INFRARED SPECTRA OF SOME COORDINATION COMPOUNDS OF SILICON AND GERMANIUM TETRAHALIDES IN THE CAESIUM BROMIDE RANGE

by

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To my wonderful wife, for her
love and support, and to my sons.

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INTRODUCTION

The spectacular progress in inorganic chemistry during the last ten to fifteen years has been due mainly to the very rich and rewarding study of coordination compounds. The transition metals (or B-group elements) have received the greatest attention partly because of the variety of spectroscopic techniques which are suitable for the study of transition metal complexes, and partly because most of these complexes are soluble in water, unlike most of the complexes of the A-group elements.

In recent years, however, more and more experimental and theoretical studies have been reported about the coordination compounds of A-group elements. For example, there are reviews by Stone on Group IIIA (1), by Beattie on Group IVA (2) and by Ingham et al on organotin compounds (3). Theoretical studies of the use of d-orbitals in bonding by A-group elements have been described by Craig and Zauli (4).

In addition, there has been a considerable amount of infrared and Raman spectroscopic research on inorganic and coordination compounds in the past decade. Much of the success in characterizing inorganic and coordination compounds has been due to spectroscopic measurements. The texts of Lawson (5) and Nakamoto (6) concerning the vibrational spectroscopy of inorganic and coordination compounds contain many examples showing the value of these techniques.

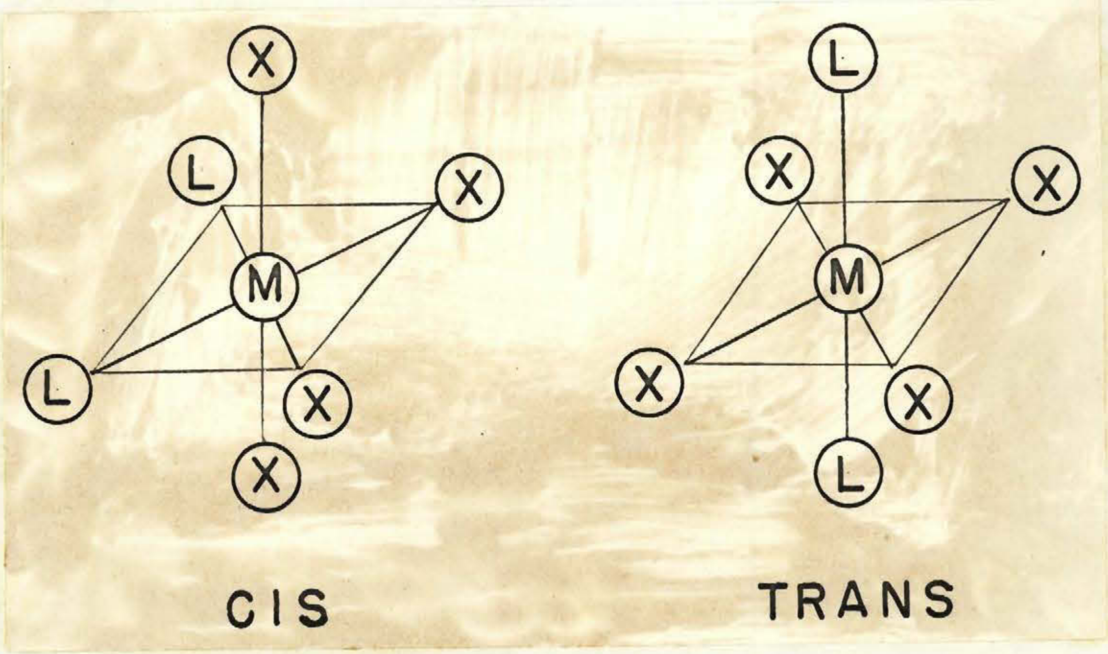
This dissertation is concerned with the study of the infrared absorption spectra of some coordination compounds of silicon and germanium tetrahalides. Unlike carbon, the other elements of Group IV can expand their valencies presumably by making use of available d-orbitals. Thus a tetrahalide, MX_4, can accept an unshared pair of electrons from a suitable donor or Lewis base, L, and form a coordination compound. The most common adducts found for the group IV halides are those with a tetrahalide to ligand mole ratio of one-to-two (viz. $MX_4 \cdot 2L$) for monodentate ligands, L, and a mole ratio of one-to-one (viz. $MX_4 \cdot LL$) for bidentate ligands, LL. In both cases, the configuration about the central atom is considered to be octahedral resulting from an sp^3d^2 hybridization of the atomic orbitals of the metal atom. Some one-to-one adducts with monodentate ligands (viz. $MX_4 \cdot L$) have also been prepared. In these compounds, either the central metal is pentacoordinated or the octahedral structure is obtained through halogen bridging (2).

A large number of amine complexes of the Group IV tetrahalides have been prepared and characterized and found, in general, to be very stable. For these reasons, it was decided that amine, and in particular, tertiary amine, adducts of SiX_4 and GeX_4 would be used for the present infrared study. Primary and secondary amines, and ammonia, react with SiX_4 or GeX_4, other than the tetrafluorides, forming substitution compounds rather than adducts (7,8). The tertiary amine adducts that will be dealt with in this dissertation are those of pyridine, isoquinoline, 2,2'-dipyridyl and tetramethylethylenediamine.

Structure and Bonding

Although many addition compounds of the Group IV tetrahalides have been prepared, comparatively little work has been done on the stereochemistry of the adducts. As mentioned previously in the one-to-one adducts of monodentate ligands, the metal atom is either pentacoordinated, resulting in a monomer, $MX_4 \cdot L$, or is octahedrally coordinated through halogen bridging, resulting in a dimer, $M_2X_8 \cdot 2L$, or higher polymers. Rivest (9) has studied a number of one-to-one adducts of titanium tetrachloride and found these to be polymeric, thus indicating halogen bridging.

In the case of the one-to-two adducts, there exists the possibility of cis-trans isomerism as shown in the following diagram.



The one-to-one adducts of bidentate ligands are thought to be cis complexes because of the inability of the ligand to span the trans positions.

Some of the experimental methods available for the determination of molecular structure of coordination compounds are: X-ray diffraction, nuclear magnetic resonance, Raman and infrared spectroscopy. These and other techniques have been used for stereochemical studies of some Group IV coordination compounds. The results are summarized briefly under separate headings, as follows.

X-ray Diffraction

The structures of a number of hexahalo ions, MX_6^{-2}, of Group IV (which may be regarded as adducts between MX_4 and $2X^-$) have been determined by X-ray diffraction studies. These include SiF_6^{-2}, GeF_6^{-2} and $GeCl_6^{-2}$ (10, 11, 12). In each case, it has been confirmed that the anions possess a symmetrical octahedral structure. The same results have been found for the complex halides of tin (13).

Although no systematic x-ray studies of MX_4 adducts have yet been made, some valuable structural information has recently been obtained. For example, the adduct between pyridine and trimethyltin chloride (viz. $Me_3ClSn{\cdot}Py$) has been shown by an x-ray analysis to possess an unsymmetrical trigonal bipyramid structure (14). The three methyl groups lie in the equitorial plane of the molecule and the chlorine and pyridine are in axial positions. The tin atom has thus been shown to be pentacoordinated in this adduct.

The phosphoryl chloride adduct of titanium tetrachloride ($TiCl_4{\cdot}POCl_3$) has been shown, by X-ray diffraction, to be a dimer (15). Double chlorine bridges exist between two titanium atoms so that there is an octahedral arrangement of bonds about each titanium atom. This is in agreement with the work of Rivest (9) who found polymeric adducts of $TiCl_4$ with substituted ureas.

The problem of cis-trans isomerism in the $MX_4{\cdot}2L$ coordination compounds has not yet been thoroughly studied by X-ray methods. The only complexes whose configurations have been established by X-ray measurements are $SnCl_4{\cdot}2POCl_3$ which is cis octahedral, and $GeCl_4{\cdot}2Py$, which is trans (16, 17).

Although X-ray diffraction is an exceedingly valuable tool for structural studies, it has two major drawbacks. Firstly, structural studies usually take a great deal of time, particularly when dealing with crystals of low symmetry. Secondly, diffraction patterns must be obtained for complexes in single crystal form which is usually very difficult to prepare.

NMR Spectroscopy

Nuclear magnetic resonance spectroscopy has been used to elucidate the structure of a number of tin and titanium tetrafluoride complexes utilizing the spin of F^{19} (18). On the basis of the splitting of the fluorine chemical shift into two peaks, indicative of two different environments of the fluorine atoms, it was concluded that these adducts have the cis octahedral configuration. These experiments were carried out in solution, however, and there exists the possibility of partial dissociation of a trans adduct (dissociation is common in the tin halide complexes (19, 20) resulting in two kinds of fluorine atom configurations in solution - square planar in the adduct and tetrahedral in free MF_4.

Brown and Kubota (20) have pointed out that it is necessary to carry out additional measurements, such as molecular weight determinations, in order to test for possible dissociation of the adducts. This is because NMR spectral studies must be made on dilute solutions of the complexes in inert solvents. In addition to the dissociation problems in solutions, most of the adducts of MX_4 have a very low solubility in the common organic solvents (2, 21).

Raman Spectroscopy

The use of Raman spectroscopy in studying the stereochemistry of group IV tetrahalide complexes has been limited to the complex hexahalo ions, SiF_6^{-2} (22, GeF_6^{-2} (23), SnF_6^{-2} (24), $SnCl_6^{-2}$ (25),

$PbCl_6^{-2}$ (26) and $TiCl_6^{-2}$ (22).

The spectra of the fluorides were obtained in aqueous hydrofluoric acid, those of the chlorides in aqueous hydrochloric acid and the bromide in aqueous hydrobromic acid. In each system the species in solution was the dibasic acid, H_2MX_6. The Raman results showed that the ions possessed regular octahedral symmetry around the central atom. This agrees with the X-ray diffraction studies carried out on salts of these anions.

The most serious difficulty in the use of Raman spectroscopy in studying the structures of adducts of MX_4 is that the materials to be studied must be either in solution or in the vapour phase. As mentioned previously, most of the MX_4 complexes are insoluble in inert solvents and, in addition, most dissociate completely on being heated in a vacuum (2). Thus Raman, like the X-ray and NMR techniques, has major limitations in structural investigations of MX_4 complexes.

Infrared Spectroscopy

There have been a number of infrared investigations of coordination compounds of MX_4. These investigations can be divided into two groups: (i) studies of the nature of the bonding between MX_4 and the ligands, and (ii) studies concerning the structures of the adducts.

The titanium tetrachloride (27) and silicon tetrafluoride (28) complexes with dimethyl formamide, a ligand which can coordinate through the oxygen or nitrogen atoms, provide good examples of the type of bonding. The infrared spectra of these adducts reveal that the carbonyl ($C = O$) stretching frequency is reduced compared with that of the free ligand. This indicates that the electron density of the carbonyl bond has been decreased on coordination, strongly suggesting that bonding takes place through the oxygen atom. Similar studies have been made on urea and thiourea complexes of MX_4 (29, 30) and on a number of ethyl acetate complexes (31).

Infrared spectroscopy has also been used to show the relative acceptor properties of some of the Group IV tetrahalides. Sheldon and Tyree (32, 33), for example, studied the interactions of phosphorous and selenium oxychloride ligands with tin and silicon tetrachlorides. With $SnCl_4$, major frequency shifts in the P = O and Se = O stretching vibrations were observed. On the other hand, there were no frequency changes observed in the spectra of the ligands dissolved in pure $SiCl_4$, indicating that $SnCl_4$ is a much stronger Lewis acid than $SiCl_4$. Similar results were obtained by Lappert and Smith using dimethyl sulphoxide (34).

Information regarding the nature of the bonding in the Group IV adducts can be derived from measurements made in the rock salt region (4000 to 650 cm^{-1}.) of the infrared spectrum only if suitable ligand bands appear in this region. In order to observe the frequencies of the metal-halogen and metal-donor atom bonds, and hence obtain structural data, it is necessary to go to lower frequencies. The potassium bromide region extends to 400 cm^{-1}., caesium bromide to 260 cm^{-1}. and caesium iodide to 200 cm^{-1}. This appears to be the practical limit for prism optics but recently Carlson (35), using a grating instrument, was able to achieve 75 cm^{-1}..

Low frequency infrared spectroscopy has been used to great advantage in studying the stereochemistry of $MX_4 \cdot 2L$ complexes. Assuming the ligands to have spherical symmetry, the molecular point group of the trans adduct is D_{4h} and that of the cis adduct is C_{2v}. Therefore marked differences will be observed in the spectra of the complexes in the region where the metal-halogen and metal-donor atom vibrational frequencies occur. In addition, infrared spectra of the solid complexes, as mulls or KBr discs, are readily obtained. This gives infrared spectroscopy a marked advantage over most of the other methods of determining structure which require the complex to be in dilute solutions or the vapour phase.

Beattie et al have measured the low frequency infrared spectra of several Group IV addition compounds. They compared the spectra of trans-$GeCl_4 \cdot 2Py$ with the cis adducts of $GeCl_4$ and 1,10-phenanthroline and 2,2'-dipyridyl (bidentate ligands) and observed one Ge-Cl stretching frequency for the trans adduct, two broad absorption bands for the 2,2'-dipyridyl adduct and three bands for the 1,10-phenanthroline adduct (19). In addition, they have shown that the silicon tetrachloride and tetrabromide adducts of pyridine (viz. $SiCl_4 \cdot 2Py$ and $SiBr_4 \cdot 2Py$) have the cis-octahedral structure (36). These results were based on a comparison of the infrared spectra of these adducts with those of the corresponding 1,10-phenanthroline and 2,2'-dipyridyl adducts.

Clark (37) has studied the infrared spectrum of the 2,2'-dipyridyl adduct of $TiCl_4$ in the CsBr region and found three Ti-Cl stretching bands. Similar results have been obtained by Gutmann et al (38) for a number of adducts of SiF_4 with various amines including 2,2'-dipyridyl. One Si-F stretching band was observed for the monodentate ligand complexes and two for the bidentate ligand complexes. Guertin (39) observed two broad bands due to Si-F stretching vibrations in the spectrum of the ethylenediamine complex of SiF_4. The ammonia adduct of SiF_4, on the other hand, showed only one Si-F stretching frequency (28).

Symmetry properties of molecules and ions are an invaluable aid in the study of infrared and Raman spectroscopy. A great deal of useful information can be gained from considerations of molecular geometry and symmetry (40). For example, the number of fundamental frequencies, their degeneracies, and the shapes of the normal modes corresponding to each frequency can be determined. In addition, the selection rules for both infrared and Raman spectra, covering the overtone and combination frequencies as well as the fundamentals, can readily be obtained from a symmetry analysis. The magnitudes of the frequency and the amplitude of a given vibration, however, cannot be derived from symmetry alone, although the use of symmetry greatly reduces the difficulties in calculating these quantities.

The present study will be concerned firstly with the determination of the metal-halogen vibrational frequencies, and secondly, utilizing these frequencies, with the determination of the structures of the complexes. The use of infrared absorption measurements in differentiating between cis and trans octahedral adducts has been demonstrated recently by Beattie et al (19, 36) who have shown the existence of cis-$SiCl_4$•2Py, trans-$GeCl_4$•2Py and trans-$SnCl_4$•2Py. In the present study, attempts will be made to explain these and other experimental results on the basis of symmetry and group theoretical considerations.

A full symmetry analysis of the cis and trans isomers of the Group IV tetrahalide complexes will be described and comparisons of the symmetry predictions and the experimental results will be shown. Assignments of the infrared absorption frequencies will be made and then utilized in determining the stereochemistry of the pyridine, isoquinoline, 2,2'-dipyridyl and tetramethylethylenediamine adducts of the fluorides, chlorides and bromides of tetracovalent silicon and germanium.

EXPERIMENTAL

The following electron-pair donors (Lewis bases) were used in reactions with the tetrahalides (Lewis acids): pyridine (Py), isoquinoline (IQ), 2,2'-dipyridyl (dipy), tetramethylethylenediamine (enMe$_4$), dimethyl formamide (DMF), triethylamine (Et$_3$N), dimethyl aniline (DMA), N-methyl pyrrole (MP) and pyrrole (Pyr.), and the following reactions were studied:

Silicon tetrafluoride (SiF_4) with IQ, dipy and Pyr.
Silicon tetrachloride ($SiCl_4$) with Py, IQ, dipy
Silicon tetrabromide ($SiBr_4$) with Py, IQ, dipy
Germanium tetrafluoride (GeF_4) with Py, IQ, dipy, enMe$_4$
Germanium tetrachloride ($GeCl_4$) with all bases except pyrrole
Germanium tetrabromide ($GeBr_4$) with Py, IQ, dipy.

Purification of Materials

(1) Lewis Bases

All Lewis bases, except 2,2'-dipyridyl, were distilled (usually twice) from calcium hydride in an atmosphere of dry nitrogen. The use of nitrogen was especially necessary in the distillation of isoquinoline which oxidizes in air even at room temperature. In all cases, the boiling points were in close agreement with those given in the literature. It was not necessary to purify the 2,2'-dipyridyl because its melting point (70-71°) compared favourably with the literature value of 69.7° (41) and an infrared spectrum revealed no impurities.

(2) Lewis Acids

Of the six Lewis acids, three were used directly and three were purified. Those used directly were $GeCl_4$ (Germanium Research Institute-Electronic grade), $GeBr_4$ (Chemicals Procurement-99.999%) and $SiBr_4$ (Anderson-Purified). Silicon tetrachloride (Fisher-Practical) was distilled twice from copper turnings. The boiling point was 57.0-57.3° compared to the literature value of 57.57° (42).

Silicon tetrafluoride (Matheson), a gas at room temperature, was purified by first bubbling it through concentrated sulphuric acid and then through a -78°C trap. Its purity was checked by vapour pressure and molecular weight measurements.

Germanium tetrafluoride was prepared by the thermal decomposition of barium hexafluogermanate according to the method of Dennis (43). It was purified in a vacuum system as follows. The bulk of any SiF_4 impurity was removed from crude GeF_4 by several distillations at -130°C. The residue of the first distillation was then condensed at -96°C with repeated flashing off of the vapours. An infrared spectrum of the purified GeF_4, measured in a gas cell equipped with KBr windows, was identical with that of a pure sample.

(3) Solvents

Carbon tetrachloride, benzene and n-hexane, used as solvents for the various preparations, were dried over calcium hydride and then fractionally distilled.

Preparations of Adducts

The free tetrahalides of Group IV and their addition compounds are very hygroscopic. To prevent hydrolysis all manipulations of MX_4 and their adducts were carried out in a dry box containing dry nitrogen or, for gaseous MX_4 compounds, in a high vacuum system. In addition, equipment such as flasks, syringes, etc., were thoroughly dried prior to use.

(1) Precipitation from Solution

Adducts of $SiCl_4$, $SiBr_4$, $GeCl_4$ and $GeBr_4$ were prepared by adding solutions of the Lewis acid to solutions of the Lewis base. The concentration of each solution was such as to insure a slight excess of base and to yield 2 to 3 g. of complex.

Upon combining the two solutions, immediate precipitation of white solids occurred except in the case of the $GeBr_4$ adducts all of which were pale yellow. The precipitates were filtered on scintered glass funnels in the dry box and washed with pure solvent and in some cases with anhydrous ether. They were dried by suction using an oil pump equipped with a liquid air trap. This method of preparation was simple and convenient.

The complex salt, caesium hexachlorogermanate (Cs_2GeCl_6) was prepared from $GeCl_4$ and CsCl according to the method of Fialkov (44).

(2) Silicon Tetrafluoride Bubbling

Adducts of silicon tetrafluoride with 2,2'-dipyridyl and isoquinoline were obtained by bubbling purified SiF_4 into n-hexane solutions of the base. The concentrations of the solutions were adjusted to yield approximately one gram of complex. The white precipitates obtained in each case were filtered in the dry box as previously described.

(3) Germanium Tetrafluoride Condensation

Adducts between GeF_4 and 2,2'-dipyridyl, isoquinoline and tetramethylethylenediamine were prepared in a high vacuum system by condensation of the Lewis acid onto a n-hexane solution of the base. Germanium tetrafluoride was condensed at liquid air temperature and the mixture was allowed to warm to -450 at which temperature a precipitate was observed. The system was recooled with liquid air and then slowly warmed to room temperature to insure complete consumption of GeF_4.

In the preparations of GeF_4•dipy and GeF_4•enMe$_4$, solvent and any unreacted fluoride were removed by pumping in the vacuum system. The solid product was then removed from the reaction flask in the dry box. The infrared spectrum of the GeF_4•dipy complex showed the presence of a small amount of unreacted (free) ligand. The spectrum of the GeF_4•enMe$_4$ complex, on the other hand, revealed that there was no excess base in the sample. The GeF_4•2IQ adduct was separated from the solvent and any unreacted starting material by filtration in the dry box.

Chemical Analysis

Halogen determinations were done on most of the complexes. The fluorine content of SiF_4•2IQ and SiF_4•dipy was obtained according to the method of Belcher (45). Potentiometric titrations using a silver-silver halide electrode and standard silver nitrate were done on the chloride and bromide adducts. Since pyridine and other strong Lewis bases readily complex with silver ion and thus interfere with the analysis, it was necessary to remove these ligands before titrating with silver nitrate.

A weighed sample of the material to be analysed was carefully dissolved in water. The solution was made alkaline with potassium hydroxide and then heated to just below the boiling point for a few hours. During the heating process (a form of steam distillation) the characteristic odours of the ligands were observed, strongly at first and then gradually disappearing. Hydrolysis occurred as follows,

$$MX_4 \cdot 2L + 2H_2O \longrightarrow MO_2 + 2LHX + 2HX$$

$$2LHX + 2HX + 4KOH \longrightarrow 4KX + 2L + 4H_2O$$

where LHX is the amine hydrohalide. The resulting solution of potassium halide was acidified to a pH of 4-5 and titrated with standard silver nitrate solution.

Infrared Spectra

A Perkin-Elmer Infracord double-beam spectrometer equipped with sodium chloride optics was used to record spectra of all compounds over the frequency range 3800-650^{-1}. A dual-grating Perkin-Elmer model 421 spectrometer was also used over this range when higher resolution and accuracy were required. Calibration of the instruments was checked using a standard polystyrene film. For the low wavenumber spectra, 714-263 cm^{-1}., the model 421 was equipped with caesium bromide optics. Prior to measurement of a spectrum in this range, the instrument was thoroughly flushed out with dry air, using a compressor pump and "Drierite" and silica gel columns. This was necessary to maintain the lowest possible concentration of water vapour in order to minimize infrared energy loss and to provide additional protection for the caesium bromide prism.

Spectra were obtained as nujol mulls spread between sodium chloride plates in the high frequency range and between caesium bromide plates in the low frequency range. Samples were prepared in the dry box. To protect the caesium bromide plates (which are easily scratched and readily susceptible to hydrolysis), thin films of polyethylene (Dow Chemical Co. "Handiwrap") were used. This material shows no absorption bands below 700 cm^{-1}. and permits approximately 75-80% transmittance. In addition, it is inexpensive and convenient to use with nujol mulls.

The spectra of a few complexes were measured as KBr discs. Thin discs of infrared quality KBr have a useful frequency range from 4000 cm^{-1}. to 263 cm^{-1}. although increased absorption was observed near 300 cm^{-1}. However, such discs showed weak absorption bands at 3400 and 1650 cm^{-1}., due to water, which is almost impossible to remove completely.

The spectra of all ligands, except 2,2'-dipyridyl, were obtained as liquid capillary films between sodium chloride and caesium bromide plates. The nujol mull technique was used for 2,2'-dipyridyl.

Spectra of the complexes in dilute solutions were not obtained because of their low solubility in inert organic solvents and spectra as thin sublimed solid films were not obtained because of a lack of a suitable low temperature infrared cell.

RESULTS

General Results

Table I contains the analytical results of those complexes for which halogen determinations were done, and the infrared results (NaCl region) of all the adducts. The term "good spectrum" signifies that the spectrum compares well with that of the free ligand and the corresponding $GeCl_4$ adduct (which because of the good analytical data, was taken as a standard of comparison) and shows no bands around 2500 cm^{-1}. due to the hydrolysis product - the amine hydrohalide salt.

Nuttall et al (46) observed a strong absorption band in the spectrum pyridinium chloride at 2450 cm^{-1}. and in the spectrum of the corresponding bromide at 2650 cm^{-1}. These bands are due to the N-H stretching vibration and the difference in frequency between the chloride and the bromide was attributed to stronger hydrogen bonding in the chloride salt.

In this work the hydrobromide salts of isoquinoline and 2,2'-dipyridyl were prepared and their spectra showed strong absorption bands at 2640 cm^{-1}. and 2580 cm^{-1}., respectively. In the spectra of $SiBr_4 \cdot 2IQ$ and $GeBr_4 \cdot 2IQ$ there was a strong band at 2640 cm^{-1}. and in the spectrum of $SiBr_4 \cdot dipy$, there was a band at 2580 cm^{-1}., indicating the presence of hydrolysis product impurities. For this reason, spectra in the CsBr region of the two amine hydrobromides were measured and in this way the infrared bands due to hydro halide impurities in the spectra of the complexes were identified and accounted for.

If a coordination compound is being reported for the first time, the word "new" appears in the reference column in Table I. If an adduct has been prepared before, the literature reference is given.

TABLE I

Analytical and Infracord Results

Complex	% Halogen Content		General Infrared Results	Reference
	Found	Calc.		
SiF_4·2IQ	28.93	29.19	Good Spectrum	47
SiF_4·dipy	20.23	20.97	" "	38
$SiCl_4$·2Py	42.60	43.22	" "	48
$SiCl_4$·2IQ	32.84	33.11	" "	47
$SiCl_4$·dipy	41.65	43.47	" "	47
$SiBr_4$·2Py	-	63.19	" "	36
$SiBr_4$·2IQ	-	52.76	Contains Some H.P.*	47
$SiBr_4$·dipy	-	63.45	" " "	47
GeF_4·2Py	-	24.77	Good Spectrum	49
GeF_4·2IQ	-	18.68	" "	New
GeF_4·dipy	-	24.93	" "	New
GeF_4·enMe$_4$	-	28.70	Unknown **	New
$GeCl_4$·2Py	37.95	37.98	Standard	50
$GeCl_4$·2IQ	29.97	30.02	"	New
$GeCl_4$·dipy	38.30	38.27	"	51
$GeCl_4$·enMe$_4$	42.35	42.91	Unknown **	New
$GeCl_4$·2OMF	39.16	39.33	Standard	New
$GeBr_4$·2Py	57.10	58.08	Good Spectrum	51
$GeBr_4$·2IQ	48.18	49.12	Contains Some H.P*	New
$GeBr_4$·dipy	57.85	58.26	Good Spectrum	51

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*H.P. = Hydrolysis product. Spectrum shows some bands due to the amine-hydrobromide.

**Complex spectrum around 2500 cm^{-1}. for GeF_4·enMe$_4$ and $GeCl_4$·enMe$_4$.

In addition to the new compounds listed in Table I, the following new systems were investigated and found to produce no addition compound when the reactants were added together in an inert solvent at room temperature:

SiF_4 - pyrrole
$GeCl_4$ - triethylamine
$GeCl_4$ - N,N-Dimethylaniline
$GeCl_4$ - N-methylpyrrole

These results are in agreement with those of Beattie and Webster (52) who obtained no adduct in the $SiCl_4$-triethylamine system, and Piper and Rochow (28) who obtained no adduct in the $SiCl_4$-N,N-dimethylaniline system.

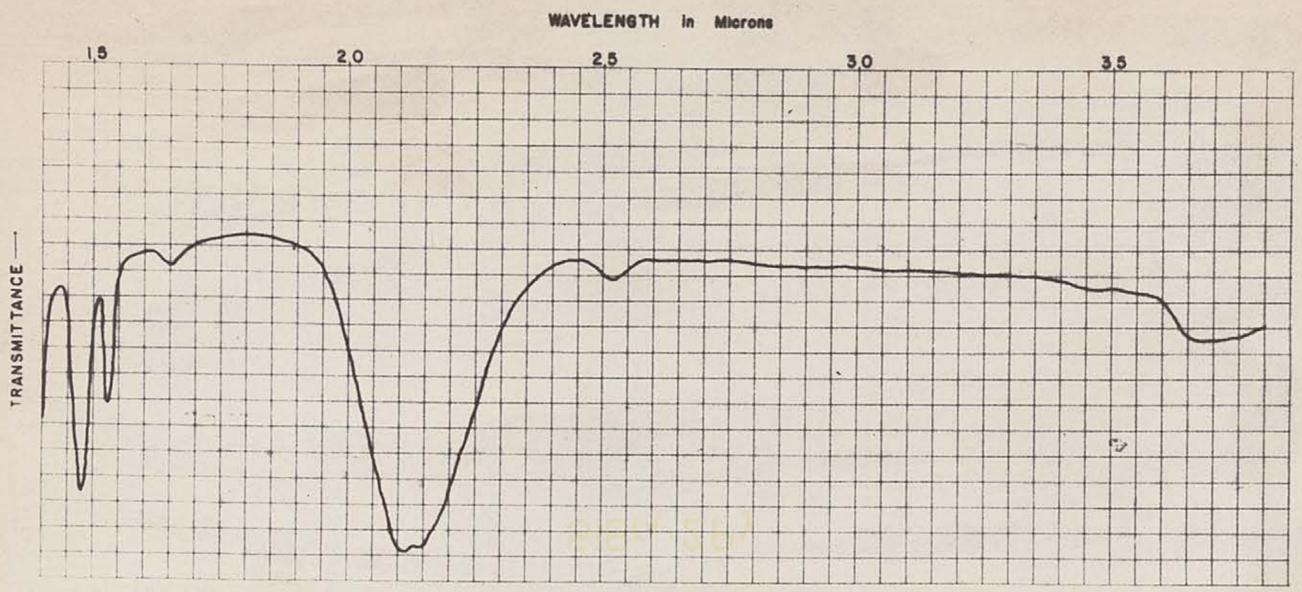
Infrared Results

The infrared spectra, in the CsBr region, of all the adducts listed in Table I are shown in Figures 1-7. The spectrum of SiF_4-2Py (Figure 1), taken from Guertin (39), has been included for comparison. In addition, the spectra in the NaCl region of the adducts, $SiF_4 \cdot 2IQ$ and $SiF_4 \cdot dipy$, are shown in Figure 8. Following each figure is a table containing the infrared band assignments of each spectrum.

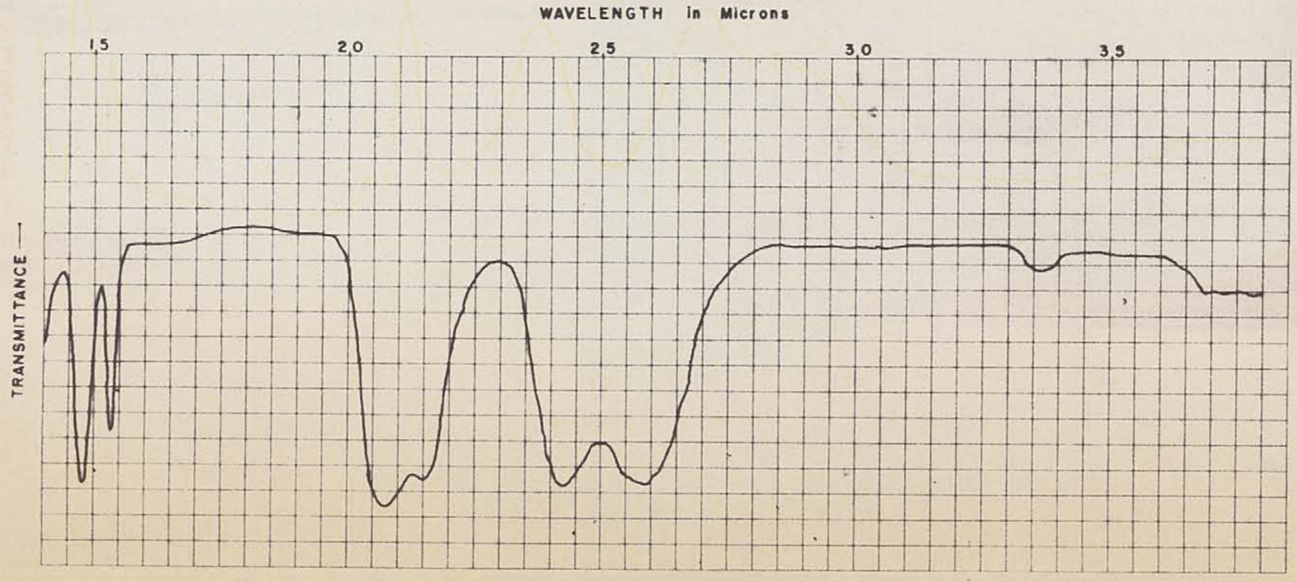
FIGURE 1

Infrared Spectra of the Pyridine Adducts of SiX_4

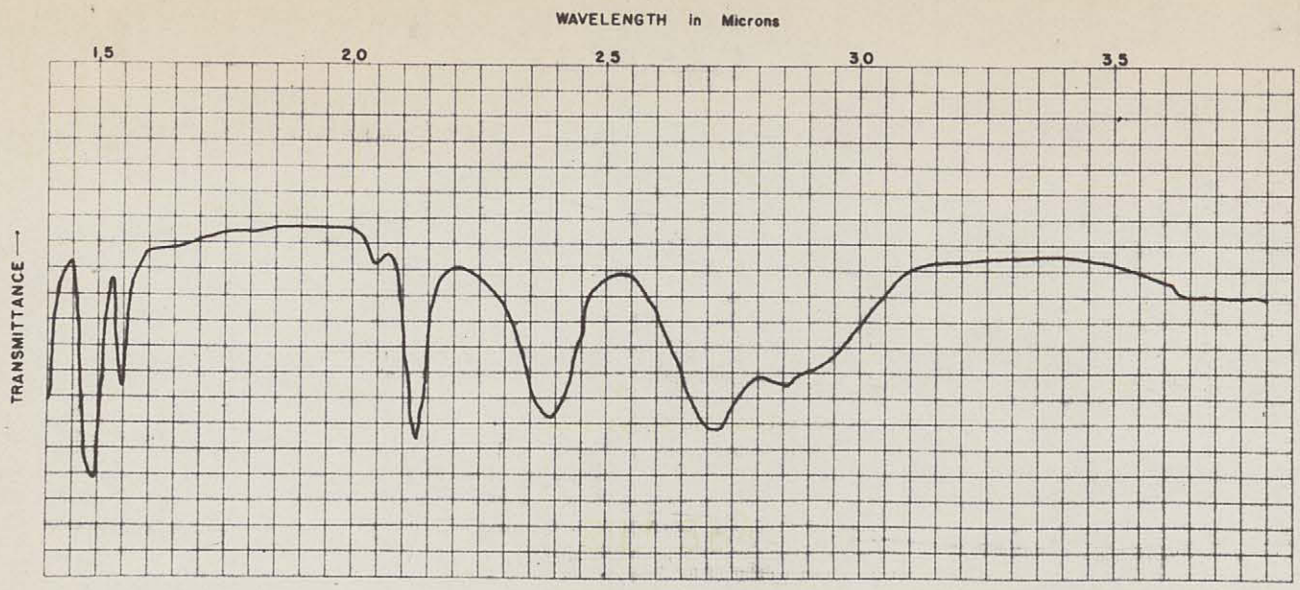
The Spectrum of $SiF_4 \cdot 2Py$ is that of Guertin (39).



$SiF_4 \cdot 2Py$



$SiCl_4 \cdot 2Py$



$SiBr_4 \cdot 2Py$

TABLE II

Infrared Bands of $SiX_4 \cdot 2Py$

$SiF_4 \cdot 2Py$

Wavelength (Microns)		Assignment
14.78	s	Ligand
15.27	m	"
16.52	w	"
21.10	vs	Si-F deformation
21.40	vs	Ligand
25.20	w	"

$SiCl_4 \cdot 2Py$

Wavelength (Microns)		
14.79	s	Ligand
15.32	m	"
16.50	vw	"
20.75	vs	Si-Cl stretch
21.50	vs	Ligand
24.25	vs	Si-Cl stretch
25.90	vs	" "
33.65	w	Unassigned*

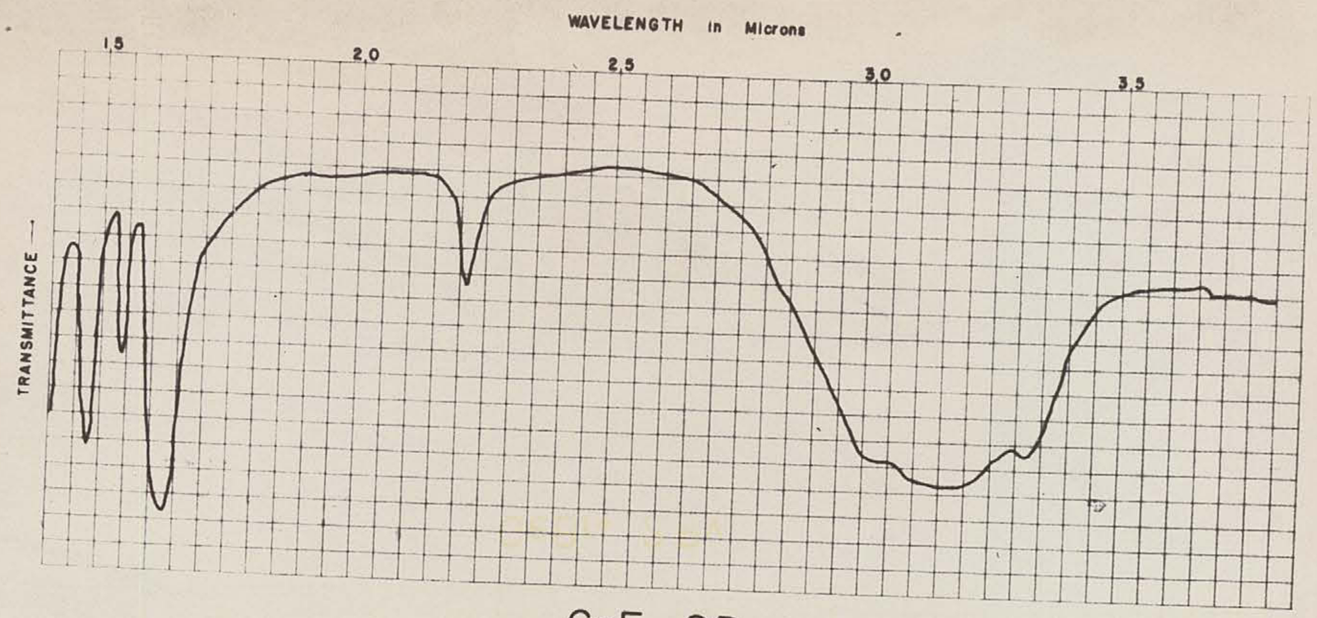
*See page 49 of the Discussion.

$SiBr_4 \cdot 2Py$

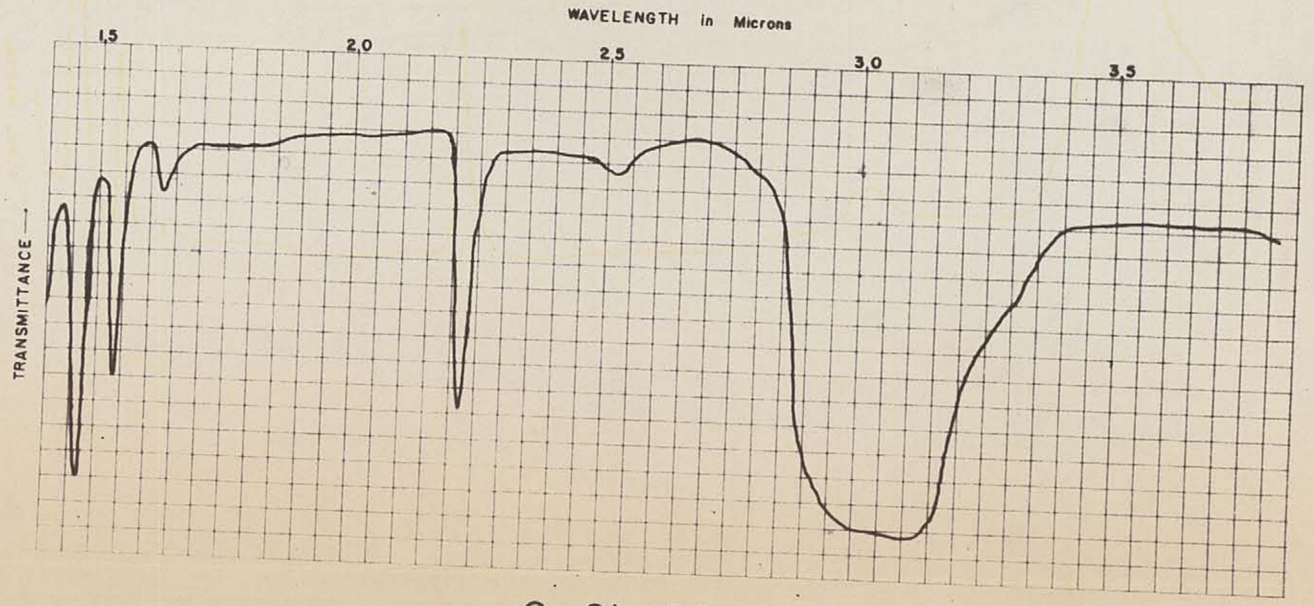
Wavelength (Microns)		
14.89	s	Ligand
15.46	m	"
16.60	vw	"
20.45	w	Unassigned
21.28	s	Ligand
23.90	s	Si-Br stretch
27.15	s	" "
28.60	s	" "

FIGURE 2

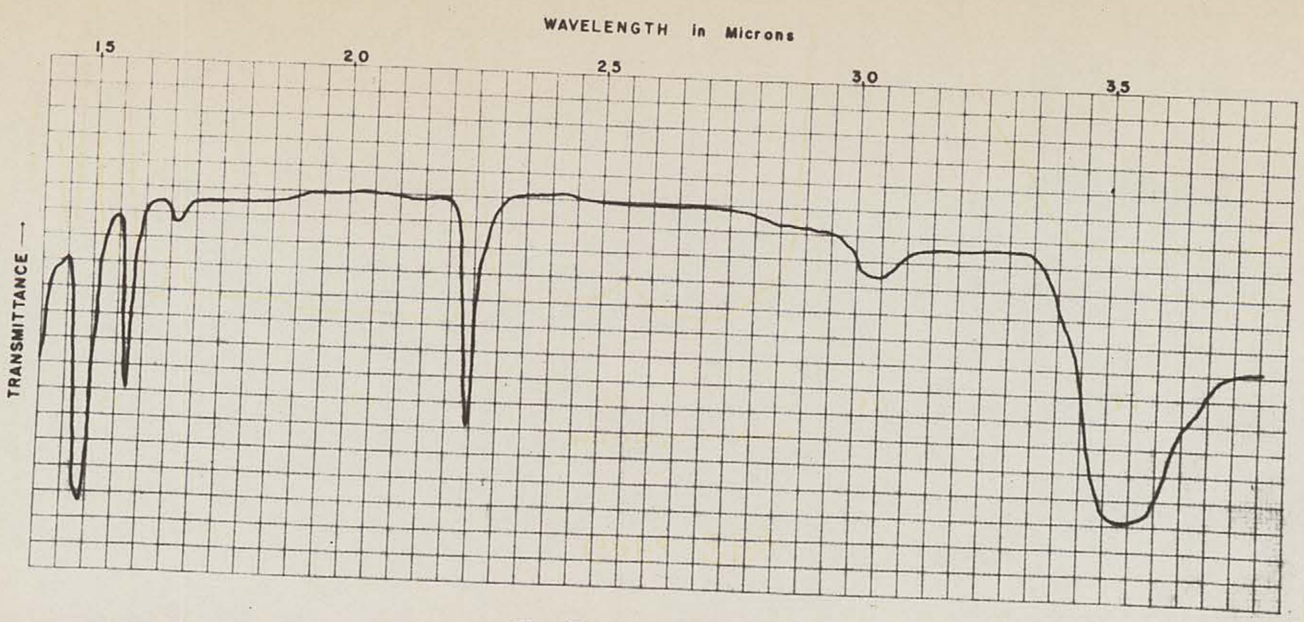
Infrared Spectra of the Pyridine Adducts of GeX_4



GeF$_4$ · 2Py



GeCl$_4$ · 2Py



GeBr$_4$ · 2Py

TABLE III

Infrared Bands of $GeX_4 \cdot 2Py$

$GeF_4 \cdot 2Py$

Wavelength (Microns)		Assignment
14.76	s	Ligand
15.40	m	"
16.28	vs	Ge-F stretch
22.13	m	Ligand
30.30	vs br.	see page 51 for the discussion of these bands
31.70	vs br.	
33.20	vs br.	

$GeCl_4 \cdot 2Py$

Wavelength (Microns)		
14.70	s	Ligand
15.35	m	"
16.25	w	"
22.20	s	"
25.20	w	"
30.60	s br.	Ge-Cl stretch

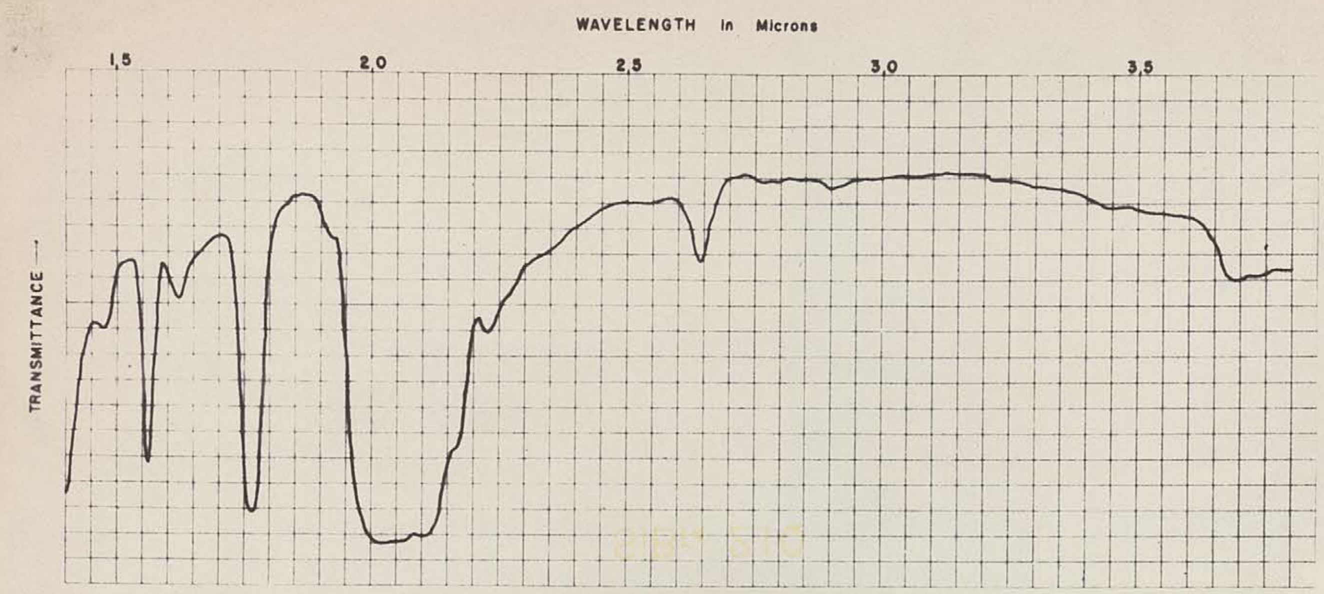
$GeBr_4 \cdot 2Py$

Wavelength (Microns)		
14.86	s	Ligand
15.60	m	"
16.60	w	"
22.42	s	"
30.40	w	Unassigned*
35.40	vs br.	G-Br stretch

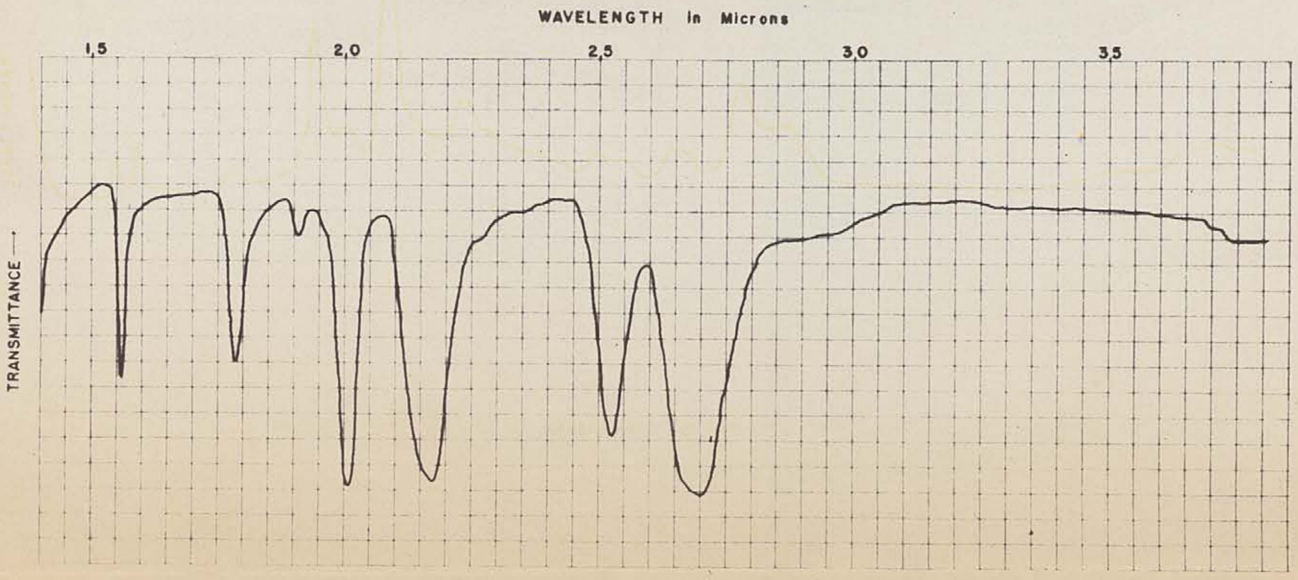
*See page 52 for a discussion of this band.

FIGURE 3

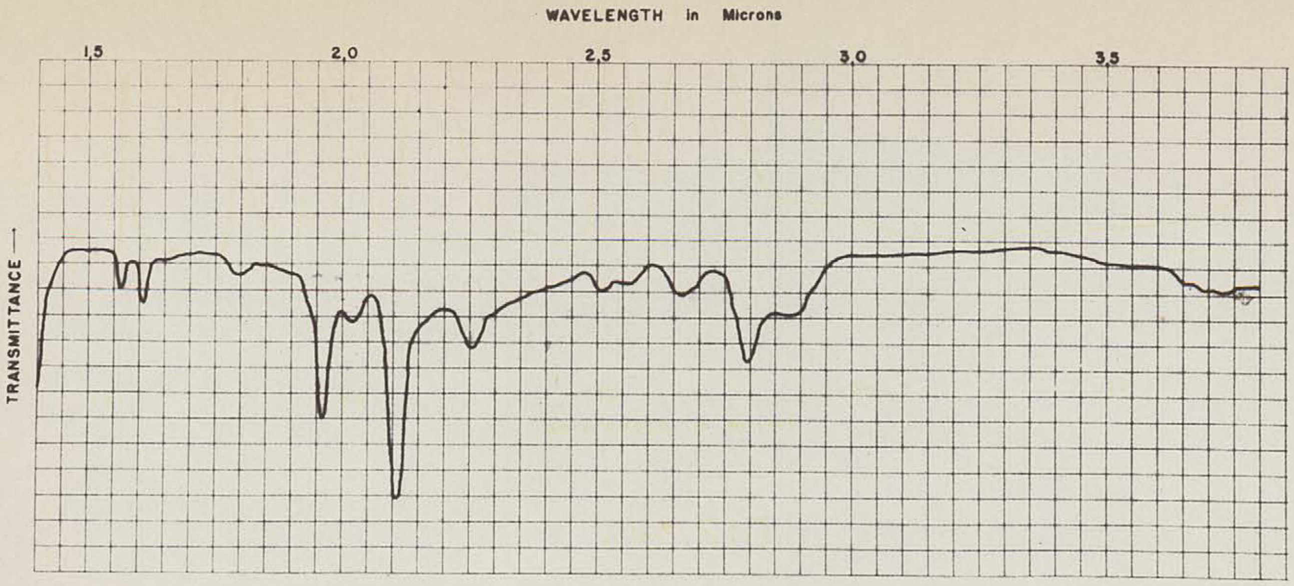
Infrared Spectra of the Isoquinoline Adducts of SiX_4



$SiF_4 \cdot 21Q$



$SiCl_4 \cdot 21Q$



$SiBr_4 \cdot 21Q$

TABLE IV

Infrared Bands of $SiX_4 \cdot 2IQ$

$SiF_4 \cdot 2IQ$

Wavelength (Microns)		Assignment
14.70	w	Ligand
15.60	s	"
16.28	w	"
17.65	s	"
19.25	w	"
20.40	vs br	Ligand + Si-F deformation
21.05	vs	Ligand
21.60	s	"
22.28	w	"
26.43	w	"
29.00	vw	"

$SiCl_4 \cdot 2IQ$

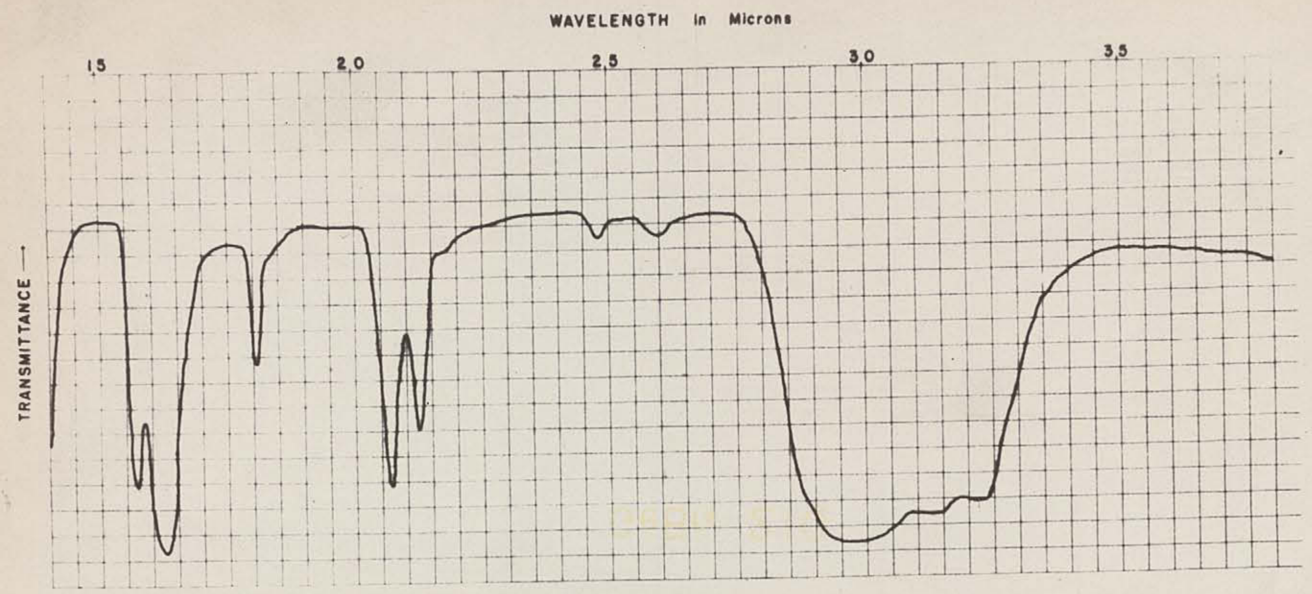
Wavelength (Microns)		
15.60	m	Ligand
17.85	m	"
19.10	w	"
20.08	vs	"
21.75	vs	"
22.50	w	"
25.25	s	"
27.00	vs	Si-Cl stretch
29.50	vw	Ligand

$SiBr_4 \cdot 2IQ$

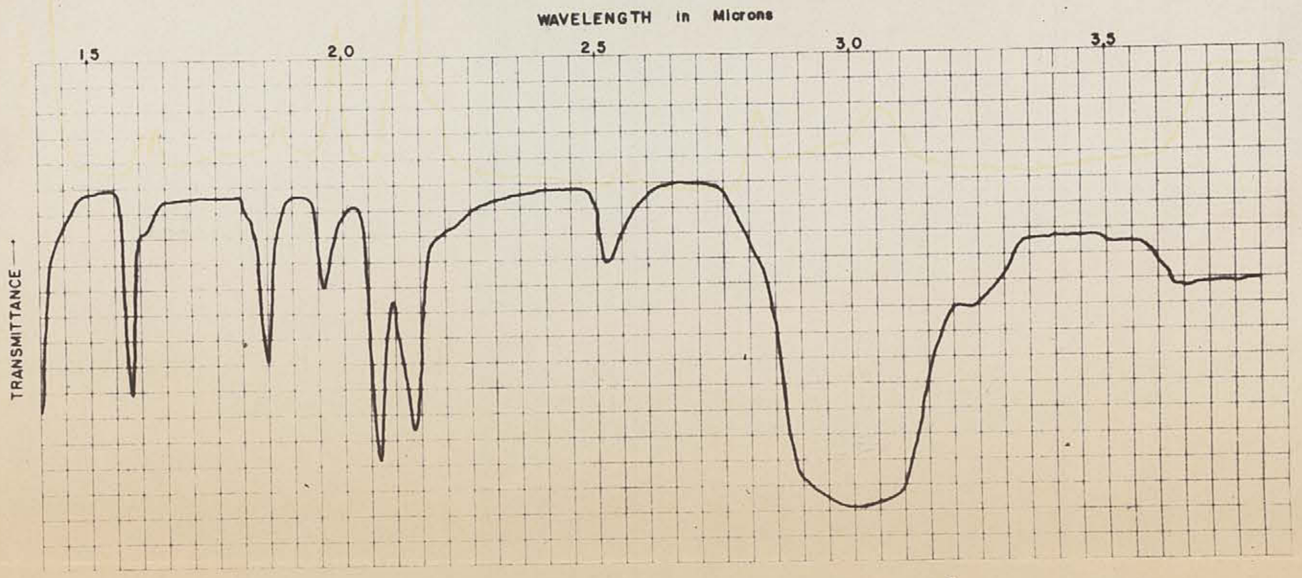
Wavelength (Microns)		
15.62	w	Ligand
16.10	w	Hydrolysis Product
17.95	w	Ligand
19.60	m	Hydrolysis Product
20.20	w	Ligand
21.07	s	Hydrolysis Product
22.55	m	Ligand
25.10	w	"
25.60	w	Hydrolysis Product
26.65	w	Ligand
27.92	m	Hydrolysis Product
28.80	m	Si-Br stretch

FIGURE 4

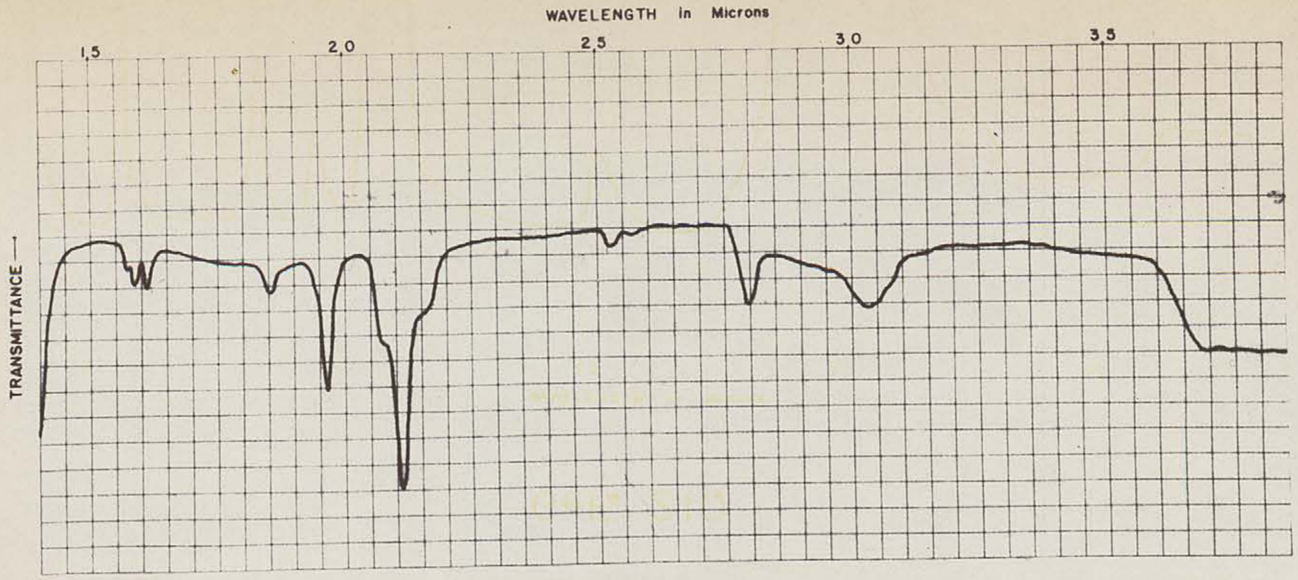
Infrared Spectra of the Isoquinoline Adducts of GeX_4



GeF$_4$ · 21Q



GeCl$_4$ · 21Q



GeBr$_4$ · 21Q

TABLE V

Infrared Bands of $GeX_4 \cdot 2IQ$

$GeF_4 \cdot 2IQ$

Wavelength (Microns)		Assignment
15.70	s	Ligand
16.25	vs	Ge-F stretch
18.05	m	Ligand
20.70	s	"
21.22	s	"
21.70	w	"
24.80	w	"
26.00	w	"
29.70	vs br	see page 57 for discussion of these bands.
31.20	vs br	
32.20	vs br	

$GeCl_4 \cdot 2IQ$

Wavelength (Microns)		
15.80	m	Ligand
16.05	w	"
18.50	m	"
19.60	m	"
20.68	s	Ligand
21.35	s	"
22.00	w	"
25.20	m	"
30.10	vs br	Ge-Cl stretch
32.30	m	Unassigned
36.40	w	"

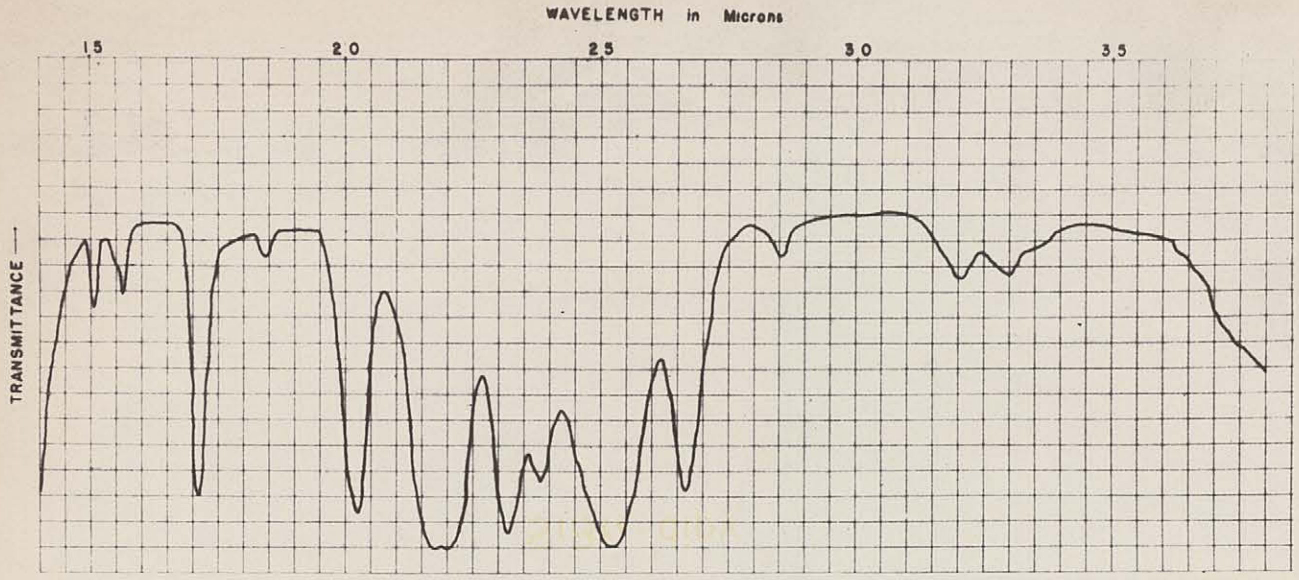
$GeBr_4 \cdot 2IQ$

Wavelength (Microns)		
15.70	w	Ligand
15.85	w	"
16.10	w	Hydrolysis Product
18.55	w	Ligand
19.62	m	Hydrolysis Product
20.80	m	Ligand
21.10	s	Hydrolysis Product
21.40	m	Ligand
25.25	w	"
25.70	vw	Hydrolysis Product
27.95	m	" "
30.30	m	Unassigned*
36.90	m	Ge-Br stretch

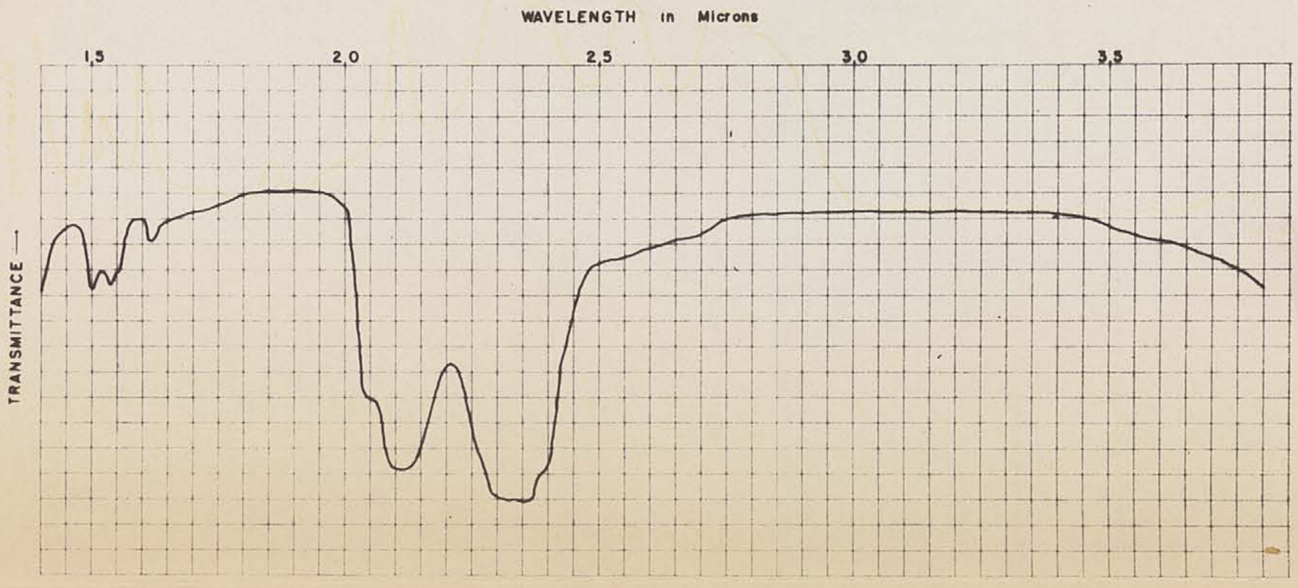
*See page 52 for the discussion of this band.

FIGURE 5

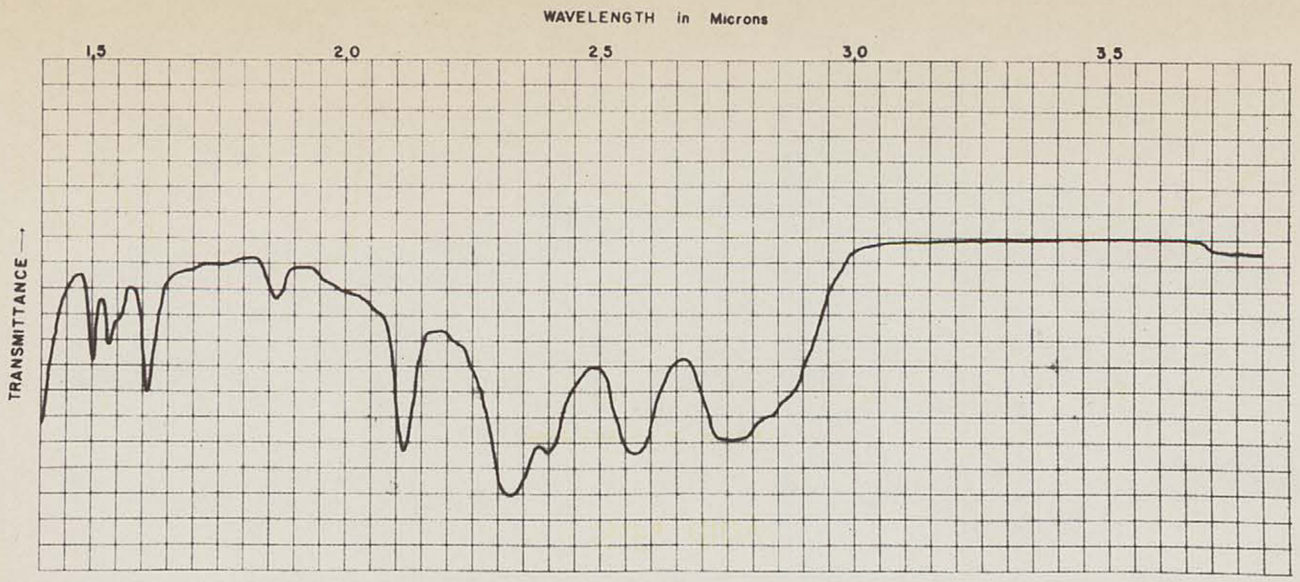
Infrared Spectra of the 2,2'-Dipyridyl Adducts of SiX_4



$\mathrm{SiF_4}\cdot$dipy



$\mathrm{SiCl_4}\cdot$dipy



$\mathrm{SiBr_4}\cdot$dipy

TABLE VI

Infrared Bands of SiX_4•dipy

SiF_4•dipy

Wavelength (Microns)		Assignment
15.06	w	Ligand
15.62	w	"
17.10	s	Si-F stretch
18.40	w	Ligand
20.25	s	Si-F deformation
21.75	vs	Ligand
20.00	vs	Si-F deformation
23.18	s	" "
23.80	s	Ligand
25.20	vs	Si-F deformation
26.65	vs	Unassigned*
28.55	w	"
32.05	w	"
33.00	w	"

*See page 59 for discussion of these bands.

$SiCl_4$•dipy

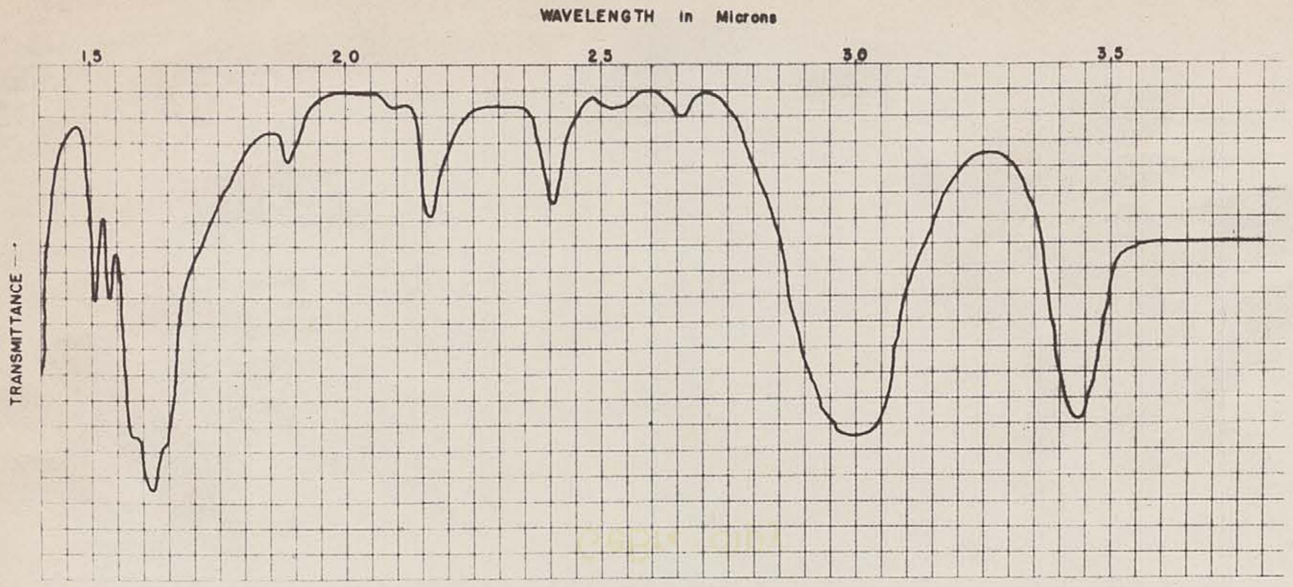
Wavelength (Microns)		
15.00	w	Ligand
15.40	w	"
16.17	w	"
20.60	s	"
21.15	s	Si-Cl stretch
23.20	vs	" "
23.55	vs	" "
23.85	s	Ligand

$SiBr_4$•dipy

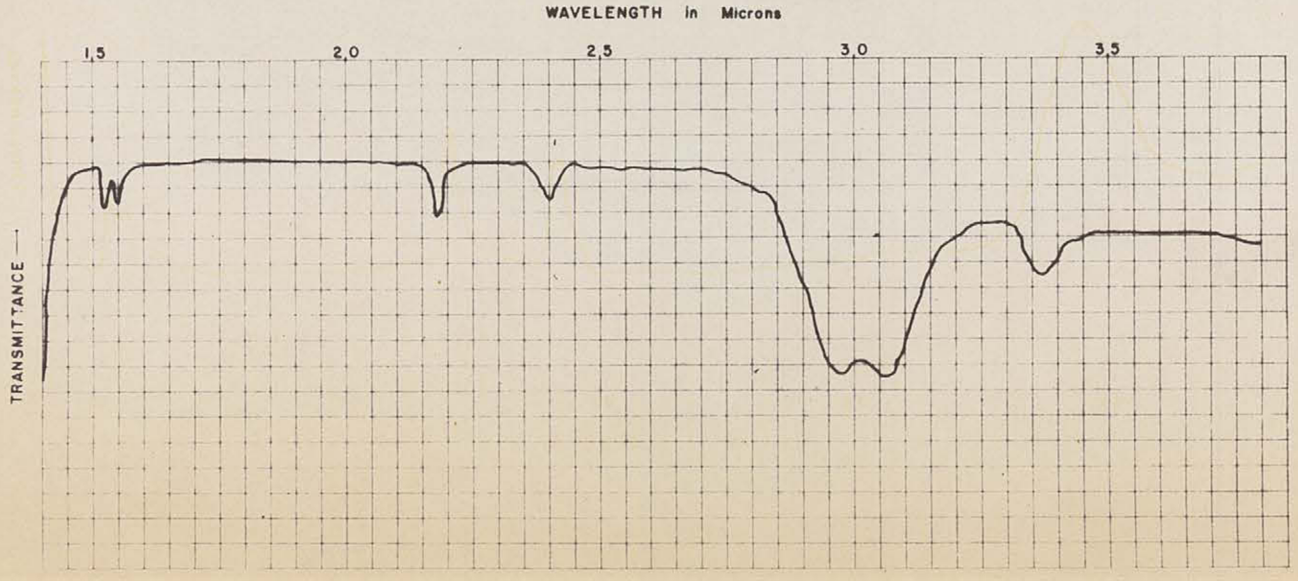
Wavelength (Microns)		
15.00	w	Ligand
15.33	w	"
16.10	m	"
18.65	w	"
21.15	s	"
23.25	vs	Si-Br stretch
24.00	s	Ligand
25.70	s	Si-Br stretch
27.60	s br	" "

FIGURE 6

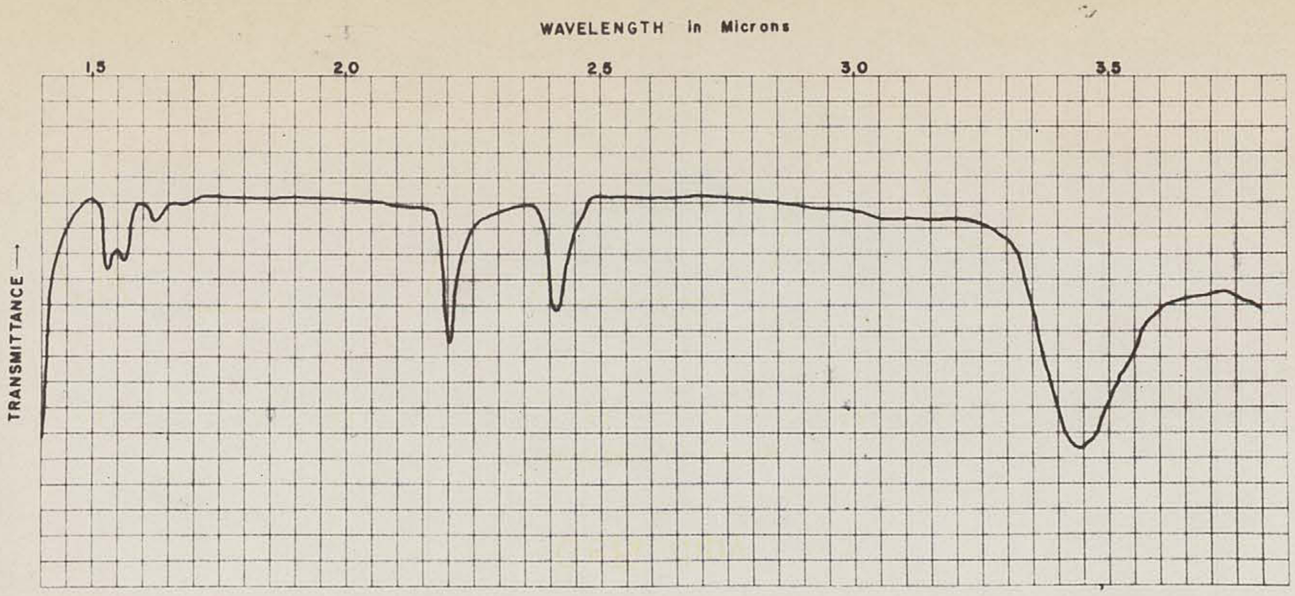
Infrared Spectra of the 2,2'-Dipyridyl Adducts of GeX_4



GeF$_4$ · dipy



GeCl$_4$ · dipy



GeBr$_4$ · dipy

TABLE VII

Infrared Bands of GeX_4•dipy

GeF_4•dipy

Wavelength (Microns)		Assignment
15.07	m	Ligand
15.35	m	"
15.80	s	Ge-F stretch
16.17	vs	" "
16.40	s	" "
18.85	w	" "
20.90	w	Ligand
21.65	m	"
24.05	m	"
25.20	w	Free ligand impurity
26.60	w	Ligand
30.00	vs br	Ge-F deformation
34.35	vs	" "

$GeCl_4$•dipy

Wavelength (Microns)		
15.20	w	Ligand
15.48	w	"
21.80	m	"
24.00	m	"
29.75	s	Ge-Cl stretch
30.60	s	" "
33.70	m	" "

$GeBr_4$•dipy

Wavelength (Microns)		
15.30	w	Ligand
15.62	w	"
16.22	vw	"
22.05	m	"
24.10	m	"
34.40	s br	Ge-Br stretch

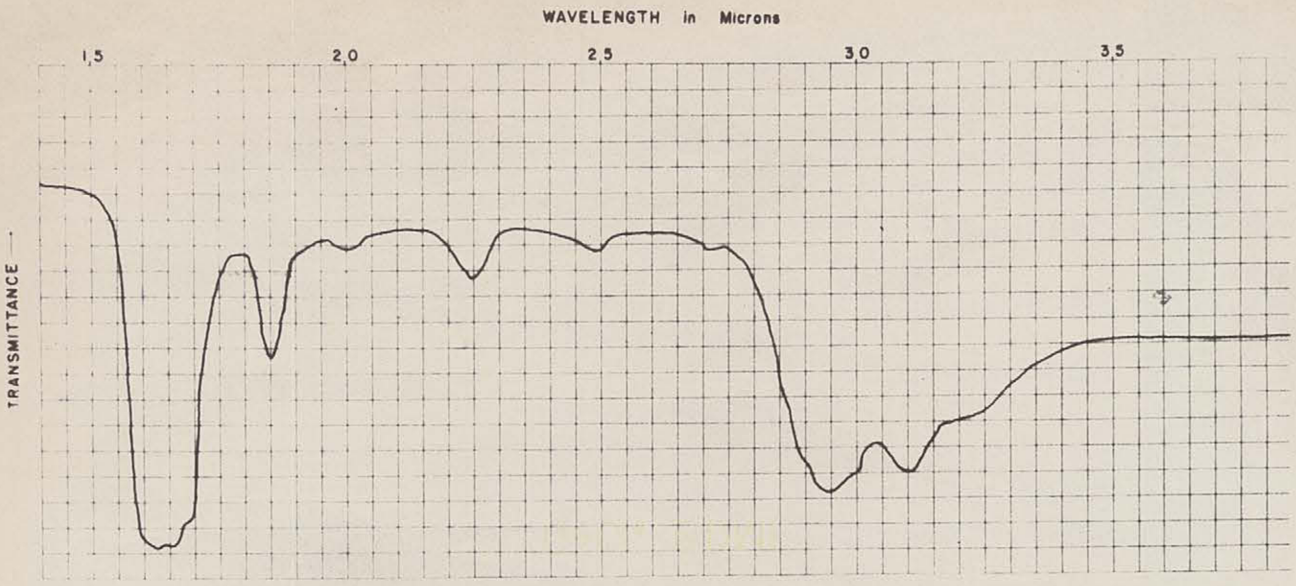
FIGURE 7

Infrared Spectra of the Adducts

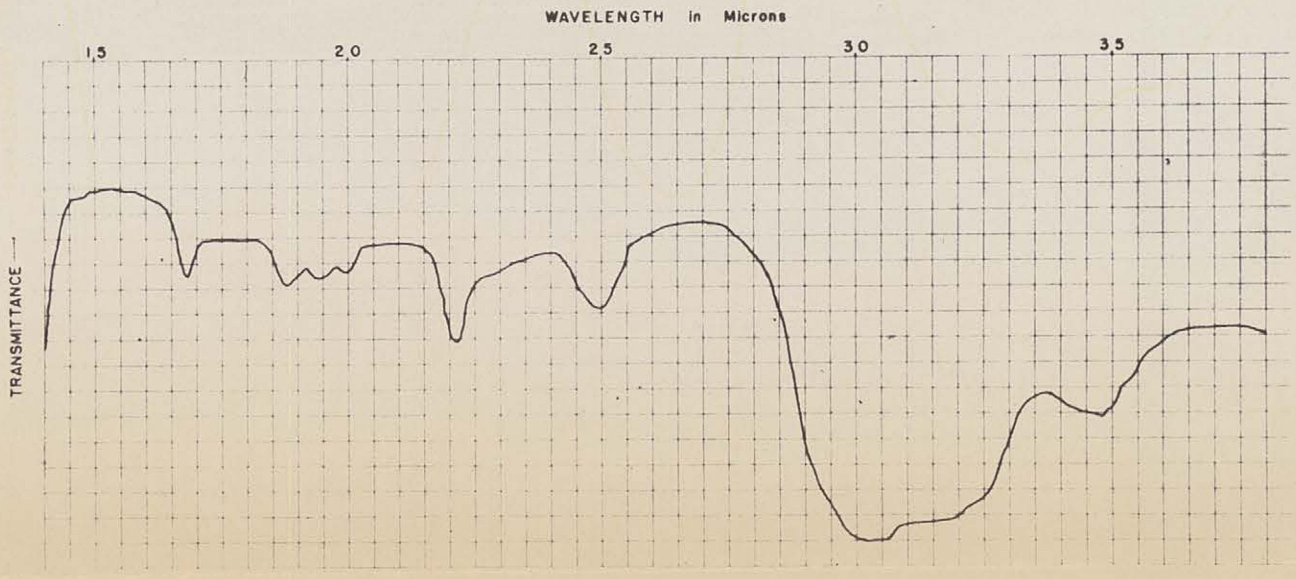
$GeF_4 \cdot enMe_4$

$GeCl_4 \cdot enMe_4$

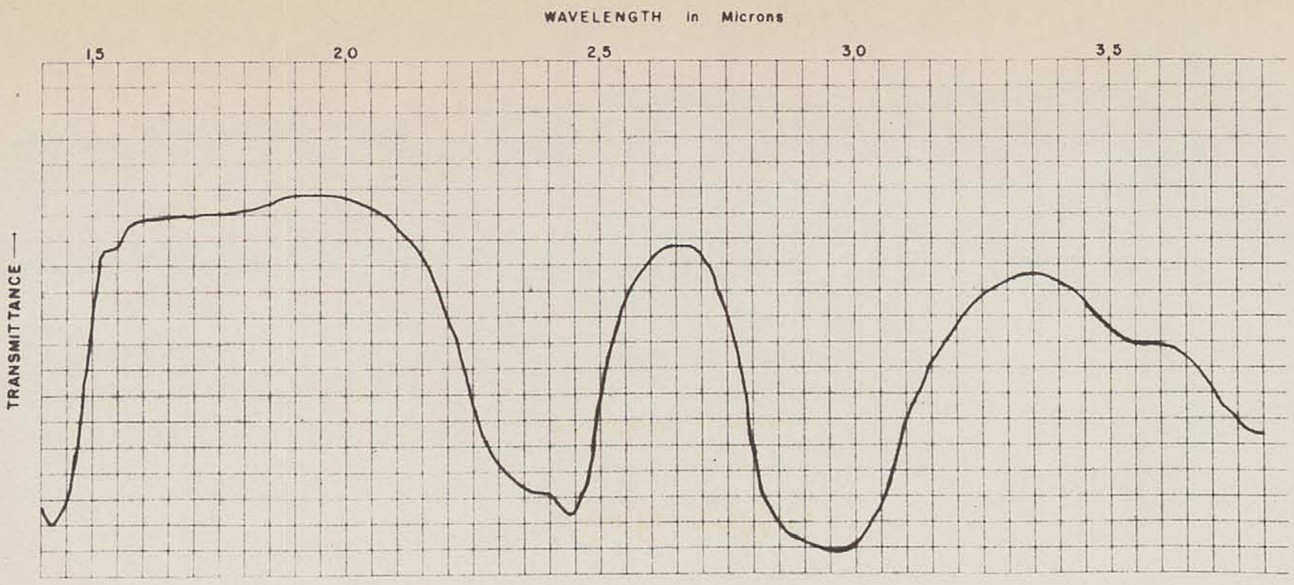
$GeCl_4 \cdot 2DMF$



$GeF_4 \cdot enMe_4$



$GeCl_4 \cdot enMe_4$



$GeCl_4 \cdot 2DMF$

TABLE VIII

Infrared Bands of $GeF_4 \cdot enMe_4$, $GeCl_4 \cdot enMe_4$ and $GeCl_4 \cdot 2DMF$

$GeF_4 \cdot enMe_4$

Wavelength (Microns)		Assignment
16.25	vs	Ge-F stretch
16.55	vs	" "
16.80	vs	" "
18.50	m	" "
20.00	w	Ligand
22.45	w	"
24.90	w	"
29.50	s	Ge-F deformation
31.00	s	" "
32.00	s br	" "

$GeCl_4 \cdot enMe_4$

Wavelength (Microns)		
16.80	w	Ligand
18.75	w	"
19.40	w	"
19.96	w	"
22.13	m	"
24.95	m	"
30.30	vs	Ge-Cl stretch
31.50	vs br	" "
34.80	s	" "

$GeCl_4 \cdot 2DMF$

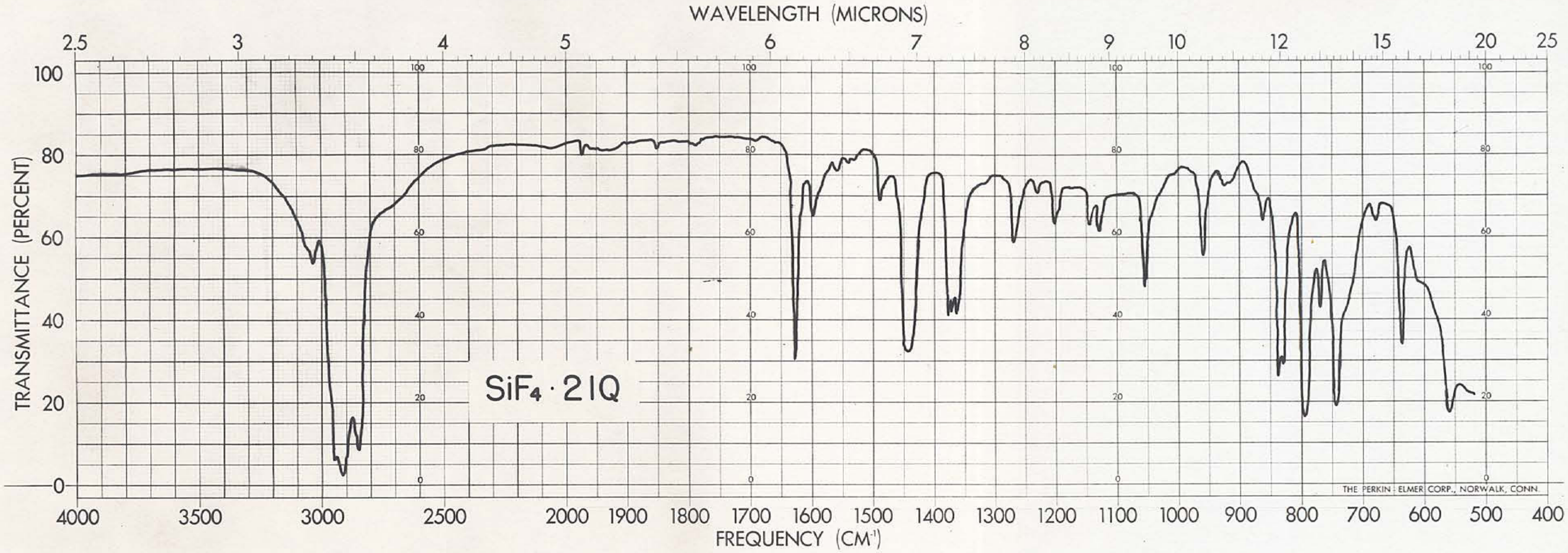
Wavelength (Microns)		
14.20	vs	Ligand
15.20	w	"
23.80	vs	"
24.40	vs	"
29.65	vs br	Ge-Cl stretch
35.50	m	Unassigned

FIGURE 8

Infrared Spectra in the NaCl Region of the Adducts

$SiF_4 \cdot 2IQ$

$SiF_4 \cdot dipy$


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
25
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
$SiF_4 \cdot 2IQ$
THE PERKIN - ELMER CORP., NORWALK, CONN.
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

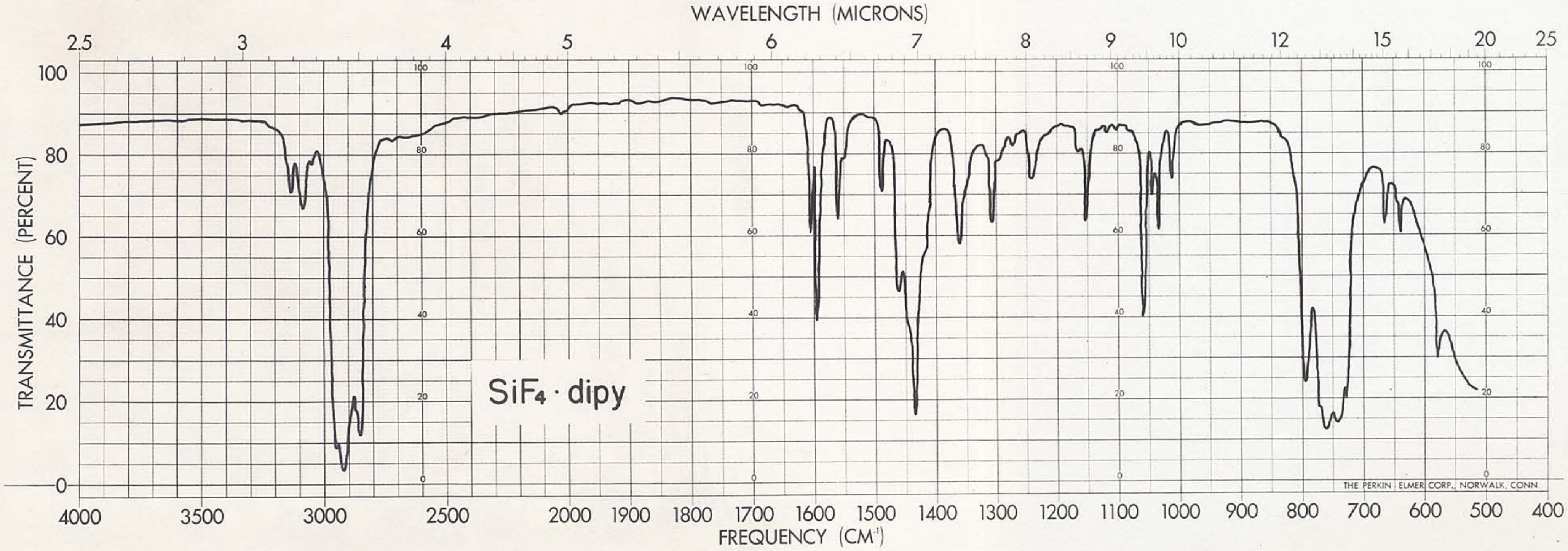

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
25
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
$SiF_4 \cdot dipy$
THE PERKIN - ELMER CORP., NORWALK, CONN.
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

TABLE IX

Infrared Bands of $SiF_4 \cdot 2IQ$ and $SiF_4 \cdot dipy$ from $850\ cm^{-1}$ to $700\ cm^{-1}$.

$SiF_4 \cdot 2IQ$

Frequency (cm^{-1}.)		Assignment
840	s	Ligand
835	s	"
795	s	Si-F stretch
770	w	Ligand
745	s	"
740	m	"

$SiF_4 \cdot dipy$

Frequency (cm^{-1}.)		
830	vw	Ligand
795	s	Si-F stretch
772	s	Ligand
765	vs	Si-F stretch
742	vs	" "
728	s	Ligand

FIGURE 9

Infrared Spectra of the Ligands in
the CsBr Region

Legend

Py = Pyridine
IQ = Isoquinoline
dipy = 2,2'-dipyridyl
$enMe_4$ = Tetramethylethylenediamine
DMF = Dimethylformamide

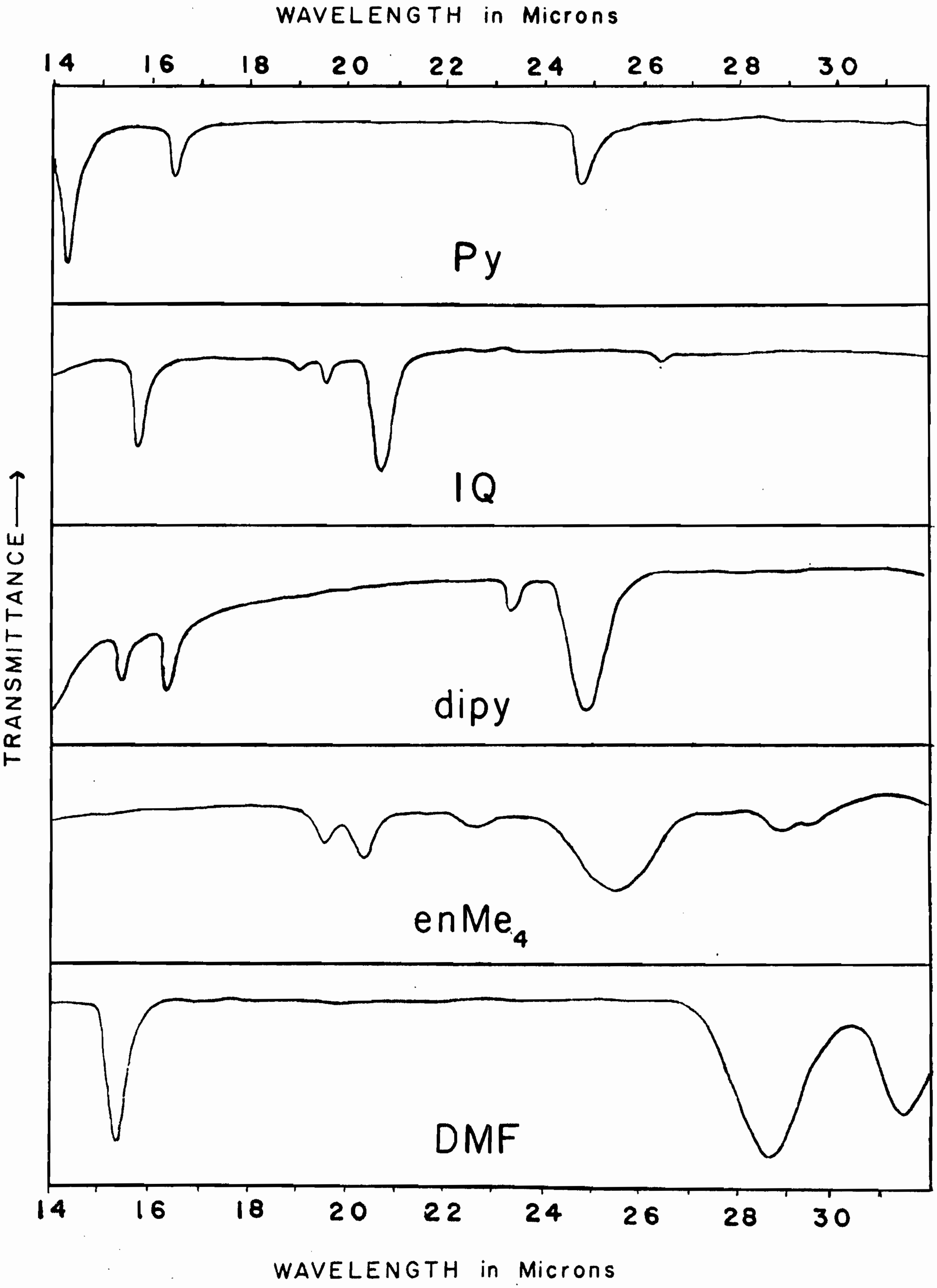

WAVELENGTH in Microns
14
16
18
20
22
24
26
28
30
TRANSMITTANCE ⟶
Py
IQ
dipy
$enMe_4$
DMF
14
16
18
20
22
24
26
28
30
WAVELENGTH in Microns

TABLE X

Infrared Bands of Free Ligands*

Pyridine (Py)	
14.40	vs
16.75	m
24.90	m

Isoquinoline (IQ)	
15.74	m
19.20	w
19.88	w
20.85	s
26.45	w

2,2'-Dipyridyl (dipy)	
15.50	m
16.25	m
23.45	w
25.00	s

Tetramethylethylenediamine ($enMe_4$)	
19.60	w
20.20	w
22.60	w
25.50	m
28.90	w
29.60	w

Dimethylformamide (DMF)	
15.42	s
28.75	s
31.50	s

*Values in microns

Table XI contains a list of the trans-$MX_4 \cdot 2L$ adducts together with their M-X stretching frequencies. These adducts, as discussed in the symmetry analysis (Appendix I), belong to the point group D_{4h} and the M-X stretching modes have the symmetry type E_u.

Table XII contains the cis-MX_4-2L adducts and the adducts of bidentate ligands together with their M-X stretching fundamentals. These compounds belong to the point group C_{2v} and the three M-X stretching fundamentals of each adduct have the symmetry types A_1, B_1 and B_2. A full discussion of the spectral interpretations and band assignments will be given in the Discussion and the results of a symmetry analysis are found in Appendix I.

TABLE XI

M-X Stretching Fundamentals of Trans Adducts

Adduct	M-X Bond	Wavelength Microns	Frequency cm^{-1}	Figure
$SiF_4 \cdot 2Py$(a)	Si-F	13.42	795	
$SiF_4 \cdot 2IQ$	Si-F	13.38	793	8
$SiCl_4 \cdot 2IQ$	Si-Cl	27.00	370	3
$SiBr_4 \cdot 2IQ$	Si-Br	28.80	348	3
$GeF_4 \cdot 2Py$	Ge-F	16.28	615	2
$GeF_4 \cdot 2IQ$	Ge-F	16.25	615	4
$GeCl_4 \cdot 2Py$	Ge-Cl	30.60	327	2
$GeCl_4 \cdot 2IQ$	Ge-Cl	30.10	332	4
$GeCl_4 \cdot 2DMF$	Ge-Cl	29.65	337	6
$GeBr_4 \cdot 2Py$	Ge-Br	35.40	282	2
$GeBr_4 \cdot 2IQ$	Ge-Br	36.90	271	4

(a)after Guertin (39)

In addition to the stretching fundamentals given in Tables XI and XII, the spectra of the tetrafluoride complexes show other absorption bands due to M-F vibrations. The spectra of trans-SiF_4-2Py (Figure 1) and trans-$SiF_4 \cdot 2IQ$ (Figure 3) contain strong bands at 21.10 microns (474 cm^{-1}.) and 20.40 microns (490 cm^{-1}.) respectively. These bands have been assigned to the Si-F deformation modes of symmetry type E_u. In the case of the cis-SiF_4-dipy adduct (Figure 5) there are a large number of Si-F bands in the CsBr region and unambiguous assignments of these are not possible. A similar situation arises in the spectra of all the complexes of GeF_4 in the vicinity of 31 microns. These results will be considered in more detail in the Discussion.

TABLE XII

M-X Stretching Fundamentals of Cis Adducts

Adduct	M-X	Wavelength Microns	Frequency cm^{-1}.	Figure
SiF_4·dipy	Si-F	13.42	795	5
		14.92	765	
		14.51	742	
$SiCl_4$·2Py	Si-Cl	20.75	482	1
		24.25	412	
		25.90	386	
$SiCl_4$·dipy	Si-Cl	21.15	474	5
		23.20	431	
		23.55	425	
$SiBr_4$·2Py	Si-Br	2390	419	1
		27.15	369	
		28.60	350	
$SiBr_4$·dipy	Si-Br	23.25	430	5
		25.70	389	
		27.60	362	
GeF_4·dipy	Ge-F	15.80	633	6
		16.17	619	
		16.40	610	
GeF_4·enMe_4	Ge-F	16.25	615	7
		16.55	605	
		16.80	595	
$GeCl_4$·dipy	Ge-Cl	29.75	336	6
		30.60	327	
		33.70	296	
$GeCl_4$·enMe_4	Ge-Cl	30.30	330	7
		31.50	318	
		34.80	288	
$GeBr_4$·dipy	Ge-Br	34.40	291	6

Spectral Comparisons

This section will deal with three infrared spectral comparisons: (i) the spectra of $GeCl_4 \cdot 2DMF$ and free dimethyl formamide; (ii) the spectra in the NaCl region, of adducts of pyridine, isoquinoline and 2,2'-dipyridyl compared to the free bases; (iii) the spectra in the CsBr region of pyridine adducts of MX_4, including tin adducts (data taken from Beattie et al (19, 36).

The Adduct $GeCl_4 \cdot 2DMF$

In order to obtain a stable oxygen-donor adduct, it was decided to attempt the preparation of the dimethyl formamide complex of $GeCl_4$. As mentioned in the introduction, this ligand can coordinate through the oxygen atom or the nitrogen atom. With titanium tetrachloride (27) and silicon tetrafluoride (28), coordination takes place through the oxygen atom.

With $GeCl_4$, a white solid, analysed as $GeCl_4 \cdot 2DMF$, was obtained. The infrared results showed that the carbonyl stretching frequency of the adduct was 1650 cm^{-1}. The free base carbonyl stretching frequency is 1676 cm^{-1}. (27) showing a decrease of 26 cm^{-1}. due to coordination. This decrease, like the similar decrease in DMF complexes of $TiCl_4$ and SiF_4, strongly suggests that bonding to the germanium atom occurs through the oxygen atom.

Pyridine, Isoquinoline and 2,2'-Dipyridyl Adducts

As observed by Hulme (17) and Gill (53), the infrared spectra in the NaCl region of the pyridine adducts of MX_4 are all very similar to each other and to the free base. The same similarities were observed in the spectra of isoquinoline and 2,2'-dipyridyl adducts.

There were some small changes in the spectra of the bases on coordination. One region of the spectrum that showed some regular changes was that between 700 and 800 cm^{-1}. where, in aromatic systems, the out-of-plane carbon-hydrogen deformation vibrations occur (54).

Table XIII shows the frequencies of the C-H out-of-plane deformation modes of the adducts of pyridine, isoquinoline and 2,2'-dipyridyl, together with those of the free bases. The positions and intensities of these bands label them as these C-H modes and, moreover, a complete infrared analysis of pyridine has shown that both the 748 cm^{-1}. and 705 cm^{-1}. bands are due to this kind of vibration (55).

TABLE XIII

C-H Out-of-Plane Deformation Frequencies*

Ligand	Free Base	Adduct
Pyridine	748	760
	705	675
Isoquinoline	740	755
2,2'-Dipyridyl	754	775
	737	722

*Frequencies expressed in cm^{-1}.

From the table, it is evident that on coordination to MX_4, some of these frequencies increase while others decrease. These results agree with those of Hulme (17) on the pyridine systems, and with Shilt and Taylor (56) and Clark (37) on the 2,2'-dipyridyl systems.

CsBr Spectra of Pyridine Adducts

In the spectra of the pyridine adducts of SiX_4 (Figure 1) there is a strong band around 21.40 microns (467 cm^{-1}.) and in those of GeX_4 (Figure 2) around 22.20 microns (450 cm^{-1}.) which is due to a ligand vibration. Beattie et al (19, 36) have observed similar results and, in addition, observed that for the tin tetrahalide adducts of pyridine, this band occurs near 23.25 microns (430 cm^{-1}.). The free base has a moderately intense band at 403 cm^{-1}. which has been interpreted as a skeletal vibration and has been labeled, ν_{16b} (55). This assignment has been applied to the above mentioned bands in the spectra of the adducts.

Table XIV contains the values of ν_{16b} for a number of MX_4 adducts of pyridine. Figure 10 shows a plot of ν_{16b} against the atomic weight of M.

TABLE XIV

ν_{16b} of $MX_4 \cdot 2Py$

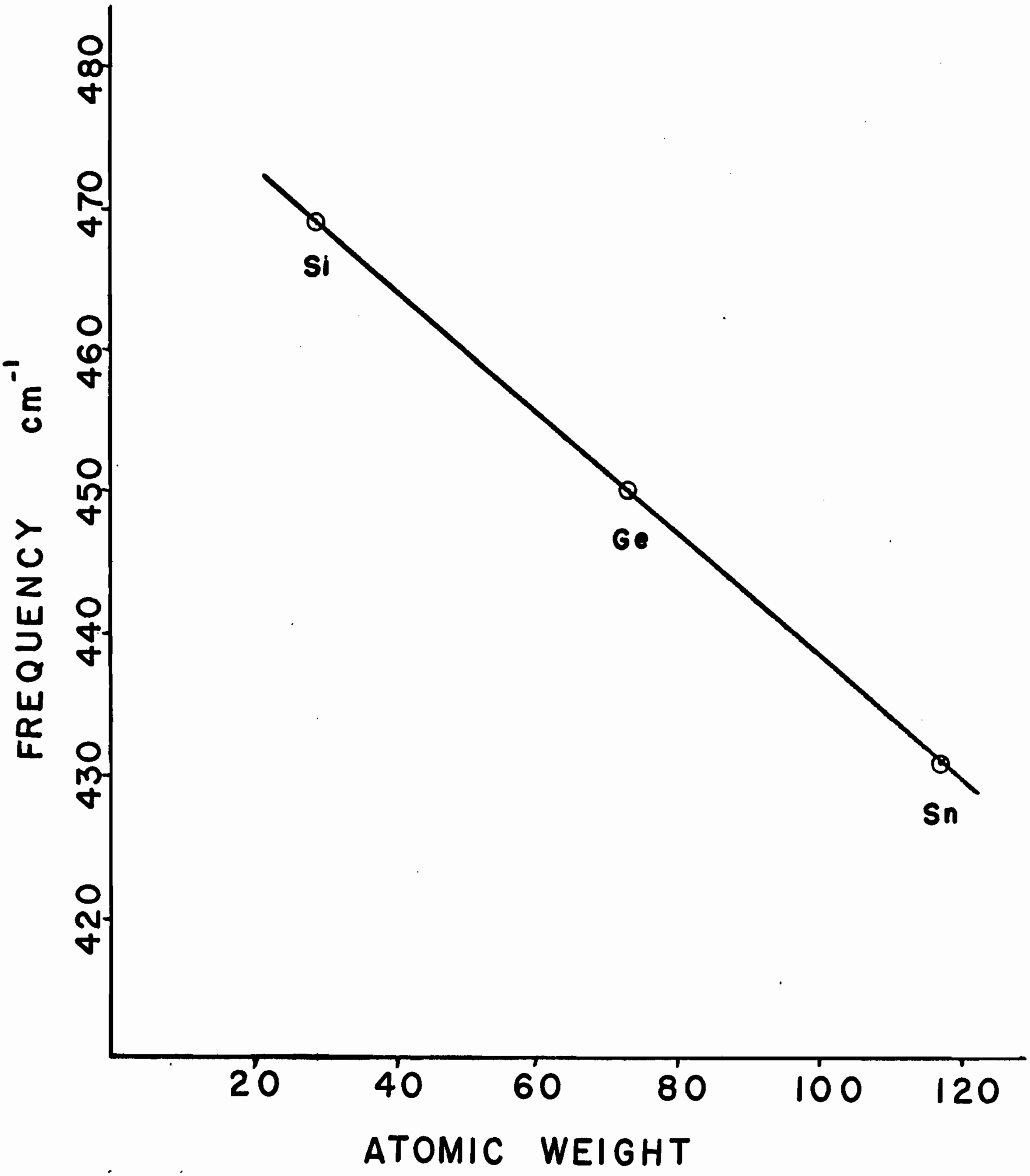
Lewis Acid	Wavelength Microns	Frequency cm^{-1}.
SiF_4	21.40	467
$SiCl_4$	21.50	465
$SiBr_4$	21.28	469
*SiI_4 (a)	21.52	465
GeF_4	22.13	452
$GeCl_4$	22.20	450
$GeBr_4$	22.42	446
$SnCl_4$ (a)	23.20	431
SnI_4 (a)	23.40	427
CH_3SnCl_3 (a)	23.40	428

*occurs as $SiI_4 \cdot 4Py$

(a) after Beattie

FIGURE 10

Graph Showing the Frequency, ν_{16b}, of Pyridine in Coordination Compounds of Silicon, Germanium and Tin Tetrachlorides Plotted Against the Atomic Weight of the Metal


FREQUENCY cm^{-1}
480
470
460
450
440
430
420
Si
Ge
Sn
20
40
60
80
100
120
ATOMIC WEIGHT

DISCUSSION OF RESULTS

The infrared spectroscopic measurements of the metal-halogen stretching frequencies, which are listed in Tables XI and XII, show that all the adducts of bidentate ligands and the pyridine adducts of $SiCl_4$ and $SiBr_4$ possess the cis-octahedral structure. The other pyridine adducts, including $SiF_4 \cdot 2Py$, and the isoquinoline adducts have the trans-octahedral structure.

This discussion will consider the above conclusions concerning the preferred stereochemistry of the addition compounds of silicon and germanium tetrahalides. The infrared absorption band assignments, which are given in Tables II to IX, will be fully discussed and alternate assignments of some of the bands will be considered because in some instances it was not possible to unequivocally assign a given band.

The symmetry properties of the adducts have played a major role in the infrared band assignments and in the differentiation between the cis and trans isomers. The symmetry analysis, given in the Appendix shows that the trans adducts (D_{4h} symmetry) have one doubly-degenerate metal-halogen stretching fundamental which is infrared active while the cis adducts (C_{2v} symmetry) have four non-degenerate metal-halogen infrared active stretching fundamentals. Schematic diagrams of these M-X stretching modes are shown in Figures 11 and 12 on pages 80 and 81 of the Appendix. In addition, all the vibrational fundamentals of the cis and trans isomers are listed in Table XVII on page 77 of the Appendix.

The selection rules used in the symmetry analysis, however, are strictly valid for the spectra of materials in the vapour phase or in dilute solution. All the spectra shown in Figures 1 to 8 were obtained from crystalline compounds and hence, as discussed in the symmetry analysis, solid state interactions complicate the interpretations of the measured spectra. Solid state effects are apparent in some spectra and these will be considered in the discussions to follow.

Another tool of group theory that has proven invaluable in the interpretation of spectra has been the Correlation Tables (57). In such a table, the irreducible representations of high symmetry groups are related to those of groups of lower symmetry. Thus the fundamental vibrational frequencies of the hexahalo complex ions of Group IV (i.e. MX_6^{-2}) which have a symmetrical octahedral structure and belong to the point group, O_h, can be related to the fundamental M-X vibrations of the trans (D_{4h}) and cis (C_{2v}) octahedral adducts of MX_4. This will be done to show the origin of the M-X bands in the spectra of the adducts.

The infrared and Raman spectroscopic results of a number of Group IV hexahalo anions are listed in Table XV. The notation used for the frequencies is taken from Nakamoto (58). The F_{1u} bands are infrared active: ν_3 is considered to be a stretching frequency and ν_4 a deformation frequency. The A_{1g}, E_g and F_{2g} are Raman active: ν_1 is the totally symmetrical stretching frequency, ν_2 is a doubly degenerate stretching frequency and ν_5 is a triply degenerate deformation frequency. The F_{2u} modes are totally inactive.

Table XV contains a reproduction of part of the Correlation Table of the point group, O_h, taken from Cotton (57).

TABLE XV

Fundamental Vibrational Frequencies of MX_6^{-2}*

Anion	A_{1g} ν_1	E_g ν_2	F_{1u} ν_3	F_{1u} ν_4	F_{2g} ν_5	F_{2u} ν_6	Reference
SiF_6^{-2}	656	510	730	480	-	-	22, 59, 19
GeF_6^{-2}	627	454	600	350	318	-	23
$GeCl_6^{-2}$	-	-	308	-	-	-	19
$SnCl_6^{-2}$	311	229	294	-	158	-	25, 60
$SnBr_6^{-2}$	185	135	-	-	95	-	25

*All values reported in cm^{-1}.

TABLE XVI

Correlation Table for O_h, D_{4h} and C_{2v}

O_h	D_{4h}	C_{2v}
A_{1g}	A_{1g}	A_1
E_g	$A_{1g} + B_{1g}$	$A_1 + A_2$
F_{1u}	$A_{2u} + E_u$	$A_1 + B_1 + B_2$
F_{2g}	$B_{2g} + E_g$	$A_1 + B_1 + B_2$
F_{2u}	$B_{2u} + E_u$	$A_2 + B_1 + B_2$

The principle is to correlate the fundamental frequencies of the MX_6^{-2} anions with those of the adducts of the corresponding MX_4. As an example, consider SiF_6^{-2}. The infrared spectrum of the potassium salt, K_2SiF_6, shows a band at 730 cm^{-1}. (59): this is ν_3. The trans adducts of SiF_4 all possess Si-F fundamental frequencies close to this value. The spectrum of $SiF_4 \cdot 2IQ$ (Figure 8) has an Si-F absorption band at 793 cm^{-1}. which from the symmetry analysis has been labeled the E_u stretching fundamental. Similarly, the adducts of $SiF_4 \cdot 2Py$ and $SiF_4 \cdot 2NH_3$ possess E_u stretching frequencies of 795 cm^{-1}. (39) and 725 cm^{-1}. (28) respectively. The correlation table shows that the F_{1u} frequency of the O_h breaks down to E_u (and A_{2u}) in D_{4h}.

Considering the M-X stretching modes in general, there is in O_h one infrared active stretching fundamental which is correlated to one infrared active M-X stretching fundamental of D_{4h}. On going from O_h to C_{2v}, however, F_{1u} breaks down into three infrared active M-X stretching modes. In addition, A_{1g} of O_h is correlated to A_{1g} of D_{4h}, both modes being infrared inactive. However, this in turn is correlated to A_1 of C_{2v} which is active in the infrared. Thus one expects that the trans adducts will have one M-X stretching fundamental frequency in the vicinity of the F_{1u} stretching frequency of MX_6^{-2} and the cis adducts will have three. In addition, the cis adducts should have a fourth M-X stretch in the infrared with a frequency close to that of the A_{1g} mode of MX_6^{-2}. In the discussion, to follow the number of experimentally observed M-X stretching bands is used to distinguish between the cis and trans octahedral structures.

Pyridine Adducts

The infrared spectra in the CsBr region of the pyridine adducts of SiX_4 and GeX_4 are shown in Figures 1 and 2 respectively. Tables II and III contain the wavelengths of the bands together with their assignments. The problem is to determine which bands are due to metal-halogen or metal-nitrogen vibrations and which are due to vibrations entirely within the ligand molecule, i.e. the "ligand bands."

The three bands near 15-16 microns in all the spectra (except that of $GeF_4 \cdot 2Py$) are clearly due to ligand vibrations. The frequencies are virtually unaffected by changes in M or X. In the silicon tetrahalide complexes there is a strong band around 21.40 microns which is also assigned to a ligand vibration: the ν_{16b} of pyridine. The corresponding band in the $GeX_4 \cdot 2Py$ spectra is found near 22.20 microns. This assignment agrees with that of Beattie (36) and will be discussed later in more detail under a separate heading.

In connection with the M-X vibrations, three definite Si-Cl and Si-Br stretching bands are found in the spectra of $SiCl_4 \cdot 2Py$ and $SiBr_4 \cdot 2Py$. The spectra of the corresponding 2,2'-dipyridyl adducts (Figure 5) also show three Si-X stretching frequencies. These results also agree with those of Beattie (36) who, in addition, observed three Si-Cl bands at 21.05, 22.60 and 23.55 microns in the spectrum of $SiCl_4$-O-phenanthroline. Thus the spectroscopic evidence strongly suggests that $SiCl_4 \cdot 2Py$ and $SiBr_4 \cdot 2Py$ possess the cis-octahedral structure.

In the spectrum of $SiCl_4 \cdot 2Py$ there is a weak band at 33.60 microns (297 cm^{-1}.) which is not present in the spectra of other pyridine adducts. Beattie (36) proposes this is a fourth

Si-Cl stretching fundamental. As discussed previously, four M-X stretching fundamentals are expected for cis adducts. However, there is no corresponding band in the spectrum of cis-$SiCl_4 \cdot dipy$. The 33.60 micron band of $SiCl_4 \cdot 2Py$ is tentatively assigned to a Si-Cl stretching fundamental but this assignment must await conformation.

The band at 21.10 microns (475 cm^{-1}.) in the spectrum of $SiF_4 \cdot 2Py$ is the doubly degenerate Si-F in-plane deformation fundamental of E_u symmetry. Table XV shows that ν_4 for SiF_6^{-2} occurs at 480 cm^{-1}. and this fundamental is correlated to the E_u mode of trans-$SiF_4 \cdot 2Py$. Guertin (39) has also observed the E_u Si-F deformation frequency at 475 cm^{-1}. in the spectrum of trans-$SiF_4 \cdot 2NH_3$.

Each of the F_{1u} fundamentals of point group O_h give A_{2u} modes in D_{4h}, in addition to the E_u modes. From the symmetry analysis it is evident that there are two A_{2u} fundamentals in the trans adducts - the M-X out-of-plane deformation and the assymetric M-L stretching mode. In general, in-plane deformation vibrations occur at higher frequencies than the out-of-plane modes, as, for example, in the carbon-hydrogen vibrations of benzene (54). The A_{2u} Si-F deformation, which is infrared active, very likely occurs at frequencies lower than 260 cm^{-1}. Beattie et al (36) claim that the force constant for the Si-N bond stretching is probably small and hence the frequency will be low, especially when the nitrogen is part of a heavy ligand molecule. In addition, this vibration probably occurs as a very weak band, especially in solid state spectra, and thus is not observed, or is masked by stronger bands.

There is a weak band at 20.45 microns in the spectrum of cis-$SiBr_4 \cdot 2Py$ which is completely masked in the spectra of the other $SiX_4 \cdot 2Py$ adducts and which is absent in the spectra of the $GeX_4 \cdot 2Py$ adducts. This band may be due to one of the two infrared active Si-N stretching modes of the cis adduct but this has not been confirmed and the band is listed as "unassigned" in Table II.

The spectrum of $GeF_4 \cdot 2Py$ shows a strong band at 16.28 microns (615 cm^{-1}.) due to the E_u Ge-F stretching fundamental of a trans adduct. This fundamental is correlated with the F_{1u} (ν_3) of GeF_6^{-2} which occurs at 600 cm^{-1}. (23). The spectrum also reveals, however, a broad absorption which is resolved into three bands at 30.30, 31.70 and 33.20 microns. Table XV shows that ν_4 of GeF_6^{-2} occurs at 350 cm^{-1}. or 28.60 microns. For a trans adduct of GeF_4, there should be one Ge-F deformation fundamental around this frequency, as observed in the trans adducts of SiF_4.

The following is an attempt to explain the origin of these three bands in the spectrum of $GeF_4 \cdot 2Py$. Solid state or D_{2h} symmetry complications as discussed in the symmetry analysis, may occur for this complex, but these should split the E_u fundamental into two non-degenerate fundamentals, and hence, two bands, closely separated, should result. There was no evidence, moreover, that the 16.28 micron band, the E_u stretching fundamental, was split into two bands. It is possible that the A_{2u} Ge-F deformation or A_{2u} Ge-N stretching mode, or both, may occur near 30 microns, but this has not been verified. Alternately, the complex might have the cis structure, and hence a larger number of infrared active fundamentals, but this seems unlikely when the band at 16.28 microns in this spectrum is compared with the corresponding three absorption bands in the spectrum of cis-GeF_4.dipy (Figure 6) and cis-GeF_4.enMe$_4$ (Figure 7).

The spectrum of $GeCl_4$.2Py shows a strong band at 30.60 microns (327 cm^{-1}.) in agreement with that of 330 cm^{-1}. obtained by Beattie et al (19). This band is due to the Ge-Cl stretching mode of E_u symmetry of a trans adduct and is correlated with ν_3 of $GeCl_6^{-2}$ occurring at 308 cm^{-1}. (19). The band is not symmetrical and shows evidence of splitting into two bands, which, if genuine, is probably due to solid state interactions. A second spectrum, at a lower nujol mull concentration, showed a more symmetrical band with no evidence of splitting. Furthermore, as stated in the introduction of this thesis, $GeCl_4$·2Py has been shown by an X-ray diffraction analysis to possess the trans-octahedral structure (17).

The corresponding E_u fundamental in the spectrum of $GeBr_4$.2Py occurs at 35.40 microns (282 cm^{-1}.). It is interesting to compare the half-widths of the three Ge-X stretching bands. The spectra are calibrated linearly in microns and hence the wavelength half-widths for Ge-Cl and Ge-Br are much larger than for Ge-F as observed. A calculation of the half-widths in wavenumbers, however, shows that the three are very similar: 26 cm^{-1}. for the Ge-F band, 35 cm^{-1}. for the Ge-Cl band and 20 cm^{-1}. for the Ge-Br band.

The only absorption band of the pyridine adducts that has not been discussed is the weak one occurring at 30.40 microns in the spectrum of $GeBr_4$·2Py. There is no band around this wavelength in the spectra of the SiX_4 adducts and the region is masked in the spectra of the other $GeX_4 \cdot 2Py$. The band may be due to the A_{2u} Ge-N stretching fundamental. There is a weak band at 30.30 microns in the spectrum of trans-$GeBr_4 \cdot 2IQ$ which may be given the same assignment. This interpretation is not definite, however, and awaits further experimental verification. More adducts of $GeBr_4$ need to be prepared and their spectra analysed in the CsBr region.

Isoquinoline Adducts

The spectrum of SiF_4-2IQ in the NaCl region is shown in Figure 8. As discussed previously, the strong band at 793 cm^{-1}. is due to the E_u Si-F stretching fundamental of a trans-octahedral adduct. The other absorption bands listed in Table IX are known to be ligand bands from a study of spectra of other MX_4-isoquinoline adducts in this frequency range and by comparison with the spectrum of pure isoquinoline.

It is interesting to compare the frequencies of the E_u stretching modes of $SiF_4 \cdot 2Py$ (795 cm^{-1}.), $SiF_4 \cdot 2IQ$ (793 cm^{-1}.) and $SiF_4 \cdot 2NH_3$ (725 cm^{-1}.). The aromatic ligand complexes have significantly higher values for this frequency than the ammonia adduct. The higher frequencies for aromatic base adducts are also observed in cis-SiF_4·dipy (Figure 5) and cis-SiF_4·en (en = ethylenediamine). The spectrum of the latter shows two Si-F stretching bands at 740 and 715 cm^{-1}. (39), one of which is an unresolved doublet.

The higher values of the Si-F stretching frequencies in the aromatic systems are due to greater Si-F stretching force constants which in turn is due to a greater electron density of the silicon-fluorine bonds. The problem is to explain why the aromatic ligands product a greater electron density in the Si-F bonds than do the aliphatic ligands. This can be explained, at least qualitatively, in one of two ways.

Firstly, if the aromatic ligands form stronger silicon-nitrogen bonds (the coordinate link), then a greater build-up of electronic charge at the silicon atom would result. This charge build-up would be partly dissipated by the strong electronic attraction of the electronegative fluorine atoms resulting in an increased charge density in the Si-F bonds. The greater the charge centered at the silicon, the greater will be the charge attracted by the fluorine atoms.

The second explanation assumes that the aromatic ligands form weaker Si-N bonds than do the aliphatic ligands. This would lead to a smaller electronic charge build-up at silicon in the aromatic systems, and this in turn would result in a greater degree of p_π-d_π back-bonding from fluorine to silicon. The greater the back-bonding the higher the electron density between the silicon and fluorine atoms.

Although neither explanation has been verified, there is more experimental evidence in support of the second. Fluorine is known to have a strong tendency to undergo supplementary partial back-bonding. For example, in the boron halides, fluorine in BF_3 forms stronger partial double bonds than do chlorine or bromine in the corresponding BCl_3 and BBr_3 (61). In addition, silicon is known to be a good back-bonding acceptor atom as evidenced in compounds like trisilylamine, $(SiH_3)_3N$ (62). Furthermore, in the reaction of these bases with protons, ammonia is known to be a stronger base than pyridine. The base constant of ammonia is 1.8×10^{-5} whereas that of pyridine is 2.3×10^{-9} (42).

There is, however, no direct experimental evidence that p_{π}—d_{π} back-bonding occurs in the adducts of SiF_4. Moreover, both the pyridine and ammonia adducts have comparable stability as evidenced by the following heats of reaction data:

$$SiF_{4(g)} + 2NH_{3(g)} \longrightarrow SiF_4 \cdot 2NH_{3(s)} \quad -\Delta H = 54.6 \text{ kcal/mole} \quad (63)$$

$$SiF_{4(g)} + 2Py_{(g)} \longrightarrow SiF_4 \cdot 2Py_{(s)} \quad -\Delta H = 50.1 \text{ kcal/mole} \quad (64)$$

Thus, the relative basicity towards SiF_4 is not of the same magnitude as the relative basicity towards protons. Clearly more experimental work is needed. In the first place, more adducts of SiF_4 with aromatic and aliphatic ligands should be prepared and their infrared spectra studied. Secondly, there is a need for experiments, such as measurements of heats of formation and heats of dissociation of the adducts, which could establish the relative strengths of the coordinate bonds.

The spectra of the isoquinoline adducts in the CsBr region, shown in Figures 3 and 4, present some difficulties in their interpretation. This is mainly due to the relatively large number of ligand bands found in the spectra of the complexes, and to the fact that the relative intensities of some of these bands appear to be different in different spectra. As a result metal-halogen bands, especially in the silicon halide adducts, cannot be assigned unequivocally. The spectra of $SiBr_4 \cdot 2IQ$ and $GeBr_4 \cdot 2IQ$ are further complicated by the presence of several bands due to the isoquinoline-hydrobromide salt, a hydrolysis product of the addition compound.

In the spectrum of $SiF_4 \cdot 2IQ$ there is a relatively broad absorption band at 20.40 microns which is not characteristic of ligand bands in this spectral region. The spectrum of $SiCl_4 \cdot 2IQ$ shows a strong sharp band at 20.08 microns while that of $SiBr_4 \cdot 2IQ$ has a band at 20.20 microns. The broad band at 20.40 microns in the spectrum of $SiF_4 \cdot 2IQ$ is thus considered to be an unresolved doublet containing the above-mentioned ligand band and the E_u Si-F deformation fundamental of the trans adduct. As discussed in the previous section, the Si-F mode occurs at 21.10 microns in the spectrum of the pyridine adduct of SiF_4.

The strong absorption band at 21.05 microns in the $SiF_4 \cdot 2IQ$ spectrum however, might possibly be due to the Si-F deformation vibration. This band corresponds more closely to the E_u Si-F deformation vibration in the pyridine adduct. However, the 21.05 micron band is probably due to a ligand vibration corresponding to the bands at 21.75 and 22.55 microns in the spectra of $SiCl_4 \cdot 2IQ$ and $SiBr_4 \cdot 2IQ$ respectively. There is an almost constant shift of about 70-80 microns toward longer wavelengths on going from the fluoride to chloride to bromide. This suggests that the modes of vibration, although influenced somewhat by the halogens, are the same in each adduct. The corresponding ligand band in the spectra of the germanium halide adducts occurs between 21.25 and 21.50 microns.

The spectrum of $SiCl_4 \cdot 2IQ$ shows two strong absorption bands at 25.25 microns (396 cm^{-1}) and 27.00 (370 cm^{-1}). The latter has been assigned as the E_u Si-Cl stretching fundamental of the trans-octahedral adduct. The 25.25 micron band is thought to be a ligand band, corresponding to the bands at 26.43 microns for $SiF_4 \cdot 2IQ$ and 25.20 microns for $GeCl_4 \cdot 2IQ$ (Figure 4). However, the intensity of the 25.25 micron band in the $SiCl_4 \cdot 2IQ$ spectrum is much greater than that of the 26.43 micron band of $SiF_4 \cdot 2IQ$ and yet the other ligand bands in the latter spectrum are more intense. Perhaps the 25.25 micron band of $SiCl_4 \cdot 2IQ$ is due to an Si-Cl stretching vibration and the two Si-Cl stretching bands result from solid state splitting of the E_u fundamental.

The E_u M-X stretching fundamentals in the spectra of the other complexes occur as follows: $SiBr_4 \cdot 2IQ$ at 28.80, $GeF_4 \cdot 2IQ$ at 16.25, $GeCl_4 \cdot 2IQ$ at 30.10 and $GeBr_4 \cdot 2IQ$ at 36.90 microns. The spectra of the two bromide adducts are complicated by the presence of several bands due to hydrolysis impurity. These bands were identified by examining the infrared spectrum of the hydrolysis product, the hydrobromide salt of isoquinoline.

As observed in the spectrum of $GeF_4 \cdot 2Py$, there are three strong absorptions around 30 microns in the spectrum of $GeF_4 \cdot 2IQ$. The previous discussion of these absorption bands in the spectrum of the pyridine adduct of GeF_4 also applies to the isoquinoline complex. Examination of the 16.25 micron band of $GeF_4 \cdot 2IQ$ reveals it is a sharp, symmetrical band, as would be expected for the E_u Ge-F stretching fundamental of a trans adduct.

In the spectrum of $GeCl_4 \cdot 2IQ$ there is a weak shoulder at 32.30 microns. This shoulder may be due to solid state splitting, although this was not observed for the pyridine adduct of $GeCl_4$. Another possibility is that this shoulder may be due to the A_{2u} Ge-N stretching mode of an adduct with trans symmetry. As mentioned previously, the bands at 30.40 and 30.30 microns in the spectra of $GeBr_4 \cdot 2Py$ and $GeBr_4 \cdot 2IQ$ respectively, may be due to the assymetric Ge-N stretching mode. In addition, one of the three bands around 30 microns in the spectra of the GeF_4 adducts of these ligands may be assigned to A_{2u} Ge-N stretching. It is likely that for similar ligands, the wavelengths of the metal-donor atom stretching vibrations would be relatively insensitive to changes in X and L.

Thus the interpretation of the infrared spectra leads one to conclude that all the isoquinoline adducts possess the trans-octahedral structure. The cis adducts of MX_4 with the bidentate ligands, 2,2'-dipyridyl and tetramethylethylenediamine show three definite M-X stretching vibrations. In addition, the pyridine adducts of $SiCl_4$ and $SiBr_4$ also have three Si-X stretching fundamentals. This is to be compared with the single (and in some spectra possibly two) M-X stretching fundamentals for the isoquinoline adducts.

In addition to the infrared evidence, Miller and Onyszchuk (64) measured calorimetrically the heats of formation of the pyridine and isoquinoline adducts of MX_4. They found that the magnitude of the heats of formation of $GeX_4 \cdot 2Py$, $GeX_4 \cdot 2IQ$ and $SiX_4 \cdot 2IQ$ followed the sequences $F > Cl > Br$ and $Ge > Si$. The pyridine adducts of SiX_4, however, showed values in the order of $Cl > Br > F$ and for the chloride and bromide systems, $Si > Ge$. The anomalously high values for $SiCl_4 \cdot 2Py$ and $SiBr_4 \cdot 2Py$ were considered to be due to their existence in cis-octahedral form.

2,2'-Dipyridyl Adducts

Examination of the spectrum of $SiF_4 \cdot$dipy in the NaCl region (Figure 8) reveals five strong absorption bands between 800 and

and 720 cm^{-1}. The bands at 772 and 728 cm^{-1} are ligand bands. This is known from studies of the spectra of other MX_4•dipy adducts. For example $SiCl_4$•dipy shows these ligand bands at 775 and 722 cm^{-1}. Hence the other three bands in the spectrum of SiF_4•dipy are unquestionably due to the three Si-F stretching fundamentals of a cis adduct. The triplet, correlated with F_{1u}, ν_3, of SiF_6^{-2} is made up of symmetry types A_1, B_1 and B_2. It is not possible, however, to assign any one of the three fundamentals to a particular symmetry type.

The fourth Si-F stretching mode, which is correlated with A_{1g}, ν_1, of SiF_6^{-2}, might occur at 17.10 microns (585 cm^{-1}), There is a strong absorption band at this wavelength in the spectrum of SiF_4•dipy (Figure 5) which is absent in all the other 2,2'-dipyridyl adducts. Table XV shows that ν_1 of SiF_6^{-2} occurs at 656 cm^{-1}. In addition, Guertin (39) obtained a moderately intense band at 601 cm^{-1}. in the spectrum of the ethylenediamine adduct of SiF_4 (C_{2v} symmetry) which may also be due to the fourth Si-F stretching mode. These assignments are not unequivocal, but they are reasonable possibilities, especially in view of the high intensity of the 17.10 micron band in the spectrum of SiF_4•dipy.

In addition to the 17.10 micron band, the spectrum of SiF_4•dipy has several bands which are not found in the spectrum of the trans adducts of SiF_4 or in the spectra of the other MX_4•dipy adducts. The bands at 21.75 and 23.80 microns are known to be ligand bands from spectral comparisons with the other 2,2'-dipyridyl adducts. This leaves five strong bands - at 20.25, 22.00, 23.18, 25.20 and 26.65 microns - and three weak bands - at 28.55, 32.05 and 33.00 microns - unaccounted for.

Three Si-F deformation modes, correlated with F_{1u}, ν_4, of SiF_6^{-2}, are expected in the vicinity of the corresponding E_u mode of the trans adducts of SiF_4. In addition, the symmetry analysis predicts a fourth infrared active Si-F deformation mode (A_1 symmetry) and an infrared inactive Si-F deformation mode (A_2 symmetry). Thus four of the five strong bands can be assigned to Si-F deformation vibrations. It is possible that the A_2 mode may also be active in the solid state spectrum, although bands arising from this kind of activity are usually weak ones (65). The assymetrical and symmetrical Si-N stretching modes, both of which are infrared active, may occur in the spectrum of SiF_4•dipy in the CsBr region. There is, however, no evidence for any Si-N vibrations in the spectra of the other adducts of SiX_4.

A complete assignment cannot be made for all bands in the spectrum of SiF_4•dipy. In addition to the solid state selection rule complication, the interpretation of this, and other, spectra is further complicated by a lack of accurate knowledge of the sample concentration in the nujol mull. Thus the three weak bands in the spectrum of SiF_4•dipy may conceivably be ligand bands which are not observed in the spectra of the other 2,2'-dipyridyl adducts, the spectra of which were taken in lower nujol mull concentrations. It is clear, however, that adducts with the cis structure produce more infrared active M-X vibrations than do those with the trans structure, in support of the predictions of the symmetry analysis.

The results obtained for the 2,2'-dipyridyl adducts of $SiCl_4$, $SiBr_4$ and $GeCl_4$ agree substantially with those of Beattie et al (19, 36). In each spectrum, the three M-X stretching bands expected for cis adducts are observed (Figures 5 and 6). The spectrum of

$GeBr_4$•dipy shows only one Ge-Br stretching band at 34.40 microns. Presumably, the other Ge-Br fundamentals occur at wavelengths beyond the range of the CsBr optics.

The spectrum of GeF_4•dipy reveals a triplet near 16 microns which is attributed to the three Ge-F stretching modes. In addition, there is a weak band at 18.85 microns which may be the fourth Ge-F band correlated to A_{1g} of GeF_6^{-2}. Table XV shows that ν_1 of GeF_6^{-2} occurs at 627 cm^{-1}. or 15.95 microns. The spectrum of the tetramethylethylenediamine adduct of GeF_4 (Figure 7) has a moderately intense band at 18.50 microns which also may be due to the fourth Ge-F stretching mode of that adduct. However, the spectra of SiF_4•dipy and $SiBr_4$•dipy also contain weak bands around 18 microns and these are ligand bands. Thus the two bands in question (for each GeF_4 adduct) are likely ligand bands, although the possibility that they might be due to Ge-F stretching cannot be ruled out entirely.

The two strong bands at 30.00 and 34.35 microns in the spectrum of GeF_4•dipy are due to Ge-F deformation modes. As shown in Table XV, the F_{1u} deformation fundamental of GeF_6^{-2} (ν_4) occurs at 350 cm^{-1}. (28.60 microns).

Tetramethylethylenediamine Adducts

Figure 7 shows the spectra, in the CsBr range, of GeF_4•enMe_4 and $GeCl_4$•enMe_4. The three Ge-F stretching bands of the cis adduct are found around 16 microns in agreement with the results for GeF_4•dipy. As discussed in the previous section, the moderately intense band at 18.50 microns may be due to the fourth Ge-F stretching mode. The spectrum of $GeCl_4$•enMe_4 does not possess a band of moderate intensity at 18.50 microns but shows three weak bands near 19 microns. The nujol mull concentration of $GeCl_4 \cdot enMe_4$ is greater than that of the GeF_4 adduct as shown by the absorption bands at 22 and 25 microns. Thus it is reasonable to propose that the 18.50 micron band of $GeF_4 \cdot enMe_4$ might not be due to a ligand vibration.

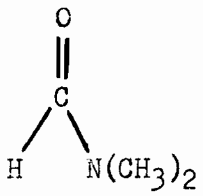
The absorption bands around 30 microns in the spectrum of $GeF_4 \cdot enMe_4$ are due to the Ge-F deformation vibrations. The three absorption bands at 30.30, 31.50 and 34.80 microns for $GeCl_4 \cdot enMe_4$ are due to the Ge-Cl stretching vibrations of a cis adduct. This agrees with the results obtained for the 2,2'-dipyridyl adduct of $GeCl_4$.

The Dimethyl Formamide Adduct of $GeCl_4$

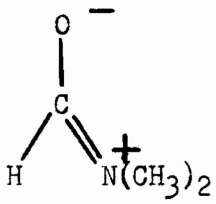
The only dimethyl formamide adduct prepared and studied in this work was that of $GeCl_4$. The band at 29.65 microns (337 cm^{-1}.) is very likely due to the Ge-Cl stretching mode of a trans adduct. The frequency of this band agrees closely with the Ge-Cl stretching bands of trans-$GeCl_4 \cdot 2Py$ and trans-$GeCl_4 \cdot 2IQ$. The two strong bands near 24 microns in the spectrum of $GeCl_4 \cdot 2DMF$ are ligand bands corresponding to the two bands at 28.75 and 31.50 microns in the spectrum of the free ligand (Figure 9).

As mentioned in the results section, the spectrum of this complex in the NaCl range shows that the carbonyl stretching band occurs at 1650 cm^{-1}., a decrease of 26 wavenumbers from that of the free base. This result strongly indicates that coordination to germanium takes place through the carbonyl oxygen atom of the ligand (27, 28).

An explanation for the lowering of the carbonyl stretching frequency on coordination is based on a consideration of the following resonance hybrids of the ligand:



I



II

If coordination takes place through the oxygen atom, structure II is enhanced and the electron density of the carbonyl bond is lowered. If coordination is through the nitrogen atom, however, structure I is enhanced and the electron density of the carbonyl bond is increased. Since the electron density and force constant are directly related and since the stretching frequency is proportional to the force constant, a decrease in electron density would result in a decrease in the stretching frequency. This result is observed in the infrared spectrum and thus the conclusion is that coordination takes place through the oxygen atom.

ν_{16b} of Pyridine

Table XIV and Figure 10 show the relationship between the frequency, ν_{16b}, of coordinated pyridine in adducts of SiX_4, GeX_4 and SnX_4 and the atomic weight of the central metal atom. The magnitude of this frequency has been found to be sensitive to changes in the central atom but insensitive to changes in the type of halogen (36).

In free pyridine, a molecule of C_{2v} symmetry, ν_{16b} (at 402 cm^{-1}) is due to an out-of-plane skelatal vibration of symmetry type B_2 (55). In this mode the nitrogen atom oscillates in a perpendicular fashion to the plane of the aromatic ring. Since the nitrogen atom is bonded to the central metal atom in the adducts, the nature of the metal atom will influence the motion of the nitrogen. The results show that the frequency of this vibration is greater in the adducts than in the free base.

The linear relationship shown in Figure 10 clearly demonstrates that the nature of the metal atom has a marked affect on the magnitude of this frequency. There are two possible explanations for this linear relationship. Firstly, the metal atom may also undergo a displacement in this mode, in which case the frequency will depend on the mass of the metal atom. Secondly, the force constant for ν_{16b} may be affected by the strength of the coordinate bond (i.e. the M-N bond) of the adduct which appears to be in the order Si < Ge < Sn (2). Thus the stronger the M-N bond, the smaller will be the force constant of ν_{16b} and hence the smaller will be the magnitude of this frequency. Both explanations are consistent with the observed changes in the magnitude of this frequency.

The Problem of the Metal-Nitrogen Vibrations

As discussed previously, the bands near 20 microns in the spectrum of cis-$SiBr_4$·2 Py, and the bands around 30 microns in trans-$GeBr_4$·2Py and trans-$GeBr_4$·2IQ could not be unambiguously assigned to ligand or metal-halogen vibrations. Consequently, the interpretation that these bands may be due to metal-nitrogen stretching modes was put forward. In addition, Ge-N bands might occur in the spectra of trans-$GeF_4 \cdot 2Py$, trans-$GeF_4 \cdot 2IQ$ and trans-$GeCl_4 \cdot 2IQ$, all in the region of 30 microns. These assignments, although appealing with respect to the predictions of the symmetry analysis, are subject to considerable doubt and must remain tentative.

Beattie and co-workers (36) have proposed two very good arguments against the presence of silicon-nitrogen vibrations in the CsBr spectra of adducts of $SiCl_4$ and $SiBr_4$. Firstly, in their spectra, there was no need for any Si-N assignments, even in the spectra of adducts having the cis structure and hence a larger number of active fundamentals. Secondly, they claim on theoretical grounds that because the silicon atom is using its 3d-orbitals as the acceptor orbitals, the Si-N bonds in the adducts would be relatively weak. This would mean a low value of the stretching force constant for these bonds and hence a low value of the stretching frequency.

Gill and co-workers studied the infrared spectra of a large number of transition metal complexes of pyridine over the frequency range 4000 to 400 cm^{-1}. (53). They observed no bands above 400 cm^{-1}. (25 microns) which they could not assign as purely pyridine vibrations. Clark and Williams (66) have obtained metal-ligand stretching vibrations of a number of pyridine and other nitrogen-donor ligand complexes of some transition metal halides in the region of 280 to 220 cm^{-1}. In addition, Bicelli, in a study involving the C-N bonds of pyridine, has predicted that the metal-nitrogen stretching modes of the pyridine-transition metal complexes would occur in the frequency range 150 to 250 cm^{-1}. (67).

These arguments, together with those discussed on page 50 invalidate the tentative assignments of the metal-nitrogen frequencies. However, it should be noted that the arguments concerning the Group IVA adducts are qualitative and have not been fully investigated. Beattie et al, for example, did not measure spectra of SiF_4 and GeF_4 adducts which might well contain bands due to Si-N and Ge-N stretching. In addition, there has been no systematic quantitative experimental work on the relative bond strengths and force constants of the coordinate links in these compounds. Clearly there is a very great need for further study of these addition compounds, especially their heats of formation, and their infrared and Raman spectra.

The Problem of the Preferred Structures

The apparent anomalous structures of $SiCl_4 \cdot 2Py$ and $SiBr_4 \cdot 2Py$ have not been explained. Why do these two adducts have the cis configuration whereas the other pyridine adducts and all the isoquinoline adducts the trans? The explanation probably involves the participation of the d-orbitals of silicon and germanium in the coordinate bonding. Two d-orbitals are used directly in bonding through the octahedral sp^3d^2 hybridization. This leaves three empty d-orbitals which may participate in further bonding by $p_\pi - d_\pi$ overlap from filled p-orbitals of the halogens or π-electron from the ligands. Perhaps the cis structure is obtained for $SiCl_4 \cdot 2Py$ and $SiBr_4 \cdot 2Py$ because this configuration leads to better $p_\pi - d_\pi$ overlap between the silicon and the halogens. Moreover, the reverse would be true for $SiF_4 \cdot 2Py$ and the pyridine adducts of the germanium tetrahalides. In addition, the isoquinoline adducts of $SiCl_4$ and $SiBr_4$, which have fairly large and bulky ligand molecules, have the trans structure because of steric effects - large ligand-ligand repulsions in the cis positions. The author is unable to explain why this kind of π-bonding would be favoured in one adduct by one structure and in another adduct by the other structure. There is a wide scope for further experimental and theoretical studies in this field with the "structural why" question taking uppermost importance.

SUMMARY

The purpose of the present investigation was to attempt to differentiate, using infrared absorption spectroscopy, between the cis and trans octahedral structures of the coordination compounds of silicon and germanium tetrahalides. The complexes were of the type $MX_4 \cdot 2L$ and $MX_4 \cdot LL$ where M is Si or Ge, X is F, Cl or Br, L is a monodentate ligand (pyridine and isoquinoline) and LL is a bidentate ligand (2,2'-dipyridyl and tetramethylethylenediamine). Theoretically, according to the symmetry properties for each structure, infrared spectroscopy can be used to distinguish between cis and trans structures and the experimental results have confirmed this.

The infrared measurements have shown that the adducts of MX_4 with the bidentate ligands possess the cis-octahedral structure. The infrared spectra obtained for these adducts are all consistent with spectra of molecules possessing C_{2v} symmetry. The pyridine adducts of $SiCl_4$ and $SiBr_4$ also show spectra consistent with C_{2v} symmetry and hence are considered to be cis isomers. On the other hand, the pyridine adducts of SiF_4 and of the three tetrahalides of germanium give infrared results which are consistent with spectra of molecules possessing D_{4h} symmetry, the symmetry of the trans-octahedral adducts. Similarly, the infrared spectra of all the isoquinoline adducts (including those of $SiCl_4$ and $SiBr_4$) show that these molecules have the trans-octahedral structure.

APPENDIX

Symmetry Analysis

Introduction

The central idea which links infrared and Raman spectroscopy to the symmetry and geometry of a molecule is the fact that each normal mode of vibration forms a basis for or "belongs to" an irreducible representation of the molecular point group. This means that the normal coordinate of a given normal mode will transform according to the symmetry properties of the irreducible representation to which that normal mode belongs. If a normal mode is found to belong to a one-dimensional irreducible representation then the frequency associated with it is non-degenerate. If, on the other hand, it belongs to a two-dimensional irreducible representation, then there are in fact, two such normal modes associated with a doubly degenerate frequency. The same applies to three-dimensional irreducible representations and triply degenerate frequencies.

Symmetry can also give the activities of the normal modes. The infrared active modes belong to the same irreducible representations as do the x, y and z basis vectors or, put in another way, transform in the same way as do the translations along the x, y and z axes. Raman active modes show the same symmetry properties as the squares and binary products of the x, y and z vectors. Examination of the character table of the point group for the relevant molecule will give the desired irreducible representations and hence the activity of each normal mode.

The selection rules for infrared and Raman spectroscopy are described in detail by Wilson, Decius and Cross (40). The fundamentals of group theory, representation of groups and their applications to spectroscopy are described by Cotton (57). It is the method outlined by Cotton that was used here in the symmetry analyses of the coordination compounds of MX_4.

This analysis is concerned with stretching and deformation vibrations of bonds attached to the central metal atom. These include M-X and M-L bonds. The relevant point group symmetry is the symmetry surrounding the central metal atom. The ligand vibrations (a term used for modes within the ligand molecule itself), because of their complexity, will not be treated in this analysis.

Before carrying out the analysis, two assumptions have to be made. Firstly, the ligand molecules are treated as single atoms (L) attached to the metal atom, and secondly, the monodentate ligands are assumed to be able to rotate freely about the M-L bonds. These assumptions are made to simplify the analysis and give the L "atom" spherical symmetry. In the adducts, however, there is a strong possibility that the ligands cannot rotate and the effect of a fixed ligand, relative to the MX_4 plane in the trans adducts, on the symmetry of the molecule will also be considered. In addition, it will also be shown that there are additional complications arising from the fact that the experimental results were obtained for solid samples and condensed phase infrared cannot be treated as simply as vapour phase and dilute solution spectra.

Symmetry Elements of the Trans Isomer

Examination of the trans-$MX_4 \cdot 2L$ (see page 3) reveals that the molecule contains the following symmetry elements:

Identity element	E
4-fold axis along the L-M-L bonds	C_4
2-fold " " " L-M-L "	C_2
2 2-fold axes along the X-M-X bonds	$2C_2'$
2 2-fold " bisecting " X-M-X angles	$2C_2''$
4-fold improper axis coincident with C_4	S_4
Horizontal mirror in the plane of MX_4	σ_h
Center of inversion at M	i
2 Vertical mirrors along the X-M-X bonds	$2\sigma_v'$
2 " " bisecting " X-M-X angles	$2\sigma_v''$

Hence the molecule belongs to the point group D_{4h}.

Symmetry Elements of the Cis Isomer

The cis-$MX_4 \cdot 2L$ (page 3) has the following symmetry elements:

Identity operation	E
2-fold axis bisecting the L-M-L angle	C_2
Vertical mirror " " L-M-L "	σ_v
" " in the plane of X_2ML_2	σ_v'

Hence the molecule belongs to the point group C_{2v}.

Symmetry Analysis

To each of the n atoms of a molecule are attached x, y and z Cartesian vectors with all x_n parallel, all y_n parallel and all z_n parallel. These are known as the Cartesian displacement vectors, or external coordinates. The symmetry operations of the group (one operation from each class of elements) are applied to these 3n displacement vectors and a reducible representation of dimension 3n is generated.

This representation is then reduced to a set of irreducible representations of the point group and this set contains all the normal modes of the molecule. From this set the six normal modes of translation and rotation (five for linear molecules) are deleted, leaving the 3n-6 genuine vibrational normal modes.

The next step is to consider the internal displacement vectors (coordinates) and 3n-6 are required. There are n-1 bonds and hence n-1 bond extensions, all of which are independent. The remaining 2n-5 coordinates are made up of the various bond angle changes of the molecule. It is necessary, however, to insure that the deformation coordinates are truly independent. For example, consider the MX_4 square plane and the in-plane angle changes. The following redundancy condition holds:

$$\Delta a_1 + \Delta a_2 + \Delta a_3 + \Delta a_4 = 0$$

where Δa_i means the change in the i^{th} angle.

This means that the four angles are not independent coordinates. The method of treating a redundancy condition of this kind is first to assume all four angles are independent and then, after the symmetry analysis on the four coordinates is completed, to delete from the list of irreducible representations the totally symmetric mode as a spurious result. All four angles are considered because of convenience in the symmetry analysis.

As in the case of the external coordinates, the internal vectors are operated on by the group elements and reducible representations are generated. These are then reduced to sets of the irreducible representations of the group and in this way, the stretching and bending contributions to the normal modes, according to their symmetry types, are deduced.

trans-$MX_4 \cdot 2L$

There are seven atoms and hence twenty-one external coordinates and the dimension of the reducible representation, Γ, is twenty-one. The following result for Γ was obtained. The elements are listed according to classes of elements as found in the character table (D_{4h}).

E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v'$	$2\sigma_v''$
21	3	-3	-3	-1	-3	-3	5	5	3

This was reduced to give the following result:

$$\Gamma_{3n} = 2A_{1g} + A_{2g} + B_{1g} + B_{2g} + 2E_g + 3A_{2u} + B_{2u} + 4E_u$$

The translational modes belong to -

$$A_{2u}\ (z) \quad \text{and} \quad E_u\ (x,\ y)$$

The rotational modes belong to -

$$A_{2g}\ (R_z) \quad \text{and} \quad E_g\ (R_x,\ R_y)$$

Hence the genuine representation is as follows:

$$\Gamma_{3n-6} = 2A_{1g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

Turning now to the internal coordinates, consider first the M-X bonds. Since there are four, the dimension of the representation is four. The following result was obtained:

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v'$	$2\sigma_v''$
Γ_{M-X}	4	0	0	2	0	0	0	4	0	0

This was reduced to give -

$$\Gamma_{M-X} = A_{1g} + B_{1g} + E_u$$

In the same way it can be shown that for the M-L stretching vibrations -

$$\Gamma_{M-L} = A_{1g} + A_{2u}$$

and for the X-M-X in-plane deformations -

$$\Gamma_{X-M-X\ (in)} = B_{1g} + E_u \quad \text{(only 3 independent vectors)}$$

For the X-M-X out-of-plane and L-M-L modes, it is more difficult to find the proper coordinates. The best way to proceed is to consider what is left over from Γ_{3n-6} (external coordinates); this is -

$$A_{2u} + B_{2u} + E_g + E_u$$

In the MX_4 square plane system (5-atomic, D_{4h}) the out-of-plane modes belong to A_{2u} and B_{2u} (68). In the linear carbon dioxide molecule, there is a doubly degenerate bending frequency of symmetry, E_u, and a doubly degenerate rotational pair of modes of symmetry type, E_g (69).

Hence we can now complete the internal coordinate analysis on the trans-$MX_4 \cdot 2L$. The X-M-X out-of-plane deformation modes are described by the following result:

$$\Gamma_{X-M-X\ (out)} = A_{2u} + B_{2u}$$

and the L-M-L deformations, by -

$$\Gamma_{L-M-L} = E_g + E_u$$

Note that the E_g modes become genuine vibrations in the trans-$MX_4 \cdot 2L$ molecule because this kind of motion will not impart angular momentum to the molecule due to the fixed position of the MX_4 plane.

cis-$MX_4 \cdot 2L$

As in the case of the trans isomer, a reducible representation of dimension of twenty-one is generated.

E	C_2	σ_v	σ_v'
21	-1	3	5

This is reduced to -

$$\Gamma_{3n} = 7A_1 + 3A_2 + 6B_1 + 5B_2$$

The translational modes belong to -

$$A_1\ (z), \quad B_1\ (x), \quad B_2\ (z).$$

The rotational modes belong to -

$$A_2\ (R_z), \quad B_1\ (R_y), \quad B_2\ (R_x).$$

Hence the genuine representation is as follows:

$$\Gamma_{3n-6} = 6A_1 + 2A_2 + 4B_1 + 3B_2$$

In the internal coordinate analysis, for the four M-X bonds, the following result is obtained:

$$\Gamma_{M-X} = 2A_1 + B_1 + B_2$$

For the M-L bond stretching -

$$\Gamma_{M-L} = A_1 + B_1$$

For the X-M-X deformations -

$$\Gamma'_{X-M-X} = 3A_1 + A_2 + B_1 + B_2$$

However, the redundancy condition removes one of the A_1 modes because only five coordinates are independent.

$$\Gamma_{X-M-X} = 2A_1 + A_2 + B_1 + B_2$$

Those modes left over from Γ_{3n-6} are -

$$A_1 + A_2 + B_1 + B_2$$

Consider now the case of water (C_{2v}). This molecule has one genuine deformation mode of symmetry type A_1 and three rotational modes of symmetries A_2, B_1 and B_2 (70). The last three become genuine vibrations when applied to the L-M-L deformations of cis-$MX_4 \cdot 2L$. Hence in this molecule, the L-M-L deformations belong to -

$$\Gamma_{L-M-L} = A_1 + A_2 + B_1 + B_2$$

Point Group D_{2h}

This alternate molecular point group of the trans isomer applies to adducts in which the ligand molecules are not free to rotate. For example, pyridine is a planar molecule (C_{2v}) and hence a rotation of 90° about the nitrogen-3-carbon axis (a C_4 operation) is not a symmetry operation. There is a possibility that the pyridine molecules (the same would hold for isoquinoline) may be held fixed through hydrogen bonding between the atoms and the halogen atoms in the MX_4 plane. It must be noted, however, that there is no experimental evidence either for or against such hydrogen bonding.

The analysis using D_{2h} symmetry yields the following genuine representation:

$$\Gamma_{3n-6} = 2A_g + B_{1g} + B_{2g} + B_{3g} + A_u + 2B_{1u} + 3B_{2u} + 3B_{3u}$$

The results of the internal coordinate analyses are listed in Table XVII, together with those of the D_{4h} and C_{2v} groups.

In addition, the activities of the various modes are given using the following notation:

Raman active	=	R
Infrared "	=	I
Both "	=	R, I
Inactive	=	N

TABLE XVII

Normal Modes of $MX_4 \cdot 2L$

Mode	D_{4h}			D_{2h}				C_{2v}			
M-X	A_{1g}	B_{1g}	E_u	$2A_g$	B_{2u}	B_{3u}		$2A_1$	B_1	B_2	
	R	R	I	R	I	I		R,I	R,I	R,I	
M-L	A_{1g}	A_{2u}		A_g	B_{1u}			A_1	B_1		
	R	I		R	I			R,I	R,I		
X-M-X	B_{2g}	E_u		B_{1g}	B_{2u}	B_{3u}		$2A_1$	A_2		
in-plane	R	I		R	I	I		R,I	R		
X-M-X	A_{2u}	B_{2u}		A_u	B_{1u}			B_1	B_2		
out-of-plane	I	N		N	I			R,I	R,I		
L-M-L	E_g	E_u		B_{2g}	B_{3g}	B_{2u}	B_{3u}	A_1	A_2	B_1	B_2
	R	I		R	R	I	I	R,I	R	R,I	R,I

As shown, the E modes in D_{4h} break down to two non-degenerate modes in D_{2h}. For example, consider the L-M-L deformations in pyridine adducts. Broadside motions (flapping) would be expected to occur at frequencies different from those of edgewise motions of the pyridine rings. This would apply to both the "gerade" and "ungerade" symmetries. With respect to the metal-halogen modes, however, it is possible that localized four-fold symmetry in the MX_4 plane may be preserved and give rise to doubly degenerate E modes involving metal-halogen bonds. The only way to make an unequivocal choice between D_{4h} and D_{2h} by spectroscopic means is to study the complete infrared and Raman spectrum and assign all the fundamentals.

Table XVII also shows that for the trans isomer (D_{4h}), there are five infrared active fundamentals, five Raman active fundamentals and one that is inactive. For the cis isomer (C_{2v}), the table shows that there are thirteen infrared active and fifteen Raman active fundamentals. Thus infrared and Raman spectroscopy should provide an excellent means of distinguishing between the two isomers. The vibrations that are particularly valuable in this connection are the metal-halogen stretching modes. The trans isomer has one infrared active M-X stretching fundamental whereas the cis isomer has four. The experimental results will show that the metal-halogen stretching frequencies of adducts of silicon and germanium tetrahalides (excluding the iodides) occur over the frequency range from 800 to 265 cm^{-1}. and that the number of bands observed in the spectrum is determined by the symmetry of the central atom.

The shapes of the normal coordinates of the M-X stretching modes are shown in Figure 11 for the trans-$MX_4 \cdot 2L$ (D_{4h}) and in Figure 12 for the cis-$MX_4 \cdot 2L$ (C_{2v}). The arrows in the diagrams represent the directions of changes in positions of the atoms but do not represent the magnitudes of such changes. Symmetry considerations alone cannot give the amplitudes of vibrations, only the directions of the motions of the atoms.

Solid State Infrared Spectra

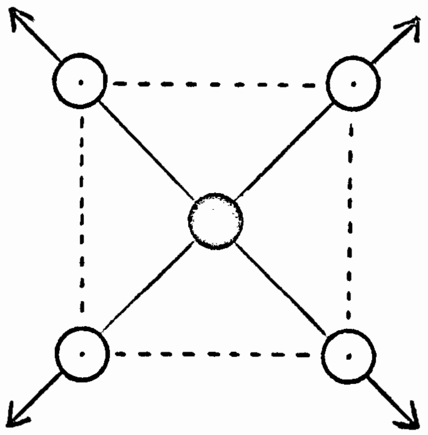
The foregoing symmetry analysis is completely general but the results concerning the activities of the normal modes are applicable only to isolated systems, i.e. vapour phase and dilute solutions. In the case of condensed phase spectra, the interactions between a given molecule and its neighbours change the selection rules (71).

In order to carry out the complete symmetry analysis on the vibrations of molecules in crystalline solids it is necessary to know the space group of the crystal and the number of molecules per unit cell of the crystal. The molecule is considered to occupy a site which is defined as a point left invariant by some of the operations of the space group and this is called the site group (71, 72).

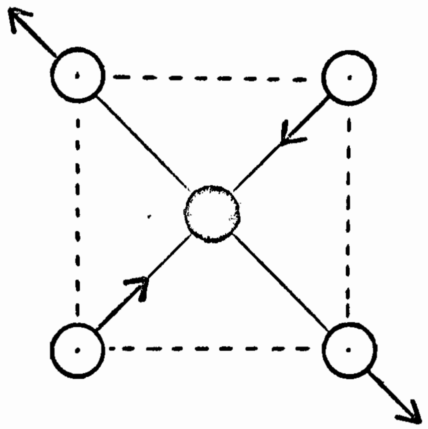
The site symmetry is the key in deducing selection rules for solid state spectra. In order that a given site group be acceptable for a symmetry analysis, it must be a sub-group of both the crystallographic space group and the molecular point group and hence in many systems an unequivocal choice is easily made. Once a suitable site group is found, the symmetry analysis is carried out on the basis of the site symmetry rather than the molecular symmetry as in the case of isolated molecules.

FIGURE 11

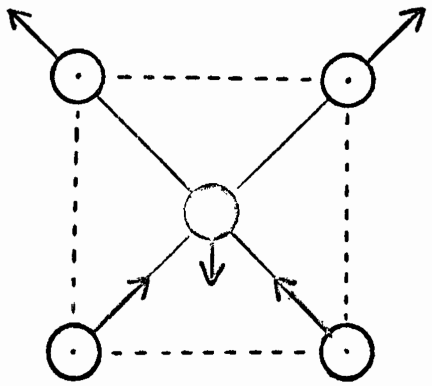
Normal Coordinates of the Metal-Halogen Stretching Modes of the Trans-$MX_4 \cdot 2L$ Point Group, D_{4h}



A_{1g}



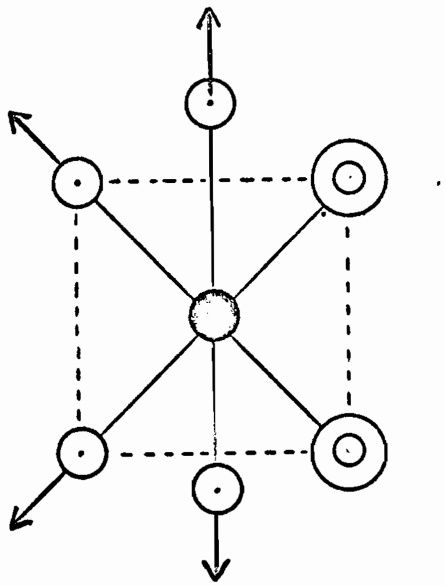
B_{1g}



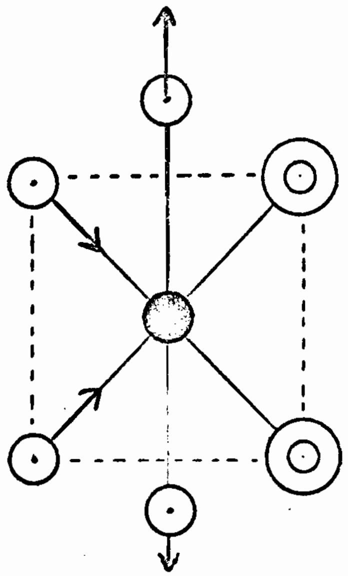
E_u

FIGURE 12

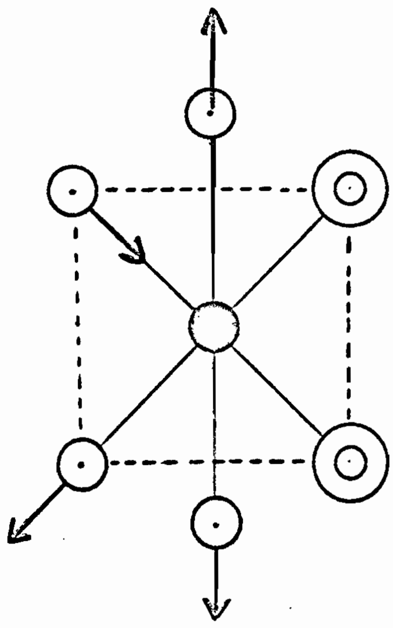
Normal Coordinates of the Metal-Halogen Stretching Modes of the Cis-$MX_4 \cdot 2L$ Point Group, C_{2v}.



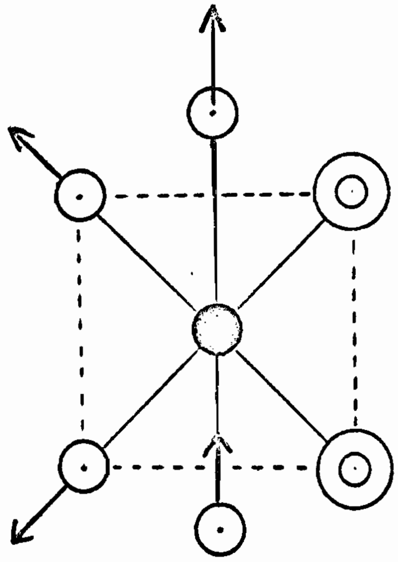
A_1



A_1



B_1



B_2

In this dissertation, however, the site symmetry approach was not considered. The only adduct, for which the space group is known, which was studied by this author, is trans-$GeCl_4 \cdot 2Py$ (17). All the systems studied in this work will be treated as isolated systems as a first approximation although mention will be made of some possible effects of site symmetries in the discussion of the experimental results.

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