greatly simplifies the preparation of this compound, improves the yield, and should make it far more readily available.

Discussion of Results.

1. PCl₅, diamine.

PCl₅ reacted with diamine in benzene solution to give an immediate pale yellow precipitate. Analysis indicated that a 1:1 adduct had been formed. Conductivity and molecular weight

measurements in nitrobenzene indicated that the material was a 1:1 electrolyte, in solution. The results of these measurements are given in table 22, page 83. Clark²⁰⁷ has briefly discussed the changes in the infrared of this ligand on co-ordination. He found that the strong band at 744 associated with C-H ring vibrations is raised by about 20cm^{-1} , and the strong bands at 560 and 579cm^{-1} are lowered by a similar amount. The infrared spectrum of the free ligand and the compound PCl_5 ,diamine are given in tables 23, 24. The spectra of the compound SnCl_4 ,diamine and 2SbCl_5 ,diamine are reported in the same tables. The band at 740cm^{-1} shifts by about 20cm^{-1} in every case, as observed by Clark. In the free ligand we observed a medium band at 689cm^{-1} , and on co-ordination this shifts to ca 720cm^{-1} . The two strong bands at 575 and 556cm^{-1} appeared as a doublet, see figure 12, and another medium band at 500cm^{-1} was observed in the free ligand. In all three compounds we observed a pattern of three bands occurring in the region ca. 600cm^{-1} and ca. 480cm^{-1} . The metal halogen vibrations at 455cm^{-1} sh. and 430cm^{-1} v.s. are very similar to the pattern observed for the adducts PCl_5 ,phen and PCl_5 ,bipy, reported in chapter 3. The Raman spectrum of this compound with bands at $356\Delta\text{cm}^{-1}$, $276\Delta\text{cm}^{-1}$ and $244\Delta\text{cm}^{-1}$ also shows excellent agreement with the spectra of PCl_5 with other bidentate ligands, see tables 18 and 19, pages 56 and 58.

The compound SnCl_4 ,diamine was prepared by mixing carbon tetrachloride solutions of the two materials. Attempts were also made to prepare compounds of the ligand with SiCl_4 and GeCl_4 , but even on distilling the tetrachloride into the ligand, on a vacuum line,

no reaction took place, and it was possible to separate the two starting materials by cold trap distillation on the vacuum line. 1:1 addition compounds of SiCl_4 and GeCl_4 with the ligands phen and bipy have been reported⁴⁶⁵, and the lack of complex formation with diamine suggests that this ligand is not as good a donor as phen or bipy, and further suggests that the PCl_4^+ ion is a better acceptor than either of the tetrahalides. The infrared and Raman spectra of SnCl_4 , diamine are reported in tables 22, 23. It was impossible to get a good Raman spectrum of this compound and only one band at $327\Delta\text{cm}^{-1}$ was definitely observed. The infrared showed three bands in the metal halogen region (352m, 325v.s., 310 sh.m.) in general agreement with that predicted for a cis MX_4L_2 molecule. Four metal halogen bands are, in fact, predicted, $2A_1 + B_1 + B_2$ for such a model, but the fourth, a symmetric stretching of trans halogens, is weak in the infrared. Clark²⁰⁴ has also reported the infrared spectrum of this compound. He observed two strong bands at 325cm^{-1} and 311cm^{-1} and also a weak band at 274cm^{-1} , which was not observed in our spectrum.

2. The System SbCl_5 -diamine

Addition of the ligand diamine to SbCl_5 in carbon tetrachloride produced a deep red precipitate. The stoichiometry and colour varied from preparation to preparation, and seemed to depend on the relative amounts of starting materials used. By adding one mole of ligand to two moles of SbCl_5 a product of approximately 2:1 (SbCl_5 :L) mole ratio was obtained, but by varying the ratio of starting materials the composition of the final product varied between 2:1 and 1:1.

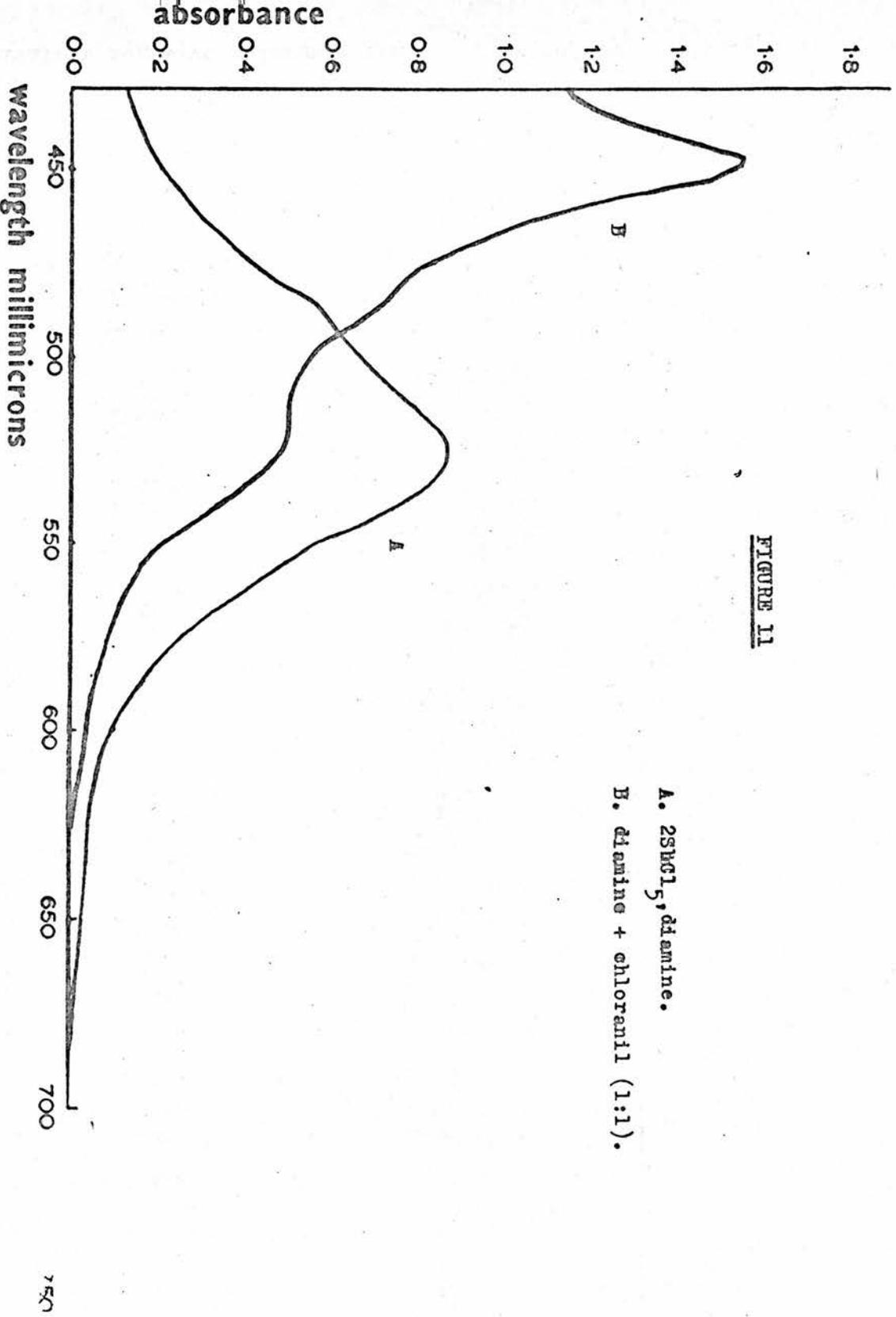


FIGURE 11

A. 2SWCl₅, diamine.

B. diamine + chloranil (1:1).

It is known that antimony pentachloride forms many coloured complexes with aromatic hydrocarbons which are paramagnetic⁴³⁶, and the appearance of colour has been explained in terms of the formation of monopositive carbonium ions⁴³⁷. Magnetic measurements, both on the solid and on methyl cyanide solutions, indicated that the compounds (of different stoichiometries) were diamagnetic and no e.s.r. signal could be detected in the methyl cyanide solution. The U.V. spectra of the compounds were recorded with a band at 527m μ , and a shoulder at 489m μ . Foster⁴³⁸ has reported the U.V. spectrum of the p-phenylenebisdimethylamine anion. He suggests that in the p-diamine chloranil complex both the mono anion and mono cation are present. Pott and Kommandeur in a recent paper⁴³⁹ have shown that the band at 500m μ , with a shoulder at 460m μ is, in fact, due to p-diamine²⁺ and the 448m μ band of chloranil is the chloranil²⁻ ion.

A solution of the o-diamine ligand with chloranil in MeCN was prepared and its U.V. spectrum recorded. Two bands were observed, one at 448, the other at 526m μ , and a shoulder at 480m μ (fig. 11). The band at 448m μ is due to the dianion of chloranil and hence the band at 526m μ is almost certainly due to the dipositive cation diamine²⁺. The molar absorptivity of the 2:1 complexes was measured, and a value of ca. 1400 for the 526m μ band was obtained. This figure is very similar to that reported by Foster for the p-diamine dianion⁴³⁸. However, Potts has shown that the crystal lattice of the system p-diamine chloranil, is built up of neutral diamine and chloranil molecules together with bivalent positive diamine ions and bivalent negative chloranil ions. They suggest a bivalent ion

concentration of about 20%. Although it is tempting to extrapolate these figures to the o-diamine SbCl_5 system, and to assume that the molar absorptivities of the ortho and para species are similar, there is no evidence to support such an assumption, and at present no estimate on the concentration of o-diamine²⁺ and its counter ion can be made. It has already been mentioned that SbCl_5 is used for the production of paramagnetic cations for e.s.r. measurements. However, there is no evidence for the presence of a paramagnetic anion, nor is the exact nature of this counter ion known.

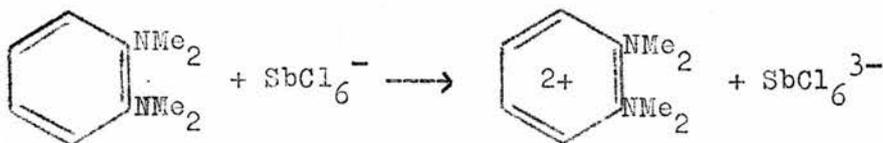
Conductivity and cryoscopic measurements in nitrobenzene were made on the 2:1 complex and are reported in table 22, page 83. The results of these measurements indicate that the material is a 1:1 electrolyte, and the infrared spectrum, fig.13B, shows one strong band at 342cm^{-1} associated with Sb-Cl stretching vibrations. When excess ligand is used and the stoichiometry is in the region of a 1:1 adduct, no band in this region of the infrared is observed. This suggests that the ligand reacts with the ion SbCl_6^- . The ligand was added slowly to a solution of $\text{PyH}^+\text{SbCl}_6^-$ in methyl cyanide, a red colour immediately developed, and the U.V. spectrum indicated the presence of the diamine dication. The infrared spectrum was recorded in the region $700 - 200\text{cm}^{-1}$ after each addition. It was observed that the $\nu_3(\text{F}_{1u})$ band of SbCl_6^- slowly decreased, and when excess ligand had been added, no trace of this band could be found.

An infrared study of the methyl cyanide solutions of the SbCl_5 -diamine system was carried out, and two interesting factors were noted. In the spectrum of the 2:1 complex a strong band was

observed at 540cm^{-1} , which is associated with the co-ordinated ligand, and also a band at 342cm^{-1} associated with Sb-Cl stretching vibrations, possibly $V_3(F_{1u})$ of SbCl_6^- . When excess ligand was added, two strong bands at 580 and 560cm^{-1} appeared and the band at 342cm^{-1} disappeared. The bands at 580 and 560cm^{-1} are associated with the free ligand, indicating that the excess ligand is unco-ordinated. On addition of more SbCl_5 to this solution co-ordination takes place and the bands due to the free ligand are no longer observed. When the ligand is added to $\text{PyH}^+ \text{SbCl}_6^-$ in methyl cyanide, free ligand is present, the presence of a medium band at 540cm^{-1} suggests that some co-ordination has taken place. The $V_3(F_{1u})$ band of SbCl_6^- is replaced by a broad, weak band with a band centre ca. 295cm^{-1} . Loss in energy made it impossible to record the spectrum in the region $300 - 200\text{cm}^{-1}$. These spectra are reported in table 25, page 88.

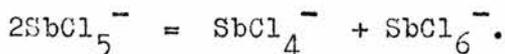
Unfortunately, when exposed to the laser Raman beam the 2:1 compound decomposed, giving a dark blue product. Even when sealed in an ampoule under high vacuum decomposition occurred slowly. The material is apparently photosensitive, but this is not surprising as the para substituted compound shows similar properties.

It is difficult to rationalize these results; the U.V. spectrum almost certainly indicates the presence of the dipositive cation, and the fact that this can be formed by reaction with SbCl_6^- makes it tempting to think in terms of an oxidation reduction reaction of the type:



The infrared and Raman spectra of the SbCl_6^{3-} ion have recently been published³⁹⁴, and the infrared active $\nu_3(\text{F}_{1u})$ band occurs at 178cm^{-1} , which is off the range of the instrument used in this study. Such a reaction would certainly account for the disappearance of the Sb-Cl stretching vibrations in these spectra.

In a recent paper Sato⁴⁷¹ has shown that phenothiazine and thianthrene form stable paramagnetic crystalline complexes with SbCl_5 . E.s.r. spectra have revealed that the origin of the paramagnetism is due to the aromatic cation radicals which are produced through oxidation with the SbCl_5 . Phenothiazine reacts with SbCl_5 to give a solid of composition $\text{C}_{12}\text{H}_9\text{NS}\cdot\text{SbCl}_4$, in which the anion is assumed to be $\text{Sb}^{(111)}\text{Cl}_4^-$. With an excess of SbCl_5 the compound $\text{C}_{12}\text{H}_9\text{NS}\cdot\text{SbCl}_5$ was obtained. Kainer and Hausser⁴⁷² have shown that 4,4'-dimethoxy-diphenylamine reacts with SbCl_5 , and suggest that SbCl_5^- is formed which then disproportionates according to the equation:



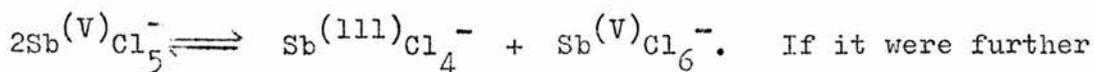
Sato⁴⁷¹ proposes a similar reaction to explain why his susceptibility measurements originate entirely from the monopositive ion radical in the above mentioned compounds.

In the compounds formed between diamine (L) and SbCl_5 there are a number of structures which must be considered.

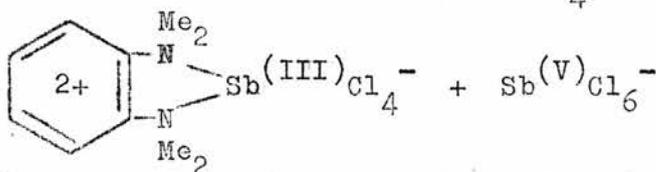
1) A straightforward 2:1 complex of the type $\text{LSbCl}_4^+ \text{SbCl}_6^-$ can be dismissed because it fails to explain the presence of the dianion observed from U.V. studies. The isoelectronic LSnCl_4 is colourless. Similarly a 1:1 complex of type $\text{LSbCl}_4^+ \text{Cl}^-$ need not be considered further.

2) For the 2:1 complex an oxidation reduction reaction of the type $\text{L} + 2\text{SbCl}_5 \rightleftharpoons \text{L}^{2+} 2\text{SbCl}_5^-$, and following the suggestion of Kainer⁴⁷²

the disproportionation of the anion would be written



assumed that the dication then reacted with SbCl_4^- to give



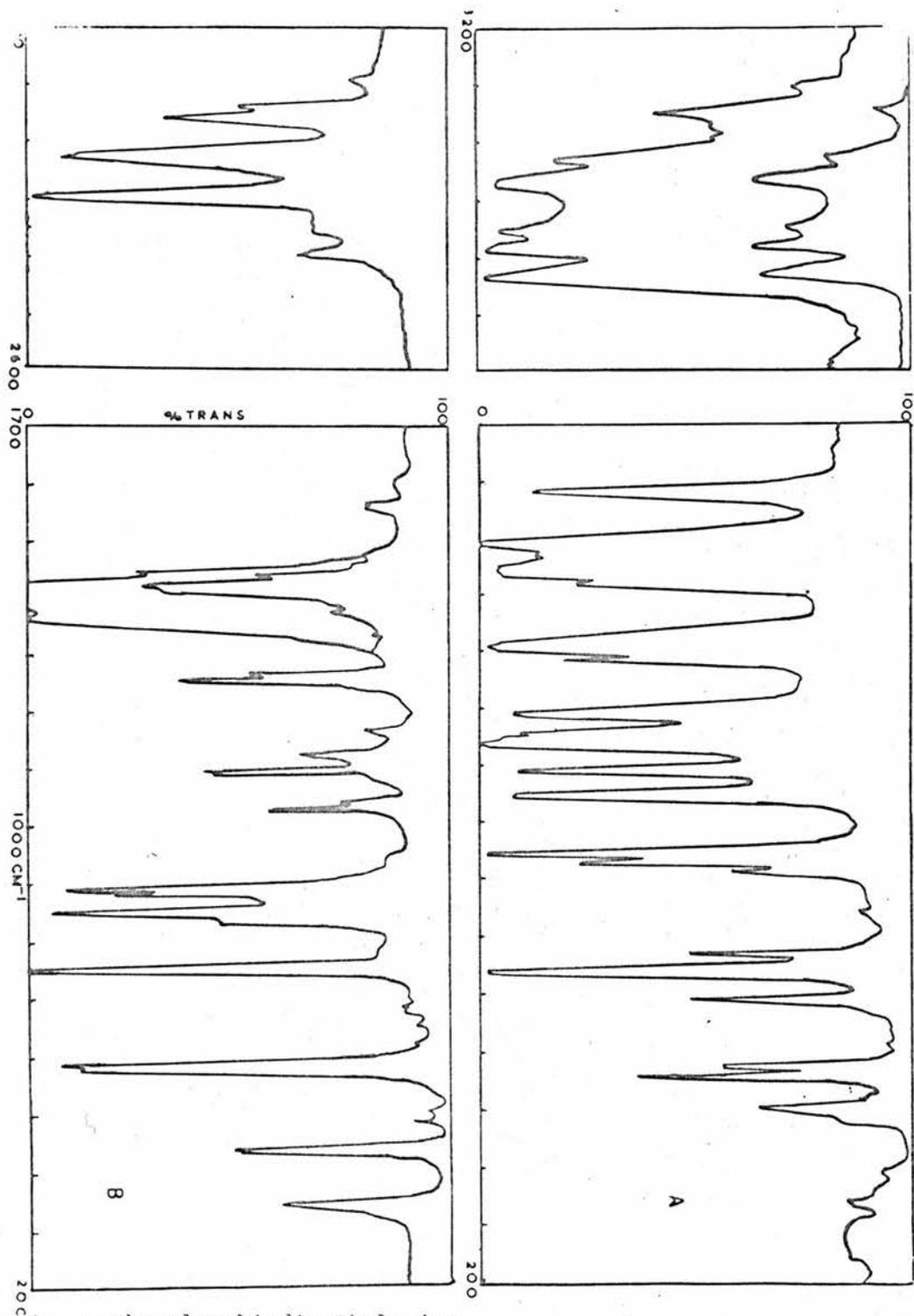
then the molecular weight, conductivity and infrared data observed could be readily explained.

For the 1:1 complex an oxidation-reduction reaction would lead to compounds of the type $\text{L}^{2+} + \text{Sb}^{(\text{III})}\text{Cl}_5^{2-}$ and since this anion is known³⁹³ and is diamagnetic, there is no need to introduce disproportionation for this ion.

In view of the difficulty experienced in interpreting the chloranil-*p*-diamine system where stable, treatable compounds are obtained, it is, with hindsight, not surprising that the *o*-diamine system with SbCl_5 should give such complex results, bearing in mind the established propensity for SbCl_5 to accept electrons.

TABLE 22: Molecular Weight and Conductivity of some diars and diamine Complexes in Nitrobenzene.

<u>Compound</u>	<u>Conductivity</u>		<u>Molecular Weight</u>		
	Molar Cond. mole litre ⁻¹ (X 10 ³)	Molar Cond. ohm ⁻¹ cm ² mole ⁻¹	Molar Conc. M. % w/w	M. found	M. calc.
PCl ₅ diamine	1.24	27	0.574	205	372.5
2SbCl ₅ , diamine	4.06 4.29	44 29.3	0.662	386	763.3
2SbCl ₅ , diars	9.32	20.4			884
PCl ₃ , diars	8.15	1.5			423



A. *o*-phenylenebisdimethylamine.

B. *o*-phenylenebisdimethylarsine.

TABLE 23: Infrared Spectra of some Diamine Complexes (1600 - 800cm⁻¹)

<u>Diamine</u> ^(a)	<u>PCl₅, diamine</u> ^(b)	<u>SbCl₅, diamine</u> ^(b)	<u>SnCl₄, diamine</u> ^(b)
	1600 br m	1610 m	
1586		1586 m	
1502 sh.w			
1492 s	1527 m.s	1540 w	
		1485 s	1482s
	1490 m.s		
1470 v.w			
1450 sh		1448 s*	
1445 s			
1420 w			
1309 s	1304 m	1305 w.sh	
1285 m-w	1284 w		1242 m-w
1192 m.s	1211 w	1210 w	
	1205 sh		
1156 w	1170 m	1164 m	1165 v.w
	1160 w		
1138 v.s	1132 w	1120 m-s	1145 v.w
	1120 w		1136 m
1090 m.s		1080 v.w	1099 v.w
			1082 m
1048 s	1060 w	1032 m-w	
		1001 w	1049 w-m
947 s	972 m	966 w	982 s
930 m-w	940 m	938 m	
911 w			905 s
	896 w	882 sh	890 w
			832 br.w

(a) liquid smear. (b) spectra were recorded as nujol mulls.

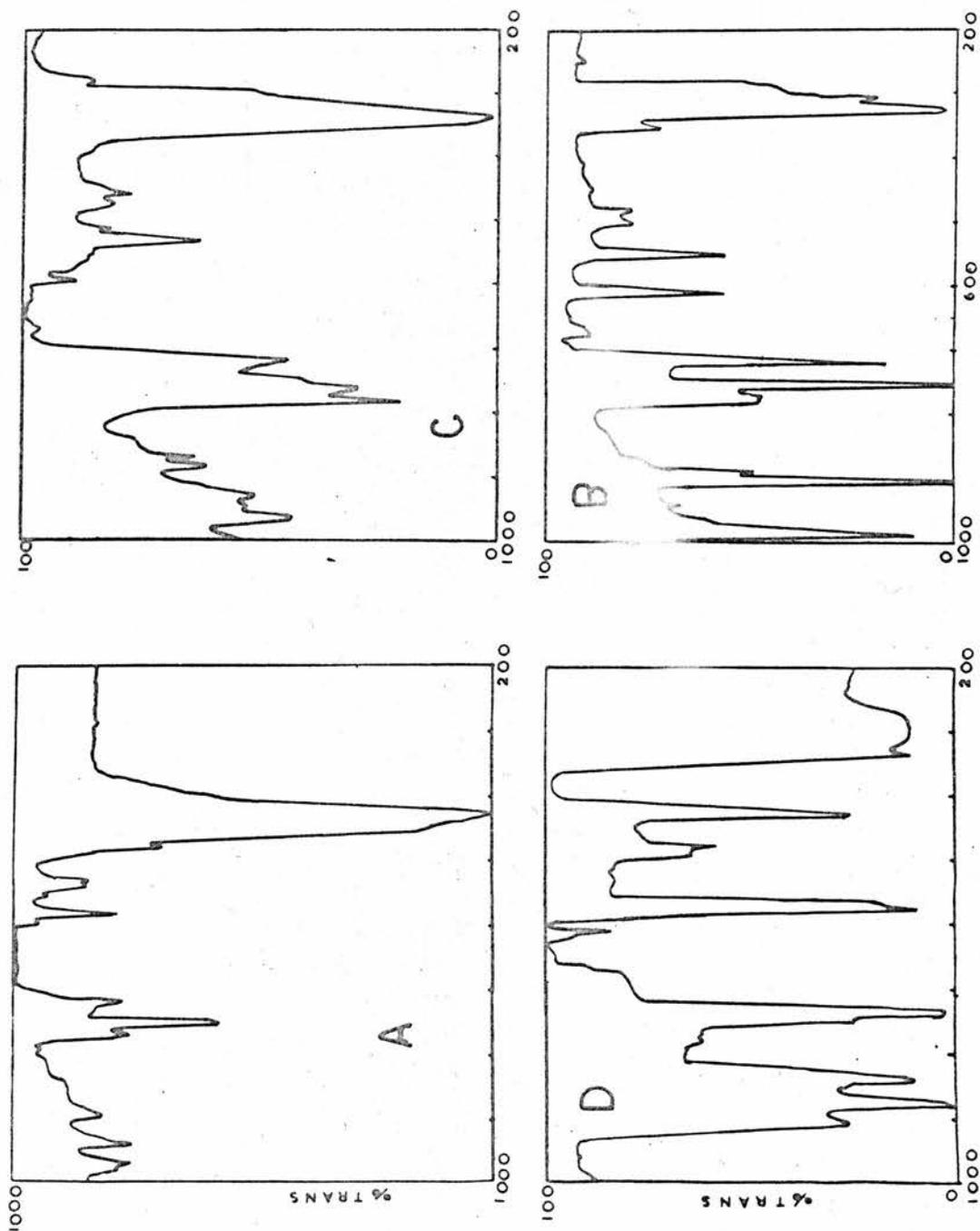


FIGURE 13. (Infrared spectra $1000 - 200\text{cm}^{-1}$)

A. PCl_5 , diamine.

. SnCl_4 , diamine.

. 2SbCl_5 , diamine.

D. 2SbCl_5 , diars.

TABLE 24: Infrared and Raman Spectra of some Diamine Complexes.i.r. 800 - 200cm⁻¹. Raman 700 - 100cm⁻¹ (6328Å)

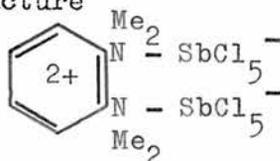
diamine	2SbCl ₅ ,diamine	SnCl ₄ ,diamine	PCl ₅ ,diamine		
i.r.	i.r.	i.r.	R.	i.r.	R.
	783 vs				
771 m-w		775 br m		774 m	
740 vs	761 s	755 s		756 s	
689 m	720 m-s	720 m-s		721 m	
	671 w	672 w			
		664 w			
	602 w	610 m			
575 m				587 m-s	
556 m-s	533 m	549 m-s		554 m	563 w
	512 w			535	
500 m-br	480 w	479 m-w		481 w	
	460 w			455 sh	
				431 vs	
338 w br	339 vs	350 sh w			358 vs
		325 vs	327 vs		
	290 sh w				
		310 m			276 s
					244 s
					168 w
					184 w

TABLE 25 Infrared spectra of System SbCl_5 -diamine in MeCN (650 - 200 cm^{-1})

2SbCl ₅ , diamine	SbCl ₅ +ex diamine	diamine + ex SbCl ₅	PyH ⁺ SbCl ₆ ⁻	PyH ⁺ SbCl ₆ ⁻ + diamine	diamine + chloranil
600w		595w	612w		
	581s	581m		581m	581s
555sh w	560s			560s	560s
539s	539w	538s		532m	
				500m	500s
480m 460m	445w sh			440m	
377v s	377v s **	377s ** 358sh	377v s **	370v s **	377v s **
342v s 325sh		341v s	340v s		
265w sh		295br sh m		295br w	

** CH_3CN solvent band.

Alternatively one can suggest covalent bonding between the nitrogen and antimony, giving a structure



However, steric requirements and the directional characteristics of the nitrogen "lone pair" immediately rule out such a possibility.

3. The System PCl_5 -diars.

An excess of diars was added to a saturated solution of PCl_5 in benzene. After 24 hours a small amount of white material had precipitated out, and chemical analysis indicated that the product was PCl_3 ,diars. This is in agreement with the work carried out by Sutton²⁰³, who reports a similar reaction in carbon tetrachloride. In an effort to prepare an authentic sample of the product, a mixture of the starting materials in benzene was allowed to stand for several hours, at which time a small amount of precipitate had settled out. The infrared of this material was identical with that obtained from the reaction with PCl_5 . Clark has observed shifts in the bands at 884, 846 (CH_3 rocking modes) and 741cm^{-1} (CH ring deformation) of the free ligand, to higher wave numbers (ca. 20cm^{-1}) on complex formation, and we observed the same effect with the compound 2SbCl_5 ,diars. However, in the compound PCl_3 ,diars, no shift in these bands was observed, which suggests that if complex formation has taken place it is very weak.

Several bands associated with P-Cl stretching modes were

observed, but it was not possible to draw any positive conclusion regarding the structure of the complex. Conductivity measurements in nitrobenzene, indicated that the material was non ionic, which agrees with the general trend observed by Sutton²⁰³ for complexes of group VB trihalides with diars.

Infrared studies in benzene solution, over the range $650 - 200\text{cm}^{-1}$ indicated that the addition of diars to PCl_5 caused immediate reduction of the pentahalide to the trihalide. This was extended to include the reaction between $\text{PCl}_4^+\text{SbCl}_6^-$ and diars, in methyl cyanide solution. Instead of chelating with the PCl_4^+ ion, as was expected, the addition of diars caused the disappearance of the band at 650cm^{-1} assigned to $\nu_3(\text{F}_{1u})$ of the PCl_4^+ ion, being replaced by a strong band at 490cm^{-1} , probably $\nu_3(\text{E})$ of PCl_3 ; even more surprising was the disappearance of the band at 340cm^{-1} $\nu_3(\text{F}_{1u})$ of SbCl_6^- , when excess ligand was added.

Once again, it is difficult to rationalize these results. It is tempting to suggest oxidation-reduction reaction as a possible explanation. Holmes^{178,180} has shown that PCl_5 is reduced by Me_3N , Et_3N and Me_3As , but not by Me_3P . The products of the reaction were $(\text{Me}_3\text{M})_2\text{Cl}_2$, ($\text{M} = \text{N}, \text{As}.$) and PCl_3 . SbCl_5 was reduced by Me_3As to SbCl_3 , and by Me_3Sb to the metal. In the light of these results it is not too surprising to suggest that the ligand diars, and also diamine, caused reduction rather than complex formation with the pentachlorides of phosphorus and antimony.

4. The System SbCl_5 -diars.

On addition of diars to a solution of SbCl_5 in carbon tetrachloride, a white precipitate was obtained which proved to be unstable, decomposing to a grey polymer-like material, and forming a black tar when exposed to moist air. By working quickly it was possible to measure the conductivity, record the infrared spectrum, and analyse for chloride, which indicated a compound of stoichiometry $2\text{SbCl}_5, \text{diars}$. A sample was sent for C and H analysis, but the poor results are probably an indication of the decomposition which takes place. The infrared and conductivity measurements suggest that the complex formed was $\text{SbCl}_4 \text{ diars}^+ \text{SbCl}_6^-$. However, the ready decomposition of the material made further investigations impossible.

TABLE 26: Infrared Spectrum of o-phenylenebisdimethylarsine.(4000 - 1000cm⁻¹) (a)

3102 w, 3060 m, 3040 m, 2974 s, 2904 s, 2850 sh.w, 2801 m,
 2450 w.br, 1948 br.w, 1910 w, 1800 m, 1601 w, 1556 m, 1440 sh.w,
 1420 s, 1370 m, 1262 m.sh, 1252 s, 1160 w, 1119 m-w, 1091 m,
 1035 sh.w, 1025 m.

(a) liquid smear.

TABLE 27: Infrared and Raman Spectra of Diars and 2SbCl₅diars.(i.r. 1000 - 200cm⁻¹; R. 150 - 1300Δcm⁻¹)

<u>Diars</u> ^(a)	<u>2SbCl₅diars</u> ^(b)	
i.r.	R.	
	1260 w	
	1165 w	
	1147 w	
	1126 w	
	1113 w	
	1037 w	
940 w	997 w	910 s
885 s		880 s
846 s		
827 sh		806 m
744 v.s	690 v.w	781 s
695 w		755 m
675 br.w	664 v.w	
648 v.w	650 w	650 w
576 v.s	576 s	590 w
570 sh		
498 v.w		480 m
433 s		420 m
340 m	344 m	340 sh.s
280 w		300 v.br.s
	231 w	
	174 w	
	126 w	

(a) liquid. (b) nujol mull.

TABLE 28 Continued

	$\text{PCl}_5 + \text{D}^b$	ppt. from $\text{PCl}_5 + \text{D}^c$	$\text{PCl}_4 + \text{SbCl}_6^-$ ^c	$\text{PCl}_4 + \text{SbCl}_6^-$ ^d	$\text{PCl}_4 + \text{SbCl}_6^- + \text{D}^d$	PCl_5^+ ^d	$\text{PCl}_5 + \text{D}^d$
	670v s *	671m	654s	650s 632sh		650s	
	590sh s	576s	588w ⁺	590w ⁺	588m ⁺ 538w	590s ⁺	590s ⁺
	490v s	490sh w 462sh w			490v s	494w	
	438m	432m				450s	
	398m	390w				392w-m	
93	361w	360sh w		370s *	374m *	378s *	378s *
	290m	295sh w			310br m		
	275w	275w		270w	270m-br	273w	
	245w	245w		245w	242w br	244w	244w

a, liquid smear.

b, solution in benzene.

c, nujol mull.

d, solution in acetonitrile.

* solvent band.

+ POCl_3 impurity.

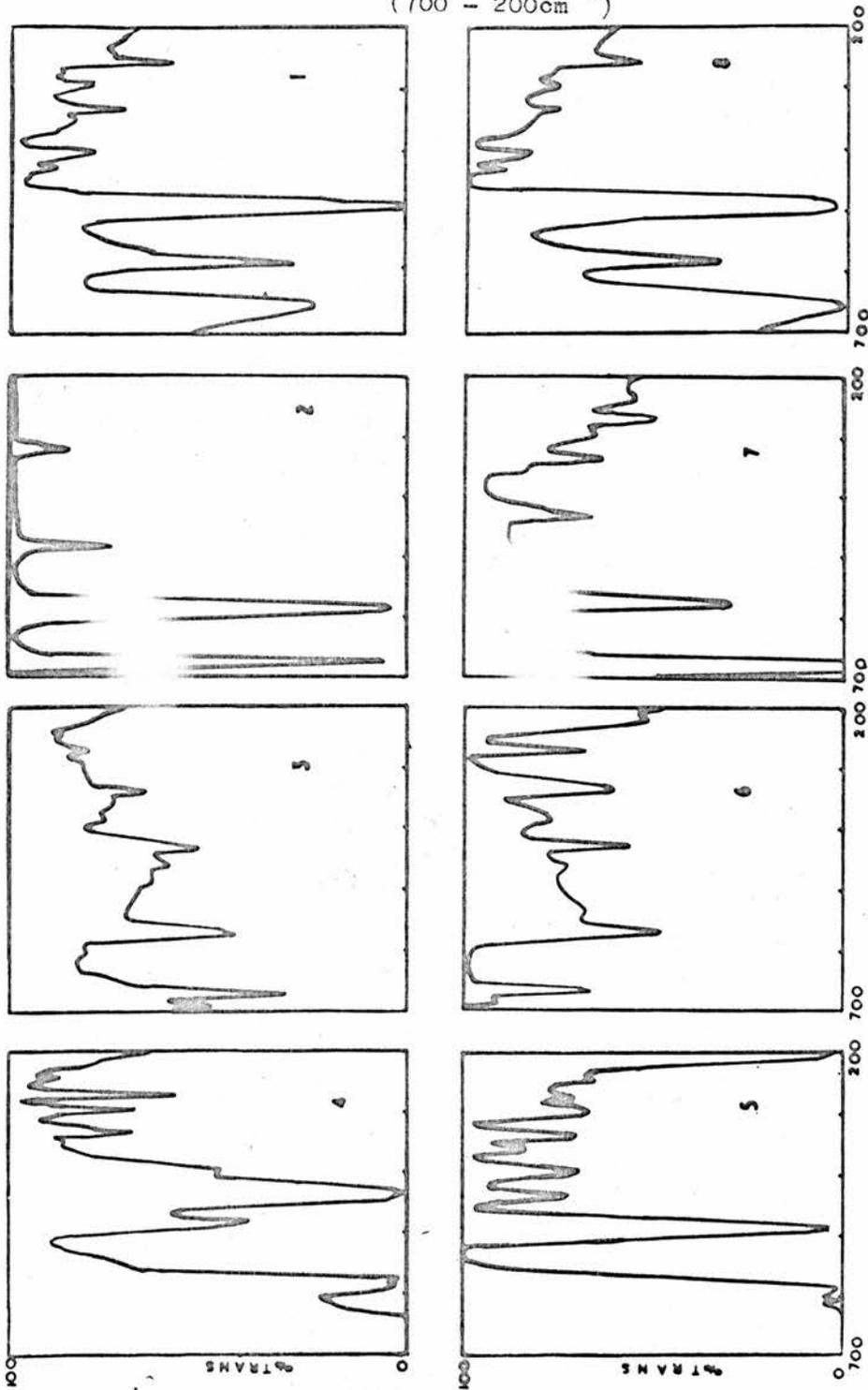
TABLE 28 Solution Spectra of the System PCl_3 -diars ($650 - 200cm^{-1}$)

PCl_3^a	PCl_3^b	diars ^a	diars ^b	$POCl_3^b$	PCl_3+D^b	PCl_3D^b	PCl_5^b
675w	660v s *			678s *	660v s *	674m	668v s *
583m ⁺	582m ⁺	575s	568s	583v s	582m ⁺	575br s ⁺	588m s ⁺ 578v s
485v s	490v s	498w	495w	487w	495br v s		483m
		465w	475w	471w		460br w	
	430w	435m	425m		432w	435m	439v s
392v w	401m				405m	390w	400sh w
	350w	342m	345sh		350br sh	340m	
332w	334m			322m w	332m ⁺		332m ⁺
	295w				295w		298m
		275w				275w	273m
258m	259m				258m	245w	245w

FIGURE 14Infrared Spectra of PCl_5 -Diars System (700 - 200 cm^{-1})

- 1) PCl_3 in C_6H_6 .
- 2) POCl_3 in C_6H_6 .
- 3) ppt. from reaction of PCl_5 with diars (nujol mull).
- 4) PCl_5 in C_6H_6 .
- 5) PCl_5 + diars (1:1 mole ratio) in C_6H_6 .
- 6) PCl_3 , diars (nujol mull).
- 7) Diars in C_6H_6 .
- 8) PCl_3 + diars (1:1 mole ratio) in C_6H_6 .

Figure 14: Solution Spectra of the PCl_3 system
(700 - 200 cm^{-1})



SECTION II

CHAPTER 5

A study of the solid systems $\text{PCl}_5\text{-SnCl}_4$

Introduction.

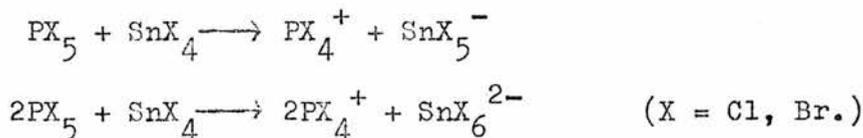
A molecular addition compound between phosphorus pentachloride and stannic chloride was reported more than a hundred years ago, by Casselmann²⁵⁶. This work was corroborated by Baudrimont^{257,258}. Both of these workers reported a 1:1 addition compound. In the original papers this complex was reported as $2\text{SnCl}_2 \cdot \text{PCl}_5$, but an atomic weight of 59.5 was used for tin instead of the correct value, 118.69. More recently, Groeneveld²⁵⁹ has reported the solid complexes $\text{SnCl}_4 \cdot \text{PCl}_5$ and $\text{SnCl}_4 \cdot 2\text{PCl}_5$. The same author has also reported a conductometric titration of SnCl_4 with PCl_5 , in POCl_3 ²⁶⁰. The titration curve showed a break after the equivalence point for one mole of PCl_5 , and one mole of SnCl_4 had been reached. Another break occurred at the mole ratio 2:1 ($\text{PCl}_5:\text{SnCl}_4$).

Bur'yanov²⁶¹ studied the system $\text{PCl}_5\text{-SnCl}_4$ in nitrobenzene and acetonitrile. The conductivity increased with increasing concentration of PCl_5 , and reached a constant value for the composition; two moles of PCl_5 to one mole of SnCl_4 . Cryoscopic measurements and viscosity determinations of nitrobenzene solutions confirmed the ratio $2\text{PCl}_5, \text{SnCl}_4$ in the complex compound. These measurements also gave some indication of a 1:1 complex.

The only reported investigation of the $\text{PBr}_5\text{-SnBr}_4$ system is a conductometric titration in acetonitrile, by Harris and Payne²⁶². These authors report inflection points at 1:1 and 2:1 mole ratios ($\text{PBr}_5:\text{SnBr}_4$). They made no attempt to isolate solid adducts and

no report of such solids has appeared in the literature.

In solution, both the 1:1 and 2:1 adducts are ionic, and the following structures, which fit the observed data, have been postulated.



There is no direct evidence for the presence of these ionic species in solution, nor has any evidence been presented indicating the type of species, ionic or molecular, present in the solid state. However, the ions PCl_4^+ and SnCl_6^{2-} are well established, and since the materials are ionic in solution, it seems reasonable to expect that these ions will be present in the solid state.

The interpretation of infrared and Raman spectra is the most generally applicable method for determining the configuration of molecules and ionic species. This method does not reveal ions inasmuch as the electron distribution is not directly measured. However, the presence of ions can easily be inferred by comparison with spectra of solids or solutions in which the ion is known to exist. Therefore a vibrational study of these compounds was carried out to investigate the structure in the solid state, and also the stereochemistry of the species present, particularly the SnCl_5^- ion.

The Tetrachlorophosphorus (V) Ion has been well characterised by crystal structure analysis²⁶⁴. It is tetrahedral, of ideal symmetry T_d . Thus there are four fundamental vibrations predicted by group theory. They are: $V_1(A_1)$, $V_2(E)$, $V_3(F_2)$, $V_4(F_2)$. These are all Raman active but only V_3 and V_4 are infrared active²³². The complete vibrational spectrum has been reported by Miller²⁶³, and is given in table 30, page 113.

The Hexachlorostannate (IV) Ion is a regular octahedron belonging to the point group O_h . Such a structure has six normal modes of vibration: $V_1(A_{1g})$, $V_2(E_g)$, $V_3(F_{1u})$, $V_4(F_{1u})$, $V_5(F_{2g})$, $V_6(F_{2u})$. Since the molecule has a centre of symmetry the rule of mutual exclusion holds. (This states that fundamentals appearing in the infrared spectrum will not appear in the Raman spectrum, and conversely, those appearing in the Raman will not appear in the infrared). It is also possible under this rule for certain transitions to be forbidden in both. Thus V_1 , V_2 and V_5 are Raman active, V_3 and V_4 are infrared active, whilst V_6 is inactive. The Raman spectrum is well known²³², and a number of workers^{233,265,266} have recently published the infrared data for this ion.

The work of Adams is of interest in that all the vibrational modes appear to be sensitive to the cation present, for example, V_1 of $SnCl_6^{2-}$ occurs at $323\Delta cm^{-1}$ in the compound K_2SnCl_6 , whereas in $(Et_4N)_2SnCl_6$ it is at $305.5\Delta cm^{-1}$, a difference of almost $20cm^{-1}$. The complete vibrational spectrum is given in tables 29, 30, pages, 111 and 113.

The Pentachlorotin (IV) anion has been reported several times in the literature. Cotter and Evans⁴⁵⁵ reported the formation of the triphenyl carbonium ion on the addition of SnCl_4 to a solution of $(\text{C}_6\text{H}_5)_3\text{CCl}$. They postulated the presence of the SnCl_5^- ion, although the dimeric ion $\text{Sn}_2\text{Cl}_{10}^{2-}$, which Gutmann²⁶⁷ has shown to be present in acetonitrile solution, can not be overlooked. Recently, however, the SnCl_5^- ion has been identified in the compound 3-chloro-1,2,3,4-tetraphenyl cyclobutenium pentachlorostannate. Byran⁴⁵⁶ has shown, by the use of X-ray crystal analysis, that SnCl_5^- is a trigonal bipyramid belonging to the point group D_{3h} .

Muetterties, in a recent monograph⁴⁵⁷, points out that for a pentaco-ordinate species there are two geometric structures worthy of serious consideration. One is a trigonal bipyramid, the other a tetragonal pyramid of symmetry C_{4v} . According to Muetterties, the difference in energy between these two structures should be small for most electronic configurations. Additionally there is the possibility of a low energy process that can interconvert the two idealised geometries. This requires only the bending process as outlined below.



This is a genuine vibration for an ML_5 species. Thus in dealing with the SnCl_5^- ion these two geometries must be considered.

D_{3h} symmetry gives rise to eight normal vibrations, $V_1(A_1')$, $V_2(A_1')$, $V_3(A_2'')$, $V_4(A_2'')$, $V_5(E')$, $V_6(E')$, $V_7(E')$, $V_8(E''')$. Six of these vibrations are Raman active (A_1' , E' , and E'''), whereas five

(A_2'' and E') are infrared active. Further, there is a coincidence of three E' vibrations. On the other hand C_{4v} symmetry requires nine normal vibrations. Thus group theory gives

$$\Gamma_{\text{vib.}} = 3A_1 + 2B_1 + 3E$$

and from the character table it can be seen that all nine are Raman active, whereas six, $3A_1 + 3E$, are infrared active. Therefore, for this model a coincidence of six vibrations is expected.

Stereochemistry by Vibrational analysis. The spatial arrangements of atoms, in ions or molecules, determines the molecular symmetry. A molecule may possess a number of symmetry elements, each element being a symmetry operation which will produce a configuration of the nuclei, indistinguishable from the original. In a vibrating molecule when such symmetry operations are carried out, the mode concerned does not necessarily lead to self coincidence; the various normal modes may thus be symmetric or antisymmetric, with respect to the symmetry elements. There are four types of symmetry elements which are discussed in many standard texts, for example, the text by Nakamoto²³². The symmetry or point group to which a discrete molecule belongs is determined by the number and type of symmetry elements it possesses. A molecule has $3N-6$ normal modes of vibration ($3N-5$ for a linear molecule), the "normal vibration" of a polyatomic system may be defined as a vibrational state, in which each atom carries out a simple harmonic motion about its equilibrium position, each atom having the same frequency of oscillation. These normal vibrations can be classified into various species according to their

symmetry properties. Of the $(3N-6)$ normal modes of a polyatomic acyclic system, $(N-1)$ may be described as, primarily, bond stretching vibrations, usually represented by V together with additional details relating to the form of the vibration. The remaining $(2N-5)$ modes are angle bending vibrations. The frequency of a vibration depends on the force constant and on the reduced mass of the atoms involved. Thus the numbers and frequencies of vibrations not only identify a molecule or ion, but also determine its stereochemistry.

This extremely simplified explanation must be treated with caution. The above discussion refers to an isolated molecule, and no consideration of intramolecular effects has been considered. The actual experimental spectral measurement is made on solids or solutions, and a number of difficulties can arise in determining the number of fundamentals from an observed spectrum. The intensities of overtones and combination bands are sometimes comparable to those for fundamentals, when they are enhanced by Fermi resonance, and fundamentals may appear weakly in the spectrum. The spectra recorded from the solid state are usually on microcrystalline samples, and therefore the problems of site symmetry and factor group or correlation field splitting must be considered. Site symmetry can be described as the local symmetry of the crystalline environment around the molecule in the unit cell. In general the site symmetry, in the solid state, is lower than molecular symmetry, hence bands forbidden in the gaseous or solution state may appear weakly, and degenerate vibrations may split in the crystalline state. Factor group or correlation splitting is concerned with interactions

between vibrations in different molecules within the same unit cell. This can introduce a further splitting of bands up to N components per non degenerate mode of the molecule, where N is the number of molecules in the unit cell.

From the foregoing discussion it can be seen that great care must be taken in assigning a stereochemical model to a molecule on the basis of its vibrational spectrum. Simple calculations of a vibrational spectrum, by the method of normal co-ordinate analysis²³², can be an added asset in assigning the stereochemistry of a molecule. However, one is nearly always faced with the problem of having more "unknowns" (i.e. force constants) than "knowns" (i.e. frequencies), and some approximations have to be made. Even then the whole procedure of transferring force constants from molecule to molecule has been questioned repeatedly, but Beattie and his school have shown the utility of such calculations, provided the numerical values of the force constants are treated with caution, and the force field simplifications are selected to make sense chemically.

The frequency of a normal vibration is determined by the kinetic and potential energies of the molecule. The kinetic energy is determined by the masses of the individual atoms and their geometrical arrangement in the molecule. The potential energy arises from interaction between individual atoms and is described in terms of force constants. By assuming a reasonable set of force constants, it is possible to calculate the frequencies, and comparison between the calculated and observed spectrum for different models can be helpful in deciding which particular model should be adopted.

Strictly speaking, force constants are not transferable from one molecule to a different type, but it does seem to work. However, it was felt that transferring force constants from SnCl_6^{2-} ion to the two different models (D_{3h} and C_{4v}) proposed for SnCl_5^- , and calculating a vibrational spectrum for each of them, would help in deciding which model best fitted this particular ion. Since the completion of this work Beattie²³³ and Green²⁶⁵ have published infrared and Raman data on this ion. Beattie calculated frequencies for SnCl_5^- (and other molecules) by transferring octahedral force constants to the axial bonds, and tetrahedral force constants from InCl_4^- to the equatorial bonds. This last step is based on the assumption that the force constants of the group III ion which is isoelectronic with SnCl_4 , will be more representative of the conditions in the species of interest than would the force constants from the uncharged SnCl_4 . That the force constant for bond stretching increases as the negative charge decreases, has been shown by Woodward⁴⁴¹ for a series of isoelectronic triads, and the recent publication of the infrared and Raman spectra of SbCl_6^{3-} ion³⁹⁴ shows, for example, that $V_3(F_{1u})$ decreases from 330 (SbCl_6^-) to 178cm^{-1} , and the stretching force constant, f_r , although not published, will presumably be lower than the value of $1.793\text{ md.}\text{\AA}^{-1}$ for SbCl_6^- (233).

Discussion of Results and Conclusions

A. Preparation of the Compounds

Several different methods of preparing these compounds were used and are described adequately in Section II, chapter 8. Gutmann prepared the 1:1 complex by addition of a solution of PCl_5 to SnCl_4 , using phosphoryl chloride as solvent, at a temperature of 70°C . Working at room temperature, in a dry box, we isolated a product of stoichiometry $3\text{PCl}_5 \cdot 2\text{SnCl}_4$. The preparation was repeated four times, and each time the same material was obtained. The 1:1 adduct was prepared by adding PCl_5 to an excess of SnCl_4 and sealing the mixture in a tube under high vacuum. The tube was heated to ensure complete reaction. Acetonitrile was found to be an ideal solvent for the preparation of the 2:1 complex.

B. The Infrared and Raman Spectra

The infrared and Raman spectra of these three compounds, along with other relevant spectra, are shown in tables 29, 30, pages 111, 113. The infrared spectra of the solids were recorded as nujol mulls. The higher frequency bands of the compound $\text{Ph}_3\text{C}^+ \text{SnCl}_5^-$ are in good agreement with earlier work⁴⁵⁸, and bands associated with the SnCl_5^- anion were identified by comparison with $(\text{Ph}_3\text{C})(\text{ClO}_4)$. The band at ca. 310cm^{-1} reported in a number of triphenylmethyl compounds⁴⁵⁹ was not observed; otherwise spectral agreement was good.

The three $\text{PCl}_5\text{-SnCl}_4$ compounds show a strong band at $648 \pm 3\text{cm}^{-1}$, and the Raman spectra have bands at 182 ± 2 , 253 ± 1 , 459 ± 1 and $660 \pm 3\text{cm}^{-1}$,

in agreement with the expected vibrational spectrum of the PCl_4^+ cation^{235,263}.

The $V_1(A_{1g})$ band of SnCl_6^{2-} , along with the other vibrational bands, has been shown by Adams²⁶⁶ to be cation dependent. We also observed this effect in our spectra. The compound $(\text{NH}_4)_2\text{SnCl}_6$ gave a strong band at $323\Delta\text{cm}^{-1}$, $(\text{Et}_4\text{N})_2\text{SnCl}_6$ at $312\Delta\text{cm}^{-1}$ and $2\text{PCl}_5\cdot\text{SnCl}_4$ at $307\Delta\text{cm}^{-1}$. All these are assigned to $V_1(A_{1g})$ of SnCl_6^{2-} , as they fall within the range observed by Adams for this Raman active band. We observed the same cation dependency for the Raman active bands $V_5(F_{2g})$, occurring in the range $158 - 184$ ²⁶⁶. The Raman spectrum of SnCl_6^{2-} reported in Nakamoto was taken from a paper by Woodward and Anderson⁴⁴², and the spectrum concerned was recorded from an aqueous solution.

Adams has reported the Raman spectra of a number of solid compounds containing the SnCl_6^{2-} ion. Although cation variation seems to affect the spectra, $V_2(E_g)$ falls in the range $241 - 250\Delta\text{cm}^{-1}$. Unfortunately, PCl_4^+ also has a strong band at $251\Delta\text{cm}^{-1}$ (235,263), assigned to $V_4(F_2)$, and as this occurs in all three compounds it is difficult to decide if the very weak band at $233\Delta\text{cm}^{-1}$, in the compound $2\text{PCl}_5\cdot\text{SnCl}_4$, should be assigned $V_2(E_g)$ SnCl_6^{2-} , or if this band occurs in the region $240 - 250\Delta\text{cm}^{-1}$, where it will be obscured by the strong PCl_4^+ band. The same ambiguity arises in the region $160 - 185\Delta\text{cm}^{-1}$, where $V_2(E)$ of PCl_4^+ and $V_5(F_{2g})$ of SnCl_6^{2-} overlap. The compound $\text{Et}_4\text{N}\text{SnCl}_6$ gives rise to a medium intense band at $160\Delta\text{cm}^{-1}$, and since the frequency of this band, as reported by Adams, seems to decrease with increaseng size of cation, it is tentatively suggested that the

band at $166\Delta\text{cm}^{-1}$, in the compound $2\text{PCl}_5 \cdot \text{SnCl}_4$, should be assigned to $V_5(F_{2g})$ of SnCl_6^{2-} . Therefore, the strong band at $183 \pm 2\Delta\text{cm}^{-1}$ in all three compounds should be assigned $V_2(E)$ of PCl_4^+ .

The incomplete spectral data collected by us for the SnCl_5^- ion makes an unambiguous assignment of its stereochemistry impossible. Infrared data could only be recorded down to 200cm^{-1} and the Raman data down to $100\Delta\text{cm}^{-1}$. It was necessary to operate the Raman instrument at maximum sensitivity when recording the spectrum of $\text{PCl}_5 \cdot \text{SnCl}_4$ and background noise made it difficult to clearly define weak peaks. The spectra (i.r. and R.) are recorded in tables 29, 30. and where any doubt exists, the band is marked "?".

Simple calculations, which are discussed in the next section, were made for both possible stereochemistries. The results of these calculations, along with the observed spectra, are given in table 31. It can be seen that without far infrared data (below 200cm^{-1}) to observe the correlation between Raman and infrared, no definite assignment is possible. The good agreement for C_{4v} depends on the three dubious bands at 310, 151 and $120\Delta\text{cm}^{-1}$.

In general the data gives better agreement with the calculated spectrum for D_{3h} than with that for C_{4v} and assignment of the observed bands to the former model gives a better correlation of the expected infrared and Raman activity, than does the C_{4v} model. Without far infrared data an unambiguous assignment cannot be made, and the possibility of the ion having a tetragonal pyramid structure, although unlikely, has not been completely ruled out.

Beattie's spectral data²³³ agrees well with that reported above,

although he does not record bands at 310, 174, 151 or $120\Delta\text{cm}^{-1}$, which we have tentatively suggested. The far infrared spectrum definitely establishes the stereochemistry of the ion as D_{3h} , in agreement with the suggestion made above. For comparison purposes, the calculated and observed spectra from Beattie's work are included in table 31, along with our observed and calculated spectra.

The solid adduct $3\text{PCl}_5, 2\text{SnCl}_4$ contains the PCl_4^+ ion with bands at 655 s and 248 m in the infrared. Its Raman spectrum contains four bands which are readily assigned to the fundamental vibrations of the PCl_4^+ ion²⁶³. The compound does not contain co-ordinated or free phosphoryl chloride, as evidenced by its infrared and Raman spectra. Co-ordinated POCl_3 shows a strong band in the region $1200 - 1300\text{cm}^{-1}$ (i.r.) or, more specifically, in the compound $\text{SnCl}_4, 2\text{POCl}_3$ it has a band at 1215cm^{-1} , and also a partially resolved doublet at 1300 and 1285cm^{-1} (446). No evidence for these bands could be found, nor was there any evidence for the strong Raman band at $523\Delta\text{cm}^{-1}$ ($\text{SnCl}_4, 2\text{POCl}_3$) in the compound $3\text{PCl}_5, 2\text{SnCl}_4$.

Vibrational spectroscopy also showed the absence of the ion PCl_6^- , and the band at 355cm^{-1} , associated with SnCl_5^- ion (V_5E') was also absent. It is suggested that the formulation $(\text{PCl}_4^+)_3(\text{Sn}_2\text{Cl}_{11})^{3-}$ is consistent with our observations. The most likely stereochemistry of such an ion would be each tin atom octahedrally co-ordinated by six chlorine atoms, with one bridging chlorine atom. The equatorial chlorine atoms could be either eclipsed or staggered. The former model belongs to the point group D_{4h} , whereas the staggered configuration, with an eight-fold rotation

reflection axis, coincident with C_4 , belongs to the point group D_{4d} .

Group theory arguments predict that the eclipsed model D_{4h} will have ten stretching vibrations:

$3A_{1g}(R) + 3A_{2u}(i.r.) + B_{1g}(R) + B_{2g}(R) + E_g(R) + E_u(i.r.)$. Two of

these modes ($A_{1g} + A_{2u}$) are associated with the bridging chlorine atom, and from consideration of molecules containing bridging atoms,

these two would be expected at lower frequency than the other

(non bridging) Sn -Cl stretching vibrations. For the staggered

model D_{4d} , nine stretching vibrations are predicted:

$3A_1(R) + 3B_2(i.r.) + E_1(i.r.) + E_2(R) + E_3(R)$. Once again, two of

these modes ($A_1 + B_2$) are associated with the bridging chlorine atoms.

For either of these models we would expect 4 infrared and 6 Raman (D_{4h}), or 4 infrared and 5 Raman bands (D_{4d}). In fact, in the infrared we observed only one very strong broad band at 315cm^{-1} associated with the anion. Three Raman bands occur in the Sn - Cl stretching region. With the possibility of accidental degeneracy, or unresolved bands occurring, and the further possibility of other active bands being too weak to be observed, it is felt that the vibrational data does not rule out the possibility of an anion of the type $\text{Sn}_2\text{Cl}_{11}^{3-}$ being present. Although the band at 355cm^{-1} (V_5E) of SnCl_5^- was missing in this compound, the Raman spectrum does not rule out the possibility of a mixture of SnCl_5^- and SnCl_6^{2-} . The medium band at 322cm^{-1} is not explained on this assumption. X-ray powder photographs of the three relevant materials were taken and the results indicate that the 3:2 compound is not a mixture of the other two. The $\sin^2 \Theta$ values for the three photographs, and also PCl_5 as a comparison, are given in table 32, page 117.

The Raman spectrum of the compound $\text{SnCl}_4 \cdot 2\text{POCl}_3$ is reported in table 30. Two previous Raman studies of this compound have been reported. Brune and Zeil⁴⁴⁷ studied a melt of $\text{SnCl}_4 \cdot \text{POCl}_3$ in POCl_3 at 30° , whereas Kinell⁴⁴⁸ studied a solution of SnCl_4 in POCl_3 (mole ratio 1:20). The agreement between the two sets of results was negligible. Kinell's results are given in a diagram without quoting frequencies. Reading from this table, the values 586, 511, 481, 337, 312, 289, 266, 208, 191, 142 and $118 \Delta \text{cm}^{-1}$ were obtained. These values show reasonable agreement with those given in table 30. and it seems unlikely that the spectrum given by Brune and Zeil was for the compound $\text{SnCl}_4 \cdot 2\text{POCl}_3$, although this is the only compound indicated in the phase diagram⁴⁶. The compound is known to be cis from X-ray data⁴⁶ with co-ordination through oxygen. The POCl_3 groups in the adduct are not appreciably different from free POCl_3 . Thus on a very simple model we would expect the co-ordinated POCl_3 to show P - Cl vibrations similar to those in the free ligand, whereas treating the acceptor part of the molecule separately, as a distorted tetrahedron of C_{2v} symmetry, four vibrations would be predicted. (See chapter 3 for a discussion of this point). The Raman spectrum of this compound shows surprisingly good agreement with this simple model, having Raman bands at 213 s (194S), 299 m-w (267), 341 s (337m), 523 s (486v.s) Δcm^{-1} . The values in brackets are the reported²³² fundamental vibrations of free POCl_3 . There are also two bands at 372 m and 322 m-s which may be associated with the acceptor part of the molecule, occurring at 372 m and 322 m-s Δcm^{-1} .

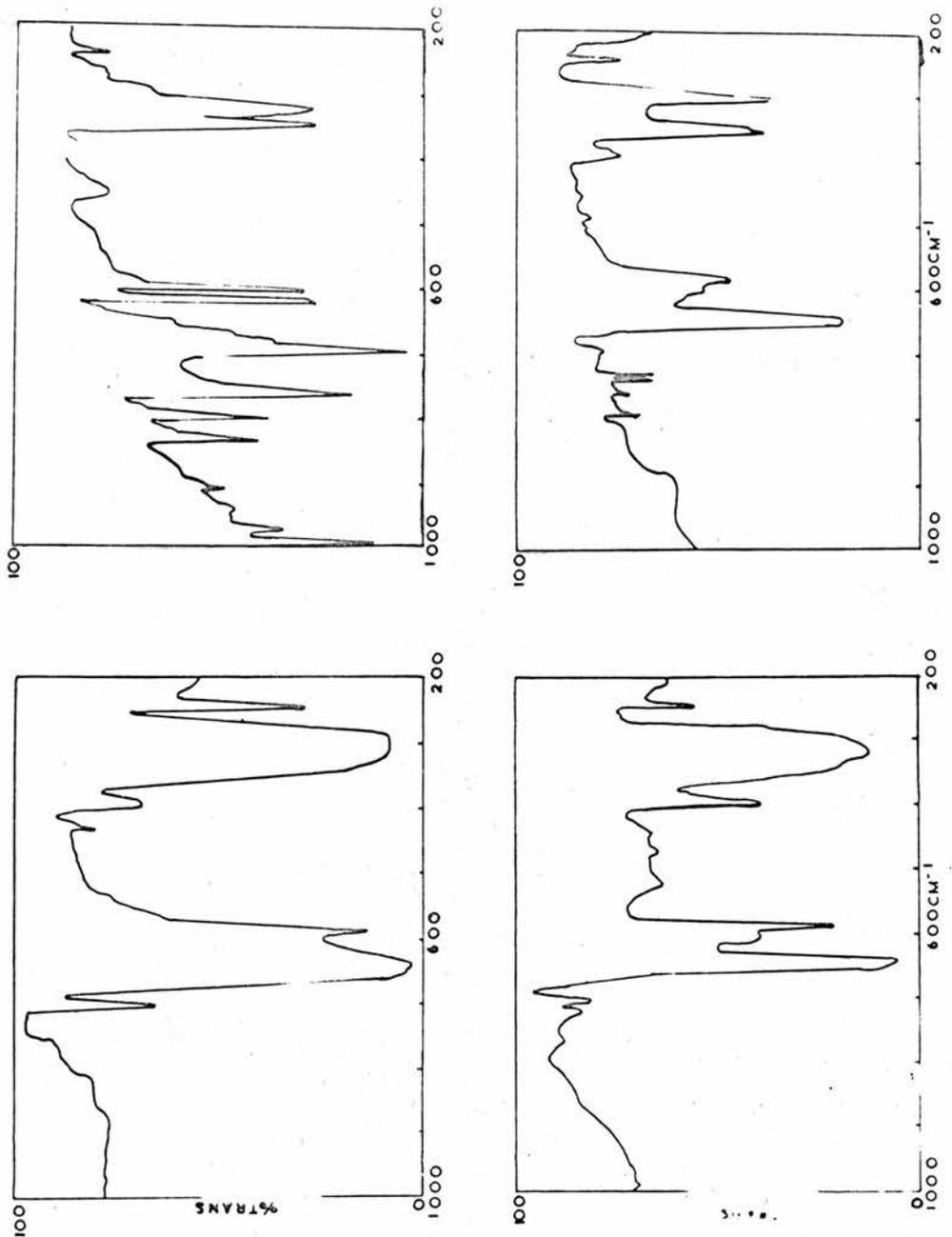
Figure 15: Infrared Spectra (1000 - 200 cm^{-1})A. $\text{SnCl}_4 \cdot 2\text{PCl}_5$ B. $\text{O}_3\text{CCl} \cdot \text{SnCl}_4$ C. $\text{O}_3\text{CCl} \cdot \text{PCl}_5$ D. $2\text{SnCl}_4 \cdot 2\text{PCl}_5$

TABLE 29 - INFRARED SPECTRA (700-210 cm^{-1}) OF THE CHLORIDE SYSTEMS

Sample	State	Principal Absorption bands (cm^{-1})													
		700m	648s(PCl_4^+)	585 \neq	395w	355s	305s	245m(PCl_4^+)	720s	690w	651s(PCl_4^+)	538 \neq	490w \neq	435s(PCl_6^-)	310sv $_3$ (F_{1u}) 173v $_4$
$\text{PCl}_5, \text{SnCl}_4$	solid ^{af}														
$2\text{PCl}_5, \text{SnCl}_4$	solid ^{af}	706m	650s(PCl_4^+)	590m \neq	485w \neq	400w	310vs, br	243m(PCl_4^+)							
$3\text{PCl}_5, 2\text{SnCl}_4$	solid ^{af}	702m	645s(PCl_4^+)	583 \neq	396m		315vs, br	243m(PCl_4^+)							
PCl_5	solid ^{af}														
SnCl_6^{2-} (b)															
$\text{Ph}_3\text{CCl}, \text{SnCl}_4$	solid ^{af} d	695s	619s	608s	475w	396w	348s	326s							
$[\text{Ph}_3\text{C}][\text{ClO}_4]$	solid ^{af}	692s	615m	604m	460w										
Ph_3CCl	solid ^{af}	690s, br	664w	625m	615m	500w									
Ph_3COM	solid ^{af}	692s	638s	580w											

a Nujol mull, d polythene windows, f CsI windows, \neq POCl_3 impurity.

(b) As Reported by Adams and Morris²⁶⁶.

TABLE 30: The Raman Spectra

PCl_4^+ (a)	SnCl_6^{2-} (b)	$\text{PCl}_5, \text{SnCl}_4$	$2\text{PCl}_5, \text{SnCl}_4$	$3\text{PCl}_5, 2\text{SnCl}_4$
		120 v.w?		
		151 v.w?		130 w
	158	166 w	166 m-s	162 m-w
		174 w?		
171 s		184 m-s	183 m-s	181 s
		200 w		
	229	242 w	233 v.w	
251 s		253 s	252 s	253 s
		310 v.w?	296 w	302 m
	311		307 s	
			321 w.sh	322 m
		339 s	339 w	337 v.s
			345 w	
		354 w		
458 s		458 s	460 v.s	460 v.s
				646 w
658 w		660 w	663 w	658 w

(a) Taken from a paper by Miller²⁶(b) As reported by Nakamoto²³².

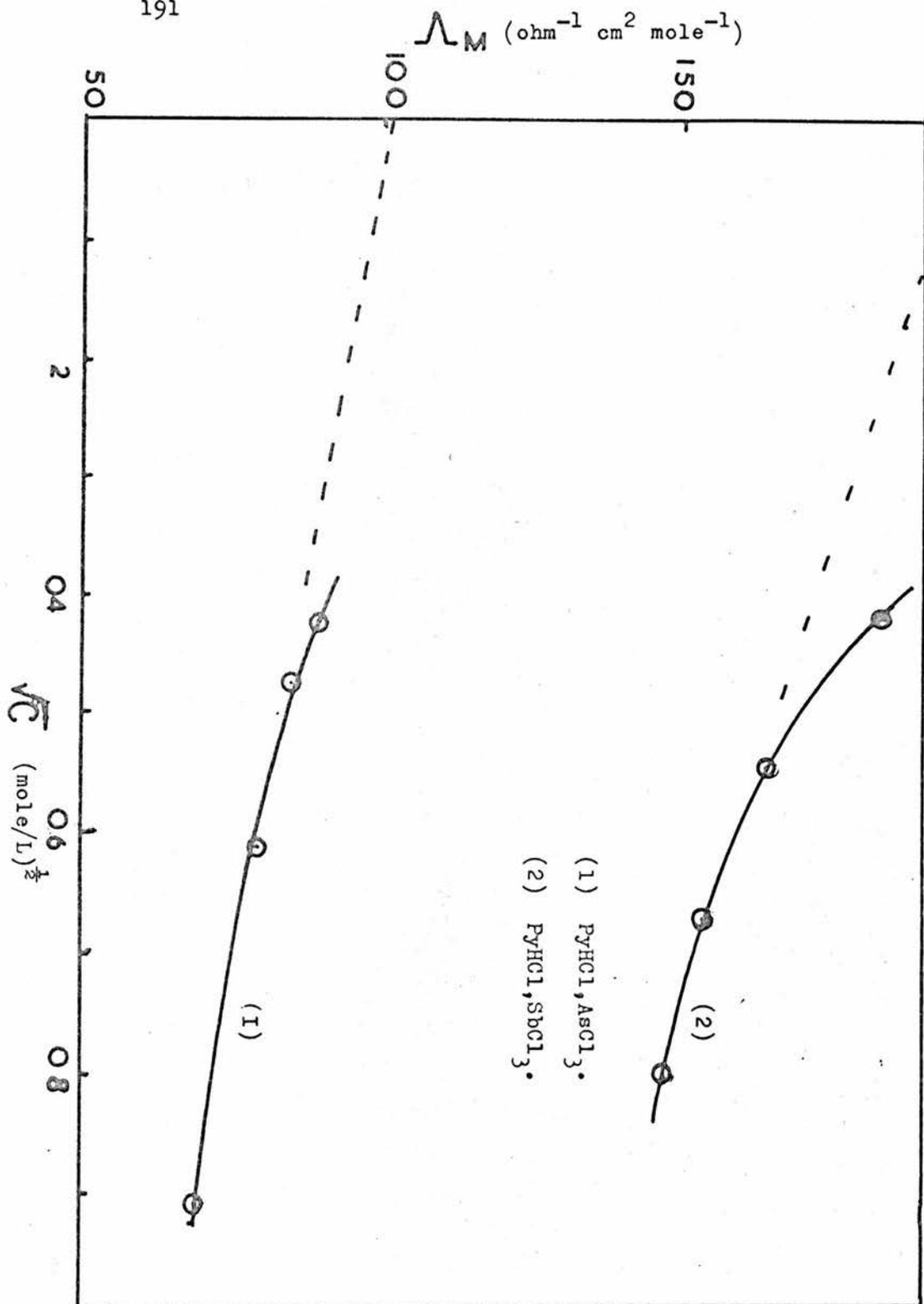
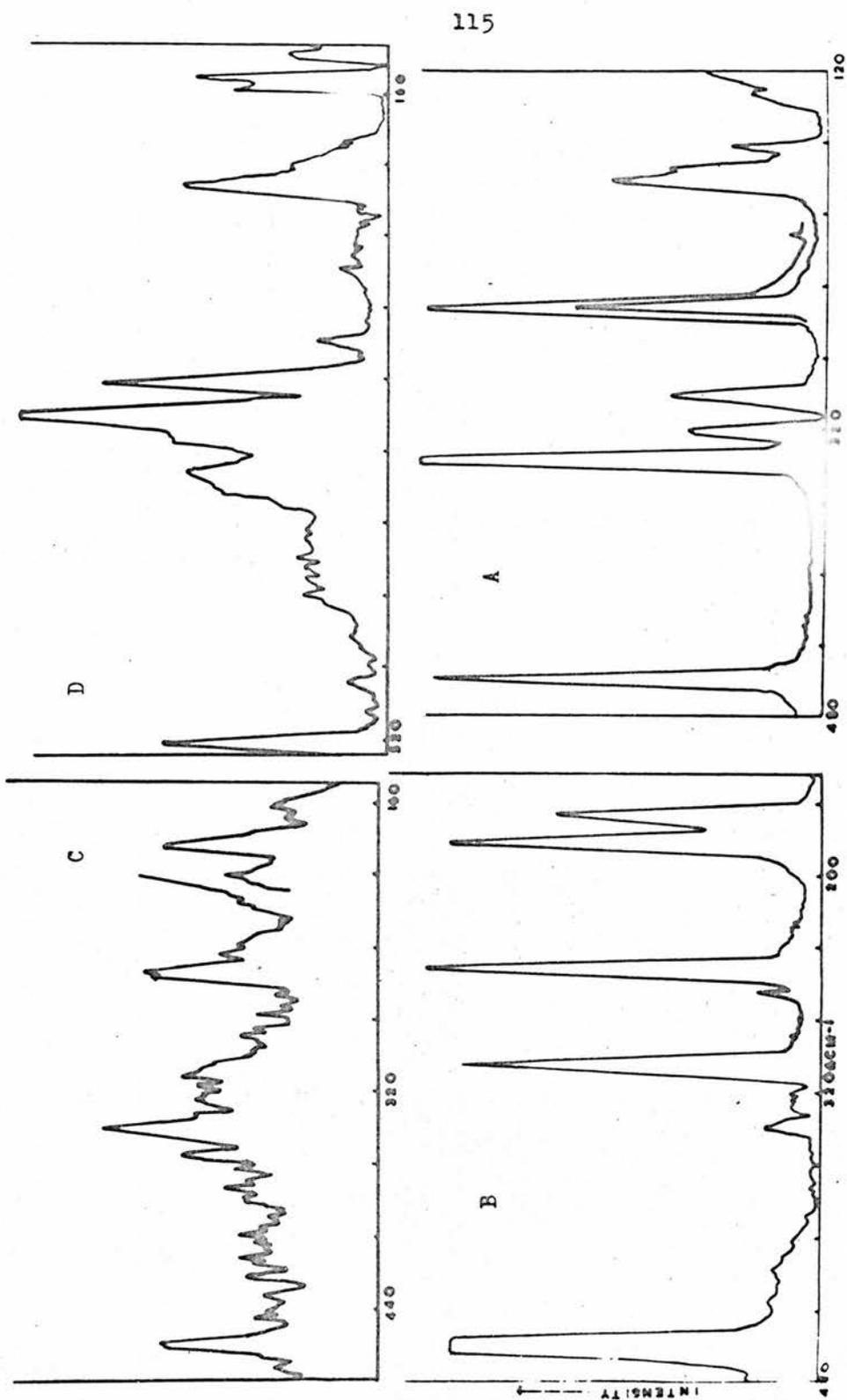


Figure 24.

(600 - 100 Δcm^{-1} of the Chloride Systems.

	$2(\text{Et}_4\text{N}^+)_2\text{SnCl}_6^{2-}$	$\text{SnCl}_4 \cdot 2\text{POCl}_3$	$\text{POCl}_3^{(b)}$	Assignment
		121 m		
		136 w		
		153 s		
160 m				$V_5(\text{F}_{2g})$ SnCl_6^{2-}
				$V_2(\text{E})$ PCl_4^+
		213 s	194 s	$V_6(\text{E})$ POCl_3
220 m-w				$V_2(\text{E}_g)$ SnCl_6^{2-}
249 v.s br				$V_4(\text{F}_2)$ PCl_4^+
			267	$V_3(\text{A}_1)$ POCl_3
		299 m-w		
312 m-s				$V_1(\text{A}_{1g})$ SnCl_6^{2-}
		322 m-s		
			337 m	$V_5(\text{E})$ POCl_3
		341 s		
		372 m		
				$V_1(\text{A}_1)$ PCl_4^+
		489 w	486 v.s	$V_1(\text{A}_1)$ POCl_3
		523 s	581 w	$V_4(\text{E})$ POCl_3
				$V_3(\text{F}_2)$ PCl_4^+

Figure 16: Raman Spectra (500 - 120 cm^{-1})



A. $2\text{SnCl}_4 \cdot 3\text{PCl}_5$. B. $\text{SnCl}_4 \cdot 2\text{PCl}_5$. C. $\text{SnCl}_4 \cdot \text{PCl}_5$. D. $\text{SnCl}_4 \cdot 2\text{POCl}_3$.

TABLE 31: Calculated and Observed Vibrational Spectrur for the
SnCl₅⁻ ion

A. A model of symmetry D_{3h}

<u>Observed</u>		<u>Calc.</u>	<u>Beattie's results</u>		<u>Assignment</u>
I.R.	R.		Obs.	Calc.	
	339 v.s	305	331	325	V ₁ (A ₁) R.
	242 w	238	252	243	V ₂ (A ₁ ') R.
305 s		302	326	301	V ₃ (A ₂ '') i.r.
		140	(~160)	148	V ₄ (A ₂ '') i.r.
355 s	310 v.w?	313	359	336	V ₅ (E') i.r., R.
	174 v.w?				
	166 w	160	~160	139	V ₆ (E') i.r., R.
	151 v.w?				
	120 v.w?	107			V ₇ (E') i.r., R.
		148		146	V ₈ (E'') i.r.

B. A model of symmetry C_{4v}

<u>Observed</u>	<u>Calc</u>	<u>Calc.</u>	<u>Assignment</u>
i.r.	R.		
355 s	339v.s	410	V ₁ (A ₁) i.r., R.
305 s	310 v.w?	290	V ₂ (A ₁) i.r., R.
		77	V ₃ (A ₁) i.r., R.
	242 w	231	V ₄ (B ₁) R.
		74	V ₅ (B ₁) R.
	166 w	158	V ₆ (B ₂) R.
(305 s)	310 v.w?	312	V ₇ (E) i.r., R.
	151 v.w?	142	V ₈ (E) i.r., R.
	120 v.w?	130	V ₉ (E) i.r., R.

TABLE 32: X-ray Powder Photographs of the System $\text{PCl}_5\text{SnCl}_4$

(The values given in the table are $\sin^2\theta$ values
for a camera of radius 57.3mm.)

$\text{PCl}_5\text{SnCl}_4$	$3\text{PCl}_5\text{,}2\text{SnCl}_4$	$2\text{PCl}_5\text{,SnCl}_4$	PCl_5
	.0124 w	.0123 w	.0128 w
			.0178 w
	.0188 s		
.0212			
	.0251 s		.0255 s
.0270 m			
			.0288 m
.0303 m			
		.0318 m	.0320 s
	.0364 m		
			.0381 m
		.0437 w	
			.0526 w
.0597 w			
.0662 w			
.0723 w	.0729 w		.0720 w
		.0742 w	
			.0751 w
	.0791 m		
		.0804 m	
.0816 w	.0816 s		.0816 v.s
	.0941 w		
		.1080 w	
.1142 w		.1385 w	
	.1297 m		
.1531 w			

The infrared spectrum of this adduct has also been reported⁴⁴⁹. A number of bands appear in the metal halogen region of the spectrum, but no intensity data for these bands is reported.

Calculation of the Vibrational Spectrum for SnCl_5^-

The principle of normal co-ordinate analysis is fully described in several text books^{232,419}, and an outline of the technique is given in appendix I. The only normal co-ordinate analysis on a tetragonal pyramid (C_{4v}) model to appear in the literature is the work of Stephenson and Jones⁴⁴³. They calculated the F and G matrix elements for a model with non 90° angles. To simplify matters it was decided in this work to use all angles at 90° . The F and G matrix elements for a model with such angles were calculated by standard techniques²³², and these calculations are given in appendix II, where the elements are listed.

Normal co-ordinate analysis for D_{3h} type molecules, using general valence force fields, has been published by Haarhoff and Pistorius⁴⁴⁴. However, several errors were found in this work and the F and G matrix elements calculated by Webster⁴⁴⁵ were used. The symmetry co-ordinates, f matrix and F and G matrix elements from this calculation are listed in appendix III.

The stretching and bending force constants were calculated for SnCl_6^{2-} using the F and G matrix elements from Nakamoto for O_h symmetry. The vibrational frequencies were taken from Nakamoto²³², and from a paper by Greenwood and Straughan⁴⁶⁰. Putting $f_{rr'} = 0$ and $f_{\alpha\alpha} = 0$

values for f_{α} , f_r and $f_{rr'}$ were obtained. The value for $f_{r\alpha}$ was obtained by calculating the f_{lu} frequencies of SnCl_6^{2-} , using the calculated values for f_r , f_{α} and $f_{rr'}$, and the values 0, 0.05, 0.1 and 0.2 ($\text{mdyn } \text{Å}^{-1}$) for $f_{r\alpha}$. $f_{r\alpha} = 0.05$ gave the best agreement with the observed spectrum and was used throughout this calculation. The inter-relationships of the various species, and the chosen force constants, are given in table 33. These values were substituted into the F matrix elements given in appendix II, and standard atomic weights were used to obtain the G matrix elements. The equations $|FG - E\lambda| = 0$ were solved on an I.B.M. 1620 computer using a programme specifically designed for this purpose. A program listing is given in appendix IV.

Phosphorus Pentabromide.

No infrared study of PBr_5 has appeared in the literature. The structure consists of $\text{PBr}_4^+ \text{Br}^-$ in the solid state,²⁶⁴ and a Raman study gave the frequencies of the PBr_4^+ ion⁴⁵⁰. The infrared spectrum of solid PBr_5 is given in table 34, and its recording is complicated by ease of hydrolysis to POBr_3 , and dissociation to PBr_3 and Br_2 in nujol. Only one band can be assigned to PBr_5 , namely, $\nu_3(\text{F}_2)$ of PBr_4^+ ion at 469cm^{-1} , in good agreement with the Raman studies. The infrared spectra of PBr_3 (451) and POBr_3 (232) have been reported previously, and our spectra are generally in good agreement with them.

When run as a nujol mull, POBr_3 gave two bands in the $\text{P} = \text{O}$ stretching region of varying intensity. These bands occurred at

TABLE 33: Interrelationship of chosen force constants

(r = equatorial, d = axial, = rv, = rd)

$\text{SnCl}_5^- (D_{3h})^a$	SnCl_6^{2-}	$\text{SnCl}_5^- (C_{4v})^b$
fr	fr	fr
frr	frr	frr
frd	frr	frd
fd	fr	fd
fdd	frr	
fd β	fr α	fr α
f β	f α	f β
fr β	fr α	fr β
f α	f α	f α

(a) Assumptions made:

$$f_{dd} = f_{\beta\beta} = f_{\alpha\beta} = f_{\alpha\alpha} = f'd = f' = 0$$

(b) As given in Appendix II.

1277 and 1241 cm^{-1} . The broad lower frequency band is associated with the solid state, and a solution of POBr_3 in nujol showed only one band at 1278 cm^{-1} . The Raman spectrum of POBr_3 in the solid state shows two bands associated with $\text{P}=\text{O}$ stretching vibrations⁴⁴⁵.

The infrared spectrum of PBr_3 showed no absorption in the $\text{P}=\text{O}$ region due to POBr_3 impurity. The nature of the species present, in solutions of PBr_5 , depends on the nature of the solvent. In acetonitrile the presence of the ions PBr_4^+ and PBr_6^- has been established by conductance and electrolysis experiments²⁶², whereas in carbontetrachloride, ethylene dichloride and carbon disulphide, an undissociated complex, $\text{PBr}_3 \cdot \text{Br}_2$ has been found⁴²⁶. In benzene solution it is fully dissociated to PBr_3 and Br_2 (454), and a similar dissociation has been observed in the vapour state⁴⁵³. The infrared spectrum of PBr_5 in benzene shows, as expected, an intense band at 388 cm^{-1} , due to PBr_3 ($\text{V}_1(\text{A}_1) + \text{V}_3(\text{E})$), and the disappearance of the 469 cm^{-1} band associated with the PBr_4^+ ion. No band was observed in the 300 cm^{-1} region, due to the low intensity of bromine absorption (the bond stretching vibration is infrared inactive under D_{2h} symmetry). The gas phase fundamental frequency of Br_2 is reported by Nakamoto²³² as 318.8 cm^{-1} .

The System $\text{PBr}_5 - \text{SnBr}_4$

The only reported investigation of this system is a conductometric titration in acetonitrile, which gave inflections at 1:1 and 2:1 mole ratios ($2\text{PBr}_5, \text{SnBr}_4$)²⁶². We have, unsuccessfully, attempted to isolate these solid complexes either by direct reaction

of components , or using a solvent (C_6H_6 , CH_3NO_2 and CH_3CN were tried). The infrared spectra of these solutions are given in table 34. Nitromethane was chosen as an ionising solvent because $SnBr_4$ is unsolvated in this medium. It was felt that the charge $SnBr_4 (T_d) \longrightarrow (SnBr_{4+X})^{X-}$ would be more easily observed with our present infrared spectrometer, than if a co-ordinating solvent (L) had been chosen, when the species present would have been of the type $SnBr_4L_2$. This would have led to a lowering of the Sn - Br stretching vibrations to a region close to that of $V_3(F_{lu})$ of $SnBr_6^{2-}$, which occurs at $206cm^{-1}$ (265). $SnBr_4$ in nitromethane shows one strong band at $280cm^{-1}$ $V_3(F_2)$, in good agreement with the published spectrum²³². Addition of PBr_5 to this solution causes a decrease in this band until the mole ratio 1:1 is reached, when no trace of this band can be found. A weak band at $253cm^{-1}$ was observed in this solution, which is presumably associated with an Sn - Br stretching vibration. By comparison with the recently published data (i.r. and R.) on the $SnBr_5^-$ ion²⁶⁵ it is tentatively assigned to $V_5 (E')$ of $SnBr_5^- (D_{3h})$. Unfortunately the solvent band at $480cm^{-1}$ completely obscures the $469cm^{-1}$ band of PBr_4^+ , and so the only evidence for complex formation which was found was the disappearance of the $V_3(F_2)$ absorption of $SnBr_4$ at $280cm^{-1}$. Neither PBr_3 nor Br_2 has any effect, individually, on the $SnBr_4$ spectrum, and we conclude that complex formation has occurred in nitromethane. In contrast to this, benzene solutions containing PBr_5 and $SnBr_4$ gave no evidence for interaction, and the 388 and $280cm^{-1}$ bands of PBr_3 and $SnBr_4$ were observed. Attempts were made to investigate the ion $SnBr_5^-$, by Raman spectroscopy, but, unfortunately, no spectral data could be obtained.

TABLE 34: Infrared Spectra (700-210cm⁻¹) of the Bromide System.

<u>Sample</u>	<u>State</u>	<u>Principal Absorption bands (cm⁻¹)</u>			
PBr ₅	solid ^{ade}	480 [†]	469	388	
PBr ₅	soln. ^{bd}	482 [†]		385	
PBr ₅	soln. ^{cd}	480 [*]		385m	265mw
PBr ₃	liquid ^{de}			380	
PBr ₃	soln. ^{bd}	482 [†]		380	
PBr ₃	soln. ^{cd}	478 [*]		387	
POBr ₃	solid ^{ade}	607w	480vs	339w	265m
SnBr ₄	solid ^{af}				280
SnBr ₄	soln. ^{bd}		398 [*]		280
SnBr ₄	soln. ^{cd}	479 [*]			280
Br ₂	liquid ^d				290br
Br ₂	soln. ^{bd}			400 [*]	300
SnBr ₄ + Br ₂ (1:1)	soln. ^{bd}				275
SnBr ₄ + PBr ₃ (1:1)	soln. ^{bd}	540w	480 [†]	378br.s	272
SnBr ₄ + PBr ₅ (1:1)	soln. ^{bd}		482 [†]	386	280
SnBr ₄ + PBr (1:1)	soln. ^{cd}		475 [*]	386	253w
CH ₃ NO ₂	liquid ^d	520w	475vs		
C ₆ H ₆	liquid ^d			400w	

(a. nujol mull, b. benzene solvent, c. nitromethane solvent, d. polythene windows, e. KBr windows, f. CsI windows, * solvent band, † POBr₃ impurity.)

SECTION III

CHAPTER 6

A survey of addition compounds of the
trichlorides of group VB

A literature survey can frequently be of value in revealing systematic changes in chemical behaviour, with the change in some parameter, and also in revealing anomalous behaviour. In the light of new techniques, it can stimulate a fresh approach to an unsolved problem, and allow reinterpretation of results. It also reveals any gaps which may be present in the literature. A number of review articles have appeared which discuss various aspects of the group VB trihalides. George²²⁹ discusses their general properties, whilst Payne has reviewed both their chemistry³¹⁸ and solvent properties⁴⁰¹. More recently, Kolditz²³¹ has discussed the trihalides of arsenic and antimony.

These trihalides appear to be capable of acting both as electron pair donors, and to a lesser degree, as acceptors. The donor properties of PF_5 are well known, but this same compound shows very weak accepting properties; in fact it will not accept a fluoride ion, nor does it show any tendency to react with potassium fluoride. Because of this dual donor acceptor property of PF_3 and PCl_3 , Holmes has very aptly described them as being amphoteric in the Lewis acid-base sense. Besides donor acceptor properties, the trihalides can also be oxidized to the pentavalent state when forming simple, stoichiometric adducts. The reaction of PCl_3 with a diene gives rise to a 1,1,1-trichlorophospholine¹⁸⁸, figure 17a.

In this review, adducts in which the group VB trihalide is acting as an electron pair donor, as in $\text{Ni}(\text{PF}_3)_4$ ⁴⁰³, or where it has been oxidized, or has undergone a chemical reaction in which the product has the stoichiometric composition of a simple adduct, have

not been included.

This review covers the literature from 1917 up to, and including June 1968. References earlier than this can be found in Mellors treatise³⁹². Popov³⁹⁰ also reports a number of adducts from the early literature. Unfortunately, no references are included with his table, and it has proved impossible to refer all the compounds back to the original authors. The data is presented in tables which follow the same format as was used in chapter 2.

Phosphorus Trihalides.

Only one addition complex has been reported in which PF_3 acts as an acceptor^{276,391}. Several such compounds have been reported for PCl_3 , PBr_3 and PI_3 react with bidentate ligands forming 1:1 complexes. These are ionic in nitrobenzene solution. Sutton has shown that *o*-phenylenebisdimethylarsine (diars) reacts with PI_3 , forming a 1:1 complex which exists in nitrobenzene solution as $(\text{PI}_2\text{diars})^+\text{I}^-$. Unlike the other trihalides of group VB no ionic species, such as PX_4^- or PX_5^{2-} , have been reported.

The Trifluorides of Arsenic and Antimony.

The work of Gutmann and his collaborators in Vienna has established, not only the trifluorides, but also the trichlorides and tribromides, as extremely useful, non aqueous solvents. Both of these trifluorides can also be used as fluorinating agents for organic and inorganic materials²³¹. Many simple salts, MF ($\text{M} = \text{K}^+, \text{Rb}^+, \text{Cs}^+$), dissolve in AsF_3 and SbF_3 to give conducting

solutions from which solids of the type KMF_4 (M = As, Sb.) can be obtained¹⁶⁸. The existence of AsF_3, SbF_5 and AsF_3, BiF_3 combined with the conductance of pure AsF_3 , lead Gutmann⁴⁰⁴ to postulate a self ionization model for this compound: $2AsF_3 \rightleftharpoons AsF_2^+ + AsF_4^-$. The compounds AsF_3, SbF_5 and AsF_3, BiF_3 ¹⁶⁸ have been postulated as ionic species, containing the ion AsF_2^+ . No evidence, direct or indirect, is available to support this. ¹⁹F. n.m.r. studies²⁷⁸ suggest a bridged structure for AsF_3, SbF_5 , whilst mixtures of AsF_3 and BF_3 , although they have a slightly enhanced conductivity, do not show resonances other than those arising from the original compounds.

X-ray crystal structures have been reported for several adducts of SbF_3 with fluorine donors. The compound $KSbF_4$ is ionic, with a tetrameric anion $(SbF_4^-)_4$ ¹⁶⁵, figure 17b. Each antimony is surrounded by five fluorine atoms in a tetragonal pyramid. The antimony atom is displaced out of the plane, as would be expected if the sixth position of the octahedron is occupied by a lone pair.

Bystrom^{344,405} has also reported X-ray data on the compounds K_2SbF_5 and $CsSb_2F_7$. The former consists of discrete K^+ and SbF_5^{2-} ions; the anion has the structure shown in figure 17c. In the latter compound two Sb atoms are linked by a fluorine bridge, giving antimony a co-ordination number, 4, figure 17d. The structure of KSb_4F_{13} has also been reported⁴⁰⁶, in this case a fluoride ion is solvated by four SbF_3 molecules, figure 17e.

No structural data has been reported for the arsenic fluorides, and it will be interesting to see if they, in fact, yield polymeric or discrete anions. Infrared and Raman spectroscopy, both in

solution and in the solid state, might well indicate whether or not these polymeric species exist in solution, or whether solvation can stabilize the discrete SbF_4^- anion.

The Trichlorides of Arsenic, Antimony and Bismuth.

The excellent solvent properties of these trihalides, coupled with their ready availability, have led to the preparation of many of their addition compounds. As can be seen in tables 40, 43 and 47, many of the reported complexes are postulated as ionic species. The discrete ions MCl_4^- (M = As, Sb, Bi.) have never been positively identified, either in solution or in the solid state.

X-ray studies have been reported for a number of SbCl_3 and BiCl_3 adducts. Porter¹⁶⁷ has shown that the complex $\text{PyHCl}, \text{SbCl}_3$ (Py = pyridine) is ionic, $n\text{PyH}^+(\text{SbCl}_4^-)_n$. The anion forms an infinite chain by use of chlorine bridges. The ion SbCl_5^{2-} has the same structure as SbF_5^{2-} (393), whereas BiCl_5^{2-} has been identified in the compound "bismuth monochloride"⁴⁰². The compound $\text{Co}(\text{NH}_3)_6\text{BiCl}_6$ is isomorphous with $\text{Co}(\text{NH}_3)_6\text{TiCl}_6$, and it thus appears that the BiCl_6^{3-} is a regular octahedron³⁹⁶. X-ray powder photographs of Cs_3SbCl_6 have been indexed as O_h^5 (395). It would appear that neither of these ions are greatly distorted by their nS^2 ($n = 6$ or 5) electrons. Beattie³⁹⁴ has reported the infrared and Raman spectra of SbCl_6^{3-} and BiCl_6^{3-} , and was able to make vibrational assignments on the basis of O_h symmetry. It is interesting to note that the $5S^2$ and $6S^2$ electrons can be stereochemically active in the five co-ordinate species, whereas they appear to be inactive in the six co-ordinate anions.

Oertel and Plane³⁸² have identified the species BiCl_4^- , BiCl_5^{2-} and BiCl_6^{3-} in aqueous solution, by Raman spectroscopy. They recorded the spectra of $\text{C}_6\text{H}_{13}\text{N}_2\text{BiCl}_4$ ³⁶⁵, $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{BiCl}_5$, $(\text{C}_2\text{H}_5\text{NH}_3)_3\text{BiCl}_6$ ³⁷⁹ and $(\text{N}_2\text{H}_5)_3\text{BiCl}_6$ ³⁷³, which were reported, on the basis of conductivity measurements, to contain the ions BiCl_4^- , BiCl_5^{2-} and BiCl_6^{3-} respectively. For BiCl_4^- they report five Raman lines, three of which are in the Bi - Cl stretching region. They assume that the ion has a distorted tetrahedral structure. In fact, according to the Gillespie - Nyholm theory of non bonding pairs⁴⁰⁷, such an ion should have a trigonal bipyramidal structure in which the lone pair occupies one of the equatorial positions, figure 4a, page 4. This model would have C_{2v} symmetry, and four metal halogen stretching vibrations are predicted for such a model. The ion BiCl_5^{2-} has a distorted tetragonal pyramidal structure. Assuming it belongs to the point group C_{4v} , then nine Raman active vibrations are predicted. Only three Raman bands are reported for this ion. A molecule with a similar structure is BrF_5 ; the Raman spectrum has been reported and all nine Raman active vibrations have been observed. The ion BiCl_6^{3-} shows three Raman active bands, and the reported spectrum shows very good agreement with Beattie's results³⁹⁴.

A number of workers have studied the systems BiX_n^{3-n} by spectrophotometric and other methods. Newman and Hume⁴⁰⁸ established the existence of the species BiCl_n^{3-n} when $n = 1-5$. Ahrland and Grenthe⁴⁰⁹ found potentiometrically that n assumes values 1-6 for both BiCl_n^{3-n} and BiBr_n^{3-n} . Solubility studies⁴¹⁰ indicate that BiCl_4^- and BiCl_6^{3-} are the only chlorobismuth complexes in solution.

Eve and Hume⁴¹¹ report BiI_4^- , BiI_6^{3-} and BiI_7^{4-} . This work is interesting in that it raises doubts about the existence of BiI_5^{2-} and also postulates seven co-ordinate bismuth.

Tables 35 - 50 show that the list of addition compounds of the trihalides is long and contains many compounds of unexpected composition, whose structures are unknown. Ions such as AsCl_9^{3-} and $\text{As}_3\text{Cl}_{11}^{2-}$ (196) have been postulated according to their composition, but no further evidence of their existence has been presented. Molecules such as AsCl_3 are highly polar, and easily form solvates. A solvate of $\text{AsCl}_5, \text{SbCl}_5$ was isolated and identified during the work presented in this thesis. This is also exemplified by the crystal structure of $\text{KSb}_4\text{F}_{13}$, fig.17e. This fact seems to have been overlooked by many authors, and the ionic structures formulated must, in many cases, be highly suspect.

The application of modern techniques to this problem should certainly help in clarifying the rather confusing position. Already X-ray crystallography has shown that the structures are not as simple as earlier workers suggested.

The Tribromides and Triiodides of Arsenic, Antimony and Bismuth.

The tribromides and triiodides behave quite similarly to the ^{chloride} trihalides. In the liquid state they have been used as non aqueous solvents.

There are a number of addition compounds reported, but the work has not been as extensive as with the trihalides.

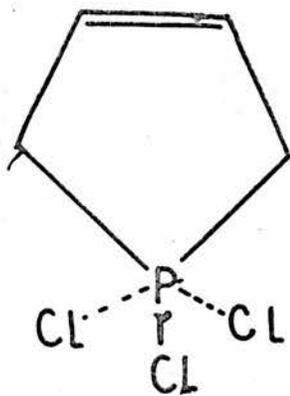
Petzold¹⁹⁶ has reported a number of adducts of AsBr_3 with amino bromides. He isolated compounds of stoichiometry 1:1 ($\text{AsBr}_3:\text{L}$), and 2:1 and postulated ionic structures containing AsBr_4^- and As_2Br_7^- , but no evidence is presented to support these structures. Popov³⁹⁰ has similarly prepared a large variety of amine hydrobromide (RNHBr), arsenic tribromide adducts. He reports compounds of the following ratios: ($\text{AsBr}_3:\text{L}$), 1:3, 2:5, 1:2, 2:3, 1:1, 2:1. He postulates ionic species for all these compounds, and suggests the presence of ions such as $\text{As}_2\text{Br}_{11}^{5-}$. Since arsenic tribromide is a highly polar molecule, it is almost certain to be a good solvating molecule, and this may account, in part, for some of the unusual stoichiometries reported in these compounds. Neither this, nor the fact that an ion containing five negative charges is most unusual, if not unique, is commented upon by this author. Several other workers^{285,296,297} have also reported complexes of AsBr_3 with amines, amine hydrobromides and aminobromides.

High frequency conductometric titrations in which a variety of organic nitrogen bases were titrated with SbBr_3 , have been reported by Riolo³⁶¹. Breaks at a mole ratio of 2:1 indicated complex formation. In some cases solids were isolated. The stoichiometry varied from base to base and did not agree with the stoichiometry indicated in solution. No rationalization of these results, on the basis of structure, was put forward.

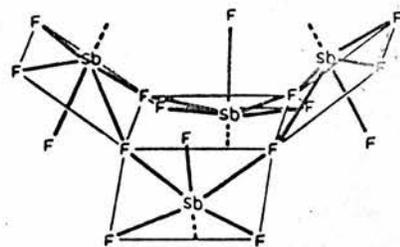
Pugh^{373,365} has prepared a wide range of complexes of MX_3 ($\text{M} = \text{Sb, Bi}; \text{X} = \text{Cl, Br, I.}$) with hydrazine halides. In his earlier paper he reports a brief study of their conductivity in acetone.

McPherson^{347,348} has published crystal structures of 2-picolinium tetrabromobismuthate and bispiperidinium pentabromobismuthate. These two compounds are reported in the literature³⁹⁰, and the presence of BiBr_4^- and BiBr_5^{2-} respectively was postulated. In fact, BiBr_4^- consists of long chains with two bridging bromine atoms per bismuth atom, fig. 17f. The bismuth is surrounded by six bromine in a regular octahedral fashion. The BiBr_5^{2-} contains a similar chain type structure, fig. 17g, with one bridging bromine atom per bismuth atom. In neither case was any effect due to the "lone pair" observed. It is interesting to note that unlike SbBr_5^{2-} , discrete BiBr_5^{2-} ions do not exist, at least not with these particular cations. In the complicated structure of $\text{Bi}_{12}\text{Cl}_{14}$ ⁴⁰² discrete BiCl_5^{2-} have been found. The compound 2-picolinium tetraiodobismuthate is isomorphous with its bromine analogue³⁴⁷.

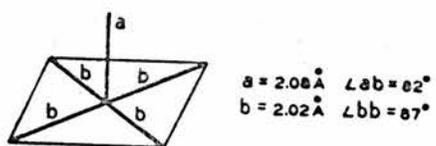
A number of interesting compounds with bidentate ligands have been reported. Sutton^{203,210} has reported 1:1 adducts of MX_3 (M= P, As, Sb; X = Cl, Br, I.) with the bidentate chelating ligand, o-phenylenebisdimethylarsine. In nitrobenzene he reports a progressive tendency towards ionization from antimony to phosphorus, and from chloride to iodide, 2-thioamidopyridinium halide with MX_3 has also been reported by the same author²¹⁰. Roper and Wilkins¹⁴ have reported a number of MX_3 adducts with 2,2'-bipyridyl(bipy). They suggest that in solution the following equilibrium holds: $\text{bipyMX}_3 \rightleftharpoons (\text{bipy}, \text{MX}_2)^+ + \text{X}^-$. The results of an X-ray structure on the compound $\text{bipy}, \text{AsCl}_3$ is reported in chapter 7. In the solid state the compound is dimeric with chlorine bridging.



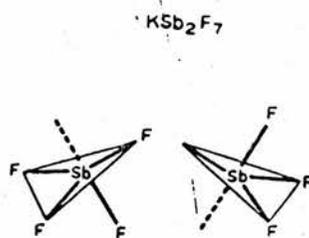
(A)

Figure 3. Structure of K_3SbF_6 .

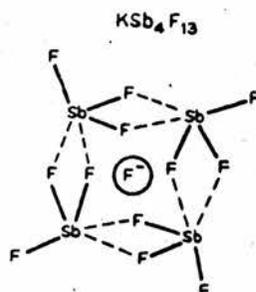
(B)

Figure 4. Structure of K_2SbF_4 .

(C)

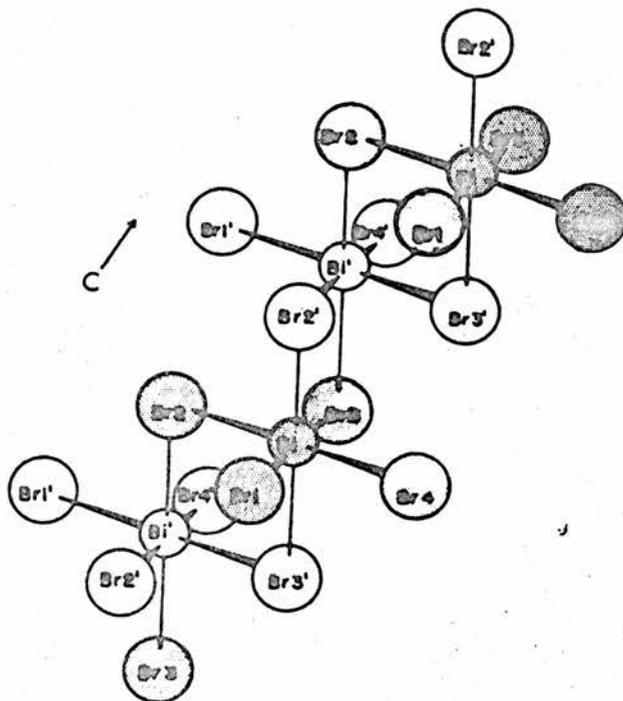


(D)

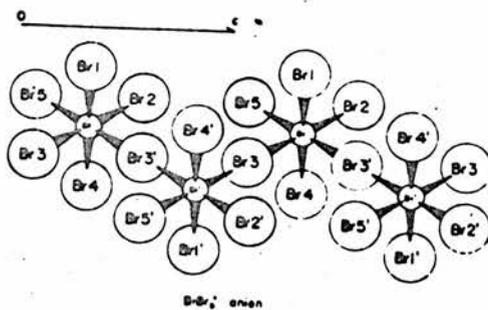


(E)

Figure 17: Continued

Schematic representation of BiBr_4^- showing infinite chain structure-

(F)



Bi-Br; anion

(G)

TABLE 35: Addition Compounds of PF₃

Other Molecule (L)	Ratio PF ₃ :L	Reference	Comments
Me ₃ N	1:1	276,391	
Et ₃ N	no reaction	276	

TABLE 36: Addition Compounds of PCl₃

(L)	PCl ₃ :L	Reference	Comments
Me ₃ N	1:1	177,179 268	
Et ₃ N	1:1 1:3	173	
Me ₃ P	1:2	178	
Me ₃ As	1:1	179,186	
POCl ₃	1:1	275	
C ₆ H ₅ CHO	1:3	322	
Crystal violet	1:1	269	U.V. in solution. 1:1 complex indicated by Jobs method.
Me ₃ NO	complex	388	

TABLE 37: Addition Compounds of PBr₃

(L)	PBr ₃ :L	Reference	Comments
Me ₃ N	1:1	179	
C ₁₀ H ₁₆ As ₂	1:1	203	L = diars. A weak electrolyte in ϕ NO ₂

TABLE 38: Addition Compounds of PI₃

Other Molecule (L)	Ratio PI ₃ :L	Reference	Comments
C ₁₀ H ₁₆ As ₂	1:1	203	Ionic in ϕ NO ₂
C ₆ H ₆ N ₂ S	1:1	210	L = 2-thioamidopyridine

TABLE 39: Addition Compounds of AsF₃

(L)	AsF ₃ :L	Reference	Comments
SbF ₅	1:1	167,168 278	AsF ₂ ⁺ SbF ₆ ⁻ bridged structure.
C ₄ H ₈ O ₂	1:1	170 171	(dioxan)
KF	1:1	168 278	K ⁺ AsF ₄ ⁻
BF ₃	1:1	168 278	AsF ₂ ⁺ BF ₄ ⁻ (in solution) no reaction.
SCl ₄	2:1	187	
SO ₃	2:3	277	
CsF	1:1	278	
TlF	1:1	278	
LiF	No reaction	278	
NaF	" "	278	
SF ₄	1:1	279 295	Suggests 3 possible structures.

TABLE 40: Addition Compounds of AsCl₃

Other Molecule (L)	Ratio AsCl ₃ :L	Reference	Comments
Me ₃ NHCl	1:1	214	Me ₃ NH ⁺ AsCl ₄ ⁻
Me ₄ NCl	1:1	166	Me ₄ N ⁺ AsCl ₄ ⁻
	3:1	174	
	2:1	172	
	5:3	172	
Me ₂ NH ₂ Cl	1:1	196	Me ₂ NH ₂ ⁺ AsCl ₄ ⁻
Et ₂ NH ₂ Cl	1:1	196	Et ₂ NH ₂ ⁺ AsCl ₄ ⁻
C ₅ H ₆ NCl	1:1	196,390	PyH ⁺ AsCl ₄ ⁻
Ph ₃ CCl	1:1	197	Ph ₃ C ⁺ AsCl ₄ ⁻
PhNH ₃ Cl	1:2	214	2PhNH ₃ ⁺ AsCl ₅ ²⁻
EtNH ₃ Cl	1:2	196	EtNH ₃ ⁺ AsCl ₅ ²⁻
CH ₃ NH ₃ Cl	2:3	196	3CH ₃ NH ₃ ⁺ As ₂ Cl ₉ ³⁻
CNHNH ₂ NH ₃ Cl	2:3	196	3CNH ₂ NH ₃ ⁺ As ₂ Cl ₉ ³⁻
(CH ₃) ₃ NHCl	3:2	196	2(CH ₃) ₃ NH ⁺ As ₃ Cl ₁₁ ²⁻
C ₉ H ₇ NHCl, H ₂ O	3:2:1	196	2(C ₉ H ₇ NH) ⁺ As ₃ Cl ₁₁ ²⁻ , H ₂ O
POCl ₃	1:1	172,197 282	POCl ₂ ⁺ AsCl ₄ ⁻
C ₉ H ₇ N, HCl	1:1:1	390	
C ₉ H ₇ N, S ₂ Cl ₂	1:1:1	197	C ₉ H ₇ NS ₂ Cl ⁺ AsCl ₄ ⁻
FeCl ₃	1:1	205	AsCl ₂ ⁺ FeCl ₄ ⁻
C ₆ H ₇ N ₂ SCl	1:1	210	2 thioamidopyridinium AsCl ₄ ⁻
NOCl	1:2	280,323	2NO ⁺ AsCl ₅ ²⁻
SbCl ₅	1:1	166	AsCl ₂ ⁺ SbCl ₆ ⁻

TABLE 40: Continued

Other Molecule (L)	Ratio AsCl ₃ :L	Reference	Comments
VC1 ₄	1:1	166	AsCl ₂ ⁺ VC1 ₅ ⁻ (solution)
PC1 ₅	1:1	176,197	PC1 ₄ ⁺ AsCl ₄ ⁻
	5:2	202	PC1 ₄ ⁺ PC1 ₆ ⁻ 5AsCl ₃
C ₁₀ H ₈ N ₂	1:1	14,16 this work	Molecular in solid state ionic in solution.
	1:2		
C ₁₀ H ₈ N ₂ ,HCl	1:1:2	281	
C ₄ H ₈ O ₂	2:3	170	
		384	
CH ₃ NO ₂	1:1	22	
CH ₃ CO ₂ C ₂ H ₅	1:1	131	(solution)
	1:3		
C ₅ H ₅ N	1:1	181	
	1:2	175	
Me ₃ N	1:1	178	
Et ₃ N	1:1	173	
	1:3		
MCl ₃	1:1	271,283	M = In, Ga, Ti.
SiCl ₄	1:2	327	The binary system was investi- gated by the f.p. method.
	1:3		
Me ₃ PO	1:1	199	
φ ₃ PO	1:2	201	
C ₁₀ H ₁₆ As ₂	1:1	203	L = diars.
C ₁₀ H ₁₆ N ₂	1:1	this work	L = <u>o</u> -phenylenebisdimethyl- amine.
	2:1		
C ₁₀ H ₈ N ₂	1:1	this work	L = phen
	2:1		

TABLE 40: Continued

Other Molecule (L)	Ratio AsCl ₃ :L	Reference	Comments
C ₆ H ₁₀ O ₂	1:1	325	
C ₄ H ₈ OS	1:1	325	L = thioxan.
Et ₂ O	1:1	385	
C ₆ H ₅ NO ₂	1:2	386	
BrCN	1:2	371	
PhNHHC(S)N: NC ₆ H ₃ RR'	1:1 2:1	211	R' = H; R = <i>o</i> -Me, <i>p</i> -Me, <i>p</i> -MeS, <i>o</i> -(MeO, PhO, HO ₂ C, PhO ₂ C). R = 2-Br, R' = 4-Br. R = 2-Me, R' = 4-Br.
C ₂₅ H ₃ N ₃ Cl	1:1	200	crystal violet, in solution.
Me ₂ CO	1:1	303	
C ₁₈ H ₁₂ N ₂ ,HCl	2:1:2	309	L = 6,6'-, or 2,3'-biquinoline.
C ₆ H ₅ N ₂ Cl	1:2	324	
C ₆ H ₅ NH ₂	1:3	326	
1,3,4-Me ₂ C ₆ H ₃ NH ₂	1:3	326	
C ₁₀ H ₇ N ₂ Cl	1:1	356	L = α or β naphthylamine diazonium chloride.
Me ₄ NCl, TeCl ₄	1:1:1	399	Me ₄ N ⁺ AsCl ₂ ⁺ TeCl ₆ ²⁻
PCl ₅ , TeCl ₄	1:1:1	400	PCl ₄ ⁺ (AsCl ₂ ⁺) ₃ (TeCl ₆ ²⁻) ₂
TeCl ₄	2:1	401	(AsCl ₂ ⁺) ₂ TeCl ₆ ²⁻
TeCl ₄ , SnCl ₄	1:1:1	401	TeCl ₃ ⁺ AsCl ₂ ⁺ SnCl ₆ ²⁻
TeCl ₄ , SbCl ₅	1:2:1	401	(TeCl ₃ ⁺) ₂ AsCl ₄ ⁻ SbCl ₆ ⁻
C ₅ H ₁₁ N, HCl, CHCl ₃	1:2:1 2:3:1	390 390	

TABLE 41 : Addition Compounds of AsBr₃

Other Molecule (L)	Ratio AsBr ₃ :L	Reference	Comments
(C ₂ H ₅) ₂ NH ₂ Br	1:1	196	(C ₂ H ₅) ₂ NH ₂ ⁺ AsBr ₄ ⁻
(CH ₃) ₃ NHBr	1:1	196	(CH ₃) ₃ NH ⁺ AsBr ₄ ⁻
C ₅ H ₆ NBr	1:1	196	PyH ⁺ AsBr ₄ ⁻
Me ₄ NBr	1:1	285	Me ₄ N ⁺ AsBr ₄ ⁻
	2:1	196	Me ₄ N ⁺ As ₂ Br ₇ ⁻
Et ₃ NHBr	1:1	285	Et ₃ NH ⁺ AsBr ₄ ⁻
Et ₄ NBr	1:1	285	Et ₄ N ⁺ AsBr ₄ ⁻
C ₄ H ₈ O ₂	2:3	170	
NH ₄ Br	2:3	196	3(NH ₄)N ⁺ As ₂ Br ₉ ³⁻
EtNH ₃ Br	2:3	196	EtNH ₃ ⁺ As ₂ Br ₉ ³⁻
C ₁₀ H ₈ N ₂	1:1 2:1	14 this work	L = 2,2'-bipy both are ionic in ϕ NO ₂
C ₁₀ H ₁₆ As ₂	1:1	203	L = diars
C ₆ H ₇ N ₂ SBr	1:1	210	(2-thioamidopyridinium) ⁺ AsBr ₄ ⁻
C ₁₀ H ₁₆ N ₂ ,HBr	1:1:2 2:1:2	281	
C ₅ H ₁₁ N,HBr	1:1:1	284	
C ₈ H ₁₁ N,HBr	1:1:1	285	L = 2, 4, 6-olidine
C ₁₀ H ₉ N,HBr	1:1:1	285	L = quinoldine
C ₇ H ₉ N,HBr	2:1:1	285	L = 2, 4-lutidine
C ₇ H ₉ N	3:2	285	
Me ₂ NPh	3:2	285	

TABLE 41: Continued

Other Molecule (L)	Ratio AsBr ₃ :L	Reference	Comments
Bu ₂ N	3:2	285	
C ₁₈ H ₁₂ N ₂ ,HBr	2:1:2 1:1:2	309	L = 2, 3'- or 6, 6'-biquinoline
PyHBr	2:5 1:2,1:1	390	5PyH ⁺ As ₂ Br ₁₁ ⁵⁻
PyHBr,CHCl ₃	1:2:1 2:3:1	390	2PyH ⁺ AsBr ₅ CHCl ₃ ²⁻
CH ₃ C ₅ H ₅ NBr	2:3 1:1 1:2	390	L = α or β picolinium bromide
PyC ₂ H ₅ Br	1:2 1:1	390	
PyC ₄ H ₉ Br,CHCl ₃	2:3:1	390	
C ₉ H ₈ NBr	1:2 1:1	390	L = quinolinium bromide
C ₉ H ₇ NC ₂ H ₅ Br	1:2 1:1 2:1	390	
C ₉ H ₇ NC ₄ H ₉ Br	1:1	390	
C ₅ H ₁₂ NBr	1:2 2:1	390	L = piperidinium bromide
C ₅ H ₁₂ NBr,CHCl ₃	1:2:1 2:3:1	390	
BrCN	1:2	371	

TABLE 42: Addition Compounds of AsI₃

Other Molecule (L)	Ratio AsI ₃ :L	Reference	Comments
C ₁₀ H ₈ N ₂	1:1	14	L = 2, 2'-bipyridyl
C ₁₀ H ₁₆ As ₂	1:1	203	L = diars
C ₆ H ₆ N ₂ SI	1:1	210	(2 thioamidopyridinium)(AsI ₄ ⁻)
(CH ₃) ₄ AsI	1:1	287	
(C ₂ H ₅) ₄ AsI	1:1	287	
(n-C ₃ H ₇) ₄ AsI	1:1	300	

TABLE 43: Addition Compounds of SbF₃

(L)	SbF ₃ :L	Reference	Comments
KF	1:1	165	4K ⁺ Sb ₄ F ₁₆ ⁴⁻
	1:2	165	K ⁺ SbF ₅ ²⁻
CsF	2:1	165	Cs ⁺ Sb ₂ F ₇ ⁻
SbF ₅	2:1	168,169	suggested (SbF ₂ ⁺) ₂ SbF ₇ ²⁻
	5:1	168	
p-MeC ₆ H ₄ SCl	1:1	334	
C ₄ H ₈ O ₂	1:1	354,355	

TABLE 44: Addition Compounds of SbCl₃

Other Molecule (L)	Ratio SbCl ₃ :L	Reference	Comments
Ac ₂ O	1:1	9	
S ₂ Cl ₂	1:1	19	S ₂ Cl ⁺ SbCl ₄ ⁻
PyHCl	1:1	307 167	Crystal structure PyH ⁺ (SbCl ₄ ⁻) _n
WCl ₆	1:1	147	Eutectic systems studied by thermal analysis
WOCl ₄	1:1	147	
CH ₃ NO ₂	1:1	22	
C ₅ H ₅ N	1:1 2:3, 1:2	328, 307 212, 291, 352	
C ₄ H ₈ O ₂	2:3 1:2 1:1 2:1	170, 291 170 291 342	L = dioxan
Et ₃ N	1:1 2:1	173, 178 178	
Me ₃ N	1:1	178	
Me ₃ P	2:1	178	
Me ₃ As	1:1	180	
GaCl ₃	1:1	195	
Et ₄ NCl	1:1	197	Et ₄ N ⁺ SbCl ₄ ⁻
Et ₃ NHCl	1:1	197	Et ₃ NH ⁺ SbCl ₄ ⁻
M ⁿ Cl _n and M ⁿ Cl _n ·H ₂ O	various	193, 194, 195	M = Na, K, NH ₄ , Hg(II), Ca, Mg, Ba, Sr, Rb, Cs, H.
Me ₃ PO	1:1 1:2	199, 303	

TABLE 44: Continued

Other Molecule (L)	Ratio SbCl ₃ :L	Reference	Comments
PCl ₅	2:1	202	PCl ₄ ⁺ PCl ₆ ⁻ 4SbCl ₃
Ph ₃ PO	1:2	201	
POCl ₃	1:1	275,335	POCl ₂ ⁺ SbCl ₄ ⁻
PSCl ₃	1:1	298	PSCl ₂ ⁺ SbCl ₄ ⁻
Ph ₃ CCl	1:1	289,290	Ph ₃ C ⁺ SbCl ₄ ⁻ (in solution)
Me ₂ CO	1:2	303	
Et ₂ O	1:2	308	
	2:1	369	
C ₅ H ₅ N, PSCl ₃	1:1:1	298	C ₅ H ₅ N, PSCl ₂ ⁺ SbCl ₄ ⁻
AcOH	1:1	340	SbCl ₂ L ⁺ Cl ⁻ solution and solid
	2:1	340	SbCl ₂ L ⁺ SbCl ₄ ⁻ in solution
CH ₂ ClCO ₂ H	1:1	339	Electric cond., viscosity and density reported.
	2:1		
CCl ₃ CO ₂ H	1:1	339	
	2:1		
Me ₂ O	2:1	369	
BrCN	1:2	371	
AsCl ₃	no reaction	372	
R ₂ S	1:1	368	R = Me, Et, Bu, Pr suggested R ₂ -S(Cl)SbCl ₂
R ₂ S, HCl	2:3:1	368	R = C ₄ H ₉ , C ₂ H ₅
MCl	2:1	366	M = methylene blue.
	3:1		
Et ₂ NH, H ₂ O	1:1:1	288	Et ₂ NH ₂ ⁺ SbCl ₃ OH ⁻
(CH ₃) ₂ NH	complex	57	

TABLE 44: Continued

Other Molecule (L)	Ratio SbCl ₃ :L	Reference	Comments
C ₁₃ H ₁₁ N	complex	57	L = benzalaniline
C ₁₅ H ₁₆ N ₂	complex	57	L = benzol- <u>p</u> '-dimethylamino- aniline.
C ₆ H ₅ CO ₂ R	1:1	131	solution, R = Me, Et.
C ₆ H ₅ COCH ₃	1:1 1:2	343	solution detm. by Jobs method.
C ₁₀ H ₈ N ₂	1:1	198	a weak electrolyte in ϕ NO ₂ . L = 2,2'-bipyridyl.
C ₁₀ H ₈ N ₂ , HCl	1:1:2	281 292	L = 2,2'-bipyridyl. L = 4,4'-bipyridyl.
R(CH ₂) ₃ NH ₂	1:1 1:3	328	R = C ₆ H ₃ , <u>m</u> -xylidine. R = CH ₃ .
<u>iso</u> -(CH ₃) ₂ CH.NH ₂	1:3	328	
C ₆ H ₅ .CH.NC ₆ H ₅	1:1	328	
(C ₆ H ₅) ₂ NH	1:1	328	
C ₁₀ H ₆ (NH ₂) ₂	2:1	328	
C ₁₀ H ₇ NH ₂	1:1	328	L = (α or β) naphthylamine.
(RC ₆ H ₃ NH ₂) ₂	2:1 2:3	328	R = H, CH ₃ , CH ₃ O.
C ₆ H ₄ (NH ₂) ₂	2:1 2:3	328	L = (<u>o</u> - and <u>p</u> -)
NH ₂ .CH ₂ .CH ₂ .NH ₂	2:1	328	
C ₄ H ₉ N	1:3	291	L = morpholine
C ₆ H ₁₃ N ₂ Cl	1:1	365	L = dimethylketazinium chloride.

TABLE 44: Continued

Other Molecule (L)	Ratio SbCl ₃ :L	Reference	Comments
RC ₆ H ₄ N ₂ Cl	1:1	330,331 299,364 367,374	R = <i>p</i> -NH ₂ , <i>p</i> -CH ₃ NH, <i>p</i> -(CH ₃) ₂ N <i>p</i> -AcNH, <i>p</i> -AcMeN, <i>p</i> -NO ₂ Me ₂ N, <i>p</i> -CH ₃ CO, H, <i>o</i> - and <i>p</i> -CH ₃ , <i>p</i> -Cl, <i>m</i> -NO ₂ , <i>p</i> -Me, <i>o</i> -Cl, <i>m</i> -Cl, <i>p</i> -Br, <i>p</i> -I, <i>o</i> -Me, <i>p</i> -Et ₂ O.
C ₁₀ H ₇ N ₂ Cl	1:1	364,356	L = (α or β) naphthalene- diazonium chloride.
C ₁₂ H ₈ N ₄ Cl ₂ ,HCl	1:1:1 2:1:2	364	L = diphenylbisdiazonium chloride
C ₁₂ H ₇ O ₂ N ₅ Cl ₂ ,HCl	2:1:2	364	L = 2-nitrodiphenylbisdiazon- ium chloride.
NH ₂ C ₆ H ₄ COOH	1:1	328	L = (<i>o</i> - and <i>p</i> -)
C ₁₈ H ₁₂ N ₂ ,HCl	1:1:2	309	L = 2,3'- or 6,6'-biquinolyl.
$\phi_3\text{PN}\phi_3\text{P}\phi_3^+\text{Cl}^-$	1:1	286,341	$\phi_3\text{PN}\phi_3\text{P}\phi_3^+ \text{SbCl}_4^-$
$\phi_3\text{PNP}\phi_3^+\text{Cl}^-$	1:1	286,341	$\phi_3\text{PNP}\phi_3^+ \text{SbCl}_4^-$
C ₁₀ H ₁₆ N ₂ ,H ₂ O	1:1:1	353	
C ₁₀ H ₁₆ As ₂	1:1	203	L = diars.
C ₁₂ H ₉ N ₂ Cl,H ₂ O	1:1:1	203	(phenH ⁺ .H ₂ O) SbCl ₄ ⁻
C ₆ H ₅ OMe	2:1	204	
C ₁₄ H ₁₃ PO	1:2	198	L = CH ₂ :CHP(O)Ph ₂
C ₁₀ H ₁₇ PO	1:2	198	L = CH ₂ :CHP(O)(C ₄ H ₉) ₂
C ₆ H ₇ N ₂ SCl	1:1	210	2-thiomidopyridinium ⁺ SbCl ₄ ⁻
C ₇ H ₈ N ₂ O ₂	1:2 2:3	216	L = 4(6)-methyl-3-nitroaniline
C ₆ H ₆ N ₂ O ₂	3:2	216	L = 2-nitroaniline

TABLE 44: Continued

Other Molecule (L)	Ratio SbCl ₃ :L	Reference	Comments
C ₂₅ H ₃₀ N ₃ Cl	1:1	200	L = crystal violet.
(CH ₃) ₃ COH	1:1 1:2	332	viscosity, density and cond. measured.
<i>p</i> -MeC ₆ H ₄ SOCl	1:1	334	
Al(OC ₂ H ₄) ₃ N	1:1	336	
C ₆ H ₇ N	1:1	328	L = α picoline.
C ₉ H ₇ N	1:1	328	L = quinoline.
C ₉ H ₇ N.HCl	1:1:1	390	
C ₉ H ₇ N.C ₂ H ₅ Cl	1:1:1	390	
C ₅ H ₁₀ NH	1:1 1:3	328 291	L = piperidine.
C ₁₃ H ₁₇ ON ₃	2:1	362	L = pyramidone.
RC ₆ H ₄ NR' ₂	1:1 1:3	328,212	R = <i>o</i> - and <i>p</i> -(CH ₃ , CH ₃ O, C ₂ H ₅ O) R = H, R' = Me, Et; R = <i>o</i> -CH ₃ R' = Me; R = <i>o</i> - or <i>p</i> -CH ₃ , <i>o</i> -NH ₂ , R' = Et.
C ₆ H ₅ NHR	1:3 1:1	328,337	R = CH ₃ , C ₄ H ₉ , H.
C ₂ H ₅ NHC ₂ H ₅	1:3	328	
C ₆ H ₅ RNH ₂	1:1 1:3	328	R = CH ₂ , NH.
RC ₃ HS ₃	1:1	344	R = 3,4-dimethoxyphenyl, 4 methoxyphenyl, 4-hydroxy-3-methoxyphenyl.
RC ₆ H ₄ N:NPh	3:2 2:1 1:1	219,220	R = <i>p</i> -Me ₂ N, H, <i>p</i> -NH ₂

TABLE 44: Continued

Other Molecule (L)	Ratio SbCl ₃ :L	Reference	Comments
p-Et ₂ OC ₆ H ₄ N:NPh,H ₂ O	2:1:2	220	
C ₂₄ H ₂₆ N ₄ O ₂ ,HCl	1:1:1	221	L = diantipyrylmethylmethane LH ⁺ SbCl ₄ ⁻
C ₂₆ H ₃₀ N ₄ O ₂ ,HCl	1:1:1	221	L = diantipyrylpropylmethane LH ⁺ SbCl ₄ ⁻
C ₂₉ H ₂₈ N ₄ O ₂ ,HCl	1:1:1	221	L = diantipyrylphenylmethane
N ₂ H ₅ Cl	1:2	373	(N ₂ H ₅) ₂ SbCl ₅ ²⁻
C ₆ H ₅ NH ₂ ,HCl	1:3:3	390	
C ₆ H ₅ NH ₂ ,HCl,H ₂ O	1:3:3:1 1:3:3:3	390	
NH ₄ Cl	1:2	393	2NH ₄ ⁺ SbCl ₅ ²⁻ X-ray crystal structure.
Co(NH ₃) ₆ Cl ₃	1:1	394,396	Co(NH ₃) ₆ ³⁺ SbCl ₆ ³⁻ i.r. and Raman.

TABLE 45: Addition Compounds of SbBr₃

Other Molecule (L)	Ratio SbBr ₃ :L	Reference	Comments
Me ₄ NBr,AcBr	1:2:1	296	
AcBr	1:1	297	Ac ⁺ SbBr ₄ ⁻
	1:3		3Ac ⁺ SbBr ₆ ³⁻
MBr	1:2	222,194	M = K, Rb, Cs.
	2:3		These were found as crystalline phases in the systems MBr-SbBr ₃
	1:3		HBr-H ₂ O and were identified by ³
	1:4,2:1		powder photography.

TABLE 45: Continued.

Other Molecule (L)	Ratio SbBr ₃ :L	Reference	Comments
C ₄ H ₈ O ₂	2:3	170	
C ₁₀ H ₈ N ₂	1:1	198	L = bipy, a weak electrolyte in solution.
C ₁₀ H ₁₆ As ₂	1:1	203	L = diars.
C ₆ H ₆ N ₂ SBr	1:1	210	C ₆ H ₆ N ₂ S ⁺ SbBr ₄ ⁻
C ₅ H ₆ NBr	1:2	213	2PyH ⁺ SbBr ₅ ²⁻
C ₁₀ H ₈ N ₂ ,HBr	1:1:2	281 292	L = 2,2'- or 4,4'- bipyridyl
Et ₄ NBr	1:1	296,297	Et ₄ N ⁺ SbBr ₄ ⁻
Sb(OAc) ₃	2:1	293	3SbBr ₂ ⁺ 3AcO ⁻ , in solution.
SbN	1:1	293	
AlBr ₃	1:1	383	an electrolyte in AsBr ₃
(PhCH ₂) ₂ NBr	1:1	296	(PhCH ₂) ₂ N ⁺ SbBr ₄ ⁻
PhMe ₂ NAcBr	1:1	296	PhMe ₂ NAc ⁺ SbBr ₄ ⁻
Et ₃ PhCH ₂ NBr	1:1	297	
EtMe ₂ PhNBr	1:1	297	
PhCH ₂ NMe ₂ PhBr	1:1	297	
PhNMe ₂	1:1 1:2	297	
N ₂ H ₅ Br	2:11 3:10 1:2 3:2,2:3	373	2N ₂ H ₅ ⁺ SbBr ₅ ²⁻
C ₄ H ₁₁ N ₂ Br	1:1	365	L = butanone hydrazoneium bromide. C ₄ H ₁₁ N ₂ ⁺ SbBr ₄ ⁻

TABLE 45: Continued

Other Molecule (L)	Ratio SbBr ₃ :L	Reference	Comments
C ₅ H ₅ N	2:1	361	High frequency conductometric titration.
2-NH ₂ C ₅ H ₄ N	2:1 1:2	361	Precipitate
C ₁₄ H ₉ N	2:1	361	L = 5,6'- or 7,8'- benzoquinoline.
C ₂₁ H ₂₀ O ₂ N ₂ (OCH ₃) ₂	2:1 1:1	361	L = brucine Precipitate.
C ₁₀ H ₇ N	2:1	361	L = quinoline or isoquinoline
CH ₃ C ₁₀ H ₆ N	2:1	361	L = quinaldine
(Me ₂ CH ₂ CH) ₂ NH	2:1 1:3	361	Precipitate.
C ₁₄ H ₁₂ N	2:1 1:2	361	Precipitate.
C ₁₂ H ₉ N ₂ Br, H ₂ O	1:1:1	203	phenH ⁺ H ₂ O SbBr ₄ ⁻
C ₅ H ₁₁ NHBr, CHCl ₃	1:2:1	284	
C ₅ H ₁₁ NHBr	1:3	284	
C ₅ H ₁₃ N ₂ Br	1:1	365	L = pentan-3-one hydrazoneium bromide. L ⁺ SbBr ₄ ⁻
M ⁿ Br _n		398	M = Na, K, NH ₄ , Cu(I), Cu(II) Ca, Sr, Cd, Hg(I), Hg(II), Sn(II), Fe(III).

TABLE 46: Addition Compounds of SbI₃

Other Molecule (L)	Ratio SbI ₃ :L	Reference	Comments
C ₅ H ₅ N	2:3	182	
C ₆ H ₅ NH ₂	1:6 1:3	191	
C ₁₀ H ₈ N ₂	1:1	198	L = bipy.
C ₁₀ H ₁₆ As ₂	1:1	203	L = diars.
C ₁₂ H ₉ N ₂ I, H ₂ O	1:1:1	203	L = 1,10'-phenanthroline iodide. phenH ⁺ H ₂ O SbI ₄ ⁻
C ₄ H ₈ S ₂	1:1 2:1	206	L = 1,4'-dithiane crystal structure.
C ₆ H ₇ N ₂ SI	1:1	210	L = 2-thioamidopyridinium iodide.
CH:CHCH:CHC(CH ₃):NHI	1:1	397	L ⁺ SbI ₄ ⁻
CH:(CH) ₃ C(NH ₂):NH	1:1	397	
R _n NH _{3-n} I	1:2	397	n = 1; R = C ₂ H ₅ , C ₄ H ₉ , C ₅ H ₁₁ , C ₆ H ₁₁ , C ₆ H ₁₃ , H ₃ N(CH ₂) ₄ , H ₃ N(CH ₂) ₆ , n = 2; R = C ₂ H ₅ .
	1:3	397	n = 1; R = CH ₃ , C ₄ H ₈ , HOC ₂ H ₄ , n = 2; R = C ₃ H ₇ .
	2:3		n = 1; R = C ₃ H ₇ , CH ₃ O(CH ₂) ₃
C ₆ H ₇ :NHI	2:3	397	

TABLE 46: Addition Compounds of SbI₃, Continued.

Other Molecule (L)	Ratio SbI ₃ :L	Reference	Comments
C ₅ H ₅ N	2:3	182	
C ₆ H ₅ NH ₂	1:6 1:3	191	
C ₁₀ H ₈ N ₂	1:1	198	L = bipy. In solution gives LSbI ₂ ⁺ I ⁻
C ₁₀ H ₁₆ As ₂	1:1	203	L = diars.
C ₁₂ H ₉ N ₂ I, H ₂ O	1:1:1	203	L = 1,10'-phenanthroline iodide. (phenH ⁺ , H ₂ O) SbI ₄ ⁻
C ₄ H ₈ S ₂	1:1 2:1	206	L = 1,4-dithiane. crystal structure.
C ₆ H ₇ N ₂ SI	1:1	210	L = 2-thioamidopyridinium iodide. L ⁺ SbI ₄ ⁻
R _n NH _{3-n} I	1:1	397	R = C ₃ H ₇ , n = 3; R = C ₄ H ₉ , n = 2.
CH:CH:CH:CH.L(CH ₃):NHI	1:1	397	L ⁺ SbI ₄ ⁻
CH:CH:CH:CH. (NH ₂):NH	1:1	397	
R _n NH _{3-n} I	1:2	397	n = 1, R = C ₂ H ₅ , C ₄ H ₉ , C ₅ H ₁₁ , C ₆ H ₁₁ , C ₆ H ₁₃ , H ₃ N(CH ₂) ₄ , H ₃ N(CH ₂) ₆ ; n = 2, R = C ₂ H ₅
	1:3		n = 1, R = CH ₃ , C ₄ H ₈ , HOC ₂ H ₄ . n = 2, R = C ₃ H ₇ .
	2:3		n = 1, R = C ₃ H ₇ , CH ₃ O(CH ₂) ₃ .
C ₆ H ₇ :NHI	2:3	397	

TABLE 47: Addition Compounds of BiCl₃

Other Molecule (L)	Ratio BiCl ₃ :L	Reference	Comments
Et ₃ N	1:1	173	
C ₅ H ₅ N	1:2	183	
Ph ₃ PO	1:2	201	
POCl ₃	1:2	275,303	
SnCl ₂	1:2	302	
N ₂ H ₅ Cl	1:1	373	N ₂ H ₅ ⁺ BiCl ₄ ⁻
	1:2		2(N ₂ H ₅) ⁺ BiCl ₅ ²⁻
	1:3		
NOCl	1:1	306	
C ₁₀ H ₈ N ₂	1:1	192	L = bipy
C ₁₀ H ₈ N ₂ ,HCl	1:1:2	281	
(C ₂ H ₅) ₄ AsCl	2:3	300	
C ₄ H ₈ O ₂	2:3	170	
C ₁₇ H ₁₀ O	1:1	112	
C ₃ H ₇ NO	1:1	140	Bonding through carbonyl oxygen L = dimethylformamide.
C ₁₃ H ₁₁ N	complex	57	L = benzalaniline.
C ₁₅ H ₁₆ N ₂	complex	57	L = benzal-p'-dimethylamino- aniline.
C ₆ H ₇ N ₂ SCl	1:2	210	2(2 thioamidopyridinium) ⁺ BiCl ₅ ²⁻
RC ₃ HS ₃	1:1	345,349	R = 4-methyl phenyl, 4-methoxy phenyl, 3,4-dimethoxy phenyl, phenyl.
C ₉ H ₇ N	1:1	217	L = quinoline.

TABLE 47: Continued.

Other Molecule (L)	Ratio BiCl ₃ :L	Reference	Comments
C ₆ H ₈ N	1:1	217	L = α or β -picoline.
C ₁₂ H ₁₂ N ₂	1:1	217	L = benzidine.
RC ₆ H ₄ N ₂ Cl	1:1	375,299,304	R = <i>p</i> -Et ₂ OC, Me ₂ N, <i>p</i> -(Me, Cl,
	1:3	376,378,363	Br, I), H, <i>o</i> -(CH ₃ , Cl, Br),
	2:1	377	<i>p</i> -(CH ₃ , Cl), <i>p</i> -(C ₂ H ₅ O ₂ C, H ₂ NSO ₂),
	1:2		<i>p</i> -C ₆ H ₅ , <i>o</i> -(CH ₃ O ₂ C, C ₂ H ₅ O ₂ C), <i>p</i> -OMe, <i>o</i> -NO ₂ , <i>m</i> -NO ₂ , <i>p</i> -NO ₂ .
C ₁₀ H ₇ N ₂ Cl	1:2	376	L = or naphthalene diazonium chloride.
R ₄ NH _{4-x} Cl	1:1 1:2 2:1 3:1 4:1 6:1	379	R = CH ₃ , x = 1,2,3,4.
Me ₃ SCl	1:1 1:3	380	
Me ₂ (PhCH ₂)SCl	1:2 2:3	380	
RNH ₃ Cl	1:3	381	R = Bu, lauryl, n - dodecyl. 3(RNH ₃) ⁺ BiCl ₆ ³⁻
RC ₆ H ₄ N:NPh	2:1 3:2	219,220	R = H, <i>p</i> -Me ₂ N
RC ₆ H ₄ N:NPh, H ₂ O	1:1:1 2:1:2 3:1:1	219	R = <i>p</i> -NO ₂ = <i>p</i> -EtO = <i>p</i> -NH ₂
<i>p</i> -Cl C ₆ H ₄ Cl	1:2	304	

TABLE 47: Continued

Other Molecule (L)	Ratio BiCl ₃ :L	Reference	Comments
C ₆ H ₁₃ N ₂ Cl	1:1	365,382	L = dimethylketazinium chloride L ⁺ BiCl ₄ ⁻
PyHCl	1:3 1:2 2:3	390	

TABLE 48: Addition Compounds of BiBr₃

(L)	BiBr ₃ :L	Reference	Comments
C ₁₇ H ₁₀ O	1:1	112	L = benzanthrone.
C ₁₀ H ₈ N ₂	1:1	198	L = bipy.
Ph ₃ PO	1:2	201	
C ₆ H ₆ N ₂ SBr	1:2	210	L = 2-thioimidopyridine 2L ⁺ BiBr ₅ ²⁻
C ₁₀ H ₈ N ₂ ·HBr	1:1:2 1:2:4	281	
(C ₂ H ₅) ₄ AsBr	2:3	300	
TeBr ₄	1:1	305	
C ₁₈ H ₁₂ N ₂ ·HBr	1:1:2 2:3:2	309	L = 6,6' or 2,3-biquinoline
C ₇ H ₇ O ₂ NHBr·H ₂ O	1:1:2	351	L = trigonelline.
C ₅ H ₁₁ O ₂ NHBr	1:2	351	L = betainium bromide.
2-CH ₃ C ₅ H ₅ NBr	1:1	347	L = 2-picolinium bromide. X-ray crystal analysis.
C ₅ H ₁₂ NBr	1:2	347	L = piperidinium bromide. X-ray crystal analysis.

TABLE 49: Addition Compounds of BiI₃

Other Molecule (L)	Ratio BiI ₃ :L	Reference	Comments
C ₁₀ H ₈ N ₂	1:1	14	
Ph ₃ PO	1:2	201	
C ₆ H ₇ N ₂ SI	1:2	210	
C ₁₀ H ₈ N ₂ HI	2:1:2	281	
(C ₂ H ₅) ₄ AsI	2:3	301	
2-CH ₃ C ₅ H ₅ NI	1:1	347	L = 2-picolinium iodide.
Co(C ₅ H ₅) ₂ ⁺ I ⁻	3:1	350	L ⁺ BiI ₄ ⁻ 2BiI ₃
C ₇ H ₇ O ₂ NHI, H ₂ O	1:1:1	351	L = trigonellum iodide.
C ₅ H ₁₁ O ₂ NHI	1:2	351	L = betainium iodide.
Cholinium iodide	1:2	351	

TABLE 50:

The following table is taken from the paper by Remy³⁷⁹ and appears to have been taken from the literature prior to 1917.

<u>Compound</u>	<u>M</u>
$M(\text{BiCl}_4)$	$M = \text{K} + (\text{H}_2\text{O}), \text{Rb} + (\text{H}_2\text{O}), \text{C}_2\text{H}_5 \cdot \text{NH}_3, \text{C}_3\text{H}_7 \cdot \text{NH}_3$. chinolinium, diethyl-phenyl-benzyl-ammonium.
$M_2(\text{BiCl}_5)$	$M = \text{Na} (+\text{H}_2\text{O}) \text{K}, \text{and } \text{K} (+2\text{H}_2\text{O}), \text{NH}_4, \text{NH}_4 (+\frac{1}{2}\text{H}_2\text{O}),$ $\text{Rb} (+2\frac{1}{2}\text{H}_2\text{O}), (\text{CH}_3)_2\text{NH}_2, \text{C}_2\text{H}_5 \cdot \text{NH}_3, \text{C}_3\text{H}_7 \cdot \text{NH}_3, \text{C}_4\text{H}_9 \cdot \text{NH}_3$. quinolinium, pyridinium, dimethylanilinium, diethylanilinium.
$M_3(\text{BiCl}_6)$	$M = \text{H}, \text{Na}, \text{NH}_4, \text{Rb}, \text{Cs}, \text{Tl}, (\text{CH}_3)_3\text{NH}, \text{C}_2\text{H}_5 \cdot \text{NH}_2$. quinolinium, anilinium, anilinium + $3\text{H}_2\text{O}$, diethylanilinium, <u>o</u> - and <u>p</u> -toluidium.
$M_4(\text{BiCl}_7)$	$M = \text{CH}_3 \cdot \text{NH}_3, (\text{CH}_3)_2\text{NH}_2, \text{C}_2\text{H}_5 \cdot \text{NH}_3, \text{C}_3\text{H}_7 \cdot \text{NH}_3$.
$M_6(\text{BiCl}_9)$	$M = \text{Tl}, (\text{C}_4\text{H}_9 \cdot \text{NH}_3)$.
$M_3(\text{Bi}_2\text{Cl}_9)$	$M = \text{Cs}, \text{CH}_3\text{NH}_3, (\text{CH}_3)_3\text{NH}, (\text{C}_2\text{H}_5)_4\text{N}, (\text{C}_2\text{H}_5)_4\text{P}, (\text{C}_2\text{H}_5)_4\text{As}$.
$M_5(\text{Bi}_2\text{Cl}_{11})$	$M = \text{NH}_4, (\text{CH}_3 \cdot \text{NH}_3)$
$M_5(\text{Bi}_3\text{Cl}_{14})$	$M = (\text{CH}_3)_4\text{N}$.

CHAPTER 7

Some addition compounds of arsenic trichloride
and tribromide

In the preceding chapter it has been shown that complexes of group VB trihalides, with other molecules, are many and various. Very little structural data has been reported on these compounds, and many of the postulated structures must be regarded with suspicion. Numerous MX_4^- ions have been postulated⁴⁷³, but so far no conclusive evidence for such a discrete ion has been reported in the literature. The X-ray data which has been reported in chapter 7 suggests that such ions are not as easily formed as it at first appeared, and it yet remains to be seen if such an ion can be isolated. Another interesting fact which has emerged is that these trihalide molecules appear to be capable of forming MX_6^{3-} ions, which are octahedral and have O_h symmetry. A number of such ions have been identified by X-ray analysis, for example, BiCl_6^{3-} (396), SbCl_6^{3-} (395) and BiBr_6^{3-} . The pentahalides MX_5^{2-} show a more varied behaviour. Some have been identified as discrete ions, for example, SbCl_5^{2-} , BiCl_5^{2-} and SbF_5^{2-} , all having a distorted tetragonal pyramidal structure, in which, presumably, the sixth position of the octahedron is occupied by a "lone pair". BiBr_5^{2-} and BiI_5^{2-} , on the other hand, do not exist as discrete ions but have chain-like structures in which each bismuth atom is octahedrally co-ordinated by six halogen atoms, with one of the halogens bridging between two bismuth atoms³⁴⁷.

Only one structural study of an arsenic trihalide adduct has appeared in the literature. Hoard and Goldstein⁴⁷⁴ have shown, by means of X-ray studies, that in the compound $\text{Cs}_3\text{As}_2\text{Cl}_9$ the arsenic trichloride molecule persists in the crystal and is built into the

structure with caesium and chloride ions. The results of this X-ray analysis have also been interpreted in terms of distorted AsCl_6 octahedrons by Kolditz²³¹. It has also been shown that the compound $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ is isostructural with its arsenic analogue⁴⁷⁶. These results seem to indicate that arsenic and antimony trichloride do not accept chloride ions quite as readily as it would appear from literature postulations. Mention has already been made of the polar nature of the trichlorides, and the ease with which they form solvates.

The stereochemistry of most non transition element compounds seems to be explained adequately by the Sigwick-Powell "non bonding electron pair repulsion theory"⁴⁰⁷. However, the theory breaks down when the problem of stereochemically inactive "lone pairs" arises. Urch⁴⁶¹ has speculated on the bonding in a number of hexa halogen complexes of non transition elements of the type SbCl_6^{3-} , TeCl_6^{3-} , SeBr_6^{2-} , all of which have a regular octahedral structure (O_h), and show no distortion from interaction with the "lone pair". He suggests that if the ns orbital (a_{1g}) of the central atom plays little part in bonding, then an extra pair of electrons may be accommodated in the a_{1g} anti-bonding molecular orbital, without distorting the O_h structure. He also suggests that electrons in such an ns orbital will decrease the effective electronegativity of the central atom, so that nd orbitals can be better used for bonding. The screening effect of electrons in an ns orbital tends to increase the electronegativity difference between a given atom and a halogen, and is important for halogens less electronegative than fluorine.

That the difference in electronegativity between the central atom and the ligand, influences the activity of the "lone pair", seems to be indicated by the fact that BiCl_5^{2-} has a stereochemically active "lone pair"⁴⁰², whereas BiBr_5^{2-} and BiI_5^{2-} (347) do not exist as discrete ions, but have chain-like structures in which each bismuth atom is octahedrally co-ordinated by six halogen atoms, with one bridging halogen atom. The "lone pair" is not stereochemically active in these last two compounds. However, the difference in electronegativity is not the only factor governing these "lone pairs", for example, in the ion SbCl_5^{2-} it is stereochemically active, whereas the ion SbCl_6^{3-} is a regular octahedron (O_h). It could be argued that the presence of five electron withdrawing groups decreases the electron density around the antimony, making it more electronegative. This does not explain the change in bonding which presumably takes place in going from SbCl_5^{2-} to SbCl_6^{3-} .

Octahedral co-ordination is usually explained in terms of six equivalent $nsnp^3nd^2$ hybridized orbitals. Pauling, in discussing the bonding in SeBr_6^{2-} , suggests that since the 4s orbital (containing a pair of unshared electrons) is unavailable for bonding, then the role of the s electron, in the hybridized orbital, is played by the 5s orbital, the bonds being $4p^34d^25s$. He suggests that the large value of the selenium radius, in SeBr_6^{2-} , which is 23 percent greater than the tetrahedral radius of selenium, supports this view. He reports a similar effect for Te^{IV} . Thus, in changing from SbCl_5^{2-} to SbCl_6^{3-} the bonding would change from $5s^25p^35d^2$ to $5p^35d^26s^2$. Similar arguments can be applied to BiCl_5^{2-} and BiCl_6^{3-} , both of

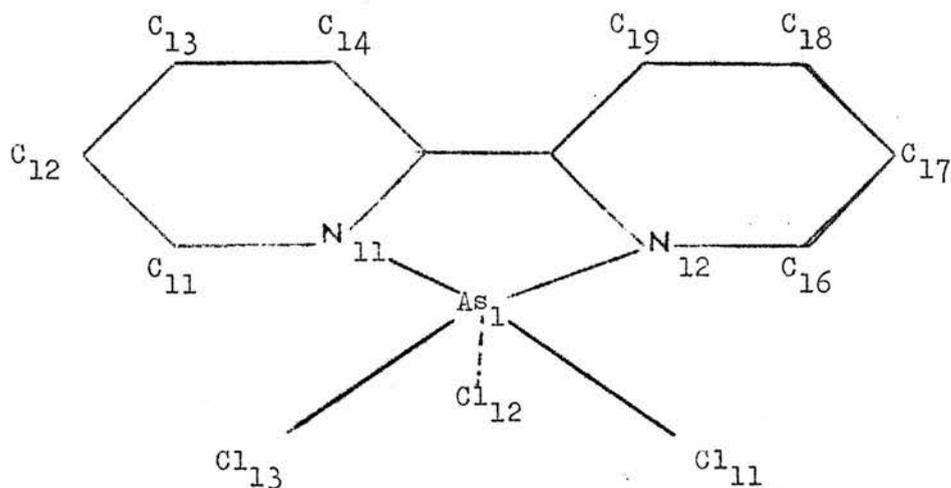
which have octahedral co-ordination, the former with a "lone pair" in one of the octahedral positions⁴⁰². Spectrophotometric⁴⁰⁸ and electrometric⁴⁰⁹ studies of complexes of BiCl_n^{3-n} , in solution, have indicated complexes with values of n from one to six, depending on chloride ion concentration. Later work suggests that the complex with n = 5 does not exist in solution^{410,411}.

The Structure of the Compound bipy,AsCl_3

The compound bipy,AsCl_3 ⁽¹⁴⁾ was prepared by us for spectroscopic study, as part of a general investigation on arsenic trichloride and tribromide adducts with several bidentate chelating ligands. An X-ray crystal analysis of this compound was carried out by J. Cameron³²⁰ in the Physics department of St. Andrews University. The results of this investigation proved to be most interesting in that the compound was shown to have a dimeric chlorine bridged structure. The structure is shown in figure 18, looking along the a, b, and c axes of the monoclinic system. The cell dimensions and relevant bond lengths and angles are reported in table 51 along with a diagram of half the molecule, indicating the nomenclature used.

There is no evidence for a stereochemically active "lone pair". It is interesting to note that from the diagram representing the structure of $\text{Cs}_2\text{As}_2\text{Cl}_9$, given by Hoard and Goldstein⁴⁷⁴, the "lone pair", once again, does not appear to be stereochemically active. It was felt that a 1:1 adduct between AsCl_3 and a bidentate chelating ligand offered a good opportunity for forming a monomeric octahedral species, in which one of the octahedral positions would be occupied by the

TABLE 51



Cell dimensions: $a = 10.07$; $b = 9.40$; $c = 9.21 \text{ \AA}$.

$\alpha = 123^{\circ}39'$; $\beta = 109^{\circ}48'$; $\gamma = 94^{\circ}12'$.

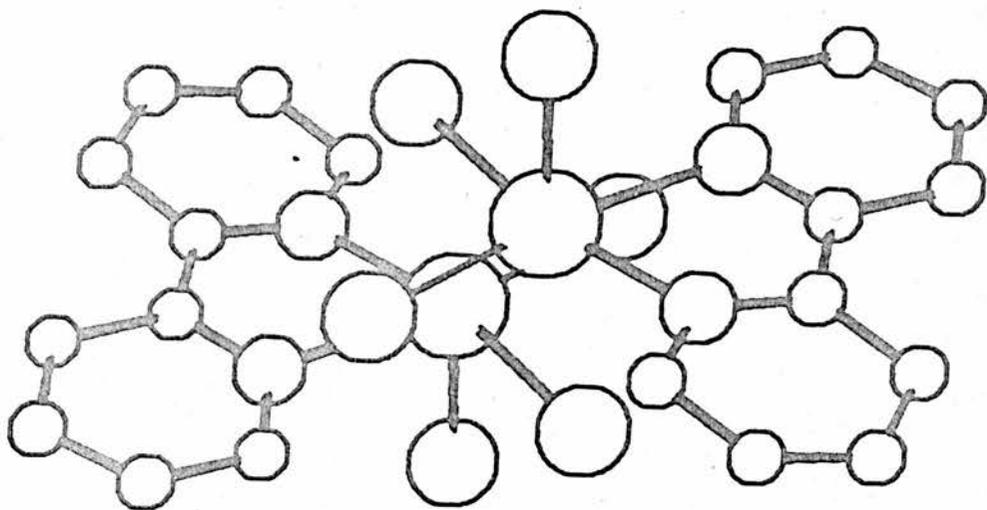
Bond Lengths

$\text{As}_1 - \text{Cl}_{11}$	=	2.958 ± 0.011
$\text{As}_1 - \text{Cl}_{12}$	=	2.302 ± 0.020
$\text{As}_1 - \text{Cl}_{13}$	=	2.5314 ± 0.021
$\text{As}_1 - \text{N}_{11}$	=	2.132 ± 0.031
$\text{As}_1 - \text{N}_{12}$	=	2.230 ± 0.048
$\text{Cl}_{11} - \text{As}_2$	=	2.817 ± 0.021
$\text{As}_2 - \text{Cl}_{21}$	=	2.9598 ± 0.011
$\text{As}_2 - \text{Cl}_{22}$	=	2.302 ± 0.020

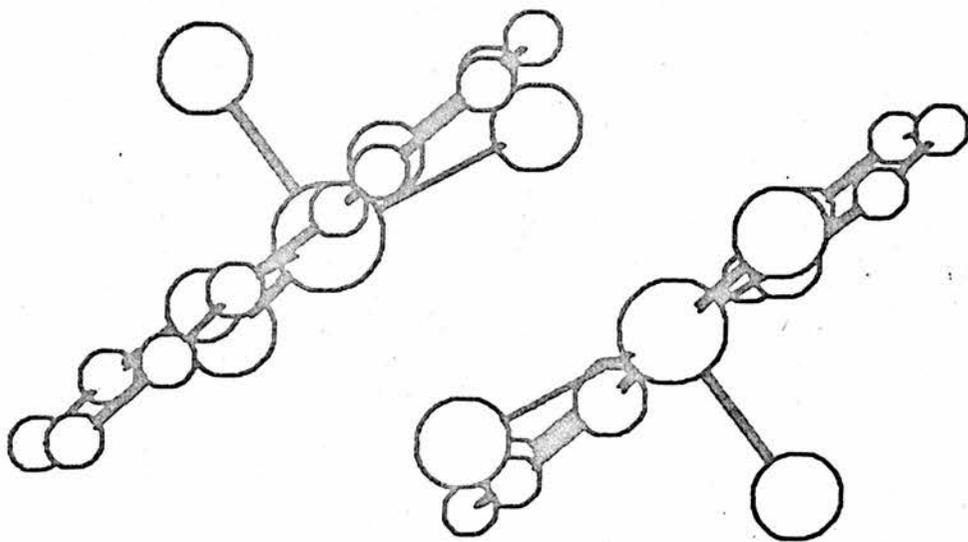
Bond Angles

$\text{Cl}_{11} - \text{As}_1 - \text{Cl}_{12}$	=	$95.38^{\circ} (\pm 0.57^{\circ})$
$\text{Cl}_{11} - \text{As}_1 - \text{Cl}_{13}$	=	$99.61^{\circ} (\pm 0.48^{\circ})$
$\text{As}_1 - \text{Cl}_{11} - \text{As}_2$	=	$87.44^{\circ} (\pm 0.47^{\circ})$
$\text{As}_1 - \text{Cl}_{21} - \text{As}_2$	=	$87.41^{\circ} (\pm 0.47^{\circ})$

Figure 18: Diagram of $(\text{bipy}, \text{AsCl}_3)_2$ shown along the a, b and c crystallographic axes

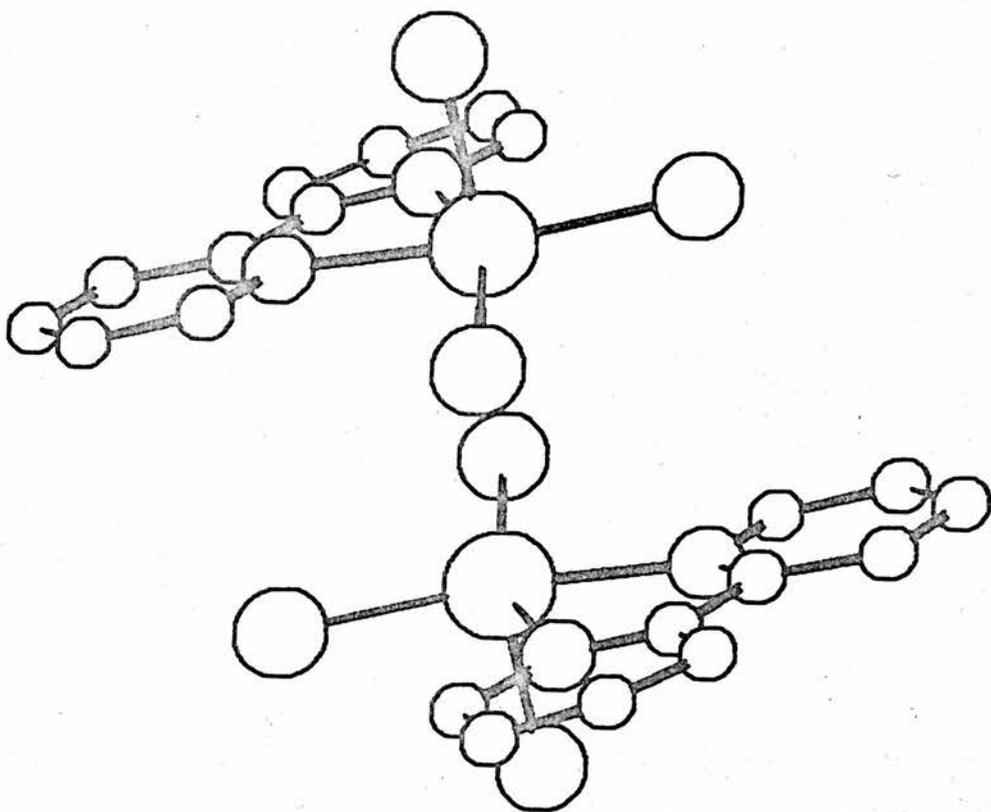


(A)



(B)

Figure 18: Continued



(c)

"lone pair". The somewhat surprising structure found suggests that AsCl_3 prefers to form compounds in which the "lone pair" is stereochemically inactive.

It is interesting to compare this structure with the isoelectronic compound $\text{SeOCl}_2, 2\text{Py}$. This latter compound has an octahedral structure with the two pyridines in trans positions and the oxygen atom bonded trans to the "lone pair" of electrons, which are stereochemically active⁴⁸¹. The ion $\text{SeCl}_3, \text{Py}_2^+$ has also been reported to have a stereochemically active "lone pair"⁴⁸².

Urch⁴⁶¹ has described three different classes depending on the interaction of the s orbital of the central element (M) with the ligand orbitals (L). In class I, the M_s orbital is more tightly bound than the ligand orbitals and interaction with the ligand orbitals is small. However, Urch is referring to octahedrally co-ordinated anions, and his suggestion that the retention of octahedral co-ordination by forming polymeric anions is caused by the large negative charge on the anion, which makes it unstable in a crystal, is obviously not applicable to the uncharged species being discussed.

Another interesting feature to be noted is the fact that the bidentate ligands occupy positions which are not symmetrical to each other, thus lowering the symmetry of the molecule.

No other X-ray structure of adducts of AsX_3 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) have appeared in the literature, nor has there been any study of these compounds by vibrational spectroscopy.

We have now prepared a number of compounds of AsX_3 ($X = \text{Cl}, \text{Br}$) with the bidentate chelating ligands phen, bipy and diamine.

Several of these compounds had been reported previously in the literature¹⁴. A series of novel compounds, L_2AsX_3 have also been prepared where L is a bidentate ligand. The infrared and Raman spectra of these compounds are reported, and discussed in the light of possible structures. Conductivity data, in nitrobenzene solution, is reported for all the compounds prepared, and molecular weight data, (cryoscopic) in the same solvent, is reported for the 2:1 adducts.

DISCUSSION OF RESULTS

A. Preparation of Compounds

In several cases both the 1:1 and 2:1 ($2AsCl_3:L$) adducts were prepared in the same solvent, simply by adding ligand to $AsCl_3$ for the 2:1 adduct, $AsCl_3$ to ligand for the 1:1 adduct. The 1:1 adduct of $AsCl_3$, bipy was prepared in acetonitrile solution, whereas the 2:1 complex was prepared in benzene solution.

B. Molecular Weight and Conductivity Measurements

It was difficult to obtain reliable molecular weight results because these compounds are only slightly soluble in nitrobenzene, the solvent used for the cryoscopic measurements. The values obtained, combined with the conductivity values, certainly suggest that the 2:1 adducts ionise in solution to give 1:1 electrolytes. These results do not exclude the possibility that the 2:1 adduct is composed of a dimeric 1:1 adduct with two molecules of AsX_3 ($X = Cl, Br$) as solvate molecules. Such a compound would, in nitrobenzene solution, give

four particles per unit molecule, and the observed molecular weight would be the same for either $(\text{bipy}, \text{AsCl}_3)_2 \cdot 2\text{AsCl}_3$ or $\text{bipy}, 2\text{AsCl}_3$. The conductivity measurements can be explained in a similar fashion. The molecular weight of $(\text{bipy}, \text{AsCl}_3)_2$ is 673 and of $(\text{bipy}, \text{AsCl}_3)_2 \cdot 2\text{AsCl}_3$ it is 1037.5. AsCl_3 is a non electrolyte in nitrobenzene so if the latter structure were the correct one for the compound $\text{bipy}, 2\text{AsCl}_3$, then the ionic species present in solution would be provided by 65% of the molecule, namely $(\text{bipy}, 2\text{AsCl}_3)_2$. Correcting the molar conductivity of $\text{bipy}, 2\text{AsCl}_3$ for this effect, and allowing for a dimeric species, gives a value $\Lambda_{0.0008} = 32.0 \text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$, which is in the same region as that obtained for a 1:1 electrolyte.

Unfortunately, molecular weight measurements could only be made on one of the 1:1 adducts; diamine, AsCl_3 . The low solubility of the other materials precluded cryoscopic measurements being made. The value obtained for this material can be interpreted in several ways. Considering the molecule as a monomer it suggests that an equilibrium such as $\text{diamine}, \text{AsCl}_3 \rightleftharpoons \text{diamineAsCl}_2^+ + \text{Cl}^-$ lies mainly to the right, in solution. However, a similar ionisation for a dimeric molecule giving rise to two cations and two anions, would give exactly half the depression in freezing point of the solvent, and exactly the same observed molecular weight. Conductivity measurements do not help in resolving this problem as the value of the molar conductivity, calculated from the observed resistance of the solvent, includes a term for the molar concentration which must be known. It is, therefore, clear that the molecular weight and conductivity data is not sufficient to indicate a possible molecular

TABLE 52: Conductivity Measurements of the Trihalide System

Compound	Molar Conc. Mole litre ⁻¹ (x10 ³)	Resistance Ohms (x10 ⁻³)	Molar Cond. Ohms ⁻¹ cm ² mole ⁻¹
phen, AsCl ₃	3.0 (1.5)	11	16.6 (33.2)
phen, 2AsCl ₃	2.94	6.4	26.7
phen, 2AsCl ₃ ^(b)	2.8	1.75	
bipy, AsCl ₃	1.0 (0.5)		19.0 (38.0)
bipy, 2AsCl ₃	1.6	14.0	24.6
diamine, AsCl ₃	2.6 (1.3)		19.4 (38.8)
diamine, 2AsCl ₃	2.9	7.0	26.3
	3.5	5.3	27.0
phen, AsBr ₃	5.64 (2.82)	5.0	17.8 (35.6)
phen, 2AsBr ₃	1.18	13.0	32.0
bipy, AsBr ₃	1.48 (0.74)	15.7	21.6 (43.2)
bipy, 2AsBr ₃	1.84	8.62	31.6
AsBr ₃	1.45	40.9	0.716
AsBr ₃ ^(b)	27.4	12.0	1.53

All measurements were carried out in nitrobenzene solution unless otherwise stated.

(b) Measurements in acetonitrile.

The figures in brackets are the molar conductivities and concentrations based on a dimeric species.

TABLE 53: Molecular Weight Determinations on the Trihalide Systems

<u>Compound</u>	<u>M</u> detm	<u>Mo</u>	<u>M/Mo</u>
phen, 2AsCl ₃	280	543	0.015
bipy, 2AsCl ₃	235	518.8	0.454
diamine, 2AsCl ₃	270	526.8	0.512
phen, 2AsBr ₃	376	809.5	0.466
bipy, 2AsBr ₃	314	785.5	0.400

All measurements made in nitrobenzene solution.

structure.

The molar conductivities for the 1:1 adducts were calculated, both on the basis of a monomeric and dimeric molecule. Both values are reported in table 52. The latter value is given in parenthesis. The values obtained on the basis of a dimeric molecule are in keeping with the value observed for the known dimer, $(\text{bipy}, \text{AsCl}_3)_2$, which suggests that the other 1:1 adducts may also prove to be dimeric.

C. Discussion of Infrared and Raman Spectra

1. Infrared study in the range $1600 - 600\text{cm}^{-1}$.

The changes which occur in the infrared spectra of the ligands phen, bipy and diamine (L) have already been discussed in chapters 3 and 4. The infrared spectra of the compounds L, AsX_3 and $\text{L}, 2\text{AsX}_3$ ($\text{X} = \text{Cl}, \text{Br}$) in the range under discussion are reported in tables 56, 57. In every case the expected changes in the ligand were observed, indicating that complex formation had taken place.

2. Infrared and Raman study in the region $600 - 100\text{cm}^{-1}$.

The unusual stereochemistry of the dimeric molecule belongs to the point group C_i having only a centre of symmetry i and a number of twofold rotation reflection axes, which are implied by the presence of a centre of symmetry. The presence of a centre of symmetry means that the mutual exclusion rule holds. Using Cartesian co-ordinates and treating bipy as two point masses located at the nitrogen atoms, i.e. a twelve atom problem, the representation for vibration is

$$\Gamma_{\text{vib}} = 15A_g + 15A_u$$

Using internal co-ordinates it was shown that each representation was composed of six stretching and nine bending vibrations. Two of these stretching vibrations were related to the singly bonded chlorines, two were related to As - N stretching vibrations, whereas the other two resulted from vibrations of the bridging chlorines.

There is little data for the comparison of terminal with bridging $V(MCl)$ frequencies, but it is generally assumed that the latter will lie lower, by analogy with the data for gaseous Al_2Cl_6 and similar molecules. In this type of molecule the bridging frequency can be as much as $100cm^{-1}$ lower than the terminal mode, but in $Cr_2Cl_9^{3-}$ the difference is only $20cm^{-1}$ (463). Clark⁴⁶³ points out that the evidence is, as yet, too sparse to conclude that bridging $V(MX)$ modes will always lie below corresponding terminal modes.

Examination of the infrared spectrum of the compound bipy, $AsCl_3$ shows a shoulder at $360cm^{-1}$ and three strong bands at 314, 278 and $234cm^{-1}$. Clark has observed that metal nitrogen stretching frequencies for this type of molecule will probably not occur above $200cm^{-1}$, and this problem has already been discussed with reference to the pentachloride adducts of phen and bipy. The strong band at $314cm^{-1}$ occurs in the region found for the $V_3(F_{lu})$ mode of $AsCl_6^-$ ion, and it seems not unreasonable to assign this band to a stretching mode of the non bonding chlorine atoms. The band at $234cm^{-1}$ can probably be assigned to a bridging chlorine stretching frequency. The weak shoulder at $360cm^{-1}$ may be due to a ligand vibration. A weak band occurs in this region in three of the reported spectra, although it is not observed in the spectrum of bipy, $2AsCl_3$, as a strong, broad,

metal halogen vibration obscures this region. It is tentatively suggested that a strong band at 278cm^{-1} is associated with a non bridging chlorine vibration, although there is no evidence to support this suggestion. The $V(\text{As} - \text{hal})$ vibrations can be associated with bands which change, with change in halogen, although it is not possible to identify bridging and non bridging halogens on this basis.

A number of bands in the $400 - 500\text{cm}^{-1}$ region occur in all four spectra and can confidently be assigned as ligand vibrations. They were also observed in other adducts of bipy. The Raman spectra of these bipy - AsX_3 adducts also show a number of bands in the region $400 - 500\text{cm}^{-1}$. They show very little change on going from chloride to bromide adducts, and can, therefore, confidently be assigned as ligand vibrations. Unfortunately it was not possible to record the spectrum of bipy, 2AsCl_3 . The Raman spectrum of the 1:1 chloride adduct shows a number of bands in keeping with the low symmetry, as determined by X-ray analysis.

It is difficult to make an assignment of the metal-nitrogen stretching frequencies from these spectra. It was felt that little change in the frequency of these vibrations would occur in changing from chloride to bromide. However, the region of interest, $150 - 200\text{cm}^{-1}$, where such vibration might be expected, is obscured by metal-bromine vibrations. The intensity of the bands at 208 and 178cm^{-1} in the 1:1 and 2:1 bromide adducts, rules out the possibility of these bands being associated with metal-nitrogen vibrations, as bands of comparable intensity are not observed in the chloride adducts.

The very strong band at 325 cm^{-1} in the 1:1 chloride adduct occurs in the same region of the spectrum as $V_1(A_{1g})$ of AsCl_6^- , and is probably associated with a non bridging chlorine vibration. Although a ligand band occurs in the region $350 - 360\Delta\text{cm}^{-1}$, the band at $364\Delta\text{cm}^{-1}$ in the 1:1 chloride adduct, can confidently be associated with a chloride rather than a ligand vibration. The intensity of the band is much higher than the ligand vibrations in the region $400 - 500\Delta\text{cm}^{-1}$, whereas in other cases it is almost of equal intensity. It is suggested that the two higher frequency bands are possibly associated with metal non bridging chlorine vibrations, and that the two bands at 271 and $233\Delta\text{cm}^{-1}$ may be due to bridging chlorine atoms. This would suggest that the As - N stretching vibrations may be associated with the medium bands at 201 and $178\Delta\text{cm}^{-1}$. However, this could not be verified; not only was this region obscured by metal bromine vibrations for the tribromide adducts, but also the pentachloride adducts, $\text{bipy}, 2\text{SbCl}_5$ and $\text{bipy}, \text{PCl}_5$, fail to collaborate this view, as no bands were observed in the region $200 - 150\Delta\text{cm}^{-1}$, which could be associated with M-N vibrations, other than the 177 cm^{-1} band in the compound $\text{bipy}, 2\text{SbCl}_5$, which is associated with $V_5(F_{2g})$ of SbCl_6^- .

The complexity of the spectra, and the low symmetry of the molecule, makes it almost impossible to assign the stereochemistry on the basis of vibrational spectroscopy.

The infrared of the 2:1 complex, $\text{bipy}, 2\text{AsCl}_3$, definitely indicates that it is not a solvated 1:1 complex as was discussed earlier. There is no evidence for solvated AsCl_3 , and, more important,

there is no evidence for the strong bands at 314, 278 and 234cm^{-1} , which occur in the 1:1 molecule. Instead, a strong, broad band occurs at 340cm^{-1} , a medium band at 374cm^{-1} whilst two weak bands were observed at 274 and 250cm^{-1} .

In comparing the spectra of the 1:1 chloride complexes of phen and bipy there is one disturbing feature, namely, the occurrence of the metal halogen stretching vibrations at higher frequencies in the phen adduct. Thus, the strongest band (As-Cl) in the infrared of the phen complex occurs at 357cm^{-1} , compared with 314cm^{-1} for the bipy complex, and the strongest Raman band is at 393 for phen, compared with 325cm^{-1} for the bipy complex. It is felt that this effect could be caused by a slightly stronger interaction with the phen ligand, giving rise to slightly larger force constants. It could also be due to different structures, although the similarity of phen and bipy makes this improbable. The general similarity in the spectra suggests that the phen adduct also has a dimeric chlorine bridged structure, but monomeric species cannot be dismissed without further consideration. There are several possibilities which must be considered for MX_3 , phen type molecules.

1. A tetragonal pyramid with the bidentate ligand occupying two cis positions, and an active "lone pair" occupying the sixth position. Two geometrical isomers can exist for such a model. Both isomers are of low symmetry and belong to the point group C_s .

2. A trigonal bipyramid in which the "lone pair" is inactive. Once again two geometrical isomers are possible, one isomer having both nitrogen atoms in the equatorial plane of the trigonal bipyramid,

and the other isomer having one nitrogen in an axial, and the other in an equatorial position. The former model belongs to the point group C_{2v} , whereas the latter has the symmetry C_s . In all four cases symmetry arguments predict three As - Cl stretching vibrations which are both infrared and Raman active. Examination of the reported spectra, table 54, suggests that this is not the case. The strong Raman band at $393\Delta\text{cm}^{-1}$ is not observed in the infrared, nor is the infrared band at 305cm^{-1} observed in the Raman spectrum. Secondly, the number of bands observed in the metal halogen stretching region is more than predicted by symmetry arguments for any monomeric species. These arguments do not prove, but they certainly suggest, that the compound phen, AsCl_3 has a dimeric structure similar to that observed for bipy, AsCl_3 .

It was not possible to obtain well resolved Raman spectra for the two diamine - AsCl_3 adducts. The frequencies of the strongest metal halogen bands, however, occurred in the same region of the spectrum as did the strongest bands for the adducts of AsCl_3 -phen. Once again, it is fairly obvious from the spectra reported in table 56 that the 2:1 adduct is not a solvated 1:1 adduct. There is no indication of free AsCl_3 , nor is there sufficient correlation between the two spectra to make such a suggestion feasible. It is felt, however, that the observed vibrational data is insufficient to make any reliable suggestions as to the stereochemistry of these adducts.

The 2:1 adducts

The 2:1 complexes have, so far, been discussed only in the light of whether or not they contain solvated AsCl_3 molecules. The foregoing discussion suggests that this possibility can be ruled out. There remain two possibilities to be considered: 1, an ionic structure of the type $\text{LAsCl}_2^+ \text{AsCl}_4^-$, 2, a halogen bridged structure.

In considering the former case it must be remembered that the AsCl_4^- ion has not been positively identified in the solid state. A recent paper by Long⁴⁷⁷ suggests that this ion exists in solution, and has been identified by vibrational spectroscopy. The compound $\text{PyHCl}, \text{SbCl}_3$ has recently been the subject of an X-ray analysis¹⁶⁷. The compound is ionic and the anion has been shown to consist of chains of SbCl_4^- units, linked together by chlorine bridging. A similar compound, $\text{PyHCl}, \text{AsCl}_3$, was first reported by Petzold¹⁹⁶. The vibrational spectra and conductance measurements are discussed in this chapter.

Comparison of the vibrational spectrum of $\text{Phen}, 2\text{AsCl}_3$ with the spectrum of the compound $\text{PyHCl}, \text{AsCl}_3$, and also with the solution spectrum of AsCl_4^- , reported by Long⁴⁷⁷, suggests that neither the ion AsCl_4^- nor $(\text{AsCl}_4)_n^{n-}$ is present in the solid state. This is supported by the conductivity measurements which give smaller molar conductivity values for the 2:1 adducts than for the 1:1 adducts, which, in at least one case, has been definitely established as a molecular compound in the solid state.

In considering halogen bridged structures several possibilities arise. In the bipy complexes the nitrogens could, possibly, donate

to different AsX_3 molecules, giving rise to a molecule in which the nitrogens were trans to each other. Such an effect has previously been suggested for one of the bipy ligands, in the compound $2TiCl_3, 3bipy$ ⁽⁴⁸³⁾. However, such an effect is not considered to be possible for the ligands phen& diamine because of the more rigid geometry of these molecules. It is also possible that the structure could be similar to the dimeric 1:1 adduct, $bipy, AsCl_3$, with one of the ligand molecules being absent. In such a molecule the centre of symmetry would no longer be present, and the mutual exclusion rule would not hold.

If the bidentate ligand is considered as two point masses located on the nitrogen atoms, then we are primarily concerned with a ten atom problem, and 24 vibrations are expected, nine of which are primarily $As - X$ stretching vibrations ($n-1$). In the compound $phen, 2AsCl_3$, ten vibrations are observed in the region $400-200cm^{-1}$ (i.r. and R.), normally associated with arsenic - chlorine stretching vibrations. Thus it is not possible, by vibrational spectroscopy, to eliminate any of the possible structures which predict this number of vibrations.

It seems possible that the 2:1 adducts have molecular, chlorine bridged structures in the solid state. In view of the low symmetry and also the low solubility which precludes solution studies, the unambiguous assignment of the stereochemistry of these compounds must await X-ray crystal analysis, if suitable single crystals can be obtained.

TABLE 54: Infrared and Raman Spectra of Phen-AsX₃ adducts
 (i.r. 500 - 200cm⁻¹, R. 80 - 500Δcm⁻¹)

Phen, AsCl ₃		Phen, 2AsCl ₃		Phen, AsBr ₃		Phen, 2AsBr ₃	
i.r.	R.	i.r.	R.	i.r.	R.	i.r.	R.
			86w				
	108m		106sh.w		99s		96m 108sh.w
	123w		113s				128w
			140w		143m		145m
			160s				160m
	173m		179w		181s		179m
			193m 205w				196m
			232m				226w 248s
	250m				244v.s		257v.s
264sh		263m	263m	265s	265w		268sh.s
	284w	290sh.w			290w	290v.s	
305m-s			313w	310w		310sh	305w
331m-w	333s	326sh.w 350sh	331m				
357s	357s	358v.s	350w 367v.s				
	393v.s	388s			406m		
418m	416s		429m		405m-s		414w 426m
438w		440m		437m	434m	437m	436w
460m	460w			455m-w	477m	455w	
		500w		496w	496m	500w	

Figure 19: i.r. and Raman Spectra of the Phen System.

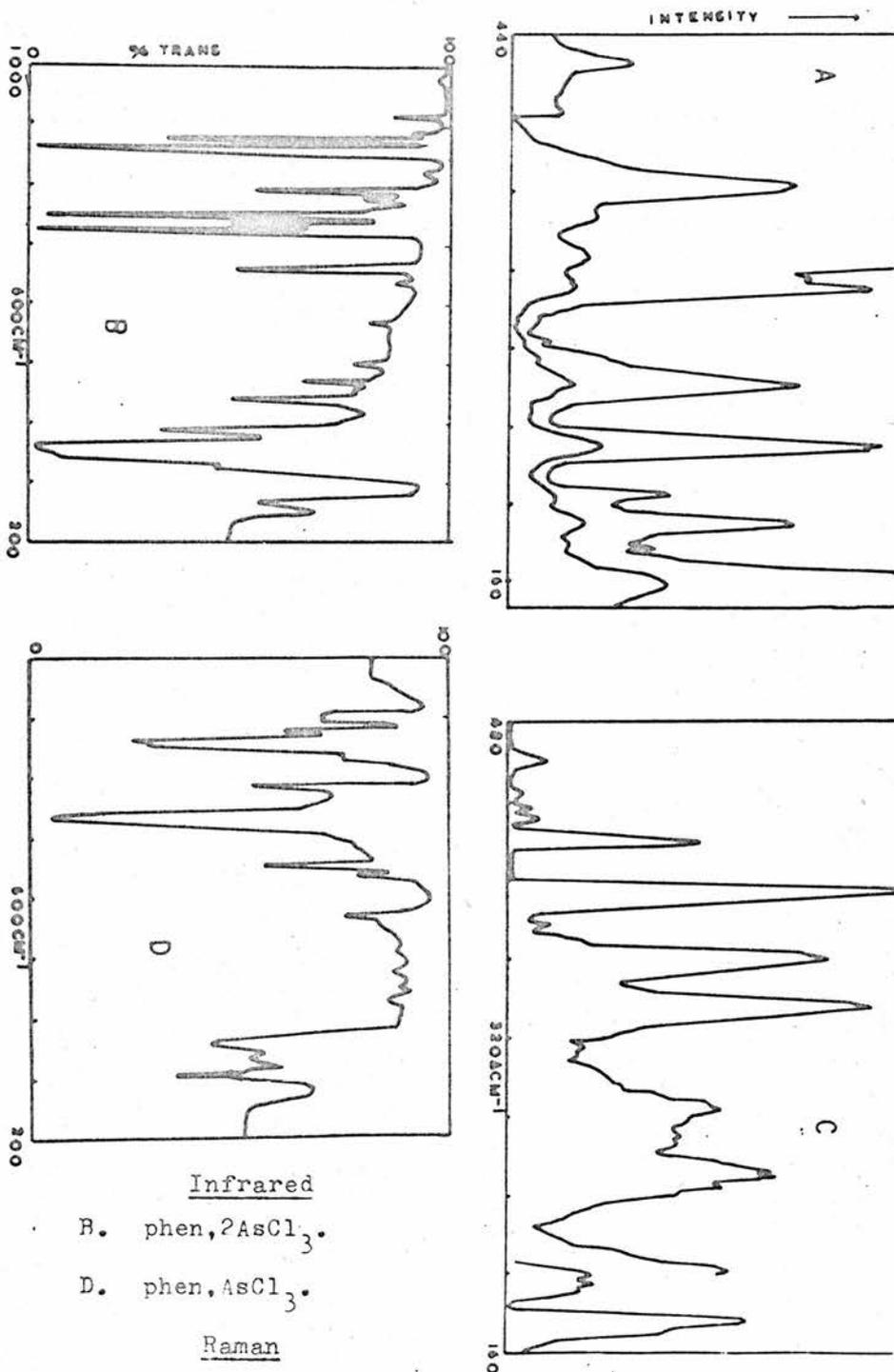
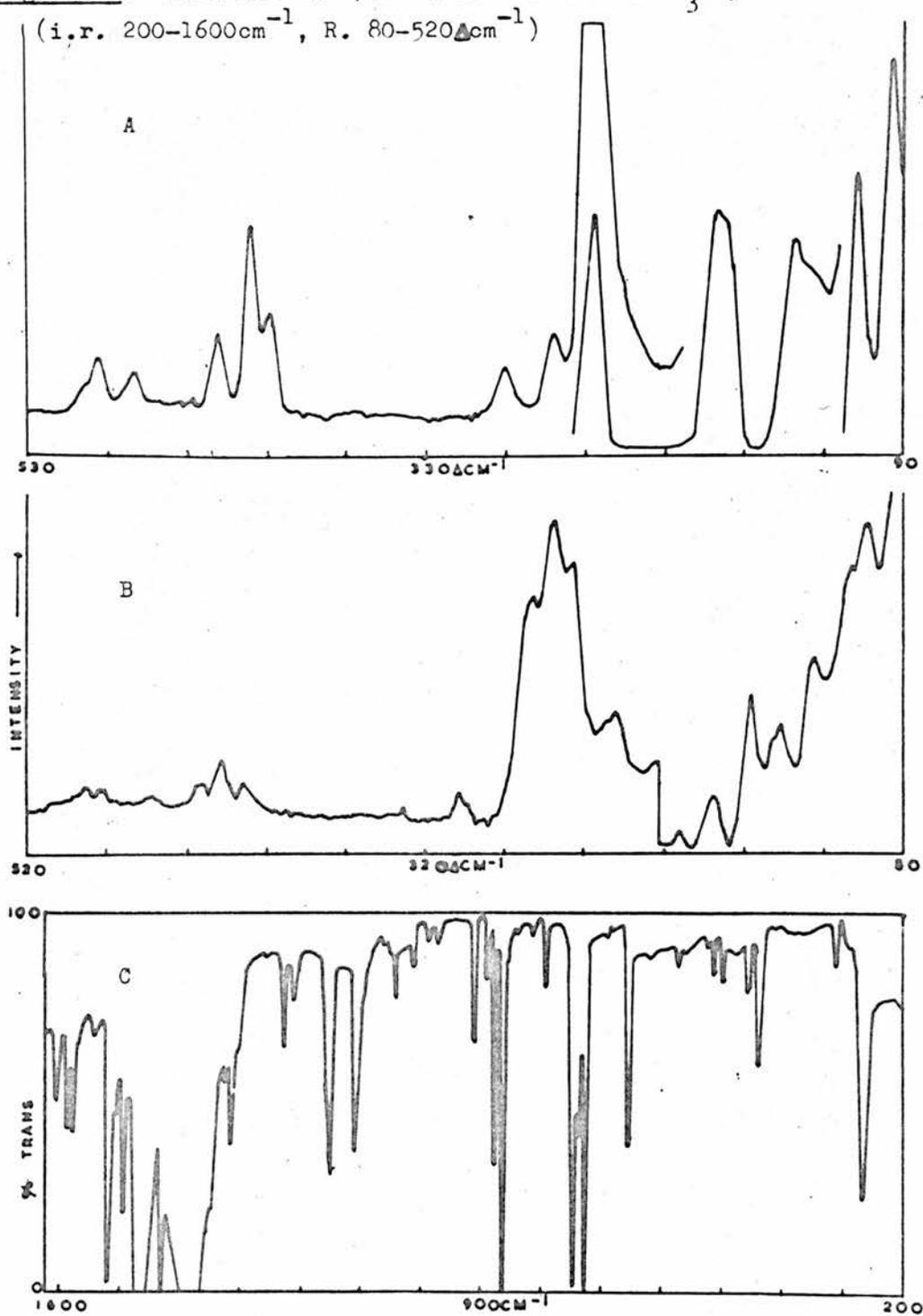


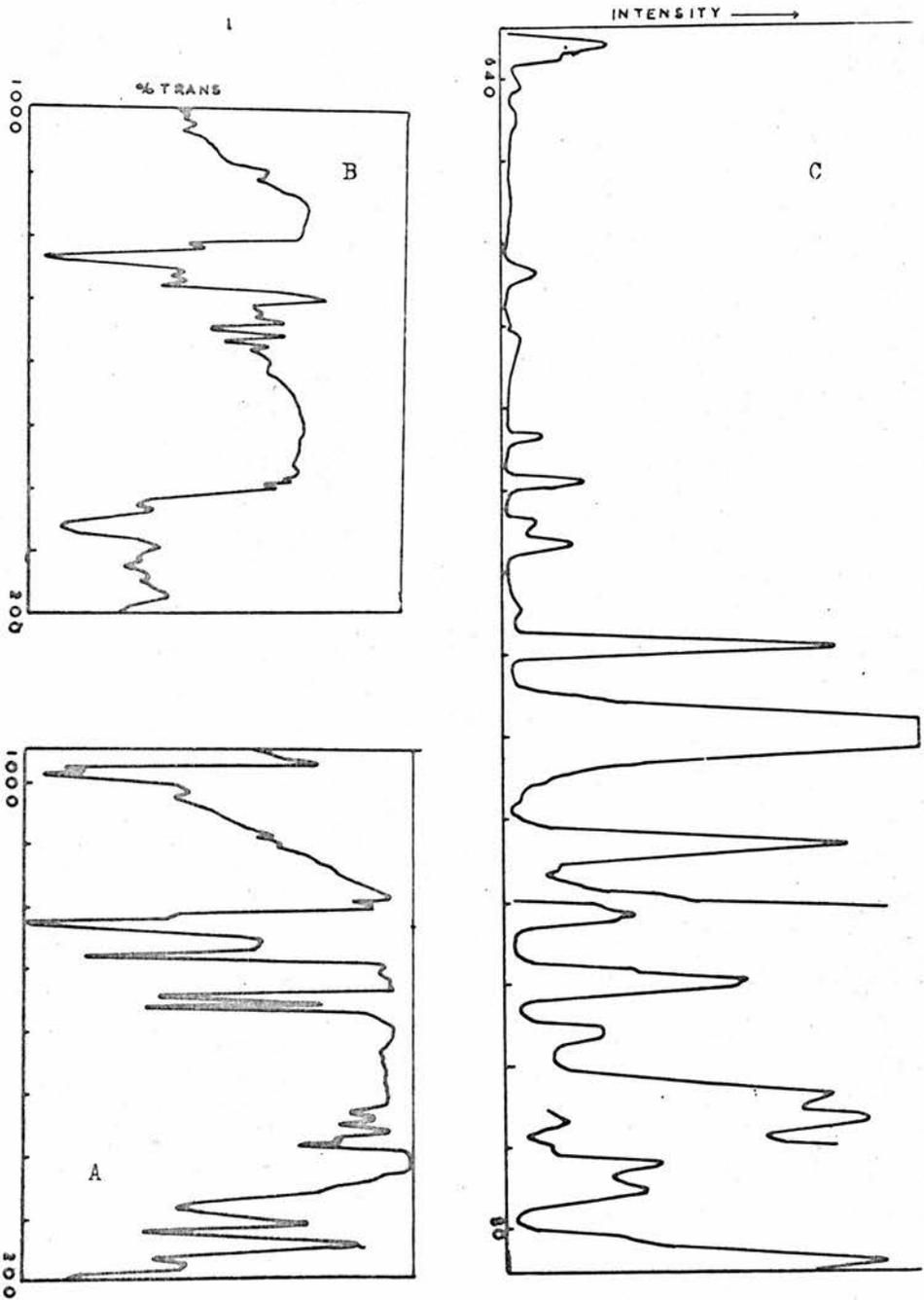
Figure 20: i.r. and R. Spectra of the Phen-AsBr₃ System

A. phen,AsBr₃. B. phen,2AsBr₃. C. phen,AsBr₃

TABLE 55: Infrared and Raman Spectra of Bipy-AsX₃ Adducts
 (i.r. 500-200cm⁻¹. R. 80-500 cm⁻¹)

<u>Bipy,AsCl₃</u>		<u>Bipy,2AsCl₃</u>		<u>Bipy,AsBr₃</u>		<u>Bipy,2AsBr₃</u>	
i.r.	R.	i.r.	R.	i.r.	R.	i.r.	R.
	69s						89w
	100s						101w.sh
	114s						
	130m						122m-s
	148m				142sh		150w
	178w-m				178s		178s
	201m				208s		208s
234s	233m						232w.sh
		250w			243s		
				255s		260s	253v.s
278s	271m	274w		276w.sh	267m		264s.sh
				285s			
314s							
	325v.s						
360sh.w	364m	340s.br		350w	362m	365w	361m-w
		374m		372w			
412m		408w					
	416w	418w		421m	414w	419m	410m-w
425sh.w	424w			431m	422w		414w
448m	447w	440w		451m	442w	465m	
465w	469w			478m	470w		

Figure 21: i.r. and R. Spectra of the Bipy System.
 (i.r. $1000-200\text{cm}^{-1}$. R. $65-650\text{cm}^{-1}$)



A. bipy, AsCl_3 . B. bipy, 2AsCl_3 . C. bipy, AsCl_3

Figure 22: i.r. and R. Spectra of the Bipy-AsBr₃ System.
(i.r. 200-1100cm⁻¹. R. as shown)

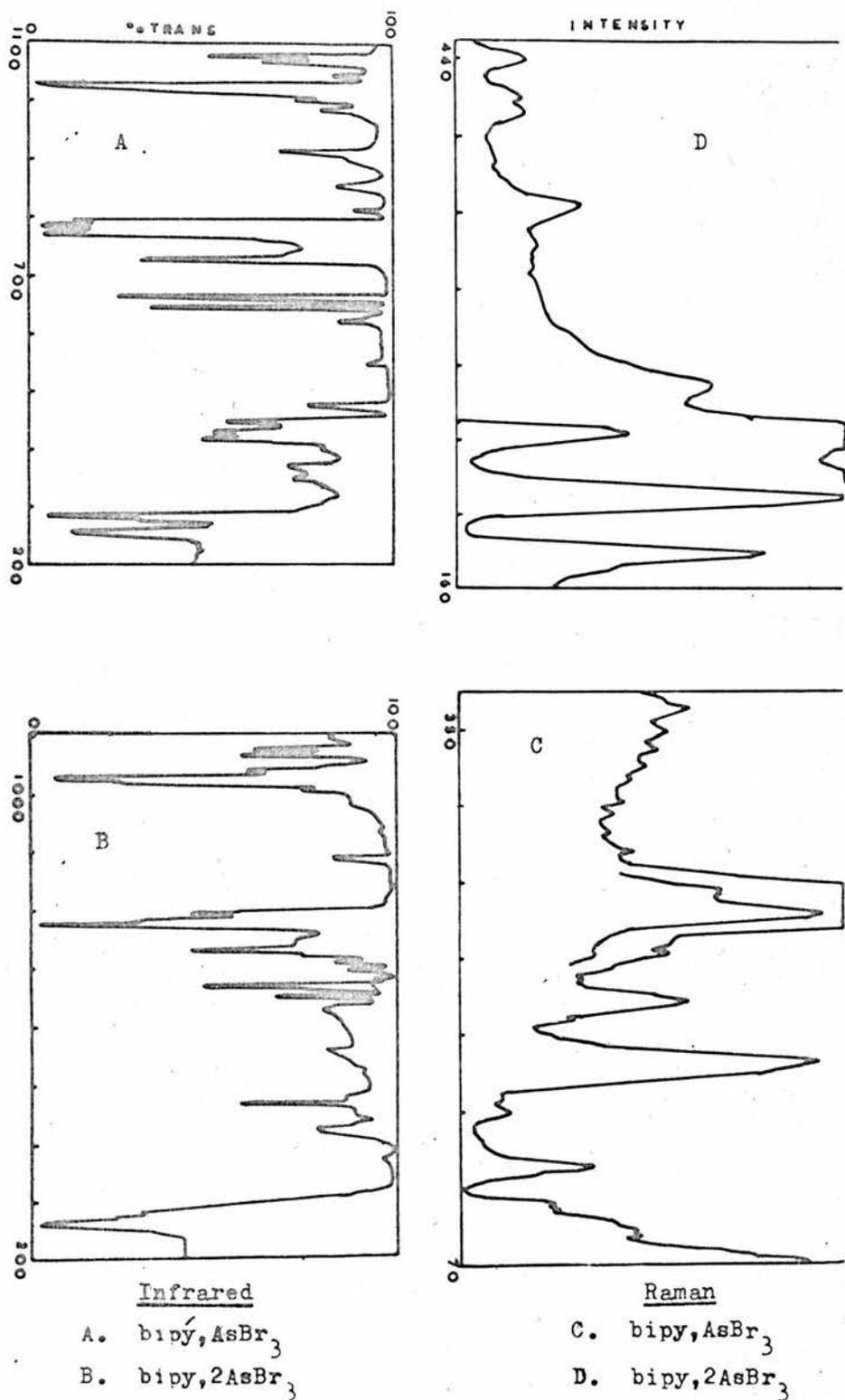
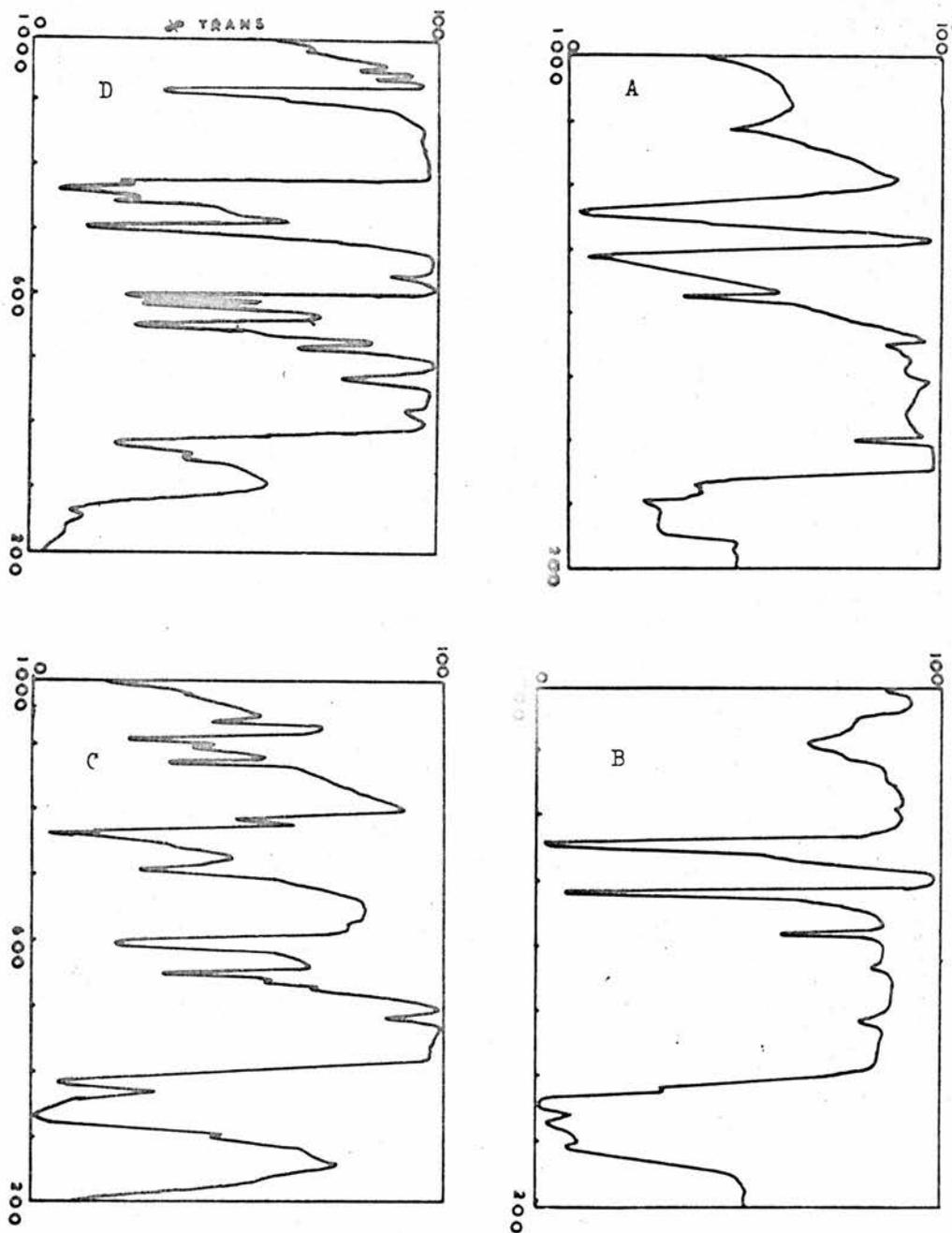


TABLE 56: Infrared Spectra of diamine - AsCl₃ adducts (800 - 200cm⁻¹)

<u>diamine, AsCl₃</u>		<u>diamine, 2AsCl₃</u>	
i.r.	Raman	i.r.	Raman
	137w 171w 181w		
265w		235sh.vw	
325sh		310w	
		335v.s	
344w.sh		348sh.s	358m
365v.s	378s	384s	386s 398sh
470m	472m 480m	480m	
519m-w		521sh	
551s	544m	549s	
584m			
597m-s		595s	
705s		710s	
746w		746s	
762s		762s	
775w		786m	

Figure 23: Infrared Spectra ($1000-200\text{cm}^{-1}$).



A. $\text{PyHCl}, \text{SbCl}_3$.

B. $\text{PyHCl}, \text{AsCl}_3$.

C. diamine, 2AsCl_3 .

D. diamine, AsCl_3 .

TABLE 57: Infrared Spectra of Bipy Adducts (1600-600cm⁻¹)

<u>bipy,AsCl₃</u>	<u>bipy,2AsCl₃</u>	<u>bipy,AsBr₃</u>	<u>Bipy,2AsBr₃</u>
1580m	1580w		
1550w	1568w-m		
1510w-m	1510w-m		
1480w.sh	1482w.sh		
1306m	1300v.w		
1271w	1268v.w	1287m	1285m-w
1242m	1238v.w	1279sh	
		1258m-s	1255m
		1230m-w	1220w
	1207v.w		
1170m	1167m-w	1179s	1175m-s
		1169s	1165m-s
1156m	1150m		
		1111m	1108m
1097m	1095w	1097w	1093w
1069m	1068w	1079m	1077m
1059m	1054w	1069m	1068m
		1048w	1039w
1019s	1118sh.s	1039s	1025s
1011s	1110m-s	1002v	1001w
975w	970w	988w	980v.w
907w		919m	
		860m	
806w		814w	
785sh	787w.sh	795sh	792m
774v.s	765v.s	788s	780sh
766sh	739sh	772v.s	772s
719s	720m-w	730s	725m
655m	652m	668s	668s
		660sh	658sh
649sh	645w	649s	645m
638s	635m	625w	620w

TABLE 58: Infrared Spectra of Phen and Diamine Adducts. (1700-600cm⁻¹)

<u>phen, AsCl₃</u>	<u>phen, 2AsCl₃</u>	<u>phen, AsBr₃</u>	<u>diamine, AsCl₃</u>	<u>diamine, 2AsCl₃</u>
1626	1626w	1624w		
1610w	1602w	1602w		
1591m	1580m	1580m	1576m	1575w
1535m	1541m	1540w	1310w	
1511m	1518m-s	1519m-s	1255w	1252v.w
1490w	1491w-m	1494m-w	1240v.w	
1312w	1312w	1316m-w	1180w	1185w
1268w	1260w	1259v.w	1162w	1160w
1235w	1230m	1230m	1145s	1140m-s
1220w		1211w		
1185w			1120w	1120sh
1140w	1156m	1151s	1085m	1083m
1098m	1110s	1110s	1046m	1040m
1030w	1040w	1041w	1008s	999s
972w	978w	971w	951w	952sh
896w	918w	911w 889w	938w	938w
881w	880s	879m	919s	911s
861w	862s	862s	902sh	898sh
850s				
842s			776w.sh	786m
818w	822w	811w	762s	762s
	795m	792w	746m.sh	745sh
770m	780w		706s	710s
	751s	745s		
	738m	738m	596m-s	596s
720s	728s	728s		
676s	662m	656m	583m	
640m	638w	618w	555s	550m
620m			518m	522sh

The Bromide systems

The vibrational spectra of the bromides are reported in tables 54 and 55, pages 177, 180, and represented in figures 20, 22, p.179,182. The spectra of phen and bipy adducts show very good agreement in the As - Br stretching region, and it seems reasonable to assume that the structures are similar. The ligand vibrations, in general, are easily assigned, although some doubt arises about the strong band observed in the Raman spectrum of phen at 244cm^{-1} . In the 1:1 adduct, phen, AsBr_3 , it is, presumably, obscured by the strong band at 248cm^{-1} . However, in the 2:1 adduct, where the As - Br stretching occurs at a higher frequency, a shoulder at 244cm^{-1} could possibly be due to the vibration observed in the free ligand.

In general, with these compounds, it has proved extremely difficult to make any assignment of ligand vibration in the arsenic halogen region. The spectra of the free ligands have been reported in tables 18 and 19, chapter 3.

Similarly, it has not been possible to assign the arsenic nitrogen vibrations, and a successful identification of these bands will require examination of molecules of higher symmetry, and more desirable solubility characteristics.

The System $\text{PyHCl}_n\text{MCl}_3$ (M = Sb, As.)

The compound $\text{PyHCl}_n\text{SbCl}_3$ has been prepared recently, and the results of an X-ray crystal analysis on this compound have been reported¹⁶⁷. In this compound the SbCl_4^- ion forms an infinite chain, and gives six-co-ordinate Sb by use of chlorine bridges. Each such chlorine is 2.64 Å from one antimony, and 3.12 Å from the next. There are two bridging chlorines per SbCl_4^- group. The other two chlorine atoms are 2.38 Å from the antimony. This shorter distance agrees closely with previous results on SbCl_3 ⁽⁴⁷⁸⁾. It is interesting to note that in this latter compound the shortest Sb - Cl distance between different molecules is 3.5 Å, whereas the van der Waal distance is about 4 Å⁽⁴⁶²⁾. It is not clear from Lindqvist's paper⁴⁷⁸ how many chlorine atoms from adjacent molecules are this close to the antimony atom, but from the diagram given it would appear that at least two, and possibly three, chlorine atoms are, in fact, closer than the van der Waal radius (excluding the three bonded chlorines). This raises the question as to whether or not the "lone pair" is actually stereochemically active in this compound. It is generally accepted as being active, so the problem of the volume occupied by a "lone pair" must be considered. In the polymeric ion $(\text{SbCl}_4^-)_n$ the bridging chlorine atoms from the next SbCl_4^- unit are 3.12 Å away from the antimony, and in this case the "lone pairs" would appear to be non active. In the compound $(\text{bipy}, \text{AsCl}_3)_2$ the normal non-bridging As - Cl distance is 2.30 Å, compared to 2.25 Å found in the compound $\text{Cs}_3\text{As}_2\text{Cl}_9$ ⁽⁴⁷⁴⁾. The bridging chlorine distance is 2.96 Å and, once again, the "lone pair" appears to be

inactive. The compound $\text{Cs}_3\text{As}_2\text{Cl}_9$ has been reported as containing AsCl_3 molecules surrounded by Cs^+ and Cl^- ions, in a cubic, close-packed structure. Although intermolecular distances are not reported, it appears, from the diagram of the unit cell, that the "lone pair" is not stereochemically active in the AsCl_3 molecules in this particular compound.

The compound $\text{PyHCl},\text{AsCl}_3$ was first prepared by Petzold¹⁹⁶. The infrared and Raman spectra of this compound, and also of $\text{PyHCl},\text{SbCl}_3$ are reported in table 61, page 197, and are reproduced in figs. 23, 25, p. 184, 196. Conductivity measurements on both of these compounds, in acetonitrile solution, are reported in table 60, page 192, and figure 24, page 191.

X-ray powder photographs of both these materials were taken, using molybdenum radiation. Attempts to use copper radiation were unsuccessful due to adsorption. The $\sin^2 \theta$ values of the most intense lines are reported in table 59. The results of this study indicate that the compounds are not isomorphous, but it must be pointed out that this does not show that they are not isostructural. A complete X-ray crystal analysis would be required to definitely establish the structure of the compound $\text{PyHCl},\text{AsCl}_3$.

Conductivity measurements were made on both of these compounds. The results, given in table 60, indicate that $\text{PyHCl},\text{AsCl}_3$ is a weak electrolyte in both nitrobenzene and acetonitrile solutions. The molar conductivities reported were calculated using the molecular weight of the monomer, and the results certainly indicate that the

TABLE 59: X-ray Powder Photographs for the System PyHCl-MCl₃

The values reported in the table are the $\sin^2 \theta$ values for a camera of 57.3mm radius (MoK $\lambda = 0.1707 \text{ \AA}$).

<u>line</u>	<u>PyHCl, AsCl₃</u>	<u>PyHCl, SbCl₃</u>
1	.0019s	.0016s
2	.0032w	.0038m
3	.0043w	
4		.0057w
5	.0062w	
6		.0090m-w
7	.0131s	.0135m
8		.0182s
9	.0267m	
10		.0355w
11	.0396m-w	

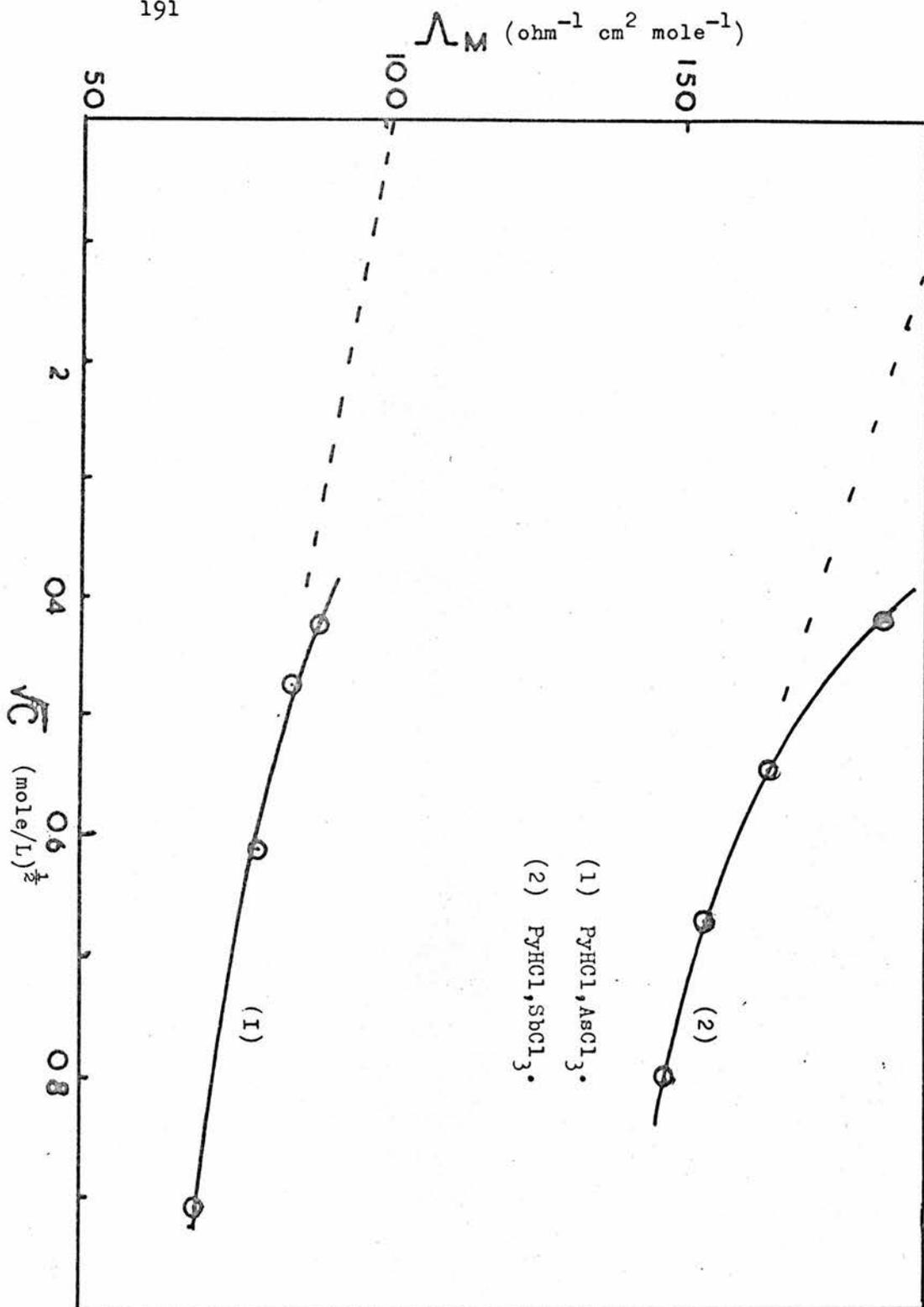


Figure 24.

TABLE 60: Conductivity Measurements of the Systems PyHCl, -MCl₃

<u>Compound</u>	<u>Molar Conc.</u> mole litre ⁻¹ (x10 ³)	<u>Resistance</u> ohms(x10 ³)	<u>Molar Cond.</u> ohm ⁻¹ cm ² mole ⁻¹
PyHCl,AsCl ₃ (a)	5.4	8.13	9.4
PyHCl,AsCl ₃ (b)	8.27	0.85	71.5
	3.82	1.71	78.8
	2.22	2.66	85.0
	1.80	3.10	89.9
PyHCl,SbCl ₃ (b)	6.4	0.53	147
	4.5	0.73	152
	2.96	1.035	164
	1.82	1.50	184

(a) nitrobenzene solution.

(b) acetonitrile solution.

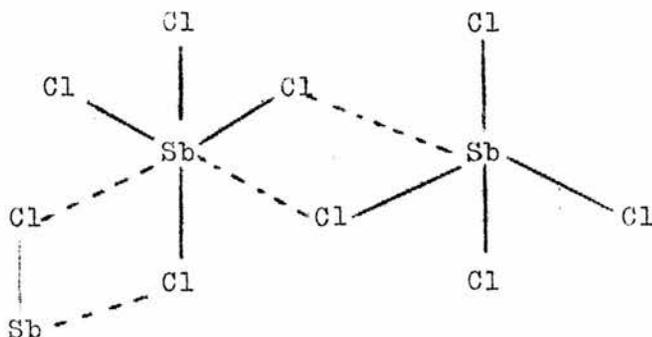
compound is not $\text{PyH}^+ \text{AsCl}_4^-$ in either of these solvents. There seems no reason to suppose that ion pair formation would be important for PyH^+ and AsCl_4^- ions. The low solubility of this compound and of $\text{PyHCl}, \text{SbCl}_3$ in nitrobenzene, made it impossible to carry out cryoscopic molecular weight measurements in this solvent.

Infrared and Raman Spectra of $\text{PyHCl}, \text{MCl}_3$ (M = As, Sb.)

In the primitive unit cell of $\text{PyHCl}, \text{SbCl}_3$ there are two SbCl_4^- units. The point group isomorphous with the factor group is C_{2h} , and since the polymeric anion has a centre of symmetry midway between the bridging chlorine atoms and the adjoining antimony atoms, the mutual exclusion rule holds. Since there are ten atoms in the anion, in a unit cell we expect $3N-3$ or 27 vibrational modes associated with the anion. In fact, five Raman active bands were observed in the antimony chlorine stretching region, whereas three infrared active bands were observed above 200cm^{-1} . Of the $3N-3$ normal vibrational modes predicted for an acyclic molecule of N atoms, $N-1$ are primarily associated with stretching vibrations, i.e. nine stretching vibrations are predicted for this model, whereas eight bands were observed in the (ir & R.) region of the spectrum, associated with antimony-chlorine stretching vibrations. The bending vibrations which are expected to occur in a ^{lower} region of the spectrum, were not observed in the Raman because of strong Raleigh scattering below $150\Delta\text{cm}^{-1}$.

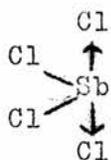
It is interesting to note that the vibrational spectra of this compound can also be interpreted in terms of a monomeric anion, SbCl_4^- of C_{2v} symmetry. As we have already observed, the anion is

polymeric, containing two long (3.12 Å) bonds from antimony to chlorine atoms, originally associated with the next antimony, as shown below

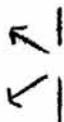


These long bonds will lead to small stretching force constants, and it is to be expected that this will give rise to vibrations at a much lower frequency than the normal antimony-chlorine region. The high frequency bands can thus be treated as the MX_4 units. The stretching vibrations for such a model have already been discussed in chapter 3, where we saw that four bands, $2A_1 + B_1 + B_2$, are predicted to occur as a closely spaced triplet, and a fourth band of lower frequency. This pattern is very similar to that observed for the Raman spectrum of this compound, shown in figure 25B, page 196. This model and the vibrational spectrum suggest that the mutual exclusion rule no longer holds. The coincidences observed can be explained as follows:

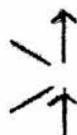
If $V(\text{Sb-Cl})$ vibrations only are considered, we have



(1)



(2)



(3)

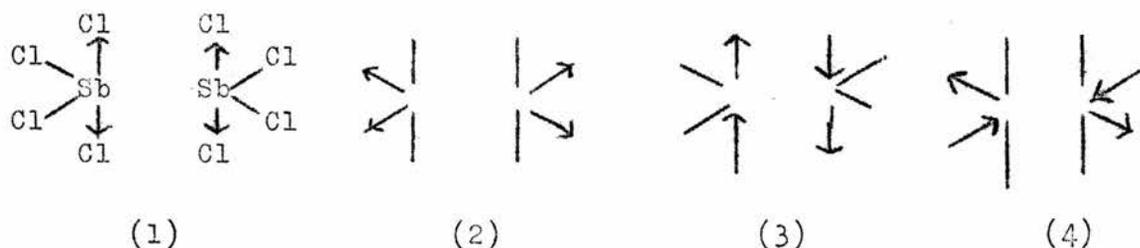


(4)

However, two SbCl_4^- units can couple in two ways:

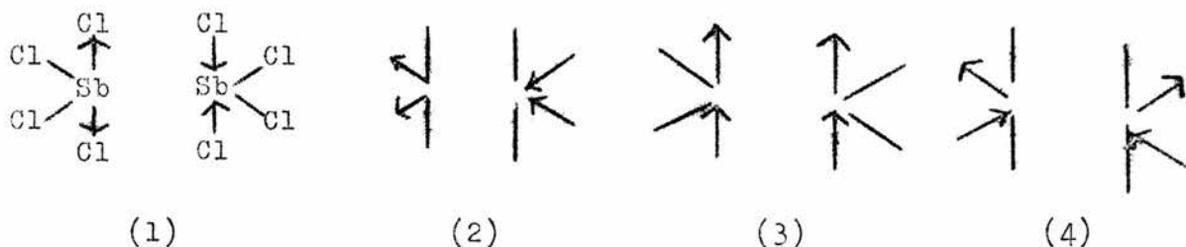
a) Raman active modes, (these are symmetric with respect to inversion in the centre of symmetry).

Schematically



b) Infrared active modes (these are antisymmetric with respect to inversion at the centre of symmetry.).

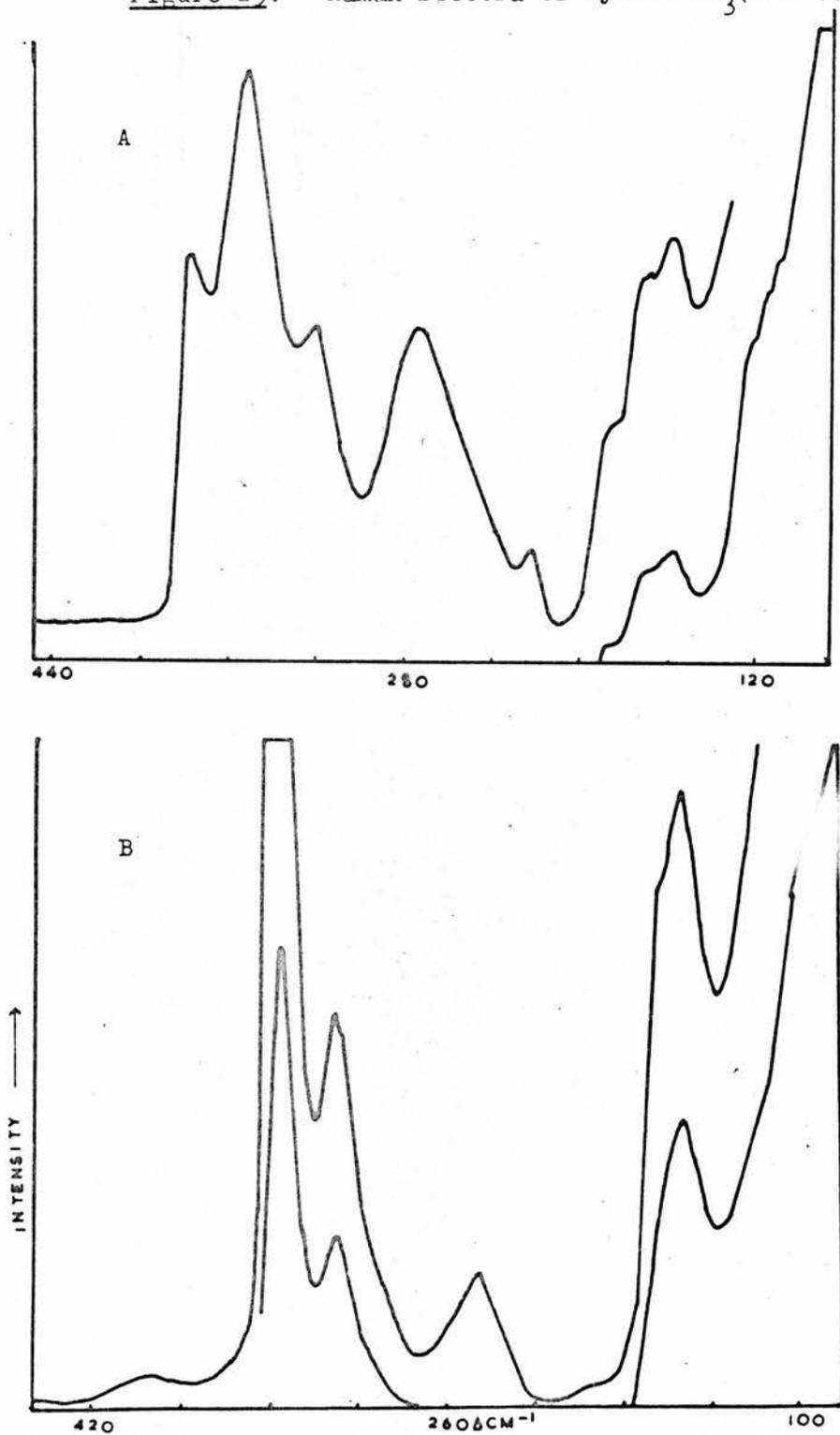
Schematically



Since these two SbCl_4^- groups are linked by a very long bond (3.12\AA), it is to be expected, for example, that (I) in (a) will have a very similar frequency to (I) in (b). This applies to all four vibrations shown above.

The vibrational spectrum of PyHCl,AsCl_3 is given in table 61. In this compound the coincidence between the infrared and Raman spectra is greater than that observed in the antimony compound, and the results could be interpreted in terms of a monomeric AsCl_4^- ion.

Figure 25: Raman Spectra of PyHCl-MCl_3 ($100-440 \text{ cm}^{-1}$)



A. PyHCl, AsCl_3 . B. PyHCl, SbCl_3 .

TABLE 61: Infrared and Raman Spectra of the System PyHCl-MCl₃

(i.r. as nujol mulls in the region 800-200cm⁻¹
Raman as solids in the range 600-150 cm⁻¹)

<u>PyHCl, SbCl₃</u> R. ^(a)		<u>PyHCl, AsCl₃</u> R. ^(b)		<u>AsCl₄</u> ^{-(c)} R.	
i.r.		i.r.		i.r.	
			110sh.v.w		
			113sh.v.w		
			117sh.v.w		
	150m-s				
	160sh		160s	160w	157v.s
			171sh		
			185sh	194m	192w
225v.w			221w	230w	229w
	240br.m			256w	
280v.br.s			276v.br.m		
		295s			291v.w
	305m-s				
325sh	331v.s	327m-s	321m		
		351v.s	352v.s	362v.s	359s
		382sh	377m	386v.s	383v.s
400w					
				407s	408s
		483w			
625m	613w	620m			
685s		685s			
755v.s		758v.s			

(c) as reported by Long⁴⁷⁷.

The conductivity measurements reported herein, however, suggest strongly that this is not so, and it is felt that the coincidences observed can be explained by the above suggestions, rather than postulating an AsCl_4^- ion in the solid state.

Long⁴⁷⁷ has recently reported a spectroscopic study on a di-n-butyl ether extract of AsCl_3 in HCl. He interprets his results as indicating the presence of a monomeric AsCl_4^- ion, and proposes a vibrational assignment for this ion which is given in table 61, page 197. It is interesting to note the reasonable agreement between this spectrum and the spectrum reported for the solid compound PyHCl,AsCl_3 .

Long did not consider polymeric species in his investigation, and the only evidence for a monomeric formulation is the ability to rationalize the observed spectrum on a monomer basis. Although not contributing directly to a knowledge of the species in solution, a structure determination on PyHCl,AsCl_3 would be of great value.

SECTION IV

CHAPTER 8

Experimental

EXPERIMENTALA. General Techniques1. Handling of materials.

All materials were handled in a dry-box or on a vacuum system, taking all possible precautions to avoid contact with moisture. Vacuum technique used was of a conventional nature. Vacuum lines were built in sections to allow easy cleaning, and cleaned with either chromic acid or an alcohol - nitric acid mixture, followed by thorough washing with tap water, and finally distilled water. These sections were oven dried (110°C) and glass blown together. The system was then tested for leaks with a "tesla coil", and finally flamed out under high vacuum for at least 30 minutes to remove absorbed molecules, particularly water.

A standard dry-box, made of perspex, with latex gloves was used throughout this work. This was flushed out with dry air before use, and kept dry by trays of phosphorus pentoxide. The air was dried by passing it through a column of molecular sieve (AEI Birlec, Ltd., adsorber type AB12.5). This was regenerated in the prescribed fashion at three weekly intervals, or as was required. Occasionally commercial oxygen-free nitrogen was used. Glassware for dry-box experiments was oven dried at 110°C whilst rubber or P.V.C. "teats", tissues, and heat sensitive materials were dried at 40°C for a number of days. Apparatus was transferred rapidly from the ovens to the air lock of the dry-box, which was then flushed out with dry air.

2. Conductance Measurements.

All conductance measurements were made with a pair of smooth platinum dipping electrodes set in glass. The solution was contained in a tube, into which the electrodes were fitted by a ground glass joint, so that atmospheric moisture could be excluded. For a typical measurement the cell was charged with ca. 15 mls of dry solvent and brought to 25° in a thermostatted bath. The solid was added from preweighed stoppered sample tubes, in the dry box, and when the solution was complete the resistance was measured, repeatedly, until constant. Sample weights were chosen to give Λ_m values in the range .001M - .01M.

The instrument used to measure the resistance between the electrodes was a Phillips PR 9500 resistance bridge, operating on 1000 c/s current. The cell constant was initially determined at 25°C using 0.01M KCl solution. It was checked from time to time and found to be constant at 0.503cm^{-1} .

3. Determination of molecular weight.

The apparatus shown in figure 26, page 234 was used for all molecular weight determinations reported. This apparatus was cleaned and dried, and the preweighed apparatus, without the Beckman thermometer, was taken into the dry-box and charged with a suitable quantity of nitrobenzene. A pressed, preweighed pellet of the sample was placed in C and a quickfit stopper in A. When the apparatus had been assembled outside the dry-box, stopper A was replaced quickly by the Beckman thermometer, which could be read to .002. The cooling curve was then plotted for the pure solvent, and by twisting the greased cone C the pellet of solute was added to the

solution. When complete solution had occurred, the freezing point curve was redetermined, and the apparent molecular weight calculated. To add further quantities of solute it was necessary to replace C with a similar cone containing another pellet, although this necessitated exposing the samples to the atmosphere it was felt that hydrolysis would be negligible, as the operation was carried out very quickly, and also the material was in compact pellet form. The following usual precautions were observed.

1. Adequate stirring. 2. Slow rate of cooling. 3. Gentle tapping of the thermometer before reading. 4. All freezing points, whether in solvent or solution, were repeated to constant ($\pm .001^\circ$) value.

The experimental results have been tabulated in tables 16B, 22, 53, and these tables are included with the discussion on each relevant section. The apparent molecular weight, M_a was calculated from the equation:

$$M_a = \frac{K_f \cdot 1000 \cdot W_2}{\Delta t \cdot W_1}$$

where Δt is the depression of freezing point in $^\circ\text{C}$ caused by the addition of W_2 grams of solute to W_1 grams of solvent. The molar cryoscopic constant (K_f) of nitrobenzene was taken as 7.10°C (262A).

4. Infrared Spectroscopy.

a. Solid Samples. The technique of dispersing a solid in a liquid such as nujol is well established, and may be used into the far infrared region, Below 650cm^{-1} NaCl windows are no longer transparent and in this work CsI

windows, transparent below 200cm^{-1} were used, unless otherwise stated. Occasionally polythene windows were used in the range $600 - 200\text{cm}^{-1}$, when reaction with the halide windows occurred. Nujol, or where required hexachlorobutadiene mulls were made up in the dry-box. Because of the hygroscopic nature of the materials handled, it was necessary to use air tight mull cells, and the type described by Webster⁴²⁴ were used. The nujol was dried by heating carefully with sodium until the sodium melted and gas evolution ceased. To determine whether a peak was due to hydrolysis, and to record these peaks, the cell, after the spectrum had been recorded, was opened, and the mull exposed to the atmosphere for 5 seconds, and the spectrum rerun. Peaks which increased in intensity, or which appeared only after this treatment, were considered as impurity peaks. This technique also gave some indication of the most moisture sensitive peaks, as these decreased most rapidly on exposure.

b. Solution spectra. Solution spectra were recorded using either teflon cells⁴²⁴ with CsI windows, or for solution work in the region $600 - 200\text{cm}^{-1}$, cells were constructed from polythene tubing, figure 26, page 234.

These were vacuum tight and it was possible to vary the path length of the solution by altering the spacing of the cell holder.

c. Gas Spectra. These were recorded using a standard 10cm gas cell. The pressure in the cell was altered to give a reasonable spectrum, and the pressure used was recorded on a manometer attached to the vacuum line.

All spectra were recorded on a Perkin Elmer 621 grating spectrophotometer. Generally, standard operating conditions were used, occasionally, ordinate expansion or high resolution was required, and these were obtained by the procedures recommended in the makers handbook.

5. Raman Spectroscopy.

Solid sample for Raman spectra were placed in glass tubes, evacuated and sealed off. In all cases it was necessary to "wet" the glass surface with glycerol to make good contact with the hemispherical lens of the instrument, see figure 26, page 234. Solution spectra were recorded in a similar manner except for the spectrum of o-phenylenebis-dimethylamine, which was sealed in a capillary tube with a flat end.

The instrument used was a Cary 81 Raman spectrometer, and unless otherwise stated the exciting radiation used was the $6328 \overset{\circ}{\text{A}}$ line of the helium/neon laser.

6. X-ray Powder Photography.

The materials were finely powdered in the dry-box and packed into lindemann tubes, the ends of which were sealed with grease. Each tube, on removal from the dry-box, was sealed in an oxygen flame, and then attached to the central axis of the camera and aligned so that it rotated in the path of the X-ray beam. The back stop was then added and when the X-ray beam had been switched on, its alignment was checked with a fluorescent screen. The copper K_{α} doublet was used as the

irradiation source, the K_{β} line being removed by a nickel filter. The X-ray generator was operated at 40K.V. and 20 Ma. The camera used was a Debye Schirrer type of radius 57.3 mm and diffraction patterns were recorded on Ilford industrial "G" film.

7. X-ray Crystallography.

Single crystals of the compound $AsCl_5$, $SbCl_5$, $AsCl_3$ were formed in pyrex capillary tubes attached to a vacuum system. The crystals were grown from $AsCl_3$ as a solvent and were sealed off for x-ray examination with a small amount of mother liquor in the capillary tube. The tube was attached to a goniometer head and one axis of the crystal set approximately parallel to the goniometer axis, which was mounted on a rotation camera, and an oscillation photograph with a two hour exposure was taken.

In this method the X-ray beam enters the camera at right angles to the goniometer axis, about which the crystal is oscillating (or completely rotating). This brings different crystal planes successively into reflecting positions. These reflections are recorded on cylindrical film surrounding the crystal. If the crystal was, in fact, aligned with a crystallographic axis along the goniometer axis, then the layer lines produced by the cones of reflection will be horizontal when the film is laid flat. However, if the crystal is not so aligned, these lines will deviate by a small angle from the horizontal position, and this is equivalent to the deviation of the crystal axis from the goniometer

axis. Once this angle had been determined, the arcs were corrected to align the crystal axis properly, a full rotation photograph was then taken. This was both to show that the crystal was properly set, and to calculate the spacing along the aligned axis, arbitrarily called the C axis.

A Weissenberg moving film photograph was then taken about the C axis. In this technique, the cylindrical film is moved bodily along the axis of rotation while the crystal is rotating. A complete to-and-fro cycle takes place during the rotation of the crystal through 180° and back. A slotted screen was adjusted to permit passage of any selected cone of reflection. Photographs were taken along the hko, ~~hkl~~ and hk2 layers. From the hko layer the spacing along reciprocal axis a^* and b^* and the angle between them, ϕ^* , were determined. The camera used was a standard motor driven Weissenberg of radius 57.3 mm. This gives a crystal rotation of 2° per mm travelled.

The goniometer head was then transferred to a precession camera, and for reasons given in Chapter IV no alteration to the setting of the axis was required.

The mass absorption coefficient μ / ρ $\text{cm}^2 \text{gm}^{-1}$ for the $\text{CuK}\bar{\alpha}$ and $\text{MoK}\bar{\alpha}$ lines are given in international tables as:

<u>Element</u>	<u>CuK$\bar{\alpha}$</u>	<u>MoK$\bar{\alpha}$</u>
As	83.4	69.7
Sb	270.0	33.1

because of the very high absorption coefficient of antimony for $\text{CuK}\bar{\alpha}$ the

MoK α line was used. A zirconium filter was used to remove the MoK β line. In fact it is the K α doublet which is used. The weighed mean of the doublet being taken as $\lambda = 0.7107\text{\AA}$.

B. Drying of Solvents

1. Nitrobenzene. For use in conductometric and cryoscopic work, analar nitrobenzene was allowed to stand over P₂O₅, with occasional shaking, for one week. It was then distilled under reduced pressure (65 - 68° ca. 2 mm), and the head and tail fractions were discarded. The middle fraction was redistilled under reduced pressure, and again the head and tail fractions discarded. The specific conductance of the middle fraction was less than $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C.

2. Methyl Cyanide. For conductivity work, the method of Forcier and Olver⁴⁶⁴ was used. The crude solvent was first refluxed over sodium hydride (1g/L) to remove acrylonitrile, acid impurities and water. It was then distilled, refluxed over phosphorus pentoxide (2g/L) to remove basic impurities, and distilled again. A final reflux over calcium hydride (2g/L), followed by distillation, removed last traces of water. For ordinary solvent requirements only the last stage was used, i.e. a prolonged reflux (12 hrs.) over calcium hydride, and distillation. In both cases a final distillation on the vacuum line was necessary to remove traces of drying agent. The specific conductivity of methyl cyanide purified by these methods varied from batch to batch, but was always around $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$. The boiling range was 81 - 82°C.

3. Other Solvents. Benzene, carbon tetrachloride, carbon disulphide, chloroform and nitromethane were refluxed for 12 hours over calcium hydride in an apparatus which was constructed to have as few quickfit joints as possible, and also to allow reflux and distillation to be carried out in the same apparatus, without exposure to the atmosphere being necessary. The apparatus was cleaned overnight in chromic acid, washed with tap water, and finally washed several times with distilled water. It was then dried in an oven at 110°C .

After the reflux period the solvent was distilled into a conical flask, quickly stoppered, and introduced into the dry box. Alternatively, it was distilled into a round bottomed flask with a break seal side arm, constriction and a vacuum tap. The tap was closed, and the apparatus transferred to a vacuum line. The flask was then cooled in a carbon dioxide acetone bath and evacuated. This procedure, freezing and pumping, was repeated several times to outgas the solvent, which was finally frozen, and the constriction sealed off. The flask was then joined to an all glass vacuum line, which was pumped down and flamed out. The break seal was smashed with a magnetic hammer, and the solvent distilled into ampoules, which were sealed off.

4. Thionyl Chloride and Phosphoryl Chloride were purified by distillation before use.

5. Ether. Diethyl ether was dried by refluxing it over sodium wire, after preliminary drying over calcium chloride. It was then stored over fresh sodium wire and redistilled before use.

C. Reagents and Starting Materials.

1. Phosphorus Pentachloride. Reagent grade PCl_5 was sublimed under vacuum to give a very pale yellow material. The tube in which this sublimation was performed was divided into several sections by constrictions. When the sublimation was completed these were sealed off, giving several ampoules of PCl_5 , which were opened in the dry-box when required.

2. Antimony Pentachloride. Reagent grade SbCl_5 was distilled into a flask with a break seal, side arm. When the distillation was finished the tap (a vacuum tap with Kel-F grease) was closed, and the flask attached to a vacuum line. This was pumped down, outgassed three times, and finally sealed off. The flask was then glass blown onto an all glass vacuum line which was then flamed out for 30 minutes. The break seal was opened with a magnetic hammer, and the SbCl_5 distilled into a flask, and then into ampoules by freeze distillation: these ampoules were sealed off and stored until required.

3. Phosphorus Trichloride, Phosphorus Tribromide, Arsenic Trichloride and Arsenic Tribromide. These were treated in a similar fashion to SbCl_5 , i.e. they were distilled, sealed off, and finally distilled

into ampoules on a vacuum line. In the distillation of AsBr_3 a warm water condenser was used, and a hot air drier was required to distill the material into ampoules.

4. Stannic Chloride was refluxed for several hours to remove any volatile hydrochloric acid. It was then distilled into a flask with a break seal side arm, containing several grams of acridine; this prevents the formation of the white crystalline pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), which otherwise tends to form. The constriction was then sealed off under vacuum, attached to a vacuum line, flamed out, the break seal opened, and the material distilled into ampoules, as described above for SbCl_5 . The same procedure was utilised for stannic bromide, except that acridine was not used. SnBr_4 is a white solid, M.Pt. 33°C , and in the distillation warm water ($\sim 40^\circ$) was used in both condensers.

5. Phosphorus Pentabromide was purified by the method of Harris and Payne²⁶². The crude material (10 grams) was dissolved in 50 ml of pure nitrobenzene at 60°C . A white insoluble residue remained, and this was removed by filtering through a sintered glass disc in an apparatus designed to exclude moisture. The solution was cooled, and the phosphorus pentabromide formed as fine yellow crystals. These were filtered off in the dry-box and washed with several portions of sodium dried ether. The material was then transferred to a test tube with a

B 24 socket, and attached to the vacuum line by means of a two way adaptor with a high vacuum tap. The excess ether was removed and the sample pumped dry. The sample was then returned to the dry-box, bottled and stored in a dessicator. Besides using commercial PBr_5 , this material was also prepared by the method of Popov and Skelly⁴²⁶ in which excess PBr_3 in carbon disulphide was brominated by adding bromine dropwise to the solution.

6. Phosphoryl Bromide was prepared by the method in "Inorganic Synthesis"⁴²⁷ and was purified by low temperature vacuum fractionation into ampoules which were sealed off.

7. Chlorine obtained from a cylinder, was dried by passage through concentrated sulphuric acid and a drying tower packed with phosphorus pentoxide.

8. Bromine. Analar bromine was purified by the method of Mataushek⁴²⁸.

9. Tetraethyl Ammonium Chloride and Tetramethyl Ammonium Chloride were recrystallised from ethanol and vacuum dried (0.01 mm Hg at 120°C).

10. Silicon Tetrachloride was distilled into a round bottomed flask with a break seal side arm, as described. The flask contained several mls of pyridine. This reacted with the SiCl_4 forming a 2:1

adduct and also reacted with any hydrogen chloride contained in the SiCl_4 . This flask was then sealed off in the usual way and attached to a vacuum line. The usual procedure of flaming out distillation etc., were followed and the ampoules sealed off. With Germanium tetrachloride, distillation followed by several distillations in vacuo was used.

11. 1,10-phenanthroline. The method of Webster⁴²⁴ was used, in which the monohydrate was sublimed in vacuum to remove water of crystallization, followed by a second vacuum sublimation. The sublimation tube was divided by a number of constrictions which were sealed off into ampoules. Commercial grade 2,2'-bipyridyl was purified by a single vacuum sublimation and sealed off in ampoules in a similar fashion.

12. Phosphorus Pentafluoride was prepared by the thermal degradation of o-chlorobenzediazonium hexafluorophosphate at 150°C under vacuum. The products p-chlorofluorobenzene, nitrogen and phosphorus pentafluoride are all volatile at this temperature. These volatile products, and any impurities, except nitrogen, were trapped in a liquid air trap. The nitrogen was removed from the system by continued pumping. The PF_5 was then purified by passing it through traps at -98°C (methanol/liquid nitrogen) to remove phosphoryl fluoride and p-chlorofluorobenzene, and then through a trap at -112°C (CS_2 /liquid N_2) to remove any SiF_4 formed by reaction with the glass walls. It was then held in a

trap at -138°C (ethyl chloride/liquid nitrogen), and any PF_3 which may have been formed is pumped away at this temperature. The vapour pressure of PF_5 at the above temperatures, calculated from the equation

$\log P = -A/T + B \log T - CT + D$, ($A = 898.9$; $B = C = 0$; $D = 7.646$), is 438.0 mm (-93.8°C), 46.8 mm (-112°C), 0.76 mm (-138°C). The infrared spectrum of this material indicated that only traces of POF_3 , PF_3 and SiF_4 were present.

13. The Compound AsCl_5 , SbCl_5 . A solution of antimony pentachloride (3 mls) in arsenic trichloride (10 mls) was prepared, and this solution was chlorinated in an apparatus designed to exclude moisture. An exothermic reaction took place and a white material precipitated out. The material was centrifuged, the supernatant liquid decanted off, in the dry-box, and the material was washed with six portions of carbon tetrachloride (which had been dried just prior to use). The material was then pumped dry under vacuum. Some loss of material was noticed at this stage, possibly due to decomposition, and consequently the pumping was not prolonged. The white material was found to be unstable, even in the dry-box, and could only be stored in ampoules under high vacuum. It was extremely reactive, reacting with nujol and polythene, and hence no infrared spectra could be recorded. Found: Cl, 62.1; As, 15.8. Calc. for AsCl_5 , SbCl_5 . Cl, 64.1; As, 16.1%.

14. Preparation of the ligand o-phenylenebisdimethylamine.

o-phenylenediamine (1.5 moles) was heated with an equimolar amount of trimethyl phosphate in a three litre flask, equipped with an air condenser, surmounted by a water condenser. This heating was at a very low rate until a fine mist was observed in the flask; at this point the flame was removed. An extremely vigorous exothermic reaction took place. As the reaction subsided heat was again applied and the reaction mixture refluxed for another two hours. To remove any primary and secondary amine, 200 gms of trimethyl phosphate (1.5 moles) was added, and the reaction mixture refluxed for another four hours. The excess phosphate was hydrolysed by refluxing with 1.5 litres of 10 N sodium hydroxide. The amine was then extracted with ether. The ether was removed on a rotary evaporator. The tertiary amine was then vacuum distilled onto molecular sieves in a stoppered flask. b.Pt. 102 - 110°/22 mm, 60 - 62°C/2 - 3 mm; 220 - 222/760 mm. (literature value; 215 - 218°/735 mm). Found: C, 72.7; H, 9.76; N, 17.8%. Calc. for $C_{10}H_{16}N_2$. C, 73.1; H, 9.30; N, 17.01%. A thin layer chromatogram on a silica base with acetone as solvent, indicated that the product was pure.

15. Preparation and Purification of o-phenylenebisdimethylarsine

o-nitrophenyl arsonic acid⁴²⁹. 100 gms. of o-nitroaniline was boiled with 650 mls of concentrated hydrochloric acid until

complete solution had occurred, giving a dark red solution. 360 mls of boiling water was added and the solution cooled to 5°C, the hydrochloride tended to precipitate out, but caused no difficulty, and was diazotized with 840 mls of normal sodium nitrite. Then normal sodium hydroxide was added, the temperature was kept below 40°C until the acid was completely neutralised (1300 mls required), and reacted red to congo red paper. During all these stages the reaction mixture was well stirred. 25 mls of ether was added to prevent excessive foaming, and 1.5 litres of 10% sodium arsenite was slowly added. At this stage it was difficult to control the foaming caused by evolution of nitrogen. To complete the reaction 2 litres of N. sodium hydroxide was added dropwise and the solution stirred. This solution was reduced to half its volume on a water bath, cooled, and made acidic with concentrated hydrochloric acid. On cooling the nitrophenyl arsonic acid crystallised as a pale yellow powder. The yield was 130 gms. Found: C, 29.0; H, 2.60; N, 5.72; Calc. for $C_6H_6O_5NaAs$. C = 29.2; N = 5.67; H = 2.43%.

b) Preparation of o-aminophenylarsonic Acid. This was prepared by the method of Jacobs⁴²⁹. 500 gms of ferrous chloride was dissolved in 15 litres of warm (40°C) water. At this stage some ferric iron was present; this was reduced by bubbling sulphur dioxide through the solution. The solution was then transferred to a five litre flask fitted with a rubber bung, and 25% sodium hydroxide solution added (ca. 500 mls) until the ferrous hydroxide mud reacted strongly alkaline

to litmus paper. 35 gms of o-nitrophenylarsonic acid was added, and the mixture shaken for five minutes. The alkaline filtrate was reduced in volume to about 200 mls on a rotary evaporator. Sodium chloride precipitated out at this stage and was filtered off, and the filtrate was made just acid with concentrated hydrochloric acid; Immediately the o-arsonilic acid precipitated out. The solution was thoroughly chilled and the acid filtered off, washed with ice water, and dried at 110°C in a vacuum oven. M.pt.: $148 - 151^{\circ}\text{C}$. Literature ⁴²⁹, 153°C . Yield, 45 gms (60%).

c. Preparation of o-phenylenediarsonic acid⁴³⁰. 55 gms of o-arsonilic acid was dissolved in 570 mls of dilute HCl (70 mls conc. acid). This solution was cooled to -8°C and 18 gms of powdered sodium nitrite was added, and the mixture well stirred until solution was complete.

65 gms of sodium arsonite in 150 mls of sodium hydroxide, diluted with 500 mls of ice water, was prepared and to this was added the diazotized solution. At the same time, 5N sodium hydroxide (about 70 mls) was added to keep the solution alkaline. The solution was decolourised with charcoal, filtered through "hyflo" and the filtrate made strongly acid. A yellow precipitate formed slowly. The yellow colour is due to traces of azobenzol o,o'-diarsonic acid. The precipitate was dissolved in 10% sodium carbonate, treated with charcoal, and once again filtered through "hyflo" and reprecipitated with concentrated hydrochloric acid to yield a very pale, yellow precipitate. M.Pt. $346 - 347^{\circ}\text{C}$ (decomposed). Literature ⁴³⁰ $> 360^{\circ}\text{C}$. Yield, 18 gms (22%).

Found: C, 24.23; H, 3.13. Calc. for $C_6H_8O_3NAs$: C, 22.2; H, 2.48%.

d. Preparation of o-phenylenebisdiarsineoxychloride.⁴³⁰ 12.5 gms of the diarsonic acid (III) in 300 mls of concentrated hydrochloric acid containing 0.2 gms of potassium iodide, was treated with a vigorous stream of sulphur dioxide until precipitation had ceased. This precipitate was filtered on a glass frit, and dissolved in carbon disulphide. A small aqueous layer was removed and the carbon disulphide evaporated on a water bath, leaving a semi-solid, dark brown mass which crystallised when triturated with a small amount of methanol. The material was then recrystallised from carbon disulphide giving pale yellow crystals. M.Pt. 142 - 148°C, literature⁴³⁰ 148°C. Yield 5.8 gms (50%). Found: Cl, 22.74; Calc. for $C_6H_4OAs_2Cl_2$; Cl, 22.67%.

e. o-Phenylenebisdichloroarsine.⁴³¹ 5 gms of the oxychloride was dissolved in 3 mls of thionyl chloride and cooled. A vigorous reaction took place, and then the solution was heated on a water bath and sodium dried cyclohexane (12.5 mls) added. When cooled, pale brown coloured crystals separated out, and these were filtered off in the dry-box under nitrogen. M.pt. 96 - 98°C, literature⁴³² 97°C. Found: Cl, 38.5. Calc. for $C_6H_4As_2Cl_4$: Cl, 38.56%.

f. Preparation of o-phenylenebisdimethylarsine⁴³¹. 3.5gms of the tetrachloride were shaken with 20 mls of ether and the clear solution was decanted from a small residue and slowly added with stirring to an

ice cold, Grignard reagent, which was prepared from 8 gms of methyl iodide and 1.34 gms of pure magnesium turnings, under nitrogen, in 300 mls of ether. Dropwise addition resulted in the formation of a red solid which readily dissolved. The solution was stirred for an hour, and the product was then hydrolysed by the addition of 17 gms of ammonium chloride in 40 mls of water. After solution had been completed the two layers were separated and the aqueous layer was extracted with 20 mls of ether, which was combined with the ethereal layer, dried with anhydrous sodium sulphate, and the solvent distilled off under nitrogen. The residue was distilled under reduced pressure and collected in ampoules which were then sealed off. B.pt., 120 - 130°C at 2 mm; literature,⁴³¹ 156°/20 mm. Found: C, 42.50; H, 5.53. $C_{10}H_{16}As_2$ requires C, 42.0; H, 5.65%.

The product was adjudged pure by thin layer chromatography on silica plates using methanol as solvent. The melting point was found to be in the range -48 to -51°C (uncorrected), literature⁴³² m.pt. -12°. N.M.R. and infrared spectroscopy were also used to identify the material.

D. Preparations

General Remarks

The compounds reported in this thesis, because of their hygroscopic nature, were prepared and handled in dry conditions, either in a dry-box, which has already been described, or on a conventional vacuum line.

Many of the preparations were very similar, in that solutions, in various solvents, were prepared in the dry-box. Addition of one of these solutions to the other produced a precipitate which was repeatedly centrifuged and washed to remove excess of starting materials. The solvent was then removed by either decanting or filtering off the solid, which was then pumped on for several hours to remove the last traces of solvent. The solid was then either bottled and stored in the dry-box, in a dessicator, or sealed off in an ampoule under high vacuum. Samples for Raman spectroscopy were prepared in this way.

To avoid unnecessary repetition, the first preparation in this section has been described in detail, and all similar preparations have been outlined. Any variations on this procedure have been described fully. To follow the sequence used in the discussion, (chapters 3, 4, 5, and 7), the preparations are divided into sections 1, 2 and 3, corresponding to the sections used earlier.

SECTION 11. 1,10-Phenanthroline-2- (Antimony Pentachloride)

A solution of phen (ca. 0.5 gm.) in 15 mls of chloroform was prepared, and to this was added, drop by drop, SbCl_5 (ca. 1 ml) in 15 mls of the same solvent. A white precipitate formed immediately. The reaction was carried out in a test tube with a B.24 socket. When precipitation was complete the test tube was stoppered, removed from the dry-box and centrifuged. The test tube was returned to the dry-box, the solvent decanted off and the compound washed with a small portion of fresh solvent. This was repeated three times, i.e. centrifuging, decanting and washing. Finally the wash liquid was decanted off and the test tube fitted with an adaptor containing a high vacuum tap, which was closed. This was removed from the dry-box, attached to the vacuum line, the system opened to high vacuum, and the solvent removed and retained in a trap, surrounded by liquid air. The pumping was continued for several hours to ensure that all traces of solvent had been removed. The system was closed, and the adaptor and test tube returned to the dry-box, where the material was bottled and stored in a dessicator. Found: phen, 22.6; Cl, 45.51, 45.89. Calc. for 2SbCl_5 , phen; phen, 23.15; Cl, 45.56%.

2. 1-10-Phenanthroline-Phosphorus Pentachloride

A solution of 0.33 gms of phen in 50 mls of benzene was prepared. On solution a small insoluble residue remained. This was filtered off.

This solution was added, dropwise, to a solution of PCl_5 (0.58 gm) in 40 mls of benzene. A white precipitate formed immediately and continued to form until most of the phen solution had been added. This precipitate was centrifuged, and washed three times with benzene. Finally it was pumped dry, and bottled. Found: Cl, 45.60, 45.25; phen, 46.46.

Calc. for PCl_5 , phen. Cl, 45.63; phen, 46.39%.

3. Tetrachloro- μ -(1,10-Phenanthroline)Arsenic(V)Hexachloroantimonate.

A freshly prepared sample of AsCl_5 , SbCl_5 , AsCl_3 was washed several times with carbon tetrachloride, to remove excess AsCl_3 . The carbon tetrachloride was then decanted off and the crystalline material dissolved in methyl cyanide. To this was added, dropwise, a solution of phen in the same solvent. An immediate orange precipitate formed, and the addition of ligand was continued until no further precipitate formed. This was centrifuged, washed three times with solvent, and pumped dry. Found: Cl, 47.17; phen, 24.59; As, 10.06, 9.92. Calc. for AsCl_5 , SbCl_5 , phen: Cl, 48.47; phen, 24.64; As, 10.2%.

4. Pyridinium Hexachloroantimonate(V) was prepared by the method of Beattie and Webster⁴⁶⁶. Found: Cl, 50.77; Calc. for $\text{C}_5\text{H}_6\text{NSbCl}_6$: Cl, 51.3%.

5. The System AsCl_3 - Cl_2 -phen.

A solution of AsCl_3 in chloroform was saturated with chlorine, and to this was added a solution of phen in the same solvent. A light brown precipitate formed, which was filtered, washed and pumped dry. Overnight this decomposed to leave a white residue which was identified as AsCl_3 , phen by comparison of its infrared spectrum with that of an authentic sample.

6. 2,2'-Bipyridyl-Phosphorus Pentachloride.

To a saturated solution of PCl_5 in benzene (0.3M) was added a solution of the ligand in the same solvent. A white precipitate was formed immediately and the material centrifuged, washed twice with benzene and pumped dry. Found: Cl, 47.0; bipy, 40.4. Calc. for $\text{C}_{10}\text{H}_8\text{Cl}_5\text{N}_2\text{P}$: Cl, 48.6; bipy, 43.2%

7. 2,2'-Bipyridyl-2-(Antimony Pentachloride).

A solution of SbCl_5 in carbon disulphide was slowly added to bipy in the same solvent. At first a yellow precipitate was formed which turned white on the addition of more SbCl_5 . The addition was continued until no further precipitate formed. After the usual treatment the material was bottled and stored in the dry-box. Found: Cl, 47.0; bipy, 20.5. Calc. for $\text{C}_{10}\text{H}_8\text{N}_2\text{Sb}_2\text{Cl}_{10}$: Cl, 47.0; bipy, 20.75%. Several preparations were required before a sample which gave reasonable analytical figures was obtained. The earlier preparations gave low chloride and bipy results (2-3% low). This, and the fact that the precipitate first formed

was yellow, indicated that a 1:1 complex may be initially formed. In an attempt to prepare this compound SbCl_5 was added to an excess of ligand and the yellow precipitate filtered, washed and pumped under high vacuum. The precipitate slowly lost its colour and left an off-white material. Found: Cl, 42.5. Calc. for SbCl_5 , bipy: Cl, 39.0%.

8. Attempted Preparation of Tetrachloro- μ -(2,2'-bipyridyl)arsenic(v) hexachloroantimonate.

To a solution of AsCl_5 , SbCl_5 , AsCl_3 in methyl cyanide was added bipy in the same solvent. After 20 minutes standing, pale yellow crystals settled out. After the usual treatment this was identified as AsCl_3 , bipy by infrared and Raman spectroscopy. Found: Cl, 31.7; bipy, 46.6. Calc. for AsCl_3 , bipy: Cl, 31.5; bipy, 46.3%.

9. o-Phenylenebisdimethylamine-Phosphorus Pentachloride.

To a saturated solution of PCl_5 in benzene was added a 1 molar solution of the ligand. The addition was made dropwise and immediately a pale yellow precipitate formed. This was treated in the normal way. Found: Cl, 51.8; C, 29.3; H, 4.9; N, 7.3. Calc. for $\text{C}_{10}\text{H}_{16}\text{Cl}_5\text{N}_2\text{P}$: Cl, 47.6; C, 32.2; H, 4.3; N, 7.5%.

10. The System o-Phenylenebisdimethylamine-Antimony Pentachloride.

Because of the difficulties involved, this particular preparation was repeated a number of times, and the analytical figures are reported below. Essentially the technique was the same in each preparation, an excess of either ligand or Lewis acid being used.

Prep. I. A solution of the ligand added to 2 mls of SbCl_5 in carbon tetrachloride gives a deep red precipitate.

Prep. II. A solution of the ligand was added to SbCl_5 in carbon tetrachloride. With the addition of the first few drops of ligand a red precipitate formed, which floated on the solvent. This was filtered off, and more ligand added. On shaking the stoppered test tube, a dark brown solid formed, almost solidifying the contents of the tube. The sample was centrifuged and washed a number of times to remove excess of starting materials, and then it was pumped dry.

Prep. III. Approximately 1 ml of diamine was added to an excess (2 mls) of SbCl_5 in carbon tetrachloride. The precipitate initially floated but finally sank. This was centrifuged and washed five times to remove excess SbCl_5 .

Prep. IV. To a large excess of amine (3-4 mls) in carbon tetrachloride was added 0.66 mls of SbCl_5 in the same solvent. A red precipitate was formed which floated initially but finally sank. This was washed a number of times to remove excess solvent.

Prep. V. An excess of SbCl_5 was added to a small quantity of ligand, then excess ligand added. This gave a purple precipitate which floated on the solvent.

<u>Element</u>	Calc.(1:1)	Calc.(2:1)	I	II	III	IV	V
Carbon	25.95	15.75	12.07	30.17	16.27	18.36	34.49
Hydrogen	3.48	2.18	1.94	4.12	2.15	2.59	4.75
Nitrogen	6.02	3.68	3.24	6.85	3.93	5.44	8.09
Chlorine	38.2	46.5	47.0	35.6	43.0	42.4	-

11. The System o-Phenylenebisdimethylarsine-Phosphorus Pentachloride

To a saturated solution of PCl_5 in benzene was added an excess of diars. On standing a small amount of white solid precipitated out. This was collected and dried. Found: C, 28.5; H, 4.22. Calc. for PCl_3 , diars: C, 28.0; H, 3.88%. The following infrared spectra, in benzene solution, were recorded in the range $700\text{-}200\text{cm}^{-1}$: (a) PCl_5 . (B) equimolar solution of PCl_5 , and diars. (C) Solution of PCl_5 with excess ligand. (D) Solution of diars. (E) Solution of PCl_3 . (F) Solutions of PCl_3 with varying amounts of ligand. The results of these spectra are given in table chapter .

12. o-Phenylenebisdimethylarsine-Phosphorus Trichloride.

From the solution prepared (see above) for spectroscopic work, a small amount of white material precipitated out. This was washed and pumped dry. Found: C, 29.9; H, 4.2. Calc. for PCl_3 , diars: C, 28.0; H, 3.88%.

13. o-Phenylenebisdimethylarsine-2(Antimony Pentachloride).

To a 15 ml solution of SbCl_5 (3 mls) in carbon tetrachloride was added, dropwise, 0.66 mls of the ligand in the same solvent. A white precipitate resulted, and on shaking a light yellow precipitate formed. This was washed a number of times with solvent and pumped dry. The material obtained was off-white in colour, but overnight in the dry-box it decomposed, giving a dark grey polymeric material which, on exposure to the air formed a black tar. By working quickly, conductivity measurements, infrared spectrum and analytical data on the initial product were obtained. Found: C, 10.6; H, 1.62; Cl, 40.2. Calc. for 2SbCl_5 , diars: C, 13.62; H, 1.83; Cl, 39.9%.

SECTION 111. Preparation of Stannic chloride-phosphorus pentachloride.

The preparation of the compound stannic chloride - phosphorus pentachloride was carried out in three different ways. All three methods are reported, but for subsequent preparations method II was found to be most convenient.

Method I.

To a solution of PCl_3 (1 ml) in thionyl chloride (1 ml), was added 1 ml of SnCl_4 in 2 mls of the same solvent. A white precipitate was immediately obtained. This was filtered off, washed three times with 5 mls portions of thionyl chloride, and pumped dry. Found: Cl, 65.4; Calc. for Cl_9PSn : Cl, 68.1%. Yield $< 8\%$. It should be pointed out that the filtrate, on standing, precipitated out more of the complex, but even including this the yield was very low, and a very poor chloride analysis was recorded.

Method II

A equimolar solution of PCl_3 in SnCl_4 was prepared in a dry nitrogen atmosphere. This was chlorinated to give a dense white precipitate. The solution was centrifuged, and pumped dry under high vacuum. Found: Cl, 67.1; Sn, 24.7. Calc. for Cl_9PSn : Cl, 68.1; Sn, 25.3%.

Method III

Phosphorus pentachloride was mixed with a calculated excess of SnCl_4 (ca. 1:4 w/w), and sealed off in a tube under vacuum. This tube was heated to 110°C in an oven for six hours, and allowed to cool slowly.

It was then centrifuged, opened, the supernatant liquid decanted off, and the precipitate pumped dry under high vacuum. An infrared spectrum of the material indicated that all the excess SnCl_4 had been removed. Found: Cl, 67.9. Calc. for Cl_9PSn : Cl, 68.1%.

2. Preparation of Stannic Chloride-2-Phosphorus Pentachloride.

To a solution of PCl_5 in methyl cyanide (0.4M) was added SnCl_4 in the same solvent, until no further precipitate was obtained. The precipitate was filtered off, washed three times with benzene and pumped dry. Found: Cl, 73.1; Sn, 17.4. Calc. for $\text{Cl}_{14}\text{P}_2\text{Sn}$: Cl, 73.3; Sn, 17.5%.

3. Reaction of Phosphorus Pentachloride with Stannic Chloride in phosphoryl chloride.

To 1 ml of SnCl_4 in 20 mls of POCl_3 , was slowly added a 0.4M solution of PCl_5 in the same solvent. After addition of 16 mls a cloudiness appeared in the solution, and by 18 mls a definite white precipitate was forming. After 36 mls of the PCl_5 solution had been added no further precipitation occurred. This gave a mole ratio of 1:5:1:: PCl_5 : SnCl_4 . This was centrifuged, washed three times with benzene, and pumped dry. Found: Cl, 71.3; Sn, 20.4. Calc. for 3PCl_5 , 2SnCl_4 : Cl, 71.2; Sn, 20.7%. Because of the unusual stoichiometry the preparation was repeated several times. The chloride analysis for two such preparations were; Cl, 71.5, 70.9%.

4. Preparation of Triphenylcarbonium Pentachlorostannate (iv)

2 gms of purified triphenylcarbinol were converted to the chloride by refluxing with 1.5 mls of acetyl chloride in 3 mls of benzene. After three hours of refluxing it was allowed to cool, and the waxy, white solid, triphenylmethylchloride, precipitated out: M.Pt., 109 - 112°C. literature⁴⁶⁷ 112 - 113°C. This solid was redissolved in benzene and two mls of stannic chloride were added. A black, oily liquid formed at the bottom of the test tube, and slowly a reddish-brown precipitate formed. This was centrifuged, washed and pumped dry. Found: Cl, 32.72. $\text{Ph}_3\text{C SnCl}_5$ requires Cl, 32.87%.

5. Triphenylcarbonium perchlorate was prepared by a standard literature method, as was ammonium hexachlorostannate (iv).⁴⁶⁸

SECTION III1. 1,10-Phenanthroline-Arsenic Trichloride Addition Compounds.

a) To a solution of phen in benzene an excess of AsCl_3 was added, in the same solvent. A yellow precipitate was formed immediately. This was filtered, washed free of excess AsCl_3 and pumped dry. Found:

Cl, 27.7; phen, 48.7. Calc. for phen, AsCl_3 : Cl, 29.4; phen 49.8%.

b) To an excess of AsCl_3 in carbon tetrachloride was added a solution of the ligand in the same solvent. The precipitate was treated in the usual way and pumped dry. Found: Cl, 38.2; phen, 30.0. Calc. for phen, 2AsCl_3 : Cl, 39.2; phen, 30.2%.

2. 2,2'-Bipyridyl-Arsenic Trichloride Addition Compounds.

The 2:1 complex was prepared by the addition of the ligand in benzene to an excess of AsCl_3 , also in benzene. Found: C, 24.02; H, 1.51; Cl, 40.03. $\text{C}_{10}\text{H}_8\text{N}_2\text{As}_2\text{Cl}_6$ requires: C, 23.2; H, 1.54; Cl, 39.0%. The 1:1 complex was isolated from the reaction of bipy with the compound AsCl_5 , SbCl_5 in methyl cyanide, and has been described earlier.

3. Preparation of Addition Complexes of o-Phenylenebisdimethylamine with Arsenic Trichloride.

On dropwise addition of AsCl_3 to the ligand (diamine) in methyl cyanide, a white crystalline material was formed, and a bright emerald green colour developed in the solvent. The supernatant liquid was decanted off and retained for a U.V. study. The precipitate was washed with two

small portions of carbon tetrachloride. It is moderately soluble in this solvent. Found: Cl, 30.8; C, 34.1; H, 4.76; N, 7.8. $C_{10}H_{16}N_2AsCl_3$ requires Cl, 30.8; C, 34.8; H, 4.76; N, 8.1%.

On addition of the ligand, diamine, to $AsCl_3$ in carbon tetrachloride, a white precipitate was obtained. Found: Cl, 40.0; C, 23.5; H, 3.04; N, 5.2%. $C_{10}H_{16}N_2As_2Cl_6$ requires: Cl, 40.4; C, 22.8; H, 3.05; N, 5.3%.

4. Preparation of the Addition Compounds of Arsenic Tribromide with 1,10-phenanthroline.

Addition of the ligand, phen, in benzene, to $AsBr_3$ in the same solvent, yielded a bright yellow precipitate. Found: Br, 58.4; phen, 21.9: $2AsBr_3$, phen requires Br, 59.3; phen, 22.3%.

1 gm of $AsBr_3$ in methyl cyanide was slowly added to 0.6 gms of phen in the same solvent. A pale yellow precipitate was formed and the excess phen removed by filtering and washing with fresh solvent. Found: Br, 47.0; phen, 35.0. $AsBr_3$, phen requires Br, 48.4; phen, 36.4%.

5. The Addition Compounds of Arsenic Tribromide with 2,2'-Bipyridyl.

The 1:1 adduct was prepared according to the method of Wilkins and Roper¹⁴. Found: Br, 49.4; bipy, 33.4. bipy, $AsBr_3$ requires: Br, 50.9; bipy, 33.2%. The 2:1 adduct was prepared by adding the ligand, bipy, to an excess of $AsBr_3$, using benzene as solvent. A yellow precipitate was obtained. Found: Br, 58.6; bipy, 20.1%. bipy, $2AsBr_3$ requires: Br, 61.0; bipy, 19.9%.

6. Preparation of Pyridinium Tetrachloroarsenate (III).

A solution of AsCl_3 in concentrated hydrochloric acid was prepared, and to this was added dry pyridine. When the solution was cooled, a white crystalline material separated out. The material was filtered, recrystallised from the same solvent which was then filtered in the dry-box, and finally the precipitate was pumped dry. Found: C, 20.62; H, 2.14; N, 4.83; Cl, 46.86. Calc. for $\text{C}_5\text{H}_6\text{NAsCl}_4$: C, 20.2; H, 2.02; N, 4.71; Cl, 47.8%.

Preparation of pyridinium tetrachloroantimonate (III) was carried out by the method of Porter¹⁶⁷. Found: Cl, 41.2. Calc. for $\text{C}_5\text{H}_6\text{NSbCl}_4$: Cl, 41.3%.

E. Analytical Techniques.

1. Microanalysis for carbon, hydrogen and nitrogen were carried out by A. Bernhardt in Germany, and later by the microanalytical laboratory in the Chemistry Department, St. Andrews University.

2. Halide analysis was carried out potentiometrically, using a silver wire as standard electrode, and a glass electrode as reference. The sample was hydrolysed in a sealed test tube as follows. A small sample tube with a thin walled glass bulb was weighed and introduced into the dry-box. The material (ca. 0.05 gm) was introduced and the stopper replaced. This was reweighed and placed in a test tube with a B 24 socket, containing 5 mls of 2M sodium hydroxide and 10 mls of distilled water. The stopper was replaced and the bulb broken by shaking vigorously.

These precautions were taken to avoid the loss of HCl gas on hydrolysis, which occasionally was quite vigorous. After hydrolysis was complete, the test tube was opened and the contents transferred quantitatively to a 400 ml beaker. The solution was diluted with distilled water to about 200 mls, made acidic with nitric acid, and finally titrated potentiometrically with standardized 0.1M silver nitrate.

3. Ligand Analysis. The ligands 1,10-phenanthroline and 2,2'-bipyridyl were determined spectrophotometrically as the phenanthroline and monobipyridyl ions in dilute hydrochloric acid. The samples were hydrolysed as described above, and transferred quantitatively to a 500 ml volumetric flask. Sufficient acid was added to make the solution 0.1M in hydrochloric acid and then made up to the mark. Calibration curves were prepared by using the pure anhydrous ligand. (Five solutions, of different concentrations were prepared for each ligand and a Beers law calibration curve was set up). The absorption band at 272 m μ was used for the phenanthroline ion and one at 238 m μ for the monobipyridyl ion. It was found that Beers law was obeyed in the range of concentration used for both compounds. The instrument was recalibrated from time to time and the curve found to be constant. A unicam SP 500 spectrophotometer operating on a 12 volt D.C. supply was used. Standard 10 mm silica cells were used, and the base line was set against distilled water.

4. Analysis for tin. Tin was determined gravimetrically as SnO_2 by the ammonium iodide method, or volumetrically by first reducing $\text{Sn (iv)} \longrightarrow \text{Sn(II)}$ using nickel metal. The Sn(II) was titrated with standard iodine solution in an atmosphere of nitrogen using a starch indicator. The titration was carried out at about 10°C ; at this temperature it was not necessary to remove the excess nickel. The iodine was standardised against a standard tin solution. Both of these techniques are described fully by Vogel⁴³³.

5. Determination of Arsenic. Arsenic was determined gravimetrically as the sulphide by precipitation from 9N hydrochloric acid solution, as described by Vogel⁴³³. Under these conditions the determination is not subject to interference by antimony.

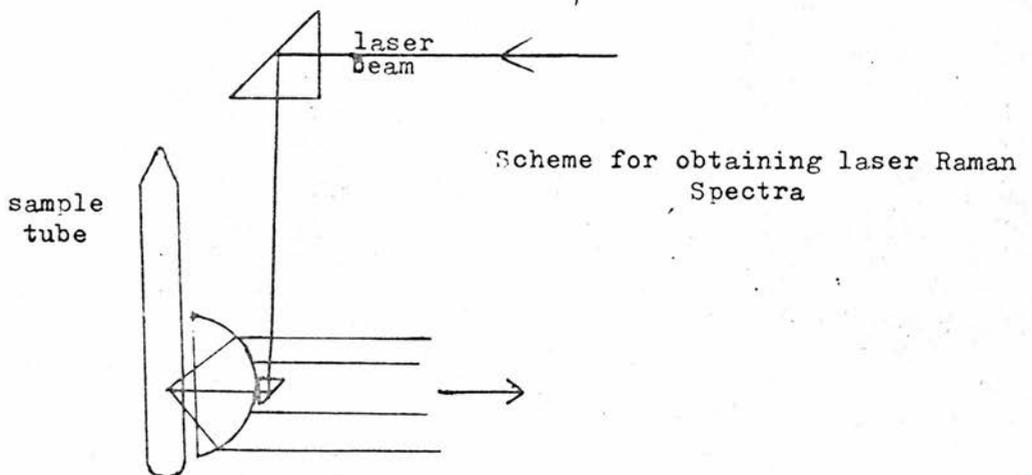
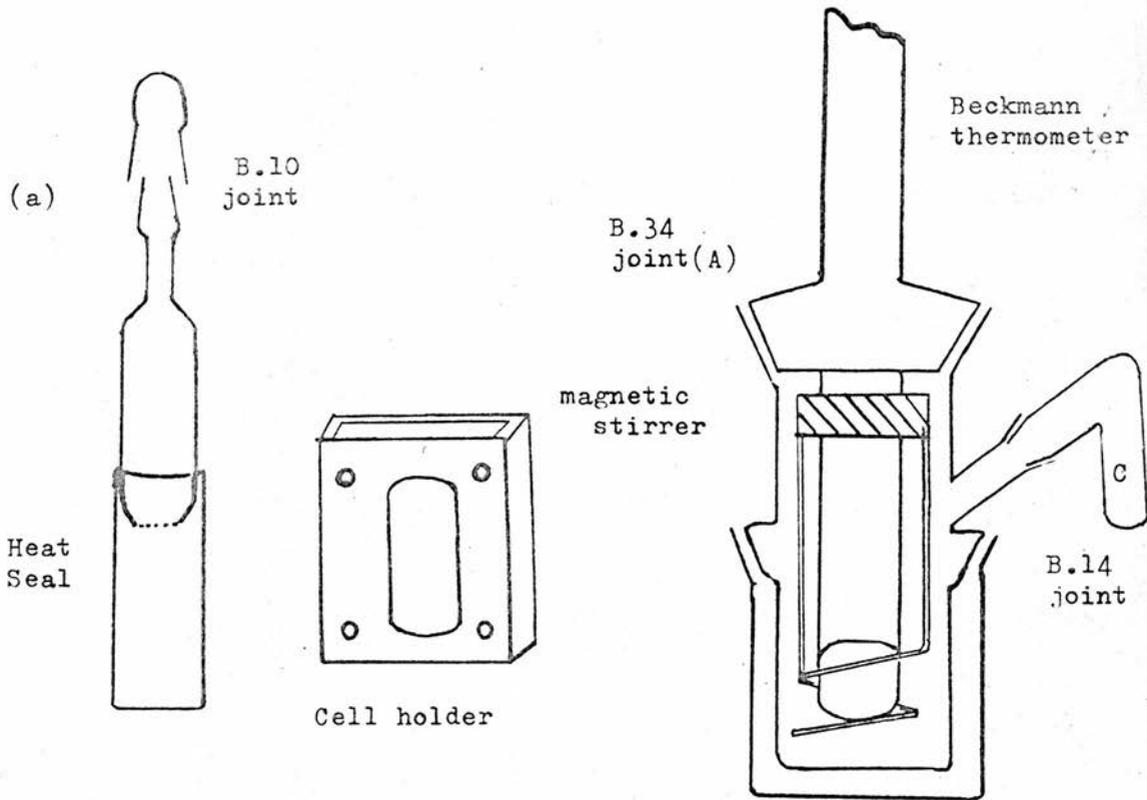


Figure 26

APPENDICES

APPENDIX I.

Principle of Normal Co-ordinate Analysis²³²

To calculate the vibration frequencies it is necessary to express the kinetic and potential energies in terms of some common co-ordinate. Internal co-ordinates, which are increments of bond lengths and bond angles, are commonly used, although other systems have been described⁴¹⁹.

Using internal co-ordinates R_i the potential energy is written

$$2 v = \underline{R}' \underline{f} \underline{R} \quad \dots\dots\dots(1)$$

where \underline{R} is a column matrix of the internal co-ordinates and \underline{R}' is its transpose. \underline{f} is a matrix whose components are the force constants.

Wilson⁴⁸⁰ has shown that the kinetic energy can be written

$$2 T = \underline{R}' \underline{g} \underline{R} \quad \dots\dots\dots(2)$$

where the \underline{g} matrix is defined as

$$\underline{g} = \underline{B} \underline{M}^{-1} \underline{B}' \quad \dots\dots\dots(3)$$

where \underline{M}^{-1} is a diagonal matrix whose components are μ_i , where μ_i is the reciprocal mass of the i^{th} atom, and the \underline{B} matrix is defined as

$$\underline{R} = \underline{B} \underline{X} \quad \dots\dots\dots(4)$$

where \underline{X} is a column matrix whose components are the rectangular co-ordinates.

Newton's equation is given by

$$\frac{d}{dt} \left(\frac{\delta T}{\delta \dot{R}_k} \right) + \frac{\delta V}{\delta R_k} = 0$$

and by combining equation (1) with this, and multiplying by $|\underline{g}|$.

$$\text{The equation, } \left| \underline{g} \underline{f} - \underline{E} \right| = 0 \quad \dots\dots\dots(5)$$

is obtained. Here \underline{E} is a unit matrix and $\tilde{\nu}$ is related to wave

number \sqrt{V} by the relation $\lambda = 4 x^2 c^2 v^2$ or $= 0.583851 \sqrt{V}^2 \cdot 10^{-6}$

It is possible to reduce the order of the f and g matrices by using symmetry co-ordinates (S), i.e. symmetrically equivalent sets of internal co-ordinates. The internal co-ordinates are transformed by $\underline{S} = \underline{U} \cdot \underline{R}$ where \underline{U} is an orthogonal matrix ($\underline{U} \underline{U} = \underline{E}$) whose elements, and hence the orthonormal symmetry co-ordinates must satisfy the relations

$$\sum_k (U_{jk})^2 = 1 \quad (\text{normalization})$$

$$\sum_k U_{jk} U_{lk} = 0 \quad (\text{orthogonality})$$

The construction of symmetry co-ordinates are fully described by Wilson Decius and Cross⁴¹⁹.

The symmetrized F and G matrices are obtained by the similarity transformation

$$\underline{F} = \underline{U} \underline{f} \underline{U}'$$

$$\underline{G} = \underline{U} \underline{g} \underline{U}'$$

The secular equation $|\underline{GF} - E\lambda| = 0$ has the same roots as 5. This new secular equation can be resolved into several equations of lower order and hence the burden of calculation is greatly reduced.

APPENDIX II

Determination of F 7 G matrix elements for a tetragonal pyramid molecule (C_4).

Figure I shows the choice of internal co-ordinates to describe the vibrations of such a molecule (ion). The corresponding f matrix, with $f_{ij} = f_{ji}$, is given in table I and defines the relevant force constants. Using Cartesian co-ordinates, and removing translational and rotational degrees of freedom the symmetry of the various normal modes for vibration was found to be:-

$$\Gamma_v = 3A_1(i.r, R) + 2B_1(R) + B_2(R) + 3E(i.r, R)$$

whereas using internal co-ordinates it was found to be:-

$$\Gamma_v^I = 4A_1 + 2B_1 + B_2 + 3E$$

so there will be one redundant co-ordinate (A_1). The symmetry co-ordinates

constructed were: A_1 $S_1 = \Delta d_5$

$$S_2 = \frac{1}{2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$S_3 = \frac{1}{2} \cdot \frac{1}{\sqrt{2}} (\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{34} + \Delta \alpha_{41} - \Delta \beta_{15} - \Delta \beta_{25} - \Delta \beta_{35} - \Delta \beta_{45})$$

$$S_3^* = \frac{1}{2} (\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{34} + \Delta \alpha_{41}) \equiv 0$$

$$B_1 \quad S_4 = \frac{1}{2} (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_5 = \frac{1}{2} (\Delta \beta_{15} - \Delta \beta_{25} + \Delta \beta_{35} - \Delta \beta_{45})$$

$$B_2 \quad S_6 = \frac{1}{2} (\Delta \alpha_{12} - \Delta \alpha_{23} + \Delta \alpha_{34} - \Delta \alpha_{41})$$

$$\begin{aligned}
 E \quad S_{7a} &= \frac{1}{2}(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4) \\
 S_{7b} &= \frac{1}{2}(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4); \\
 S_{8a} &= \frac{1}{2}(\Delta \beta_{15} + \Delta \beta_{25} - \Delta \beta_{35} - \Delta \beta_{45}) \\
 S_{8b} &= \frac{1}{2}(\Delta \beta_{15} - \Delta \beta_{25} - \Delta \beta_{35} + \Delta \beta_{45}) \\
 S_{9a} &= \frac{1}{2}(\Delta \alpha_{12} + \Delta \alpha_{23} - \Delta \alpha_{34} - \Delta \alpha_{41}) \\
 S_{9b} &= \frac{1}{2}(\Delta \alpha_{12} - \Delta \alpha_{23} - \Delta \alpha_{34} + \Delta \alpha_{41})
 \end{aligned}$$

The symmetry co-ordinates S can be defined in terms of the matrix \underline{R} by the transformation matrix \underline{U} so that $\underline{S} = \underline{U} \underline{R}$ or $\underline{U} = \underline{S} \tilde{\underline{R}}$ (3)

and the \underline{F} matrix is given by $\underline{F} = \underline{U} \underline{f} \tilde{\underline{U}}$ (4)

where f is a matrix whose components are the force constants given in table IA. By generating the \underline{U} matrix according to eqn (3) and substituting this in eqn (4), the following values of \underline{F} elements were obtained.

A_1	$F_{11} = fd$	$F_{22} = 2(fr + 2frr)$
	$F_{12} = 2frd$	$F_{23} = d/\sqrt{2} \quad fra$
	$F_{13} = F_{31} = 0$	$F_{33} = d^2fa$
B_1	$F_{11} = fr - 2frr$	
	$F_{12} = dfr\beta$	
	$F_{22} = d^2f\beta$	
B_2	$F_{11} = d^2fa$	
E	$F_{11} = fr$	$F_{22} = d^2f\beta$
	$F_{12} = rfr\beta$	$F_{23} = 0$
	$F_{13} = rfra$	$F_{33} = d^2fa$

cont on p 242

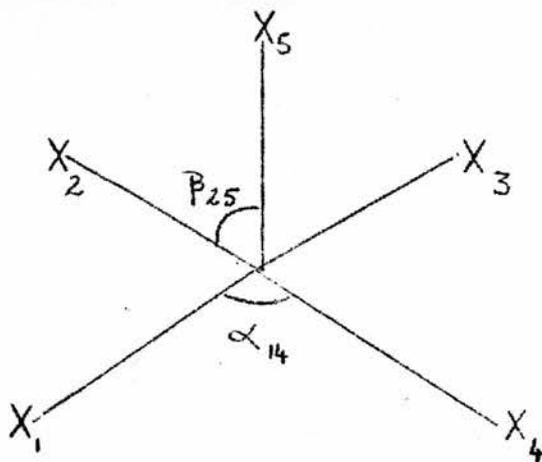


Figure 1A

 Δd $\Delta r_1, \Delta r_2, \Delta r_3, \Delta r_4$ $\Delta \alpha_{12}, \Delta \alpha_{23}, \Delta \alpha_{34}, \Delta \alpha_{14}$ $\Delta \beta_{15}, \Delta \beta_{25}, \Delta \beta_{35}, \Delta \beta_{45}$

This gives thirteen internal co-ordinates, whereas only twelve are needed to define the configuration.

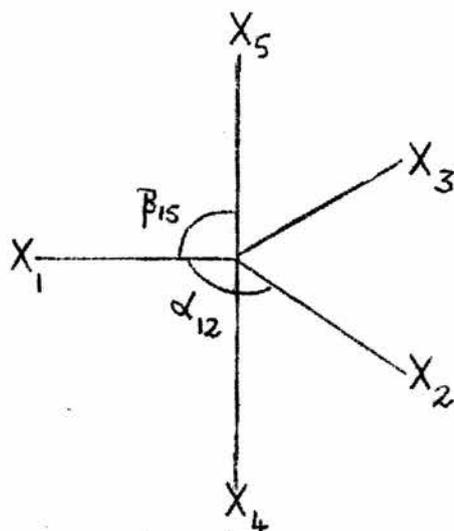


Figure 2A

internal co-ordinates.

 $\Delta d_1, \Delta d_2$ $\Delta r_1, \Delta r_2, \Delta r_3$ $\Delta \alpha_{12}, \Delta \alpha_{23}, \Delta \alpha_{13}$ $\Delta \beta_{14}, \Delta \beta_{24}, \Delta \beta_{34}, \Delta \beta_{15}, \Delta \beta_{25}, \Delta \beta_{35}$

TABLE 2A

	r_1	r_2	r_3	α_{12}	α_{23}	α_{31}	β_{41}	β_{42}	β_{43}	β_{51}	β_{52}	β_{53}	d_1	d_2
f	r_1	r_2	r_3	α_{12}	α_{23}	α_{31}	β_{41}	β_{42}	β_{43}	β_{51}	β_{52}	β_{53}	d_1	d_2
r_1	fr	frr	frr	0	0	0	$fr\beta$	0	0	$fr\beta$	0	0	frd	frd
r_2		fr	frr	0	0	0	0	$fr\beta$	0	0	$fr\beta$	0	frd	frd
r_3			fr	0	0	0	0	0	$fr\beta$	0	0	$fr\beta$	frd	frd
α_{12}				fr	fra	fra	$fr\beta$	$fr\beta$	0	$fr\beta$	$fr\beta$	0	0	0
α_{23}					fr	fra	0	$fr\beta$	$fr\beta$	0	$fr\beta$	$fr\beta$	0	0
α_{31}						fr	$fr\beta$	0	$fr\beta$	$fr\beta$	0	$fr\beta$	0	0
β_{41}							$fr\beta$	$fr\beta$	$fr\beta$	$fr\beta$	0	0	$rd\beta$	0
β_{42}								$fr\beta$	$fr\beta$	0	$fr\beta$	0	$rd\beta$	0
β_{43}									$fr\beta$	0	0	$rd\beta$	0	
β_{51}										$fr\beta$	$fr\beta$	0	$rd\beta$	
β_{52}											$fr\beta$	$fr\beta$	0	$rd\beta$
β_{53}												$fr\beta$	0	$rd\beta$
d_1													rd	rd
d_2														rd

$$f_{ij} = f_{ji}$$

APPENDIX III

The internal and symmetry co-ordinates, f matrix and \underline{F} and \underline{G} matrix elements for a trigonal bipyramidal molecule of symmetry (D_{3h}).

Figure 2A shows the choice of internal co-ordinates and the corresponding f matrix with $f_{ij} = f_{ji}$ is given in table 2A.

The ortho-normal symmetry co-ordinates are:

$$\begin{aligned}
 A'_1 \quad S_1 &= \frac{1}{\sqrt{3}} (\Delta r_1 + \Delta r_2 + \Delta r_3) \\
 S_2 &= \frac{1}{\sqrt{2}} (\Delta d_1 + \Delta d_2) \\
 A''_2 \quad S_3 &= \frac{1}{\sqrt{2}} (\Delta d_1 - \Delta d_2) \\
 S_4 &= \frac{d}{\sqrt{6}} (\Delta\beta_{14} + \Delta\beta_{24} + \Delta\beta_{34} - \Delta\beta_{15} - \Delta\beta_{25} - \Delta\beta_{35}) \\
 E' \quad S_{5a} &= \frac{1}{\sqrt{6}} (2\Delta r_1 - \Delta r_2 - \Delta r_3) \\
 S_{5b} &= \frac{1}{\sqrt{2}} (\Delta r_2 - \Delta r_3) \\
 S_{6a} &= \frac{d}{\sqrt{6}} (2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{31}) \\
 S_{6b} &= \frac{d}{\sqrt{2}} (\Delta\alpha_{31} - \Delta\alpha_{12}) \\
 S_{7a} &= \frac{d}{\sqrt{12}} (2\Delta\beta_{14} - \Delta\beta_{24} - \Delta\beta_{34} + 2\Delta\beta_{15} - \Delta\beta_{25} - \Delta\beta_{35}) \\
 S_{7b} &= \frac{d}{2} (\Delta\beta_{24} - \Delta\beta_{34} + \Delta\beta_{25} - \Delta\beta_{35}) \\
 E'' \quad S_{8a} &= \frac{d}{\sqrt{12}} (2\Delta\beta_{14} - \Delta\beta_{24} - \Delta\beta_{34} - 2\Delta\beta_{15} + \Delta\beta_{25} + \Delta\beta_{35}) \\
 S_{8b} &= \frac{d}{2} (\Delta\beta_{24} - \Delta\beta_{34} - \Delta\beta_{25} + \Delta\beta_{35})
 \end{aligned}$$

Using the appropriate matrix multiplication between the above equations and table 2A, the following \underline{F} & \underline{G} Matrix elements were obtained.

To determine the \underline{G} matrix elements it is necessary to first generate the \underline{B} matrix elements where $R = BX$, where \underline{R} and \underline{X} are column matrices whose components are the internal and rectangular co-ordinates respectively, and from equation 3 (appendix I) the \underline{g} matrix is generated.

$$\text{Now } \underline{G} = \underline{U} \underline{g} \tilde{\underline{U}}$$

and from this the following \underline{G} matrix elements were determined:-

A_1	$G_{11} = \mu_x + \mu_y$	$G_{22} = \mu_x$
	$G_{12} = 0$	$G_{23} = 0$
	$G_{13} = (\sqrt{2}/d)\mu_y$	$G_{33} = \mu_x/2d^2 + 2\mu_y/d^2$
B_1	$G_{11} = \mu_x$	$G_{12} = 0$
	$G_{22} = \mu_x/d^2$	
B_2	$G_{11} = 4\mu_x/d^2$	
E	$G_{11} = \mu_x + 2\mu_y$	$G_{22} = 3\mu_x/d^2 + 2\mu_y/d^2$
	$G_{12} = -2\mu_y/d$	$G_{23} = 2\mu_y/d^2$
	$G_{13} = -2\mu_y/d$	$G_{33} = 2\mu_x/d^2 + 4\mu_y/d^2$

G Matrix elements

$$A'_1 \quad G_{11} = \mu_y$$

$$G_{12} = 0$$

$$G_{22} = \mu_y$$

$$A''_2 \quad G_{33} = 2\mu_x + \mu_y$$

$$G_{34} = -2\sqrt{3}\mu_x$$

$$G_{44} = 6\mu_x + 2\mu_y$$

$$E' \quad G_{55} = \mu_y + 3/2 \mu_x$$

$$G_{56} = 3\sqrt{3}/2 \mu_x$$

$$G_{57} = -3/2 \mu_x$$

$$G_{66} = 3\mu_y + 9/2 \mu_x$$

$$G_{67} = -3\sqrt{3}/2 \mu_x$$

$$G_{77} = 3\mu_x + 3/2 \mu_y$$

$$E'' \quad G_{88} = 7/2 \mu_y$$

F Matrix elements

$$F_{11} = fr + frr$$

$$F_{12} = \sqrt{6} frd$$

$$F_{22} = fd + fdd$$

$$F_{33} = fd - fdd$$

$$F_{34} = \sqrt{3} fd\beta$$

$$F_{44} = f\beta + 2f\beta\beta - f'\beta\beta$$

$$F_{55} = fr - frr$$

$$F_{56} = 0$$

$$F_{57} = \sqrt{2} fr\beta$$

$$F_{66} = f\alpha - f\alpha\alpha$$

$$F_{67} = -\sqrt{2} f\alpha\beta$$

$$F_{77} = f\beta - f\beta\beta + f'\beta\beta$$

$$F_{88} = f\beta - f\beta\beta - f'\beta\beta.$$

TABLE IA

The f matrix for a Tetragonal pyramid (C_{4v}) molecule.

	f	r ₁	r ₂	r ₃	r ₄	d	α ₁	α ₂	α ₃	α ₄	β ₁	β ₂	β ₃	β ₄
r ₁	fr	fr	0	fr	fr	frd	frα	0	0	frα	frβ	0	0	0
r ₂	fr	fr	fr	0	frd	frα	frα	frα	0	0	0	frβ	0	0
r ₃	fr	fr	fr	fr	frd	0	frα	frα	frα	0	0	0	frβ	0
r ₄	fr	fr	fr	fr	frd	0	frα	frα	frα	0	0	0	0	frβ
d	fd	fd	fd	fd	fd	fd	rdα	rdα	rdα	rdα	rdβ	rdβ	rdβ	rdβ
α ₁							r ² _{fα}	0	0	0	0	0	0	0
α ₂							r ² _{fα}	0	0	0	0	0	0	0
α ₃							r ² _{fα}	0	0	0	0	0	0	0
α ₄							r ² _{fα}	0	0	0	0	0	0	0
β ₁											r ² _{fβ}	0	0	0
β ₂											r ² _{fβ}	0	0	0
β ₃											r ² _{fβ}	0	0	0
β ₄											r ² _{fβ}	0	0	0

$$f_{ij} = f_{ji}.$$

```

*LIST PRINTER
C GF MATRIX PROGRAM SET --- PART A.
C WAIT-SLEZAK
C G F MATRIX PROGRAM
  DIMENSION G(10,10),F(10,10),H(10,10),VL(10),VLINV(10),
1 TEMPV(10),VECT(10),VECTNU(10),PCT(10,10),PRODL(10,10)
C N IS ORDER OF MATRIX, MAX = 10
1000 READ 1,N
1 FORMAT(I2)
  IF(N-10)2,2,999
2 DO 4 I=1,N
4 READ 3,(G(I,J),J=1,N)
  DO 5 I=1,N
5 READ 3,(F(I,J),J=1,N)
3 FORMAT(5F14.8)
  DO 6 K=1,N
  DO 6 I=1,N
  H(I,K)=0.0
  DO 6 J=1,N
6 H(I,K)=H(I,K)+G(I,J)*F(J,K)
  PRINT 800,((G(I,J),I=1,N),J=1,N)
800 FORMAT(/39X,21HKINETIC ENERGY MATRIX/(4F20.8))
801 FORMAT(/37X,23HPOTENTIAL ENERGY MATRIX/(4F20.8))
802 FORMAT(/46X,8HH MATRIX/(4F20.8))
  PRINT 801,((F(I,J),I=1,N),J=1,N)
110 PRINT 802,((H(I,J),I=1,N),J=1,N)
120 NCOL=1
7 DO 10 I=1,N
  TEMPV(I)=0.0
  VECTNU(I)=0.0
10 VECT(I)=0.0
  TEMPV(NCOL)=1.0
  NCOUNT =1
24 DO 15 I=1,N
  VECT(I)=0.0
  DO 15 J=1,N
15 VECT(I)=TEMPV(J)*H(I,J)+VECT(I)
12 DO 17 I=1,N
  Z=VECTNU(I)-VECT(I)
  IF(ABSF(Z)-.10E-4)17,17,16
17 CONTINUE
  NTAG=1
  GO TO 20
16 NTAG=0
  DO 18 I=1,N
18 VECTNU(I)=VECT(I)
20 EIGVL=VECT(1)
  DO 21 I=2,N
  Y=ABSF(VECT(I))-ABSF(EIGVL)
  IF(Y)21,21,23
23 EIGVL=ABSF(VECT(I))
21 CONTINUE
  DO 22 I=1,N

```

```

22   TEMPV(I)=VECT(I)/EIGVL
      NCOUNT = NCOUNT + 1
      IF(NCOUNT-900)998,998,950
950  PRINT 951
951  FORMAT(19HTOO MANY ITERATIONS)
      GO TO 1000
998  IF(NTAG-1)24,30,999
30   WAVEN=1302.832*SQRTE(EIGVL)
      PRINT 31, EIGVL,WAVEN
31   FORMAT(//21X,11HEIGENVALUE=F12.8,10X,11HWAVENUMBER=F8.2//
130  CONTINUE
C    GENERATING L AND L INVERSE VECTORS
      DSQ=0.0
      DO 32 I=1,N
      DO 32 J=1,N
32   DSQ=TEMPV(I)*TEMPV(J)*F(I,J)+DSQ
      D=SQRTE(DSQ/EIGVL)
      PRINT 421
421  FORMAT(46X,8HL VECTOR//)
      DO 33 I=1,N
      VL(I)=TEMPV(I)/D
33   PRINT 42, VL(I)
42   FORMAT(44X,F20.8)
      DO 34 I=1,N
      VLINV(I)=0.0
      DO 34 J=1,N
34   VLINV(I)=VL(J)*F(J,I)+VLINV(I)
      PRINT 381
381  FORMAT(//42X,16HL INVERSE VECTOR//)
      DO 35 I=1,N
      VLINV(I)=VLINV(I)/EIGVL
35   PRINT 42, VLINV(I)
140  CONTINUE
      DO 40 I=1,N
      DO 40 J=1,N
      PRODL(I,J)=VL(I)*VL(J)
40   PCT(I,J)=PRODL(I,J)*F(I,J)/EIGVL
      PRINT 995
995  FORMAT(//12H EIGENVALUE=   )
      DO 996 I=1,N
150  DO 996 J=1,N
996  PRINT 997, PRODL(I,J),I,J
997  FORMAT (F20.8,2HF(,I2,1H,,I2,1H) )
      PRINT 43,((PCT(I,J),I=1,N),J=1,N)
43   FORMAT(//35X,29HPOTENTIAL ENERGY DISTRIBUTION//(5F20.8))
160  DO 36 I=1,N
      DO 36 J=1,N
36   H(I,J)=H(I,J)-VLINV(J)*VL(I)*EIGVL
170  NCOL=NCOL+1
      IF(NCOL-N)7,7,1000
999  CALL EXIT
      END

```

REFERENCES

- 1) P.M. Gates and E.F. Mooney, J. Chem. Soc., 4648, 1964.
- 2) G.L. Gard and G.H. Cady, Inorg. Chem., 3, 1745, 1964.
- 3) K. Bott, Angew. Chem., Internat. Edn., 3, 804, 1964.
- 4) J.C. Thayer and R. West, Inorg. Chem., 4, 114, 1965.
- 5) A. Zweig, Proc. Chem. Soc., 417, 1964.
- 6) S.J. Kuhn and J.S. McIntyre, Can. J. Chem., 43, 375, 1965.
- 7) E.L. Muetterties and W. Mahler, Inorg. Chem., 4, 119, 1965.
- 8) D. Cook, Can. J. Chem., 43, 741, 1965
- 9) R.C. Paul, K.C. Malhotra and O.C. Vaidya, Indian J. Chem.,
3, 1, 1965.
- 10) N. Wiberg and K.H. Schmid, Angew. Chem., Internat. Ed.,
3, 444, 1964.
- 11) S.N. Nabi and M.A. Khaleque, J. Chem. Soc., 3626, 1965.
- 12) J.V. Hatton, Y. Saito and W.G. Schneider, Can. J. Chem.,
43, 47, 1965.
- 13) J.K. Ruff, J. Amer. Chem. Soc., 87, 1140, 1965.
- 14) W. Roper and C.S. Wilkins, Inorg. Chem., 3, 500, 1964.
- 15) S.R. Jain and S. Soundararajan, Z. Anorg. Allgem. Chem.,
337, 214, 1965.
- 16) C.D. Schmulbach, Inorg. Chem., 4, 1232, 1965.
- 17) I.R. Beattie, K. Livingston and M. Webster, J. Chem. Soc.,
7421, 1965.
- 18) M.J. Deveney and M. Webster, Inorg. Nuc. Chem. Letters,
3, 195, 1967.

- 19) R.A.Wiggle and T.H.Norris, Inorg.Chem., 3, 539, 1964.
- 20) V.Gutmann, G.Hampel and W.Lux, Monatsh. Chem., 96, 533, 1965.
- 21) B.Cohen, T.R.Hooper, D.Hugill and R.D.Peacock, Nature, 207,
748, 1965.
- 22) R.C.Paul, R.Kaushal and S.S.Pahil, J.Indian Chem. Soc., 42,
483, 1965.
- 23) J.Strahle and K.Dehnicke, Z.Anorg.Allgem. Chem., 338, 287, 1965.
- 24) R.C.Paul and R.Dev, Indian J. Chem., 3, 315, 1965.
- 25) B.A.Voitovich and N.F.Lofovskaya, Ukr. Khim. Zh., 31, 1136, 1965
C.A. 64, 13449f.
- 26) J.Masaguer and C.Rodriguez, Anales Real Soc. Espan. Fis. Quim. Ser.
B61, 891, 1965. C.A. 64, 7657d.
- 27) W.M.Pasika, Chem. Ind., 2041, 1965.
- 28) E.Allenstein and A.Schmidt and V.Beyl, Chem. Ber., 99, 431, 1966.
- 29) W.M.Pasika, Tetrahedron, 22, 557, 1966.
- 30) Y.Yakamoto, S.Kusabryashi, T.Nogaito, K.Ito and H.Mikawa,
Bull. Chem. Soc. Japan, 38, 2015, 1965.
- 31) L.Kolditz and W.Rehak, Z.Anorg. Chem., 342, 32, 1966.
- 32) H.Selig, Inorg. Chem., 5, 183, 1966.
- 33) R.F.Copeland, S.C.Conner and E.A.Meyers, J.Phys. Chem., 70, 1288,
1966.
- 34) F.P.Boer, J.Amer. Chem. Soc., 88, 1572, 1966.
- 35) I.K.Gregor, Chem. Ind., 385, 1965.
- 36) I.K.Gregor, Aust. J.Chem., 18, 1485, 1965.
- 37) I.K.Gregor, Aust. J. Chem. 18, 2035, 1965.
- 38) R.A.Goodrich and P.M.Treichel, J. Amer. Chem. Soc., 88, 3509, 1966.

- 39) A. Meisters and J.M. Swan, Aust. J. Chem., 18, 155, 1965.
- 40) H.L. Slaters and N.L. Wendler, J. Med. Chem., 8, 886, 1965.
- 41) J.J. Pitts S. Kongpricha and A.W. Jache, Inorg. Chem., 4, 257, 1965.
- 42) K.O. Christè, A.E. Pavlath and E.G. Wallace; 1 A.A. Accession No. N64, 22542, C.A. 62, 8522f.
- 43) G.J. Sutton, Aust. J. Chem., 12, 122, 1959.
- 44) K.O. Christè and A.E. Pavlath, Z Anorg. Allgem. Chem. 335, 210 1965.
- 45) M. Schmeisser and W. Ludovici, Z. Naturforsch., 20B, 602, 1965.
- 46) C.I. Branden, Acta Chem. Scand., 17, 759, 1963.
- 47) A. Steininger and V. Gutmann, Monatsch. Chem., 97, 171, 1966.
- 48) A. Steininger and V. Gutmann, Monatsch. Chem., 96, 1173, 1965.
- 49) V. Gutmann and E. Wychera, Inorg. Nuc. Chem. Letters, 2, 257, 1966.
- 50) A. Schmidt, Chem. Ber., 99, 2976, 1966.
- 51) E. Allenstein and A. Schmidt, Spectrochim. Acta, 20, 1451, 1965.
- 52) V. Gutmann, A. Steininger and E. Wychera, Monatsch. Chem., 97(2), 460, 1966.
- 53) W.E. Tolberg, R.T. Rewick, R.S. Stringham and M.E. Hill, Inorg. Nuc. Chem. Letters, 2, 79, 1966.
- 54) K.O. Christè, J.P. Guertin and A.E. Pavlath, Inorg. Nuc. Chem. Letters, 2, 83, 1966.
- 55) W.B. Fox, J.S. McKenzie and N.E. Vanderkooi, J. Amer. Chem. Soc., 88, 2605, 1966.
- 56) G.A. Olah and M.B. Comisarow, J. Amer. Chem. Soc., 88, 3313, 1966.

- 57) L.A. Kazitsyna, A.A. Nil'son, N.B. Kupletskaya and O.A. Reutov, Vestn. Mosc. Univ. Ser. 11 Khim. 21, 95, 1966. C.A. 65, 11742e.
- 58) G.A. Olah and M.B. Comisarow, J. Amer. Chem. Soc., 88, 4442, 1966.
- 59) J.K. Ruff, Inorg. Chem., 5, 1791, 1966.
- 60) R.J. Gillespie and K.C. Moss, J. Chem. Soc. (A) 1170, 1966.
- 61) H. Volz and M.J. Volz de Lecca, Tetrahedron Letters, 3413, 1965.
- 62) H. Volz and H.W. Schwell, Angew. Chem. Internat. Edn., 77, 873, 1965.
- 63) R.C. Paul and S.L. Chadha, Spectrochim. Acta, Part A, 23, 1243, 1967.
- 64) K. Bott, Tetrahedron, 22, 1251, 1966.
- 65) R. West, A. Sado and S.W. Tobey, J. Amer. Chem. Soc., 88, 2488, 1966.
- 66) A. Roedig, M. Schlosser and H.A. Renk, Angew. Chem. Internat. Edn. 5, 418, 1966.
- 67) H.W. Roesky, O. Glemser and D. Bormann, Chem. Ber., 99, 1589, 1966.
- 68) I.K. Gregor, Aust. J. Chem., 20, 775, 1967.
- 69) R.C. Paul, D. Singh and K.C. Malhatra, J. Indian Chem. Soc., 41, 541, 1964.
- 70) N.D. Bondarchuk, V.I. Shevchenko and A.V. Kirsanov., Zh. Obshch. Khim. 35, 713, 1965. C.A. 63, 5549b.
- 71) G.I. Derkach, V.P. Rudavskii, Zh. Obshch. Khim. 35, 1202, 1965. C. A. 63, 11398a.
- 72) A. Slawisch and H. Becke Gohring, Z. Naturforsch., 21B, 589, 1966.
- 73) R. Baumgartner, W. Sawodny and J. Goubeau, Z. Anorg. Allgem. Chem., 340, 246, 1965.
- 74) A.S. Barabonova and B.A. Voitovich, Ukr. Khim. Zh. 30, 1298, 1964. C. A. 65, 13915f.
- 75) D.B. Copley, F. Fairbrother and A. Thompson, J. Less-Common Metals. 8, 256, 1965.

- 76) D.L. Kepert, R.S. Nyholm, J. Chem. Soc., 2871, 1965.
- 77) R. Clark, D. Kepert and R. Nyholm, J. Chem. Soc., 2877, 1965.
- 78) J. Desnoyers and R. Rivest, Can. J. Chem., 43, 1879, 1965.
- 79) F. Fairbrother, K.H. Grundy and A. Thompson, J. Less-Common Metals, 10, 38, 1966.
- 80) D. Copley, F. Fairbrother and A. Thompson, J. Chem. Soc., 315, 1964.
- 81) A. Edwards, J. Holloway and R. Peacock, Noble Gas Compounds, 71, 1963.
- 82) S.J. Kuhn. Can. J. Chem., 45, 3207, 1967.
- 83) I.R. Beattie and H. Chudzynska, J. Chem. Soc.(A), 984, 1967.
- 84) J.V. Dilorenzo and R.F. Schneider, Inorg. Chem., 6, 766, 1967.
- 85) G.L. Breneman and R.D. Willett, 153rd. A.C.S. Meeting, 1967.
- 86) K.E. Pullen and G.H. Cady, Inorg. Chem., 6, 2267, 1967.
- 87) H. Selig, Science, 144, 537, 1964.
- 88) R.A. Penneman, Inorg. Chem., 6, 431, 1967.
- 89) A.R. Young and D. Moy, Inorg. Chem., 6, 178, 1967.
- 90) F. Tebbe and E. Muetterties, Inorg. Chem., 6, 129, 1967.
- 91) W. Sawodny and K. Dehnicke, Z. Anorg. Allgem. Chem., 349, 169, 1967.
- 92) A.J. Edwards and G.R. Jones, Chem. Commun., 1304, 1967.
- 93) H. Dess, R. Parry and G. Vidale, J. Amer. Chem. Soc., 78, 5730, 1956.
- 94) F. Fairbrother, K. Grundy and A. Thompson, J. Chem. Soc., 765, 1965.
- 95) G. Olofsson, Acta Chem. Scand., 21, 2143, 1967.
- 96) I. Beattie, K. Livingston and T. Gibson, J. Chem. Soc. (A), 1, 1968
- 97) Ciba Ltd., Fr. Addn. 87155 (1966), C.A. 66, 29535b.
- 98) E. Ya. Gorenbein and I.L. Aberbarchuk, Zh. Neorg. Khim., 11, 2230, 1966. C.A. 66, 14520u.
- 99) L.A. Kazitsyna, N.B. Kupletskaya, V. Ptitsyna and V. Reutor, Vestn. Mosc. Univ. Ser. 11 Khim., 21(4), 117, 1966. C.A. 67, 58841z.

- 100) V.N. Tolmachev, O. Boberov and V. Lavrushin, Dopov. Akad. Nauk. Ukr. RSR 14.54 1966 C.A. 66, 60470a.
- 101) J. Weidlein and K. Dehnicke, Z. Anorg. Allgem. Chem., 348, 278, 1966.
- 102) R. Paul and S. Chadha, Spectrochim Acta Part A, 23, 1249, 1967.
- 103) B. Cohen and R. Peacock, J. Inorg. Nuc. Chem. 28, 3056, 1966.
- 104) K.J. Wynne and W.L. Jolly, A. C. S. Abstracts 152nd. Meeting.
- 105) D. Cook, Spectrochim Acta, 22, 419, 1966.
- 106) R. Weiss and B. Chevrier, Chem. Commun., 145, 1967.
- 107) G. Olah and M. Comisarow, J. Amer. Chem. Soc., 89, 2694, 1967.
- 108) A. Fratiello, D. Miller and R. Schuster, Mol. Phys. 12, 111, 1967.
- 109) F. Walker and A. Pavlath, U.S. Pat. No. 3, 321, 537. C.A. 67, 63715R.
- 110) G. Olofsson, Acta Chem. Scand., 21, 1114, 1967.
- 111) Y. Hermodsson, Acta Chem. Scand., 21, 1313, 1967.
- 112) R.C. Paul, R. Parkash and S.S. Sandhu, Z. Anorg. Allgem. Chem., 352, 322, 1967.
- 113) H. Binas, Z. Anorg. Allgem. Chem., 352, 271, 1967.
- 113a) V. Gutmann, G. Hampel and W. Lux, Monatsch. Chem., 96, 533, 1965.
- 114) J. MacCordick and R. Rohmer, C.R. Acad. Sci., Paris, Ser., C263, 1369, 1966. C. A. 66, 51810j.
- 115) G.J. Moody and H. Selig. J. Inorg. Nuc. Chem. 28, 2429, 1966.
- 116) S. Khorasani and A. Rauf, Z. Anorg. Allgem. Chem., 350, 326, 1961.
- 117) J. Canterford and T. O'Donnell, Inorg. Chem., 6, 541, 1967.
- 118) M.J. Frazer and Z. Goffer, J. Chem. Soc. (A), 544, 1966.
- 119) P.W.N.M. Van Leeuwen, Rec. Trav. Chim., 86, 201, 1967.
- 120) P.W.N.M. Van Leeuwen and W. Groeneveld, Rec. Trav. Chim., 85, 1173, 1966.
- 121) J.M. Le Carpentier and R. Weiss, Chem. Commun., 596, 1968.

- 122) O.F. Bobrov, V.L. Tolmachov and V.L. Lavrushin, Dopov. Akad. Nauk Ukr. RSR 1966, 1315. C. A. 66, 43291a.
- 123) K.O. Christe, Inorg. Chem., 6, 1706, 1967.
- 124) G.A. Wiley and W.R. Stine, Tetrahedron Letters, 2321, 1967.
- 125) W. Wieker and A. Grimmer and L. Kolditz, Z. Chem., 7, 434, 1967.
- 126) E. Lindner, R. Lehner and H. Scheer, Chem. Ber., 100, 1331, 1967.
- 127) W. Jolly, Amer. Chem. Soc. Div. Fuel Chem., Part 1. 11, 125, 1967.
C. A. 66, 111172q.
- 128) A. Schmidpeter and K. Dull, Chem. Ber., 100, 1116, 1967.
- 129) J. Gerbier and V. Lorenzelli, C. R. Acad. Sci., Paris, Ser. A.B.
264B, 690, 1967.
- 130) J. Guertin, K. Christe and A. Pavlath, Inorg. Chem., 5, 1921, 1966.
- 131) G. Michel and G. Duyckyaerts, Spectrochim. Acta, 21, 279, 1965.
- 132) L. Riesel and H.A. Lehmann, Z. Chem., 7, 316, 1967.
- 133) H. Imai, Nippon Kagaku Zasshi., 88, 730, 1967. C.A. 67, 94498b.
- 134) O. Glenser and U. Biermann, Chem. Ber., 100, 2484, 1967.
- 135) M.J. Taylor, Inorg. Nuc. Chem. Letters, 4, 33, 1968.
- 136) O. Maslov and V. Legasov, Zh. Fiz. Khim., 41, 1832, 1967.
C. A. 67, 103240r.
- 137) R. Schneider and J. Dilorenzo, J. Chem. Phys., 47, 2343, 1967.
- 138) G. Galchenko, B. Timofeev, D. Gedakyan and K. Grinberg, Izv. Akad. Nauk SSSR, Neorg. Materialy, 2, 1410, 1966. C.A. 65, 19367a.
- 139) L. Kolditz and I. Beierlein, Z. Chem. 7, 468, 1967.
- 140) S.J. Kuhn and J. McIntyre, Can. J. Chem. 43, 375, 1964.
- 141) H. Gerding and J. C. Duinker, Rev. Chim. Miner., 3, 815, 1966.
- 142) T. Kesavadas and D.S. Payne, J. Chem. Soc. (A)., 1001, 1967.
- 143) E. Kwiatkowski, Roczniki. Chem., 38, 169, 1964. C.A. 61, 7763b.
- 144) H. Meerwein, K. Zenner and R. Gipp, Ann. Chem., 688, 67, 1965.

- 145) B. Fohlisch and P. Burgle, Tetrahedron Letters, 2661, 1965.
- 146) R.C. Paul and B. Sreenathan, Inorg. Nuc. Chem., 28, 1225, 1966.
- 147) B. Korshunov and V. Bezuevskaya, Zh. Neorg. Khim., 12, 1304, 1967.
- 148) G. Olofsson, Acta Chem. Scand., 21, 93, 1967.
- 149) R. Hollzmann, Abstr. 3rd. Int. Symp. Fluorine Chem. Munich, 82, 1965.
- 150) J.G. Malm, Proc. 3rd. Int. Symp. Fluorine Chem. Munich, 1965.
- 151) S. Morrow and A. Young, Inorg. Nuc. Chem. Letters, 2, 349, 1966.
- 152) J.M. LeCarpentier and R. Weiss, Compt. Rend., 265, 796, 1967.
- 153) G. Olofsson, Acta Chem. Scand., 21, 1887, 1967.
- 154) N.D. Chikarov and L. Kazberova, Zh. Neorg. Khim., 12, 2509, 1967.
C. A. 68, 6850c.
- 155) S. Prasad and K. Upadhaya, Proc. Nat. Acad. Sci. India, 30, 72, 1961.
- 156) P. Reich and H. Preiss, Z. Chem., 7, 115, 1967.
- 157) W. Wieker and A. Grimmer, Z. Naturforsch, 22B, 983, 1967.
- 158) T.N. Polynova, N. Bokii, M.A. Poraikoshits, Zh. Strukt. Khim., 6,
878, 1965. C. A. 64, 11978f.
- 159) E. Allenstein, Ber. Chem., 96, 3230, 1963.
- 160) D.G. Farnum, M.A. Tyrell Heybey and B. Webster, J. Amer. Chem. Soc.,
86, 673, 1964.
- 161) L.I. Katzin, J. Chem. Phys., 36, 3034, 1962.
- 162) W. Libus and D. Puchalska, J. Phys. Chem., 71, 3549, 1967.
- 163) S. Frankel and P. Lowy, Chem. Ber., 46, 2546, 1913.
- 164) H.H. Perkampus and E. Baumgarten, Z. Physik. Chem., 39, 1, 1963.
- 165) A. Bystrom, S. Baklund and K. Wilhelmi, Ark. Kemi. 4, 175, 1952.
- 166) V. Gutmann, Z. Anorg. Allgem. Chem., 266, 331, 1951.
- 167) S.K. Porter and R. Jacobson, Chem. Commun., 1244, 1967.
- 168) A.A. Woolf and N.N. Greenwood, J. Chem. Soc., 2200, 1950.

- 169) O. Ruff and W. Plato, Chem. Ber., 37, 673, 1904.
- 170) C.J. Kelley and P.A. McCusker, J. Amer. Chem. Soc.,
65, 1307, 1943.
- 171) J. Doak, J. Am. Pharm. Ass., 23, 541, 1936.
- 172) M. Agermann, L.H. Anderson, I. Lindqvist and M. Zackrisson,
Acta Chem. Scand., 12, 477, 1958.
- 173) W.R. Trost, Can.J. Chem., 32, 356, 1954.
- 174) I. Lindqvist and L. Andersson, Acta Chem. Scand., 8, 128, 1954.
- 175) W.B. Shirey, J. Amer. Chem. Soc., 52, 1720, 1930.
- 176) A.W. Cronander, Chem. Ber., 6, 1466, 1873.
- 177) R.R. Holmes, J. Phys. Chem., 64, 1295, 1960.
- 178) R.R. Holmes and E.F. Bertaut, J. Amer. Chem. Soc., 80, 2980, 1958.
- 179) R.R. Holmes, J. Amer. Chem. Soc., 82, 5285, 1960.
- 180) R.R. Holmes and E.F. Bertaut, J. Amer. Chem. Soc., 80, 2983, 1958.
- 181) C.S. Gibson, J. Dobney, A. Johnson and D.C. Vining,
J. Chem. Soc., 1710, 1930.
- 182) F. Watari, Sci. Repts. Res. Inst., Tohoku Univ. Ser. A.,
13, 330, 1961.
- 183) P. Walden, Z. Physik. Chem., 43, 385, 1903.
- 184) A.H. Cowley and S.T. Cohen, Inorg. Chem., 4, 1200, 1965.
- 185) A.F. Armington, J.R. Weiner and G.H. Moates, Inorg. Chem.,
5, 483, 1966.
- 186) R.F. Mitchell, J.A. Bruce and A.F. Armington, Inorg. Chem.,
3, 915, 1964.
- 187) O. Ruff, Chem. Ber., 37, 4513, 1904.

- 188) U. Hasserodt, K. Hunger and F. Korte, Tetrahedron,
19, 1563, 1963.
- 189) G.B. Lindahl and W.L. Jolly, Inorg. Chem., 3, 1634, 1964.
- 190) G.W. Chantry, A. Finch, P.N. Gates and D. Steele,
J. Chem. Soc. (A)., 896, 1966.
- 191) D. Hass, Z. Anorg. Allgem. Chem., 337, 43, 1965.
- 192) A. Schmidpeter and H. Brecht, Angew. Chem., Internat. Ed.,
6, 564, 1967.
- 193) S. Prasad and N. Singh, J. Indian Chem. Soc., 42, 195, 1965.
- 194) G.V. Zimina, V.E. Plyushchev and S.B. Stepina,
Dokl. Akad. Nauk. S.S.S.R., 163, 887, 1965. C.A. 63, 10972d.
- 195) A. Chretien and J.C. Couturier, Rev. Chim. Minerale, 2, 487, 1965.
- 196) W. Petzold, Z. Anorg. Allgem. Chem., 214, 355, 1933.
- 197) H. Spandau and H. Hattwig, Z. Anorg. Allgem. Chem.,
311, 32, 1961.
- 198) F.J. Welch and H.J. Paxton, J. Polymer Sci. (A)., 3, 3427, 1965.
- 199) I. Lindqvist and G. Olofsson, Acta Chem. Scand., 13, 1753, 1959.
- 200) A. Basinski and E. Kwiatkowski, Rocz. Chem., 41, 175, 1967.
C.A. 67, 68168z.
- 201) M.J. Frazer, W. Gerrard and R. Twaits, J. Inorg. Nuc. Chem.,
25, 637, 1963.
- 202) L. Kolditz, Z. Anorg. Allgem. Chem., 289, 118, 1957.
- 203) G.J. Sutton, Aust. J. Chem., 11, 420, 1958.
- 204) G. Herzberg. "Infrared & Raman Spectra", D. Van Nostrand,
New York, 1945.
- 205) V. Gutmann, J. Phys. Chem., 63, 378, 1959.

- 206) T. Bjorvatten, Acta Chem. Scand., 20, 1863, 1966
- 207) R.J.H. Clark and W. Errington, J. Chem. Soc.(A)., 258, 1967;
- 208) V.S. Tsivunin, S.V. Fridland, T.V. Zykova and G. Kamai,
Zh. Obshch. Khim., 36, 1424, 1966. C.A. 66, 28843p
- 209) Y.D. Fridman, R.A. Veresova and A.N. Luk'yanets, C.A. 64, 13453f.
- 210) G.J. Sutton, Aust. J. Chem., 19, 733, 1966.
- 211) L.S. Pupko and P.S. Pel'kis, Zh. Obshch. Khim., 33, 3635, 1963.
C.A. 60, 7896f.
- 212) I. Kijima and N. Takahashi, Kogyo Kagaku Zasshi., 67, 1092,
1964. C.A. 61, 14515a.
- 213) P.P. Popov, Ya.I. Ivashentsev, Tr. Tomskogo Gos. Univ. Ser. Khim.,
157, 6-7, 1963. C.A. 61, 7946e.
- 214) P.P. Popov, S.I. Gromov and Ya.I. Ivashentsev, Tr. Tomskogo
Gos. Univ., Ser. Khim., 157, 3, 1963. C.A. 61, 6986d.
- 215) G.V. Zimina and S.B. Stepina, Zh. Neorg. Khim., 11, 1107, 1966.
C.A. 65, 6365g.
- 216) D.P.N. Satchell and J.L. Wardell, J. Chem. Soc., 739, 1965.
- 217) K.L. Jaura, K.K. Tewari and R.L. Kaushik, J. Indian Chem. Soc.,
40, 1008, 1963. C.A. 60, 10181e.
- 218) O.B. Skaar, Acta Chem. Scand., 18, 47, 1964.
- 219) L.A. Kazitsyna, N.B. Kupletskaya, V.A. Ptitsyna, M.N. Bochkareva
and O.A. Reutov, Zh. Organ. Khim., 2, 571, 1966. C.A. 65, 8313d.
- 220) A. Kazitsyna and N.B. Kupletskaya, Zh. Organ. Khim.,
2, 565, 1966. C.A. 65, 8313b.
- 221) A.I. Busev and E.S. Bogdanova, Zh. Analit. Khim., 19, 1346, 1964.

- 222) V.E. Plyushchev, S.B. Stepina, G.V. Zimina and V.G. Zhilyakov, Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met., 7, 112, 1964. C.A. 62, 2497a.
- 223) D. Brown, J.F. Easey and J. DuPreez, J. Chem. Soc.(A), 258, 1966.
- 224) K.L. Baker and G.W.A Fowles, J. Chem. Soc.(A), 801, 1968.
- 225) K. Feenan and G.W.A. Fowles, J. Chem. Soc., 2449, 1965.
- 226) E.L. Meutterties and W.D. Phillips, J. Amer. Chem. Soc., 81, 1084, 1959.
- 227) L. Brun and C.I. Branden, Acta Cryst., 20, 749, 1966.
- 228) E.L. Meutterties, T.A. Bither, M.W. Farlow and D.D. Coffman, J. Inorg. Nuc. Chem., 16, 52, 1960.
- 229) J.W. George, Progress in Inorg. Chem., 2, 33, 1960.
- 230) M. Webster, Chem. Rev., 66, 87, 1964.
- 231) L. Kolditz, "Halogen Chemistry", Vol. 2, Academic press, V. Gutmann, Ed., London, 1967.
- 232) K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds", John Wiley & Sons, Inc., New York, 1963.
- 233) I.R. Beattie, T. Gibson, K. Livingston, V. Fawcett and G. Ozin, J. Chem. Soc.(A), 712, 1967.
- 234) M.J. Taylor and L.A. Woodward, J. Chem. Soc., 4670, 1963.
- 235) G.L. Carlson, Spectrochim. Acta, 19, 1291, 1963.
- 236) C. Dragulescu, O. Solomon, S. Zugraevescu and E. Berol, Bul. Inst. Politeh. "Gheorghe Gheorghiu Dej.", Bucuresti, 29, 49, 1957.
- 237) M. Webster and M.J. Deveney, J. Chem. Soc.(A), in press.
- 238) J. Weidlein and K. Dehnicke, Z. Anorg. Allgem. Chem., 337, 113, 1965.

- 239) W. Biltz and E. Meinecke, Z. Anorg. Allgem. Chem., 131, 1, 1923.
- 240) V. Gutmann, Monatsch. Chem., 82, 473, 1951.
- 241) R.R. Holmes, J. Inorg. Nuc. Chem., 19, 363, 1961.
- 242) J.H. Owens and R.E. Johnson, J. Inorg. Nuc. Chem., 2, 260, 1956.
- 243) R.C. Paul, R. Parkash, S.S. Sandhu, Indian J. Chem., 3, 277, 1965.
- 244) R.C. Paul, S.C. Ahluwalia, S.K. Rehani and S.S. Pahil,
Indian J. Chem., 3, 207, 1965.
- 245) R.C. Thompson, J. Barr and R.J. Gillespie, Inorg. Chem.,
4, 1641, 1965.
- 246) S. Ahrland, J. Chatt and N.R. Davies, Quart. Rev., 12, 265, 1955.
- 247) A.P. Zuur and W.L. Groeneveld, Rec. Trav. Chim., 86, 1089, 1967.
- 248) L. Kolditz and G. Heuthe, "Halogen Chemistry", Vol. 2, Ed.
V. Gutmann, Academic press, London, 1967.
- 249) L. Kolditz and W. Roehnsch, Z. Anorg. Allgem. Chem., 318, 17, 1962.
- 250) K. Dehnicke and J. Weilein, Z. Anorg. Allgem. Chem., 323, 267, 1963.
- 251) K. Dehnicke and J. Weidlein, Chem. Ber., 98, 1087, 1965.
- 252) H. Preiss, Z. Chem., 6, 350, 1966.
- 253) H. Preiss, Z. Anorg. Allgem. Chem., 346, 272, 1966.
- 254) E.E. Sutton, (Ed.), "Interatomic Distances and Configurations
in Molecules and Ions", Chem. Soc. special publ. No. 11, 1958.
- 255) R.A. Condrate and K. Nakamoto, Bull. Chem. Soc. Japan,
39, 1108, 1966.
- 256) W.J. Casselmann, Liebigs Ann. Chem., 83, 257, 1852.
- 257) E. Baudrimont, Compt. Rend., 55, 361, 1863.
- 258) E. Baudrimont, Ann. Chim. Physique, (4), 2, 5, 1864.
- 259) W.L. Groeneveld, Rev. Trav. Chim., 71, 1152, 1952.

- 260) W.L. Groeneveld and A.P. Zuur, Rec. Trav.Chim., 72, 617, 1963.
- 261) Ya.B. Bur'yanov, Zhur. Obshchei. Khim., 26, 1363, 1956.
C.A. 51, 1763f.
- 262) G.S. Harris and D.S. Payne, J. Chem. Soc., 4613, 4617, 1956.
- 262A) G.S. Harris, "Ph.D. Thesis", Glasgow Univ. 1959.
- 263) F.A. Miller, Pure Appl. Chem., 7, 125, 1963.
- 264) H.M. Powell and D. Clark, Nature, 145, 971, 1940.
- 265) J.A. Creighton and J.H. Green, J. Chem. Soc.(A), 808, 1968.
- 266) D.M. Adams and D.M. Morris, J. Chem. Soc.(A), 1669, 1967.
- 267) V. Gutmann, M. Baas and O. Kunze, Monatsch, Chem., 93, 1142, 1962.
- 268) C.B. Lindahl, AEC Accession No. 35254, C.A. 63, 236a, 1965.
- 269) E. Kwiatkowski and A. Basinski, Roczniki. Chem., 36, 1011, 1962.
C.A. 58, 9689g.
- 270) N.N. Greenwood and P.G. Perkins, J. Chem. Soc., 4345, 1957.
- 271) N.N. Greenwood and P.G. Perkins, Pure Appl. Chem., 2, 55, 1961.
- 272) A.G. Garrett and C. Urry, Inorg. Chem., 2, 400, 1963.
- 273) M.L. Hair and P.L. Robinson, J. Chem. Soc., 106, 1958.
- 274) A.F. Armington, J.R. Weiner and G.H. Moates, U.S. Clearinghouse.
Fed. Sci. Tech. Inform. A.D. 645468. C.A. 67, 78562n.
- 275) B.A. Voitovich, Zhur. Neorg. Khim., 6, 1914, 1961. C.A. 56, 4344d.
- 276) R.R. Holmes and R.P. Wagner, Inorg. Chem., 2, 384, 1963.
- 277) A. Engelbrecht, A. Aignesberger and E. Hayek, Monatsch Chem.,
86, 470, 1955.
- 278) E.L. Muetterties and W.D. Phillips, J. Amer Chem. Soc.,
79, 3686, 1957.

- 279) A.L. Oppegard, W.C. Smith, E.L. Muetterties and V.A. Engelhardt,
J. Amer. Chem. Soc., 82, 3835, 1960.
- 280) J. Lewis and D.B. Sowerby, J. Chem. Soc., 1617, 1957.
- 281) P.P. Popov, Trudy Tomsk. Univ., 126, 136, 1954. C.A. 52, 18056e.
- 282) J.C. Sheldon and S.Y. Tyree, J. Amer. Chem. Soc., 81, 2290, 1959.
- 283) V. Gutmann, M. Baaz and O. Kunze, Monatsch Chem., 93, 1142, 1962.
- 284) P.P. Popov and V.A. Sidorov, Uchenye. Zapiski. Tomsk. Univ.,
26, 119, 1955. C.A. 53, 5262e.
- 285) G. Jander and K. Gunther, Z. Anorg. Allgem. Chem., 297, 81, 1958.
- 286) N. Wiberg and K.H. Schmid, Angew. Chem., Internat. Ed., 6, 953, 1967.
- 287) J. Cahours, Annalen., 122, 207, 1862.
- 288) G. Mahapatra and C. Nanda, J. Indian Chem. Soc., 35, 148, 1958.
- 289) M. Baaz, V. Gutmann and J.R. Masaguer, Monatsch Chem., 92, 582, 1961.
- 290) V. Gutmann and G. Hampel, Monatsch. Chem., 92, 1048, 1961.
- 291) H. Funk and H. Koehler, J. Prakt. Chem., 14, 226, 1961.
C.A. 56, 10011f.
- 292) V.K. Ermakov and E.N. Zykov, Uch. Zap. Tomskogo. Gos. Univ.,
29, 93, 1959. C.A. 56, 15019b.
- 293) E.C. Puente, Anales Real Soc. Espan. Fis. y Quim. (Madrid),
57, 259, 1961. C.A. 56, 11200a.
- 294) J. Havir, Collection Czechoslov. Chem. Commun., 25, 695, 1960.
C.A. 56, 5392e.
- 295) W. Smith and E. Muetterties, U.S. 3,000, 694. C.A. 56, 3123b.
- 296) R.C. Paul, S.S. Sandhu and G. Singh, J. Indian Chem. Soc.,
38, 89, 1961.

- 297) R.C. Paul, J. Kaur and S.S. Sandhu, J. Indian Chem. Soc.,
38, 93, 1961.
- 298) R.C. Paul, K.C. Malhotra and G. Singh, J. Indian Chem. Soc.,
37, 105, 1960.
- 299) A.F. Gremillion, H.B. Jonassen and R.J. O'Connor,
J. Amer. Chem. Soc., 81, 6134, 1959.
- 300) J. Newton Friend(Ed.), "Textbook of Inorganic Chemistry",
Vol. XI. part II, Griffin and Co. Ltd., London, 1930.
- 301) M. Jorgensen, J. Prakt. Chem., 3, 340, 1871.
- 302) L.A. Nisel'son, B.N. Ivanov-Emin and L.E. Larionova, Zhur. Neorg.
Khim., 6, 186, 1961. C.A. 56, 8277i.
- 303) M. Zackrisson and K.I. Alden, Acta Chem. Scand., 14, 994, 1960.
- 304) L.A. Kazitsyna, O.A. Reutov and Z.F. Buchkovskii, Zhur. Obsheei.
Khim., 6, 2065, 1961. C.A. 56, 1065h.
- 305) E. Montignie, Z. Anorg. Allgem. Chem., 315, 102, 1962.
- 306) H. Rheinboldt and R. Wasserfuhr, Chem. Ber., 60, 732, 1927.
- 307) P. Pfeiffer and K. Schneider, Chem. Ber., 68, 50, 1935.
- 308) R. Paul and K. Malhotra, Z. Anorg. Allgem. Chem., 325, 302, 1963.
- 309) O.A. Terekhova, Uchenye Zapiska Tomsk. Gosudarst. Univ. im
V.V. Kuybysheva, 1959, No. 29, 116-20. C.A. 55, 13153c.
- 310) E. Lindner and H. Kranz, Chem. Ber., 99, 3800, 1966.
- 310) D. Martin, C.R. Acad. Sci., Paris, Ser., C265, 919, 1967.
- 312) J. Moore, H. Baird and H. Miller, J. Amer. Chem. Soc., 90, 1358, 1968.
- 313) W. Wieker and A. R. Grimmer, Z. Naturforsch., 22B, 1220, 1967.
- 314) K.O. Christie and W. Sawodny, Inorg. Chem., 6, 1783, 1967.
- 315) R. Eberts and F. Pink, J. Inorg. Nuc. Chem., 30, 457, 1958.

- 316) A. J. Edwards and G.R. Jones, Chem. Commun., 346, 1968.
- 317) R.S. Drago, J. Phys. Chem., 62, 353, 1958.
- 318) D.S. Payne, Quart. Revs., 15, 173, 1961.
- 319) Yu. A. Buslaev, M. Gluskova, M. Ershova and V. Bocharova,
Zh. Neorg. Khim., 13, 63, 1968.
- 320) J. Cameron, unpublished work.
- 321) P. Baumgarten and W. Bruns, Chem. Ber., 80, 517, 1947.
- 322) N.A. Trifonov and F.F. Faizullin, Uchenye Zapiski Kazan.
Gosudarist. Univ., 112, 131, 1953. C.A. 49, 2167g.
- 323) J. Lewis and D.B. Sowerby, Rec. Trav. Chim., 75, 615, 1956.
- 324) O.A. Reutov and Yu.G. Bundel, Izvest. Akad. Nauk. S.S.S.R.
Otdel. Khim. Nauk., 1041, 1952. C.A. 48, 623d.
- 325) W.A. Waters and J.H. Williams, J. Chem. Soc., 18, 1950.
- 326) F. Pushkin, Zhur. Obsheei. Khim., 18, 1599, 1948. C.A. 43, 6899h.
- 327) H.H. Sisler, B. Pfahler and W.J. Wilson, J. Amer. Chem. Soc.,
70, 3825, 1948.
- 328) S. Prasad, G. B. Rao, S. Kumar, V. Reddy, K. Kacker,
J. Indian Chem. Soc., 36, 129, 1959.
- 329) V.S. Galinker and A. Fiks, J. Gen. Chem. U.S.S.R., 25, 433, 1955.
- 330) L.C. Anderson, J.W. Steedly, J. Amer. Chem. Soc., 76, 5144, 1954.
- 331) L.C. Anderson and B. Manning, J. Amer. Chem. Soc., 77, 3018, 1955.
- 332) V.P. Borov, Zh. Neorg. Khim., 12, 2872, 1967.
- 333) P. Bender and R.E. Bunde, J. Amer. Chem. Soc., 72, 2273, 1950.
- 334) D.L. Chamberlain and N. Kharasch, J. Amer. Chem. Soc., 77, 1041, 1955.
- 335) V. Gutmann, Z. Anorg. Allgem. Chem., 269, 279, 1952.
- 336) Fr. Hein and P. Albert, Z. Anorg. Allgem. Chem., 269, 67, 1952.

- 337) A.S. Naumova and S. Zhitkov, Zhur. Obsheei. Khim., 19, 1429, 1949.
C.A. 44, 919d.
- 338) O.A. Reutov and O. Ptitsyna, Doklady Akad. Nauk. SSSR, 89, 877, 1963.
- 339) M. Usanovich and T. Sumarokova, Zhur. Obsheei. Khim., 21, 1214, 1951.
- 340) M. Usanovich, T. Sumarokova and V. Glushchenko,
Zhur. Obsheei. Khim., 21, 987, 1951. C.A. 48, 178c.
- 341) N. Wiberg and K.H. Schmid, Angew. Chem. Internat. Ed., 6, 953, 1967.
- 342) P.V. Zimakov and E.V. Girshberg, Doklady. Akad. Nauk. USSR,
58, 1661, 1947. C.A. 46, 4843c.
- 343) G. Leclere zur Medden, Spectrochim. Acta, 24A, 473, 1968.
- 344) A. Bystrom, K.A. Wilhelmi, Ark. Kemi., 3, 461, 1951. C.A. 47, 19i.
- 345) Y. Mollie and N. Lozach, Bull. Soc. Chim. France, 1076, 1952.
- 346) I.R. Beattie, P.J. Jones and M. Webster, J. Chem. Soc.(A),
submitted for publication.
- 347) B.K. Robertson, W. McPherson and E.A. Meyers, J. Phys. Chem.,
71, 3531, 1967.
- 348) W. McPherson and E. Meyers, J. Phys. Chem., 72, 532, 1968.
- 349) M. Voronkov, A. Broun and G.B. Karpenko, Zhur. Obsheei. Khim.,
19, 1927, 1949. C.A. 44, 1955h.
- 350) E.O. Fischer and R. Jira, Z. Naturforsch., 8B, 1, 1953.
- 351) G. Sandri, Atti. Accad. Sci. Ferrara., 30, 59, 1953.
- 352) R. Das and S. Pani, J. Indian Chem Soc., 33, 538, 1956.
C.A. 51, 4864b.
- 353) S.P.¹/₂ Sinha, Z. Chem., 4, 150, 1964.
- 354) D.W. Breck, J.L. Harvey and H.L. Haendler, J. Phys. & Colloid Chem.
53, 906, 1949.

- 355) H.M. Haendler, R.H. Glazier and D.W. Breck, J. Amer. Chem. Soc.,
75, 3845, 1953.
- 356) A.B. Bruker, Zhur. Obsheei. Khim., 18, 1297, 1948. C.A. 43, 4647c.
- 357) I.R. Beattie, Chemistry in Britain, 347, 1967.
- 358) I.R. Beattie, M. Webster and G. Chantry, J. Chem. Soc., 6172, 1964.
- 359) J.A. Walmsley and S.Y. Tyree, Inorg. Chem., 2, 312, 1963.
- 360) I. Lindqvist, N. Zackrisson and S. Eriksson, Acta Chem. Scand.,
13, 1758, 1959.
- 361) C. Riolo, T.F. Soldi and C. Occhipinti, Ann. Chim.(Rome),
51, 1178, 1961. C.A. 56, 1091b
- 362) H. Wachsmuth, J. Pharm. Chim. L. 383, 1941. C.A. 38, 2340.
- 363) J.V. Supniewski and R. Adams, J. Amer. Chem. Soc., 48, 507, 1926.
- 364) P. May, J. Chem. Soc., 101, 1037, 1912.
- 365) W. Pugh, J. Chem. Soc., 3445, 1953.
- 366) R. Ralea, Ann. Sci. Univ. Jassy, Pt.I., 23, 283, 1937. C.A. 32, 5840
- 367) A.S. Nesmeyanov and K.A. Kocheshkov, Bull. Acad. Sci. U.R.S.S.
Classe Sci. Chim., 416, 1944. C.A. 39, 4320.
- 368) P.C. Ray, N. Adhikari and A.N. Roy, Indian Chem. Soc., 8, 711, 1931.
- 369) M. Usanovich and F. Terpugov, J. Gen. Chem.(USSR), 2, 443, 1932.
C.A. 27, 1259.
- 370) D. J. Loder and K.E. Walker, U.S., 2052, 889, 1936. C.A. 30, 7255.
- 371) F. Oberhauser, Ber. Chem., 60, 1434, 1927.
- 372) A.A. Woolf, J. Chem. Soc., 252, 1954.
- 373) W. Pugh, J. Chem. Soc., 1385, 1954.
- 374) W.H. Gray, J. Chem. Soc., 3174, 1926.

- 375) A.S. Nesmeyanov, K.A. Kocheshkov and V.A. Klimova,
Ber., 68, 1877, 1935.
- 376) H. Gilman and H.L. Yablunsky, J. Amer. Chem. Soc., 63, 949, 1941.
- 377) K.A. Kocheshkov and A.N. Nesmeyanov, J. Gen. Chem.(USSR),
6, 144, 1936. C.A. 30, 4833.
- 378) H. Gilman and A.C. Svigoon, J. Amer. Chem. Soc., 61, 3586, 1939.
- 379) H. Remy and L. Pellens, Chem. Ber., 61, 862, 1928.
- 380) F.E. Ray and J.L. Farmer, J. Org. Chem., 8, 391, 1943.
- 381) I.A. Shevchuk, N.A. Kerimbekova and A.V. Kerimbekova,
Zh. Neorg. Khim., 12, 3111, 1967. C.A. 68, 4446p.
- 382) R.P. Oertel and R.A. Plane, Inorg. Chem., 6, 1960, 1967.
- 383) E.Ya. Gorenbein and E.E. Kriss, Zhur. Fiz. Khim., 25, 791, 1951.
C.A. 46, 2380d.
- 384) M.S. Malinovskii, J. Gen. Chem.(USSR), 10, 1202, 1940.
C.A. 35, 2852.
- 385) M. Usanovich and R.G. Rozentreter, J. Gen. Chem.(USSR),
2, 864, 1932. C.A. 27, 3382.
- 386) B.P. Kondratenko, J. Gen. Chem.(USSR), 4, 244, 1934. C.A. 29, 988.
- 387) P.L. Timms, Inorg. Chem., 7, 387, 1968.
- 388) A.B. Burg and J.H. Bickerton, J. Amer. Chem. Soc., 67, 2261, 1945.
- 389) A. Stieber, Compt. Rend., 195, 610, 1932.
- 390) P. Popov, Zhur. Obshchei. Khim., 19, 47, 1949. C.A. 44, 1980b.
- 391) J.E. Griffiths and A.B. Burg, J. Amer. Chem. Soc., 82, 1507, 1960.
- 392) J.W. Mellor, "A Comprehensive Treatise on Inorganic and
Theoretical Chemistry", vol. IX, Longmans, 1929.

- 393) M. Edstrand, M. Inge and N. Ingri, Acta Chem. Scand., 9, 122, 1955.
- 394) T. Barrowcliffe, I.R. Beattie, P. Day and K. Livingston,
J. Chem. Soc.(A), 1810, 1967.
- 395) P. Day, Inorg. Chem., 2, 452, 1963.
- 396) M. Atoji and T. Watanabe, J. Chem. Phys., 20, 1041, 1952.
- 397) R.D. Whealy and J.B. Blackstock, J. Inorg. Nuc. Chem., 26, 243, 1964.
- 398) S. Prasad and L.P. Pandley, J. Indian Chem. Soc., 4, 771, 1964.
- 399) V. Gutmann, Monatsh., 83, 159, 1953.
- 400) V. Gutmann, Monatsh., 84, 1191, 1953.
- 401) D.S. Payne, Halides and Oxyhalides of Group V Elements as
Solvents, "Non Aqueous Solvent Systems", ed. T.C. Waddington,
Academic press, 1965.
- 403) J. Chatt and A.A. Williams, J. Chem. Soc., 3061, 1951.
- 402) A. Hershaft and J.D. Corbett, Inorg. Chem., 2, 979, 1963.
- 404) V. Gutmann and M Baaz, Angew. Chem., 71, 57, 1959.
- 405) A. Bystrom and K.A. Wilhelmi, Arkiv. Kemi., 3, 373, 1951.
C.A. 46, 3363i.
- 406) A. Bystrom and K. Wilhelmi, Arkiv. Kemi., 3, 17, 1951.
C.A. 45, 5482d.
- 407) R.J. Gillespie and R.S. Nyholm, Quart. Rev., 11, 339, 1957.
- 408) L. Newman and D.N. Hume, J. Amer. Chem. Soc., 79, 4576, 1957.
- 409) S. Ahrland and I. Grenthe, Acta Chem. Scand., 11, 1111, 1957.
- 410) G.P. Haight, C.H. Springer and O.J. Heilmann, Inorg. Chem.,
3, 195, 1964.
- 411) A.J. Eve and D.N. Hume, Inorg. Chem., 6, 331, 1967.

- 412) I.R. Beattie, G.P. McQuillan, L. Rule and M. Webster,
J. Chem. Soc., 1514, 1963.
- 413) H. Clees and F. Huber, Z. Anorg. Allgem. Chem., 350, 35, 1967,
- 414) A.A. Schilt and R.C. Taylor, J. Inorg. Nuc. Chem., 9, 211, 1959.
- 415) D.M. Murray-Rust, H.J. Hadow and H. Hartley, J. Chem. Soc.,
215, 1931.
- 416) R.G. Inskeep, J. Inorg. Nuc. Chem., 24, 763, 1962.
- 417) R.J.H. Clark, J. Chem. Soc., 1377, 1963.
- 418) R.J.H. Clark and C.S. Williams, Spectrochim. Acta, 21, 1861, 1965.
- 419) E.B. Wilson, J.C. Decius and P.C. Cross, "Molecular Vibrations",
McGraw Hill, New York, 1955.
- 420) P. Reich and H. Preiss, Z. Chem., 7, 115, 1967.
- 421) L.J. Bellamy, "The Infrared spectra of complex molecules",
Methuen, London, 1958.
- 422) I.R. Beattie and L. Rule, J. Chem. Soc., 2995, 1965.
- 423) J.A. Evans and D.A. Long, J. Chem. Soc.(A), 1688, 1968.
- 424) M. Webster, "Ph.D. Thesis", University of London, 1962.
- 425) R.J.H. Clark, J. Lewis and R.S. Nyholm, J. Chem. Soc., 2460, 1962.
- 426) A.I. Popov and N.E. Skelly, J. Amer. Chem. Soc., 76, 3916, 1954.
- 427) H.S. Booth and C.G. Seegmiller, "Inorganic Synthesis", vol.II,
McGraw Hill, New York, 1946, p151.
- 428) K. Matauschek, Z. Anorg. Allgem. Chem., 337, 48, 1965.
- 429) W.A. Jacobs, M. Heidelberger and I.P. Rolf,
J. Amer. Chem. Soc., 40, 1580, 1918.
- 430) L. Kalb, Ann., 423, 39, 1921.
- 431) J. Chatt and F.G. Mann, J. Chem. Soc., 610, 1939.

- 432) K.C. Eberly and G. Smith, J. Org. Chem., 22, 1710, 1957.
- 433) A.I. Vogel, "A Textbook of Quantitative Inorganic Analysis",
Longmans, Green and Co., London, 3rd. ed. 1965.
- 434) S. Brownstein, Can. J. Chem., 45, 2403, 1967.
- 435) G.M. Begun and A.C. Rutenberg, Inorg. Chem., 6, 2212, 1967.
- 436) S.I. Weissman, E. de Boer and J.J. Conradi, J. Chem. Phys.,
26, 963, 1957.
- 437) W.I. Aalbergsberg, G.J. Hoijtink, E.L. Meckor and W.P. Weijland,
J. Chem. Soc., 3049, 3055, 1959.
- 438) R. Foster and T.J. Thompson, Trans. Faraday Soc., 58, 860, 1962.
- 439) G.T. Pott and J. Kommandeur, J. Mol. Phys., 13, 373, 1967.
- 440) C.K. Jorgensen, Acta Chem. Scand., 11, 166, 1957.
- 441) L.A. Woodward, Trans. Faraday Soc., 54, 1271, 1958.
- 442) L.A. Woodward and L.E. Anderson, J. Chem. Soc., 1284, 1957.
- 443) C.V. Stephenson and E.A. Jones, J. Chem. Phys., 20, 1830, 1953.
- 444) P.C. Harrhoff and C.W. Pistorius, Z. Naturforsch., 14A, 972, 1959.
- 445) M. Webster, "personal communication".
- 446) J.C. Sheldon and S.Y. Tyree, J. Amer. Chem. Soc., 80, 4775, 1958.
- 447) M.A. Brune and W. Zeil, Z. Phys. Chem.(Frankfurt), 32, 384, 1962.
- 448) O. Kinell, I. Lindqvist and M. Zackrisson, Acta Chem. Scand.,
13, 1159, 1959.
- 449) I.R. Beattie and L. Rule, J. Chem. Soc., 3267, 1964.
- 450) H. Gerding and P.C. Nobel, Rec. Trav. Chim., 77, 472, 1958.
- 451) P.N. Davis and R.A. Oetjin, J. Mol. Spec., 2, 253, 1958.

- 453) G.S. Harris and D.S. Payne, J. Chem. Soc., 3732, 1958.
- 454) G. Oddo and M. Tealdi, Gazzetta, 33, 435, 1903.
- 455) J.L. Cotter and A.G. Evans, J. Chem. Soc., 2988, 1959.
- 456) R.F. Bryan, J. Amer. Chem. Soc., 86, 733, 1964.
- 457) E.L. Meutterties and R.A. Schunn, Quart. Rev., 20, 245, 1966.
- 458) D.W.A. Sharp and N. Sheppard, J. Chem. Soc., 674, 4804, 1957.
- 459) R.E. Weston, A. Tsukamoto and N.N. Lichtin, Spectrochim. Acta,
22, 433, 1966.
- 460) N.N. Greenwood and B.P. Straughan, J. Chem. Soc.(A), 962, 1966.
- 461) D.S. Urch, J. Chem. Soc., 5775, 1964.
- 462) L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press,
Ithaca, New York, 3rd ed., 1960, p251.
- 463) R.J.H. Clark, Metal Halogen Vibration Frequencies, "Halogen
Chemistry", V. Gutmann, ed., vol.3, Academic press, London, 1967.
- 464) G.A. Forcier and J. Walmer, Anal. Chem., 37, 1447, 1965.
- 465) I.R. Beattie, T. Gibson, M. Webster and G.P. McQuillan,
J. Chem. Soc., 238, 1964.
- 466) I.R. Beattie and M. Webster, J. Chem. Soc., 38, 1963.
- 467) H.P. Leftin and N.N. Lichtin, J. Amer. Chem. Soc., 79, 2475, 1957.
- 468) G. Brauer, "Handbook of preparative Inorganic Chemistry",
Academic press, New York, vol. I., 1963.
- 471) Y. Sato, M. Kimoshita, M. Sana and H. Akamoto, Bull. Chem. Soc.
Japan, 40, 2539, 1967.
- 472) H. Kainer and K.H. Hausser, Ber. Chem., 86, 1563, 1953.
- 473) R.R. Holmes, J. Chem. Ed., 40, 125, 1963.
- 474) J.L. Hoard and L. Goldstein, J. Chem. Phys., 3, 117, 1934.

- 475) H.M. Powell and A.F. Wells, J. Chem. Soc., 1008, 1935.
- 476) H. Yamatera and K. Nakatsu, Bull. Chem. Soc. Japan, 27, 243, 1954.
- 477) J.E. Davies and D.A. Long, J. Chem. Soc.(A)., 1757, 1761, 1968.
- 478) I. Lindqvist and A. Niggli, J. Inorg. Nuc. Chem., 2, 345, 1956.
- 479) R. Mecke, R. Joeckle, G. Klingenberg, Z. Electrochem., 66, 239,
1962.
- 480) E.B. Wilson, J. Chem. Phys., 7, 1047, 1939.
2, 76, 1941.
- 481) I. Lindqvist and G. Nahringsbauer, Acta Cryst., 12, 638, 1959.
- 482) A.W. Cordes and T.V. Hughes, Inorg. Chem., 3, 1640, 1964.
- 483) G.W.A. Fowles, R.A. Hoodless and R.A. Walton,
J. Inorg. Nuc. Chem., 27, 391, 1965.