SOME PROPERTIES OF
VANADIUM AND NIOBium PENTAFuORIDES

by

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ABSTRACT

SOME PROPERTIES OF VANADIUM AND NIOBium PENTAFUORIDES

The reactions of various amines with vanadium and niobium pentafluoride have been studied. Pyridine and ammonia reacted with vanadium pentafluoride reducing vanadium from the pentavalent to the tetravalent state and forming monosolvated complexes of vanadium tetrafluoride. The products isolated were pyridinetetrafluorovanadium IV, (Py)VF₄, and amminotetrafluorovanadium IV, (NH₃)VF₄. Ethylenediamine also reduced vanadium pentafluoride to the tetravalent state but formed a more highly solvated derivative of vanadium tetrafluoride. The product was identified as tris(ethylenediamine)tetrafluorovanadium IV and has been formulated as the octahedral complex \([V(en)_3]F_4\).

Niobium pentafluoride reacted with ammonia to form a 2:1 adduct of niobium pentafluoride, diammonopentafluoronioibium V, (NH₃)₂NbF₅. The product formed on reaction of ethylenediamine with niobium pentafluoride had the composition NbF₅(en)₁.₆. It has been considered as a highly solvated 1:1 adduct ethylenediaminepentfluoronioibiium V. No reduction of niobium has been observed in amine reactions.

The infrared spectra and magnetic susceptibilities of the complexes have been measured and the dissociation pressure of diamminopentafluoronioibiium V has been determined. The solubilities and melting points of the complexes were also investigated.
The pentafluorides of vanadium and niobium, in contrast to the highest chlorides of the same metals, are not solvolysed by the amines studied here. This common behaviour of fluorides, coupled with an apparent maximum coordination number of six for vanadium has been used to explain the reduction of vanadium pentafluoride by the amines.

The reduction of vanadium occurs because the association of vanadium pentafluoride in the liquid state has saturated the coordination number of vanadium, so that any solvated product formed by the amines has an unstable coordination number which must be lowered. The fact that solvolysis, which provides a method of reducing the coordination of the central atom without reducing its valence state, can not occur with fluorides, requires that the reduction in coordination number of vanadium must proceed through an alternate mechanism with concomitant reduction of the valence of vanadium. This interpretation is consistent with the behaviour of niobium pentafluoride which forms solvated derivatives in which niobium has increased its coordination number to seven or eight, the probable maximum coordination number of niobium.

Structures have been suggested for the products of the amine reactions. The properties of the pyridine and ammonia derivatives of vanadium pentafluoride, \((\text{Py})\text{VF}_4\) and \((\text{NH}_3)\text{VF}_4\), plus the improbable coordination of five for vanadium in the monomer suggests that the compounds are
polymers. The most probable structure is a long chain of $\text{VF}_4$. Base units linked by fluorine bridge bonds such as have been proposed to explain association of vanadium pentafluoride. The ethylenediamine derivative of vanadium pentafluoride, $[\text{V(en)}_3]^4_4$, is probably a monomeric compound, for there is no need to postulate association to increase the coordination number of vanadium to six. The many complex ions formed by ethylenediamine suggest that it is reasonable to postulate the formation of the $[\text{V(en)}_3]^4_4$ ion. This is the first hexacoordinate cationic complex of tetravalent vanadium, with the exception of vanadyl complexes, to be reported. The niobium pentafluoride complexes $(\text{NH}_3)_2\text{NbF}_5$, (en)NbF$_5$ may be septacoordinate monomers, isostructural with iodine heptafluoride, or octacoordinate fluorine bridged polymers. The proposed structures are based only on the few qualitative properties that are available for the compounds. Complete structure determinations are required for verification of the structures proposed.

A nuclear magnetic resonance study of vanadium pentafluoride has yielded only the $F^{19}$ chemical shift of vanadium pentafluoride of -335 ppm relative to trifluoroacetic acid. The broad nuclear resonance absorption obtained has been explained in terms of rapid fluorine exchange occurring in conjunction with quadrupole broadening due to the electric quadrupole moment of vanadium.
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# CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Coordination and Structure of Transition Metal Fluorides</td>
<td>10</td>
</tr>
<tr>
<td>3. Ammonia Derivatives of Vanadium and Niobium Pentasfluorides</td>
<td>19</td>
</tr>
<tr>
<td>4. Pyridine Derivatives of Vanadium and Niobium Pentasfluorides</td>
<td>30</td>
</tr>
<tr>
<td>5. Ethylenediamine Derivatives of Vanadium and Niobium Pentasfluorides</td>
<td>37</td>
</tr>
<tr>
<td>6. A Survey of the Amine reactions</td>
<td>43</td>
</tr>
<tr>
<td>7. Nuclear Magnetic Resonance of Vanadium Pentasfluoride</td>
<td>53</td>
</tr>
<tr>
<td>8. Experimental</td>
<td></td>
</tr>
<tr>
<td>(i) General Techniques</td>
<td>57</td>
</tr>
<tr>
<td>(ii) Analytical Methods</td>
<td>62</td>
</tr>
<tr>
<td>(iii) Fluorine Supply</td>
<td>66</td>
</tr>
<tr>
<td>(iv) The preparation of Vanadium and Niobium Pentasfluorides</td>
<td>68</td>
</tr>
<tr>
<td>(v) The reaction of Vanadium Pentasfluoride with Ammonia</td>
<td>71</td>
</tr>
<tr>
<td>(vi) The reaction of Niobium Pentasfluoride with Ammonia</td>
<td>74</td>
</tr>
<tr>
<td>(vii) The reaction of Vanadium Pentasfluoride with Pyridine</td>
<td>76</td>
</tr>
<tr>
<td>(viii) The reaction of Vanadium Pentasfluoride with Ethylenediamine</td>
<td>79</td>
</tr>
<tr>
<td>(ix) The reaction of Niobium Pentasfluoride with Ethylenediamine</td>
<td>81</td>
</tr>
<tr>
<td>(x) The Nuclear Magnetic Resonance Spectrum of Vanadium Pentasfluoride</td>
<td>83</td>
</tr>
<tr>
<td>References</td>
<td>85</td>
</tr>
</tbody>
</table>
In 1946 reliable commercial supplies of fluorine became readily available, thus stimulating research in a branch of chemistry which had been neglected since the early part of the twentieth century. Apart from the pioneering studies of fluorine and its compounds by Moissan and Ruff very little work had been done on fluorine compounds, particularly the fluorides of the transition metals. Recent years have seen great activity in all branches of fluorine chemistry; many new compounds have been reported and the meagre and contradictory information available for many known fluorides has been supplemented by more reliable data. Fluorides of the transition metals have excited much interest in the last fifteen years and will continue to do so in the future because of their extremely reactive nature.

The subject of this thesis is a study of the chemical behaviour of vanadium pentafluoride and a related compound, niobium pentafluoride, with nitrogen containing, electron donor molecules.

Vanadium pentafluoride was first reported by Ruff and Lickfett (1) to be a non-volatile orange solid which did not melt in sealed tubes below 200°C. This result was not compatible with the observed melting points of
other group VB pentafluorides, niobium and tantalum pentafluorides which melt at 78.9°C (3) and 91.5°C (2) respectively. Recent work (4, 5) has shown that vanadium pentafluoride is actually a white solid which melts in sealed tubes to a pale straw coloured liquid at 19.5°C, in agreement with the expected increase in melting point with increasing molecular weight within a subgroup. Vapor pressure measurements of vanadium pentafluoride (4, 5) give an extrapolated boiling point of 48.3°C which, when combined with the latent heat of vaporisation determined from the same data, yields a Trouton constant of 33.1 cal/mole/deg. much higher than the normal value of 22 or 23 cal/mole/deg.

Many liquid fluorides have been found to have high Trouton constants, that is they have a high entropy of vaporisation. Abnormal Trouton constants, are found in liquids with high viscosities and relatively high boiling points, and are generally indicative of association of some type in the liquid. These fluorides are thought to associate through the formation of fluorine bridge bonds (6). Through association of this type dimeric or polymeric structures of the fluoride unit are formed in which the central atom achieves a higher coordination state. In this manner vanadium pentafluoride can form
dimers (V₂F₁₀) in which two of the fluorine atoms are situated in between the two vanadium atoms to form two fluorine bridge bonds. The structure of the resulting dimer can be visualized as two VF₆ octahedra joined by a common edge. In this structure each vanadium atom is hexacoordinate and presumably utilizes approximately d²sp³ hybridisation with a resulting octahedral configuration. Association to polymers, of the type (VF₅)ₙ, must also be considered. Here the VF₆ octahedral units can be visualized as sharing non-adjacent apices so that the resultant structure is a long chain polymer. The vanadium atom is also hexacoordinate in the polymeric structure. Present evidence on the nature of the association of vanadium pentafluoride however is not sufficient to indicate whether dimers or polymers are formed.

The fluorine bridge bond is at present postulated only on the basis of the qualitative evidence of association in liquid fluorides. No quantitative confirmation of this type of bonding has been obtained, thus its status is similar to that of the hydrogen bond some forty years ago. It has proved to be useful in explaining association phenomena without the presence of unlikely metal — metal bonds. Some verification of fluorine bridging has been obtained in solids where
X-ray studies have shown fluorine atoms occupying bridging positions (7). Little quantitative information is available for liquids, in fact the best evidence for fluorine bonds in liquid fluorides is obtained from the nuclear magnetic resonance study of antimony pentafluoride (8).

Antimony pentafluoride is a liquid at room temperatures with an extremely high viscosity, approaching that of glycerol. It has a high Trouton's constant of 25.9 cal/deg/mole. On this qualitative evidence alone it is probable that antimony pentafluoride is highly associated in the liquid state. There is no evidence to support the formation of Sb - Sb bonds so presumably antimony pentafluoride is associated through the formation of fluorine bridge bonds. The nuclear magnetic resonance spectrum consists of three peaks with relative intensities of 1:2:2. The structure consistent with the nuclear magnetic resonance spectrum and the high viscosity is a long polymeric chain of octahedral SbF₆ groups joined at two orthogonal apices by fluorine bridges. There are then three groups of non equivalent fluorine atoms; one bridge fluorine per SbF₅ unit; two fluorines trans to the bridge fluorine, and two fluorines trans to each other. Hoffman et al. (8) point out that the bridge bonds are cis to each other.
(ie orthogonal apices of the octahedral unit are involved in the bridge formation) in order to utilize the most favourable bonding orbitals.

Many other fluorides have been studied with nuclear magnetic resonance techniques (9) but in no other case can the results be directly interpreted in terms of a fluorine-bridged structure. The resolved spectra have, in many instances, yielded much information as to the structure of the fluoride monomer and the collapse of the resolved spectra has been explained in terms of fluorine bridging. The nuclear resonance spectra of many fluorides consists of a broad, unresolved peak which is generally attributed to field averaging, exchange phenomena. Broadening of F$^{19}$ resonances in simple fluorides is generally attributed to exchange involving intermediates associated via fluorine bridge formation (9). Resolution of exchange broadened peaks has been accomplished in several cases by cooling the sample to a temperature where the rate of exchange is sufficiently slow to permit the observation of the nuclear resonances in the absence of an averaging effect. Because of the high melting points of many of the fluorides studied, sufficient cooling could only be obtained using hydrocarbon solvents with extremely low melting points. The use of solvents in studies of the nuclear resonance spectrum has indicated that the simple
dissociation process:

\[ MF_n \rightleftharpoons MF_{n-1}^+ + F^- \]
does not occur because the solvents are not fluorinated.

Approximate rate studies of the exchange (9) indicate that a second order process is involved, thus supporting the associative mechanism in preference to the above dissociation mechanism. It must also be recognized, however, that transfer of a fluoride can occur through a self-ionising mechanism of the type:

\[ (MF_n)_2 \rightleftharpoons MF_{n-1}^+ + MF_{n+1}^- \]

which is thought to occur in many fluorides.

Much evidence has been obtained from electrical conductivity studies of fluorides to support this self-ionisation. An exchange process of this type would also broaden nuclear resonance signals and account for a high Trouton constant.

Association and self-dissociation are not mutually exclusive processes. Energy requirements indicate that dissociation of the type:

\[ MF_n \rightleftharpoons MF_{n-1}^+ + F^- \]

which would account for the observed conductivities does not occur, hence self-ionisation must involve some form of association prior to the formation of ions. Both fluorine bridge association and self-dissociation could be involved in many fluorides and it is not possible in
the light of present knowledge to consider one process to be more important than the other.

Vanadium pentafluoride has been shown to have an appreciable electrical conductivity. Its specific conductivity \( \kappa_{sp} = 2.3 \times 10^{-4} \ \text{ohm}^{-1} \ \text{cm}^{-1} \) (4) is slightly less than that of bromine trifluoride (10) which has been shown to be a self-ionizing solvent (10, 11, 12). It has therefore been suggested (4) that vanadium pentafluoride self-ionizes according to the equilibrium:

\[
(VF_5)_2 \rightleftharpoons VF_4^+ + VF_6^-
\]

thus forming an acid-base solvent system. In this system compounds containing the \( VF_4^+ \) ion are defined as acids, those containing the \( VF_6^- \) ion as bases. The dissociation of vanadium pentafluoride probably involves a preliminary association into fluorine bridge dimers followed by transfer of the bridging fluorines from an intermediate position between two vanadium atoms onto one of the vanadium atoms, thus producing the \( VF_4^+ \) and \( VF_6^- \) ions.

Niobium and tantalum pentafluorides, on the basis of their electrical conductivities (specific conductivities: \( \text{NbF}_5 = 1.63 \times 10^{-5} \) ; \( \text{TaF}_5 = 1.5 \times 10^{-5} \ \text{ohm}^{-1} \ \text{cm}^{-1} \) (13)), also appear to self-ionize in a similar manner to vanadium pentafluoride:

\[
(MF_5)_2 \rightleftharpoons MF_4^+ + MF_6^-
\]
The Trouton constants are higher than normal (\(\text{NbF}_5 = 25.4\); \(\text{TaF}_5 = 25.9\) cal/mole/deg (2)) but not as high as that for vanadium pentafluoride, which suggests that niobium and tantalum pentafluorides may not be as highly associated as vanadium pentafluoride.

To prove the existence of acid-base solvent system in the group VB pentafluorides it is necessary to fulfill three criteria. First it must be possible to obtain compounds containing the \(\text{MF}_4^+\) and \(\text{MF}_6^-\) ions and to show that these compounds are, at least, partially ionic. Second, the combination of compounds containing the acidic (\(\text{MF}_4^+\)) and basic (\(\text{MF}_6^-\)) ions must result in the formation of a salt and the solvent. Thirdly, it must be possible to perform neutralization reactions having definite end-points when equivalent amounts of acid and base have been mixed.

The only evidence available in support of a self-ionizing solvent system for the group VB pentafluorides is the isolation of compounds presumably containing the basic (\(\text{MF}_6^-\)) anion (14,15). No compounds containing the acidic (\(\text{MF}_4^+\)) ion are known. It is therefore not possible to conclude that the group VB pentafluorides form new acid-base solvent systems on the basis of existing evidence. Little is yet known about the relative importance of self-ionization and fluorine bridge association in determining the properties of vanadium, niobium and tantalum pentafluorides, and
clearly much more information is required in order to obtain a fuller understanding of their properties.
CHAPTER 2: COORDINATION AND STRUCTURE OF TRANSITION METAL FLUORIDES

The word coordination has many meanings in structural chemistry which are essentially similar in that they describe the stereochemical relationships between the structural units. A somewhat restricted definition, which will suffice for a discussion of the properties of transition metal fluorides, results when coordination is considered as it applies to coordination complexes of the type $\text{Cr} (\text{NH}_3)_6 \text{Cl}_3$. In all compounds in which coordination occurs, it is generally considered that the resulting bonding possesses both ionic and covalent characteristics, and so it is convenient to discuss the interpretation of coordination number and structure in terms of the set of simple or hybridised orbitals used in the covalent contribution to the bonding. The coordination number then frequently implies the utilization of a certain set of hybridised orbitals which are highly directional and possess a definite stereochemical configuration so that the coordination number can be related to the structure.

In order to understand more fully the influence of coordination number on structure and reactivity
it will be necessary to consider the major factors influencing the coordination state. For present purposes this may be done only qualitatively.

The assumption that there is some covalent character in the bonding involved in complexes requires that a sufficient number of bonding orbitals be available on the central atom for covalent bond formation. In a discussion of complexes of the transition metals however, there are usually more orbitals available than required for the formation of coordinate bonds. The formation of coordination complexes of the transition metals will then be influenced primarily by the relative sizes of the ligand and the metal involved.

For a constant size of metal the size of the ligand will be an important factor in determining the coordination number of the complex formed. Likewise the size of the metal atom will govern the number of ligands that can be arranged around it. If the ligands are small, such as F\textsuperscript{-}, NH\textsubscript{3} etc. and bonding hybrid orbitals are available, the size of the metal atom will govern the maximum number of ligands that can be bonded to the central metal atom or ion. The maximum number of ligands that can be attached is the maximum coordination number. The
Effect of size can be readily observed in a comparison of transition metals of the first and second long periods. Assuming that maximum coordination is achieved in fluoroanions, which appears to be generally true from qualitative evidence, the transition metals of the first long period, such as vanadium, chromium, manganese, and iron, form the hexacoordinate ions $\text{VF}_6^-$, $\text{CrF}_6^{3-}$, $\text{FeF}_6^{3-}$. No heptafluoroanions are observed in the first long period. In the second long period, heptafluoroanions are often formed, such as $\text{ZrF}_7^{-2}$ and $\text{NbF}_7^{-2}$. The increase in coordination number from a maximum of six to a maximum of seven or higher can be attributed to the increase in size of the metal atom. For example in group Vb, vanadium, which has a radius of 1.23 Å (34) forms hexacoordinate fluoroanions, and niobium, which has an atomic radius of 1.34 Å (34) and forms heptacoordinate fluoroanions.

If the assumption that the fluoroanions exhibit the maximum coordination of a metal is correct (comparison with other ligands shows that higher coordination is never obtained), then it is apparent from the above examples that vanadium has a maximum coordination number of six whereas niobium can assume a higher coordination state. The significance of this maximum will be demonstrated in the results of
the present studies. It is apparent that where a maximum stable coordination state exists, any structure with a higher coordination state formed in a reaction will be unstable and tend to decompose in order that the central atom can revert to its maximum stable coordination state. The products of a reaction involving an increase in coordination will be simple and straightforward only if the higher coordination state is stable. If the higher coordination state is unstable, the intermediate formed will tend to revert to the lower coordinate state by decomposition.

The structures of polyatomic molecules and ions are clearly determined by the coordination number of the metal atom. The most important coordination states are four and six. Of lesser importance are two, three, five, seven and eight. For a discussion of the influence of coordination on structure and reactivity for the group VB pentafluorides it will be of value to review briefly the higher coordination states, from five to eight inclusive.

Of the coordination states considered, penta-coordination is the least common. A few molecules are known to be pentacoordinate in the gaseous phase. An example is phosphorous pentafluoride which has a trigonal bipyramidal structure, presumably utilizing
sp\(^3\)d orbital hybridization. Although a trigonal bipyramid is the most likely structure for a pentacoordinate molecule, square pyramids, involving d\(^2\)sp\(^2\) hybridization are also possible but no examples of this structure are known. Presumably a trigonal bipyramidal configuration of atoms is preferable to a square planar configuration because of the reduced repulsion of the ligands. Other examples of pentacoordinate, trigonal bipyramidal molecules are NbCl\(_5\) and MoCl\(_5\) (17) but in general very few pentacoordinate molecules are known.

Pentacoordination has only been verified in a few molecules in the vapor state, but no pentacoordinate molecules have been found in the liquid or solid states. The reason for the absence of pentacoordinate structures in the condensed phases can be attributed to intermolecular interaction leading to an increase in coordination. Thus in the condensed phases, where association is likely (or in solution where solvent molecules can interact with the solute increasing its coordination) a pentacoordinate structure can become a hexacoordinate structure. In the vapor phase, where interaction is greatly reduced, increase in coordination will be unlikely hence pentacoordinate structures will be found. The increase in stability
accompanying the formation of hexacoordinate structures must be considerable because many examples of association are found in apparently pentacoordinate molecules. The group V pentfluorides such as VF\textsubscript{5} and SbF\textsubscript{5}, which have been discussed previously, show a marked tendency to associate through the formation of fluorine bridge bonds and thus increase the coordination state of the central atom. A self-dissociation process such as that postulated for VF\textsubscript{5} is also aided by the increased stability of the coordination states produced. Thus VF\textsubscript{5} can achieve more stable coordination states for vanadium by dissociating into the tetra-coordinate VF\textsubscript{4}\textsuperscript{+} ion, which is probably tetrahedral, and the hexacoordinate, octahedral VF\textsubscript{6}\textsuperscript{−} ion. Both ions exist in coordination states which are very common and thus more stable than the uncommon pentacoordinate state.

Some examples of pentacoordination in solids have been suggested. For instance Fowles and Pleass (19) suggested that the complex, VCl\textsubscript{3}·2\textsuperscript{NMe₃} could be pentacoordinate. This however was not supported by a structure determination and in a later paper (20) they suggested the possibility of dimensation. Complexes such as TiCl\textsubscript{4}·\textsuperscript{NEt₃} are suggested by
Gillespie and Nyholm (17) as examples of pentacoordination. Muetterties (18) suggests that complexes of the group IV fluorides, e.g. TiF₄·CH₃CN, are not pentacoordinate as indicated by their stoichiometry but are rather polymeric structures in which the central atom is hexacoordinate. Thus pentacoordination appears to be an unlikely coordination state in solid and liquid materials and suggestions of pentacoordination must be accepted with reservation.

Hexacoordination is the most common coordination state. Many examples of hexacoordinate structures are known, for instance neutral molecules such as MoF₆, WF₆, SF₆, SeF₆ etc., and complex ions such as VF₆⁻, NbF₆⁻, Cr(NH₃)₆⁺³ etc. The structure in all cases is basically octahedral utilizing d²sp³ bonding hybrids. Slight distortion is found in some structures because of steric interference by the ligands or interference of non-bonding electrons with the bond orbitals, but an octahedral structure is generally recognizable. The stability of the hexacoordinate state is indicated by the lack of any tendency of the hexacoordinate fluorides of group VIB (MoF₆, WF₆) to associate in the liquid state (6). The frequency of occurrence of hexacoordinate molecules also supports the greater stability of hexacoordinate structures over pentacoordinate or heptacoordinate structures.
A few examples of coordination states higher than six have been verified. Higher coordination states generally are found in complex anions such as $\text{TaF}_7^-$, $\text{ZrF}_7^-$, $\text{Mo(CN)}_8^{-4}$ etc. (17). The orbital hybridisation is not fully understood in these compounds. The $\text{ZrF}_7^-$ ion has a pentagonal bipyramid structure involving $d^3sp^3$ hybridization. A face-centered trigonal-prism structure involving $d^4sp^2$ hybrids has been suggested for the heptacoordinate $\text{TaF}_7^-$ anion. The octacoordinate anion $\text{Mo(CN)}_8^{-4}$ presumably has a square antiprism structure formed by $d^5p^3$ hybridisation. Few neutral molecules have a coordination number greater than six, however iodine heptafluoride is an example of a septacoordinate molecule. Hence steric considerations indicate that coordination states of seven or greater will be stable if the central atom of the complex is large (eg. iodine) or if the overall size of the complex is expanded due to the presence of a charge on the complex.

In reviewing the various coordination states it is apparent then that many molecules, exhibiting the unusual pentacoordinate state are actually more highly coordinated than their stoichiometry would indicate. A more common, and presumably more stable, coordination state is then formed by association or some other means. Because of such intermolecular interaction to produce higher coordination states, the rigorous assignment of coordination numbers
is always dependent on a complete structure determination.
CHAPTER 3: AMMONIA DERIVATIVES OF VANADIUM AND NIOBIUM PENTAFLUORIDES

Ammonia is the simplest of the nitrogen bases considered. Its ability to act as an electron pair donor is well known. It reacts with simple electron pair acceptors such as borontrifluoride forming well defined adducts (eg NH₃, BF₃) and it also forms coordinate bonds with transition metals having vacant d orbitals. Examples of ammonia complexes formed with transition metals are the complex cations such as \([\text{Cr(NH}_3\text{)}_6]^{3+}\).

Some transition metal fluorides are known to form complex compounds with ammonia. For example, tungsten hexafluoride gives the product WF₆·4NH₃ in liquid ammonia (16). The exact nature of this compound, however, is not fully understood.

Ammonia, in addition to its electron donor properties, is also recognized as an acid-base solvent system. It is thought to self-dissociate to form acidic and basic ionic species in solution:

\[
2\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^- 
\]

Thus solvolysis can occur in liquid ammonia in addition to the formation of donor-acceptor complexes. Compounds which are soluble in ammonia are often solvolyzed, existing as hypothetical acids or bases in the liquid ammonia system.

The relative stability of ammonia with fluorides makes it a good choice for the study of electron accepting
properties of compounds such as the transition metal fluorides. Vanadium and niobium pentafluorides are theoretically capable of forming adducts because the unoccupied d orbitals in the metal atom can accept electrons from a donor.

Vanadium pentafluoride has been found to react immediately with liquid ammonia at -50°C to form a reddish-brown solid which was insoluble in liquid ammonia. Throughout the reaction, multi-coloured solid products are produced which become reddish brown when complete reaction has occurred. The reddish-brown solid loses ammonia readily until a pale grey-brown product is obtained. The solid is paramagnetic and X-ray powder photographs indicate the presence of ammonium fluoride. On removal of ammonium fluoride by sublimation the grey-brown solid becomes a darker brown and approximates to the composition \( \text{VF}_4(\text{NH}_3) \).

This powdery dark brown solid with the composition \( \text{VF}_4(\text{NH}_3) \) is paramagnetic with a magnetic moment of 2.14 Bohr magnetons, slightly greater than that expected for tetravalent vanadium. All known tetravalent vanadium compounds have magnetic moments close to the spin only value of 1.73 Bohr magnetons (26). Titration of a sample of the solid immediately upon dissolving in dilute sulphuric acid solution indicates approximately 8% trivalent vanadium is present in addition to tetravalent vanadium which would account for the slightly high value of the observed magnetic moment.
Reduction of vanadium pentfluoride with ammonia to form principally amminotetrafluorovanadium IV, \((\text{NH}_3)\text{VF}_4\), is strange in view of the tendency of ammonia to solvolyze transition metal halides. Fowles and Nicholls (24) have found that liquid ammonia solvolyzes vanadium tetrachloride producing a mixture of amidobasic vanadium chloride and ammonium chloride:

\[
\text{VCl}_4 + 6\text{NH}_3 \rightarrow \text{VCl}((\text{NH}_2)_3 + 3\text{NH}_4\text{Cl}
\]

Similarly tungsten hexachloride, according to Fowles and Osborne (25), is solvolyzed by liquid ammonia, producing a mixture of ammoniated amidobasic tungsten chlorides \((\text{WCl}_5(\text{NH}_2), 2\text{NH}_3\) and \(\text{WCl}_4(\text{NH}_2)_2, 2\text{NH}_3\)) and ammonium chloride. Similarly niobium pentachloride according to Fowles and Pollard (22) is solvolyzed:

\[
\text{NbCl}_5 + 4\text{NH}_3 \rightarrow \text{NbCl}_3((\text{NH}_2)_2 + 2\text{NH}_4\text{Cl}
\]

On the basis of these studies it would be reasonable to expect solvolysis of vanadium pentfluoride. This is not observed and the reaction instead apparently involves reduction and solvation.

Reduction of vanadium in the reaction with ammonia must be accompanied by an oxidation of some component. The oxidation product must be sufficiently volatile to pass through a liquid nitrogen trap in an evacuated system because no oxidation products volatile or involatile, were found in the solid product or the volatile materials.
It is possible that ammonia was oxidized to nitrogen and the resulting hydrogen atoms used in formation of hydrogen fluoride which in liquid ammonia yields ammonium fluoride. The equation for reaction is then:

\[ 6VF_5 + 14NH_3 \rightarrow 6VF_4(NH_3) + N_2 + 6NH_4F \]

One mole of ammonium fluoride is produced per mole of amminotetrafluorovanadium IV which is in agreement with the observed loss in weight, of approximately 20%, on removal of ammonium fluoride by sublimation.

A mechanism for the oxidation reaction can only tentatively be suggested in view of the fact that the oxidation product is unknown. If ammonia was oxidized to nitrogen as suggested above, it could occur through the formation of fluoramine and hydrazine and their subsequent decomposition to nitrogen and ammonium fluoride according to the equations:

\[ 6VF_5 + 6NH_3 \rightarrow 6VF_4(NH_3) + 6F \]
\[ 6F + 6NH_3 \rightarrow 3NH_2F + 3NH_4F \]
\[ NH_2F + 2NH_3 \rightarrow N_2H_4 + NH_4F \]
\[ 2NH_2F + N_2H_4 \rightarrow N_2 + 2NH_4F \]

Adding \[ 6VF_5 + 14NH_3 \rightarrow 6VF_4(NH_3) + N_2 + 6NH_4F \]

It is only possible to speculate upon a mechanism until more is known of the products.

In contrast to the reduction of vanadium pentfluoride, niobium pentfluoride reacts with liquid ammonia to form
a stable adduct, diamminopentafluoroniobium \( V, (NH_3)_2NbF_5 \), in which no reduction of niobium has occurred.

\[ NbF_5 + 2NH_3 \rightarrow (NH_3)_2NbF_5 \]

The solid is diamagnetic indicating pentavalent niobium.

There is no ammonium fluoride present, according to the X-ray powder photograph, which eliminates the possibility of the product being a mixture of \( NbF_4(NH_2) \) and \( NH_4F \).

It was mentioned earlier that niobium pentachloride was solvolysed by liquid ammonia (22) yielding the amido-basic chloride, \( NbCl_3(NH_2)_2 \). Niobium pentachloride, in contrast to the pentachloride is not solvolysed but rather solvated. This lack of solvolysis can be attributed to the inability of a \( NH_2^- \) group to replace a \( F^- \) group.

Considering that the first step in a solvolysis reaction is probably the formation of a solvated intermediate, it is more accurate to say that base-catalyzed elimination of hydrogen fluoride from the solvated intermediate does not seem to occur.

The impossibility of base-catalyzed elimination of hydrogen fluoride thus accounts for the formation of solvated products in the reactions of ammonia with vanadium and niobium pentafluorides. The observation that vanadium pentafluoride is reduced while niobium pentafluoride is not and the difference in the composition
of the reaction products, \((NH_3)_2VF_4\) and \((NH_3)_2NbF_5\); can be explained by the influence of coordination on a reaction. This will be discussed later.

Amminotetrafluorovanadium IV, the brown powdery solid which remained after removal of ammonium fluoride by sublimation, was a slightly hygroscopic compound which dissolved quickly in water to give green coloured solutions. It was not soluble in solvents such as carbon tetrachloride, ethanol (100\%), benzene, ether, nitrobenzene or pyridine. It did not melt on heating in a sealed tube but rather decomposed to a lustrous, powdery black solid accompanied by extensive etching of the tube.

Diamminopentafluoroniobium V was a brilliant yellow diamagnetic solid which was quite hygroscopic and decomposed visibly in moist air. It was not soluble in liquid ammonia which suggests that the compound cannot be formulated as \(NH_4^+ [NbF_5(NH_2)]\). The observation that solvolysis by liquid ammonia does not appear to occur with fluorides would also tend to support formulation as a donor-acceptor adduct rather than formulation as an ionic compound. Diamminopentafluoroniobium V, in contrast to amminotetrafluorovanadium IV and dipyridine pentafluoroniobium V (15), which decompose on heating, appears to melt at approximately 300° to 310°C. Moderate attack of the
glass tube occurs at this temperature which obscures the melting point so this result is not reliable.

The dissociation pressure of diamminopentafluoroniobium V has been determined. A plot of \( \log P \) vs. \( 1/T \) gives a straight line between 50° and 100°C which obeys the equation

\[
\log_{10} P(\text{mm}) = 5.62 - \frac{1720}{T}
\]

Assuming that the compound dissociates completely according to the equation:

\[
(NH_3)_2NbF_5 (s) \rightleftharpoons NbF_5 (g) + 2NH_3 (g)
\]

the heat of dissociation, calculated from the dissociation pressure data, is \( \Delta H = 7,870 \text{ cal/mole} \). Other thermodynamic data can be calculated using standard relations. The results are tabulated below along with the thermodynamic data for dipyridine pentafluoroniobium (27). (Table I)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H ) (cal/mole)</th>
<th>( K_p ) ( (85°C) )</th>
<th>( \Delta F ) (cal/mole)</th>
<th>( \Delta S ) (cal/mole)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (NH_3)_2NbF_5 )</td>
<td>7,870</td>
<td>8.85x10^-8</td>
<td>11,540</td>
<td>10.3</td>
<td>(85°C)</td>
</tr>
<tr>
<td>( (Py)_2NbF_5 )</td>
<td>22,940</td>
<td>2.84x10^-7</td>
<td>9,640</td>
<td>41.2</td>
<td>(50°C)(27)</td>
</tr>
</tbody>
</table>

From the above thermochemical data it is apparent that the ammonia complex is much more stable than the pyridine complex. This result is to be expected because ammonia is a stronger donor than pyridine, due to the reduction in donor strength of pyridine through delocalization of the electrons of the lone pair. Ammonia is a smaller
molecule than pyridine hence the steric interferences are expected to be much less in the ammonia complex. The formation of Π bonds does not appear to be an important factor since the derivative of pyridine, which is capable of forming Π bonds with the metal, is much less stable than that of ammonia.

The infrared spectra of amminotetrafluorovanadium IV and diammino pentafluoroniobium V are very similar and will be considered together. It has been possible to assign the frequencies using qualitative arguments because of the simplicity of the spectra. The assignments are based on the spectral data for transition metal ammine complexes (28, 29). The absorption frequencies and assignments are listed in Table II.

<table>
<thead>
<tr>
<th>ASSIGNMENT</th>
<th>FREQUENCY</th>
<th>(NH₃)VF₄</th>
<th>(NH₃)₂NbF₅</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3250 (s,b)</td>
<td>3100 - 3300 (s,b)</td>
<td>asymmetric N-H stretch</td>
</tr>
<tr>
<td></td>
<td>3100 (s,b)</td>
<td>2850 (sh)</td>
<td>symmetric</td>
</tr>
<tr>
<td></td>
<td>1650 (w,b)</td>
<td>1650 - 70 (w,b)</td>
<td>degenerate NH₂ deformation</td>
</tr>
<tr>
<td></td>
<td>1425 (s)</td>
<td>1420 (s,b)</td>
<td>symmetric NH₂ deformation</td>
</tr>
<tr>
<td></td>
<td>1075 (vw)</td>
<td>1055 (vw,b)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>980 (s)</td>
<td>937 (s,d)</td>
<td>M - NH₃ rock</td>
</tr>
<tr>
<td></td>
<td>913</td>
<td>800 (m,b)</td>
<td>-</td>
</tr>
</tbody>
</table>

b = broad, d = partially resolved doublet, m = medium; s = strong, sh = shoulder, vw = very weak, w = weak.
The strong absorptions in the 3200 cm\(^{-1}\) region are the N-H stretching frequencies. When resolved, as in the case of \((\text{NH}_3)\text{VF}_4\), the highest frequency is assigned to the asymmetric N-H stretch (which is observed at 3414 cm\(^{-1}\) in gaseous ammonia) and the lower to the symmetric N-H stretch (3170 cm\(^{-1}\) in gaseous ammonia). The assignment of the other frequencies is less straightforward.

In the transition metal ammine complexes, the doubly degenerate \(\text{NH}_2\) deformation frequency is little changed from the frequency of the corresponding vibration in gaseous ammonia. In gaseous ammonia the value is 1627.5 cm\(^{-1}\). In twenty-eight ammines of the first long period transition metals this vibration appears between 1560 and 1650 cm\(^{-1}\) (28, 29). This absorption frequency does not change markedly on substituting negative ligands for neutral ammonia ligands, nor does it change appreciably with the valence state or mass of the metal atom. The absorption profile of the degenerate \(\text{NH}_2\) deformation is broad and of moderate intensity (29). It therefore is reasonable to assign the 1650 cm\(^{-1}\) broad and relatively weak absorptions in the ammonia derivatives to the degenerate \(\text{NH}_2\) deformation frequency.

The symmetric deformation frequency, which appears as a doublet at 931 and 968 cm\(^{-1}\) in gaseous ammonia, was found to range from 1150 to 1350 cm\(^{-1}\) in twenty-eight transition metal ammines (28,29). The absorption profile of this
frequency is generally sharp and intense. This frequency is extremely sensitive to the oxidation state of the central atom, generally shifting to higher wave numbers with increasing valence of the central metal ion. For a constant valence of the metal, exchange of a neutral ligand for a negative ligand shifts the frequency very slightly to lower wave numbers, but the effect is small compared to the shift accompanying oxidation. On this evidence, the 1420 - 1425 peaks in the ammonia derivatives are assigned to the symmetric NH$_2$ deformation frequency.

The remaining intense bands occurring at 980 cm$^{-1}$ in (NH$_3$)$_2$VF$_4$ and at 937 - 943 in (NH$_3$)$_2$NbF$_5$ are assigned to the metal-ammonia rocking frequency. In the metal ammines that have been studied this vibration occurs between 650 and 950 cm$^{-1}$ (28,29). This frequency is also extremely sensitive to the nature and oxidation state of the central metal ion as would be expected, but it is not possible to predict any trends on the data available. The absorption profile of the rocking vibration is generally broad and intense. The assignment seems reasonable but the position of the rocking frequencies is under study (28). The reason for the doublet in the rocking frequency of (NH$_3$)$_2$ NbF$_5$ is not known. It seems very unlikely that there would be a M-NH$_3$ rocking frequency for each ammonia ligand.

Several bands are still unassigned. The source of the 2850 cm$^{-1}$ shoulder on the N-H stretching frequencies
of both derivatives is unknown. Similarly the very weak bands at 1055 cm\(^{-1}\) for \((\text{NH}_3\text{)VF}_4\) and 1075 cm\(^{-1}\) for \((\text{NH}_3\text{)}_2\text{NbF}_5\) are not identifiable. A medium intensity band at 800 cm\(^{-1}\) in \((\text{NH}_3\text{)}_2\text{NbF}_5\) also remains unassigned. It must be emphasised that the assignments are based on qualitative data obtained from only a few compounds which are not essentially of the same type. The ammonia derivatives of vanadium and niobium pentafluorides, for the basis of comparison, may be assumed to behave similarly to the transition metal ammines, but this assumption may not be justified. It is however the only one that can be made with presently available information.
CHAPTER 4: PYRIDINE DERIVATIVES OF VANADIUM AND NIOBIUM PENTAFLUORIDES

Pyridine is a strong electron donor molecule and forms many donor-acceptor complexes. In contrast to ammonia there are no hydrogen atoms bonded to the nitrogen so pyridine can be regarded as a tertiary amine, even simple aliphatic tertiary amines, and is subject to less steric interaction. The pyridine ring system is extremely stable. It is stabilized in a similar manner to benzene and exceeds benzene in stability thus making pyridine a good donor molecule for the study of such reactive acceptors as vanadium pentafluoride. Many transition metal fluorides are known to form complexes with pyridine. Tungsten hexafluoride is reported to form a complex with the formula WF$_6$.3Py (16). Niobium and tantalum pentafluorides are reported to form dipyridine adducts with the formulae NbF$_5$.2Py and TaF$_5$.2Py (15).

Pyridine, as a liquid or vapour, reacts with vanadium pentafluoride to form pyridinetetrafluorovanadium IV, (Py)VF$_4$, a dark brown, powdery solid. The reduction of vanadium pentafluoride was confirmed by the magnetic moment of 1.67 Bohr magnetons found for the solid product. Tetravalent vanadium has one unpaired electron and thus a magnetic moment of 1.73 Bohr magnetons.
The loss of a fluorine atom in the reaction is puzzling. No fluorinated pyridine derivatives were found in the volatile fractions but a trace of an unidentifiable reactive fluoride was found along with pyridine removed from the reaction vessel. This situation is similar to that encountered by Wardlaw and Webb (30) in the reaction of molybdenum pentachloride with pyridine. The product obtained by Wardlaw and Webb was a tetravalent molybdenum compound with the composition $\text{MoCl}_4 \cdot 3\text{Py}$. No trace of the remaining chlorine was found and it was suggested that an indeterminate additive complex was formed between free chlorine and pyridine and was removed with the excess pyridine. The possibility of inadvertent hydrolysis obscuring the reaction can be excluded because Wardlaw and Webb were careful to ensure the dryness of their reagents before any reaction.

The formation of an addition complex between a fluorine atom and pyridine would explain the removal of a fluorine atom, in the reaction with vanadium pentafluoride, without the formation of fluorinated pyridine derivatives. A fluorine atom trapped in such a complex would probably give a positive test for fluoride in the presence of traces of moisture.
In a study of the reactions of vanadium tetrachloride with aliphatic amines, Fowles and Pleass (20) found that at low amine concentrations, mono and dimethylamines formed 1:1 addition compounds with vanadium tetrachloride in solution. On increasing the amine concentrations, chloride was found to be replaced by amine residues suggesting a base catalysed elimination of hydrogen chloride:

\[ \text{VCl}_4 + \text{Me}_2\text{NH} \rightarrow \left[ \text{VCl}_4 \cdot \text{HNMe}_2 \right] \rightarrow \text{VCl}_3 \cdot \text{NMe}_2 + \text{HCl} \]

Both products are solvated with dimethylamine. No reduction of vanadium occurs with either methylamine or dimethylamine.

Trimethylamine, however, reacts with vanadium tetrachloride to form a trivalent vanadium compound, \( \text{VCl}_3 \cdot 2\text{NMe}_3 \). A chlorine atom was lost in the reaction and, as in the case of the pyridine-\( \text{MoCl}_5 \) reaction, was never found. Base catalyzed elimination of \( \text{HCl} \) can not occur with a tertiary amine, except through breaking of a C-H bond and the formation of unsaturated amines; therefore chlorine atoms are removed by some obscure mechanism.

If we consider pyridine to be a tertiary amine, the similarity of the reaction of trimethylamine with vanadium tetrachloride and the reaction of pyridine with vanadium pentafluoride becomes apparent. In
both cases the covalent halide is reduced to a lower halide (with a more ionic character) and a halogen atom is lost in the process.

A reduction reaction must be accompanied by the oxidation of one of the reaction components. However in the reaction of vanadium pentafluoride with pyridine, in which vanadium has been reduced to the tetravalent state, it has not been possible to identify the oxidised species. Therefore a consideration of the reaction mechanism must await further study of the reaction particularly with a view to identifying the oxidation product.

The pyridine derivative of vanadium pentafluoride, (Py)VF₄, is a dark-brown, powdery solid which is insoluble in non-reacting solvents. It dissolves in water giving green solutions which have an odour of pyridine. On exposure to moist air, pyridine-tetrafluorovanadium IV quickly decomposed leaving greenish coloured residues. On heating in a sealed tube (Py)VF₄ did not melt, but rather decomposed leaving similar greenish coloured residues which appeared to be quite inhomogeneous.

It is unlikely that (Py)VF₄ would undergo the simple dissociation:

\[
(Py)VF_4 \rightleftharpoons VF_4 + Py
\]
because vanadium tetrafluoride has been reported (1) to disproportionate to the triand pentafluorides:

$$\text{VF}_4 \rightleftharpoons \text{VF}_3 + \text{VF}_5$$

This report has never been verified. If such a disproportionation occurs however the VF$_4$ produced in the dissociation would probably disproportionate to VF$_3$ and VF$_5$, with VF$_5$ reacting again with pyridine and repeating the preparation of (Py)VF$_4$. The greenish colours of the decomposition products may be due to vanadium trifluoride. The decomposition of (Py)VF$_4$, because of its complex nature, was not investigated further.

There is a marked difference between the behaviour of niobium pentafluoride and vanadium pentafluoride with pyridine. Clark and Emeleus (15) have reported that pyridine reacts with niobium pentafluoride to form a 2:1 adduct, dipyridine-pentafluoroniobium V, (PY)$_2$NbF$_5$. This adduct is thus similar to the adduct formed between ammonia and niobium pentafluoride, diammonopentafluoroniobium V, which was described in an earlier chapter. The pyridine adduct is less stable than the ammonia adduct as evidenced by the difference in their dissociation pressures. Unlike the ammonia adduct, the pyridine adduct of niobium pentafluoride does not melt but rather decomposes at 100°C. (15)
Fowles and Pleass (21) have also studied the reactions of niobium pentachloride with various aliphatic amines. The results are similar to the reactions of vanadium tetrachloride (20). Mono and dimethyl amines undergo base-catalyzed elimination of HCl thus solvolyzing the chloride with amine residues. An example is the reaction of niobium pentachloride with dimethylamine:

\[
\text{NbCl}_5 + \text{Me}_2\text{NH} \rightarrow [\text{NbCl}_5\cdot\text{NHMe}_2] \rightarrow \text{NbCl}_4\cdot\text{NMe}_2 + \text{HCl}
\]

\[
\text{NbCl}_4\cdot\text{NMe}_2 + \text{Me}_2\text{NH} \rightarrow [\text{NbCl}_5\cdot\text{NMe}_2\cdot\text{NHMe}_2] \rightarrow \text{NbCl}_3\cdot(\text{NMe}_2\cdot\text{NHMe}_2) + \text{HCl}
\]

A further solvation step occurs forming \([\text{NbCl}_3(\text{NMe})_2\cdot\text{NHMe}_2]\) but HCl is not eliminated, probably because it is sterically impossible to bond three amine residues to niobium.

This solvolysis reaction is only possible when it is possible to eliminate HCl following solvation. A tertiary amine is unable to undergo solvolysis because there are no replaceable hydrogens on the nitrogen atom. Reactions with tertiary amines follow a different course as evidenced by the reduction of vanadium tetrachloride with trimethylamine (20) and the reduction of vanadium pentafluoride with pyridine. Similarly niobium halides react differently with tertiary amines as compared with primary and secondary amines. Niobium pentafluoride forms the dipyridine...
adduct, niobium pentachloride forms no definite product with trimethylamine (21).

Pyridine reacts with vanadium and niobium pentafluorides then to solvate the pentafluorides as would be expected for a substance incapable of undergoing solvolysis. The marked difference in final product, the apparently pentacoordinate tetravalent, vanadium compound \((\text{Py})\mathrm{VF}_4\) as against the apparently heptacoordinate, pentavalent niobium compound \((\text{Py})_2\mathrm{NbF}_5\) can be attributed to the effect of the coordination state on the reaction. This will be more fully discussed in a later chapter.
Up to now only the reactions of unidentate donor molecules, that is molecules with one donor group, have been considered. Each coordinate bond formed thus involves the attachment of one molecule to the metal atom. Ethylenediamine is a bidentate donor molecule, that is it has two donating groups per molecule, and thus can form two coordinate bonds with one molecule. Very stable complexes are therefore formed on donating two electron pairs to the same metal atom because the five-membered ring so formed is relatively free from strain. Its small size combined with the stability of the resultant five-membered ring permits ethylenediamine to form complexes in which maximum covalency is attained.

In addition to its chelating properties ethylenediamine is a primary amine with chemical properties similar to other aliphatic amines. It was therefore of interest to investigate the reactions of ethylenediamine with vanadium and niobium pentafluorides.

Vanadium pentafluoride reacted quickly with ethylenediamine to form a tetravalent vanadium compound with the composition $\text{VE}_4\text{.3en}$. A magnetic susceptibility measurement of the paramagnetic compound confirmed the
tetravalent state of vanadium. The magnetic moment of 2.0 Bohr magnetons is slightly higher than the spin-only value of 1.73 Bohr magnetons expected for tetravalent vanadium. As all known tetravalent vanadium compounds have magnetic moments close to the spin-only value (26) it seems unlikely that this high value is due to spin-orbit coupling or other interactions. The high value is probably due to experimental errors in the determination of susceptibility or to the presence of small amounts of trivalent vanadium. It was not possible to determine chemically the oxidation state of the product because it was necessary to remove ethylenediamine with strong oxidising conditions before estimating vanadium.

The product of the reaction, tris(ethylenediamine)-tetrafluorovanadium IV, can be formulated as $[\text{V(en)}_3]F_4$ containing the octahedral complex ion $[\text{V(en)}_3]^+$. This is reasonable in view of recent studies on the reactions of ethylenediamine with vanadium chlorides. Fowles and McGregor (23) report that ethylenediamine reacts with vanadium trichloride to yield a similar type of compound, tris(ethylenediamine) trichlorovanadium III:

$$\text{VCl}_3 + 3\text{en} \rightarrow [\text{V(en)}_3] \text{Cl}_3$$
in which the octahedral complex ion $[\text{V(en)}_3]^{+3}$ is obtained. Vanadium tetrachloride however apparently reacted with ethylenediamine (23) but no definite product was isolated. To explain the different behaviour of vanadium trichloride and vanadium tetrachloride with ethylenediamine Fowles and McGregor (23) suggested that the more covalent halide, that is vanadium tetrachloride, was solvolysed by ethylenediamine whereas the ionic halide, $\text{VCl}_3$, was solvated by ethylenediamine.

The fluorides, of course, behave differently from the chlorides but we can tentatively advance a similar hypothesis to explain the reaction product. The covalent fluoride, $\text{VF}_5$, in contrast to the covalent chloride will not be solvolysed however because there are indications in the ammonia and pyridine reactions that solvolysis of fluorides does not occur. Ethylenediamine will react in the same manner as pyridine and ammonia, reducing $\text{VF}_5$ to $\text{VF}_4$, the "more ionic" fluoride. The more ionic fluoride $\text{VF}_4$ is solvated by ethylenediamine, in the same manner as the more ionic chloride, $\text{VCl}_3$, was solvated, to form the hexacoordinate $[\text{V(en)}_3]^{+4}$ ion as the fluoride $[\text{V(en)}_3]\text{F}_4$.

If the formulation of the product as $[\text{V(en)}_3]\text{F}_4$ is correct then this is the first cationic complex of tetravalent vanadium, with the exception of vanadyl complexes, to be reported. Ethylenediamine forms the trivalent hexacoordinate complex, $[\text{V(en)}_3]\text{Cl}_3$, with vanadium trichloride but no complexes with vanadium tetrachloride. Presumably
the formation of a tetrapositive complex ion is stabilized by the higher charge density of the fluoride ions compared to chloride ion. Further studies are necessary to verify the presence of the complex ion \( [V(\text{en})_3]^+^4 \) in this product but at present none of the observed properties conflict with this formulation.

Only a few properties of the complex compound, tris-(ethylenediamine) tetrafluorovanadium IV, are known. It is a brown powdery solid insoluble in excess ethylenediamine, and insoluble in polar and non-polar organic solvents such as nitrobenzene, ether, alcohol, pyridine, benzene and carbon tetrachloride. It is very soluble in water, presumably with hydrolysis because the presence of unoccupied 3d orbitals on vanadium would make the complex labile (31). No evidence however is available to support hydrolysis so the complex ion \( [V(\text{en})_3]^+^4 \) may be stable in aqueous solution. Generally, however, vanadium exists in aqueous solution as the complex oxygen containing ions: \( \text{VO}^{++} \); \( \text{VO}_3^- \), etc. When heated in a sealed tube \( [V(\text{en})_3]_2\text{F}_4 \) decomposes at approximately 160°C. It is often found that compounds containing complex ions decompose when heated rather than show a definite melting point.

Vanadium is obviously reduced in the reaction with ethylenediamine just as with ammonia and pyridine. The mechanism of the reaction is not clear and again a fluorine
atom has been removed in the reaction without a trace appearing in the volatile materials or the solid product. This suggests that the reaction does not involve solvolysis, that is elimination of hydrogen fluoride, as would be expected with a primary amine and indicates again that amines and ammonia do not solvolyse fluorides. The reaction probably involves solvation by ethylenediamine in the first step followed by reduction to tetravalent vanadium because of the unstable nature of the solvated product. Solvation of the more ionic, tetravalent fluoride without further reduction then occurs to produce the complex compound, \([V(en)_3]F_4\).

The infrared spectrum of \([V(en)_3]F_4\) was measured and the peaks observed are listed in the experimental section. A rough comparison with the spectra of ethylenediamine complexes of other transition metal ions reported by Powell and Sheppard (32) shows many similarities. The spectra are complex as would be expected from the nature of the ethylenediamine molecule and as Powell and Sheppard have not yet published the assignments of their spectra it was not possible to assign the absorption peaks of \([V(en)_3]F_4\).

Niobium pentafluoride reacts with liquid ethylenediamine forming a viscous brown syrup from which ethylenediamine could only be removed with difficulty. A product of composition \(\text{NbF}_5(\text{en})_{1.6}\) was obtained after prolonged
heating under vacuum to remove ethylenediamine. Assuming that the product is similar to other nitrogen base derivatives, it can be formulated as the 1:1 complex, \( \text{NbF}_5(\text{en}) \), which is highly solvated with excess ethylenediamine.

Amines then do not solvolyse niobium pentafluoride whereas according to Fowles and Pleass (21) niobium pentachloride is solvolysed by aliphatic primary and secondary amines. In this respect niobium pentafluoride differs from the pentachloride. Ethylenediamine then solvates niobium pentafluoride and because the solvated product is stable, solvation is not followed by reduction of niobium.

The product is then presumed to be a highly solvated 1:1 complex between niobium pentafluoride and the bidentate nitrogen base, ethylenediamine. This formulation is in agreement with the products formed by other nitrogen bases and niobium pentafluoride, eg: \((\text{NH}_3)_2\text{NbF}_5\) and \((\text{Py})_2\text{NbF}_5\), in which niobium has a minimum coordination of seven. The solvated reaction product, \( \text{NbF}_5(\text{en})_{1.6} \), was soluble in water and presumably was hydrolysed. On heating in a sealed tube the compound decomposed about 240°C yielding an inhomogeneous residue. Ethylenediamine was apparently liberated and obscured the behaviour of the complex, \((\text{en})\text{NbF}_5\). No further information could be obtained from the impure product.
CHAPTER 6: A SURVEY OF THE AMINE REACTIONS

The reactions of vanadium pentafluoride with different nitrogen bases are similar in that vanadium was always reduced to the tetravalent state. The products that were obtained from the reactions are solvated complexes of vanadium tetrafluoride. Ammonia and pyridine formed 1:1 complexes; amminotetrafluorovanadium IV, (NH$_3$)VF$_4$, and pyridinetetrafluorovanadium IV, (Py)VF$_4$, whereas ethylenediamine formed the highly solvated complex, tris(ethylenediamine)tetrafluorovanadium IV which has been formulated as the complex compound $\left[V(en)_3\right]F_4$. Niobium pentafluoride formed addition complexes with the same amines in which no reduction of niobium occurred. The solvated products obtained were diamminopentafluoroniobium V, (NH$_3$)$_2$NbF$_5$, and ethylenediaminepentafluoroniobium V, (en)NbF$_5$. The pyridine product, dipyridinepentafluoroniobium V, (Py)$_2$NbF$_5$, has been previously reported (15).

It is noteworthy that vanadium and niobium pentafluorides behave similarly with the amines in that only solvated products were obtained and no evidence of solvolysis by the amines was found. This is in marked contrast with the behaviour of the highest chlorides of vanadium and niobium which, according to Fowles and co-workers (20 to 25 inc.), are extensively solvolyzed by ammonia and primary or secondary amines and are solvated only by tertiary amines which are incapable of solvolysis.
Niobium pentfluoride formed simple addition complexes in which the minimum coordination of niobium was increased from five to seven. Vanadium pentfluoride, on reaction with amines, formed solvated products in which, except for the case of \([V(en)_3]F_4\), the apparent coordination number of vanadium remained at five. The product of the ethylenediamine reaction is an exception to the behaviour of the amines in that vanadium has apparently formed a hexacoordinate complex cation.

It was indicated in an earlier chapter that pentacoordinate structures are extremely rare, especially in the liquid and solid states. In view of this and because of the association that has been postulated for liquid vanadium pentfluoride it is therefore unlikely that the compounds (Py)VF₄ and (NH₃)VF₄ are pentacoordinate, monomeric complexes. Muetterties (18) has suggested that the 1:1 amine complexes of the group IV tetrafluorides, which are insoluble, non-melting solids, are probably polymers. Because of the known tendency of simple fluorides to associate, presumably by formation of fluorine bridge bonds, Muetterties also suggested that the most likely mode of polymerization of the 1:1 complexes was fluorine bridge bond formation. It seems reasonable to suggest therefore, that the 1:1 amine complexes formed from vanadium pentfluoride, namely (Py)VF₄ and (NH₃)VF₄, which are also insoluble in
common solvents and have no definite melting points, are also fluorine bridged polymers. Through association of this type, vanadium then would be hexacoordinate rather than pentacoordinate. Thus vanadium pentafluoride, in which vanadium is thought to be hexacoordinate through the formation of fluorine bridges, reacts with amines to form complexes in which vanadium is also hexacoordinate, either in a monomeric complex such as $[V(\text{en})_3]^+$ or through the formation of fluorine bridged polymers proposed for $(\text{NH}_3)\text{VF}_4$ and $(\text{Py})\text{VF}_4$. There is apparently no net change in the coordination of vanadium on reaction of vanadium pentafluoride with amines which is in agreement with the proposal that the maximum coordination number of vanadium is six as suggested in an earlier chapter.

Niobium pentafluoride forms the complexes $(\text{NH}_3)_2\text{NbF}_5$, $(\text{Py})_2\text{NbF}_5$ and $(\text{en})\text{NbF}_5$ in which the minimum coordination number of niobium is seven. An increase in the maximum coordination number with increasing size of the metal atom accounts for the formation of septacoordinate complexes by niobium whereas vanadium appears to have a maximum coordination number of six.

Niobium pentafluoride is thought to be associated through the formation of fluorine bridge bonds in the same manner as vanadium pentafluoride so that in niobium pentafluoride, niobium would be hexacoordinate rather than in
the relatively unknown pentacoordinate state. Also the amine complexes of niobium pentafluoride may be fluorine bridged polymers because in general they do not have definite melting points. In this respect however, evidence for polymerism in the niobium pentafluoride complexes is less reliable than that for the vanadium pentafluoride derivatives. If the niobium pentafluoride adducts are fluorine bridged polymers, then niobium would be octacoordinate, which is probably the highest coordination number possible for niobium. Certainly, no compounds are known in which the coordination number of niobium is greater than eight. The reactions of amines with vanadium and niobium pentafluorides can then be considered to form complexes in which the metal atom achieves the highest coordination number possible.

It has been suggested that all the amine derivatives of niobium and vanadium pentafluorides, with the exception of the product \([V(en)_3]F_4\), are polymers, probably through the formation of fluorine bridge bonds. The formation of polymers through the formation of metal-nitrogen-metal bridges must not be overlooked for this is a possibility in ammonia and ethylenediamine complexes. The difficulty of visualizing such a bond in the pyridine complexes coupled with the similarity of pyridine and ammonia complexes suggests that M-N-M bridges are not formed and that the
alternative of fluorine bridge bond formation is more likely.

The structures of the VF₄·Base compounds are probably very similar. The most likely structure for both is a long chain of V-F-V bridge bonds with an octahedral configuration of ligands about each vanadium atom. The base molecules probably occupy position on the chain so that they are trans to one another thus minimizing the steric interactions between base molecules. The structure of the polymer would then be similar to the structure of the antimony pentafluoride polymer (8) except that one fluorine on each central atom has been replaced by a base molecule. The formation of such a structure would also suggest that liquid vanadium pentafluoride may be a long chain polymer, similar to antimony pentafluoride.

The structure of the ethylenediamine complex of VF₄ has been considered throughout as a simple hexacoordinate complex compound in which all three ethylenediamine ligands are coordinated to the same vanadium atom. This suggestion may be an oversimplification because the ethylenediamine may coordinate to two different vanadium atoms forming ethylenediamine bridges, hence this amine complex may also be polymeric. In view of the known ability of ethylenediamine to form monomeric, hexacoordinate complex ions, it is reasonable to assume the simplest structure, that of the hexacoordinate ion $\left[ V(\text{en})_3 \right]^{+4}$.
for the complex. If this ion is formed, this is the first cationic complex of tetravalent vanadium, with the exception of the vanadyl complexes, to be reported.

The structures of the niobium complexes include many more possibilities. They may be septacoordinate monomers in which case the most likely structure of the ammonia and pyridine complexes is a pentagonal bipyramid with base molecules occupying positions on either side of the pentagonal plane for a minimum of steric interference. If the ethylenediamine complex exists as a pentagonal bipyramid then the most likely arrangement of the nitrogen atoms would consist of one in the pentagonal plane and one at an apex of the bipyramid. Also in this case the formation of ethylenediamine bridges must not be excluded, but it is unlikely. The complexes may be fluorine bridged polymers, in which case niobium is octacoordinate. A possible structure would be a long chain of niobium - fluorine - niobium bridge bonds, as proposed for the vanadium polymers, with an octacoordinate configuration of ligands about the niobium atom. The most probable octacoordinate configuration is a square antiprism (17) although other structures must not be excluded.

The structures that have been proposed are based only on the qualitative information available for the compounds.
A complete structure determination is required to verify the proposed fluorine bridge bonds and to decide on the true coordination number of the metal atom.

The formation of the products isolated from the reaction can be explained by considering the effect of a maximum coordination number on the reaction. The initial step in the reaction between an amine and the pentafluoride is presumably the coordination of the nitrogen base to the metal atom, thus increasing the coordination number of the metal atom. If the coordination state so formed is stable, as in the case of niobium pentafluoride, then coordination will continue until the maximum coordination has been achieved. Thus niobium pentafluoride forms simple adducts with amines in which the coordination number of niobium is increased to a minimum of seven.

If on the other hand the coordination complex formed by the initial solvation of the pentafluoride is unstable because the maximum coordination number of the metal has been exceeded, as with vanadium pentafluoride, then the solvated complex will decompose to a more stable coordination state. With vanadium pentafluoride the formation of a stable coordination state is accompanied by reduction of vanadium to the tetravalent state. If solvolysis of the fluorides could occur, the coordination number of vanadium
in the solvated intermediate could be decreased without a reduction in the valence of vanadium. However it has been observed that fluorides are not solvolysed by amines so that stabilisation of the coordination state follows a mechanism probably similar to that involved in the reaction of vanadium tetrachloride with trimethylamine (20). Trimethylamine, with no replaceable hydrogens, cannot undergo solvolysis so that stabilisation of the coordination state was effected by the loss of a chlorine atom and reduction of vanadium to the tervalent state.

\[
\text{VCl}_4 + \text{Me}_3\text{N} \rightarrow [\text{VCl}_4 \cdot \text{Me}_3\text{N}] \rightarrow \text{VCl}_3\text{NMe}_3 + [\text{Cl}^0]
\]

The formation of the complex \([\text{V(en)}_3]F_4\), can be attributed to the high solvating power of ethylenediamine which solvates the vanadium tetrafluoride produced by the initial reduction of vanadium pentafluoride with ethylenediamine. In the initial stages of the reaction, ethylenediamine probably resembles ammonia and pyridine.

It is not possible with the available information to propose a detailed mechanism for the reactions of the pentfluorides with amines. This is especially true of the vanadium pentafluoride reactions where the oxidised species in the reactions have not been identified. The reactions must be investigated more fully before any mechanism can be suggested.

It has been noted that vanadium and niobium pentafluorides are not solvolysed by amines whereas the
corresponding chlorides are. The fact that amines with replaceable hydrogens such as ammonia and ethylenediamine do not solvolyse the fluorides suggests that the difference may be due to the difference in the strength of the metal-halogen bond. This difference in energy need not be very great for there are other energy terms involved in the reaction, such as the lattice energy of the solid product, and the difference in metal-halogen bond energy may be sufficient to shift the reaction from solvolysis to solvation. It is difficult to explain however, in the vanadium pentafluoride reactions with ammonia and ethylenediamine, why a fluorine atom is removed and remains as a reactive species in an amine with replaceable hydrogen atoms available to form hydrogen fluoride.

It has also been implied that the fluorine bridge bond, which is thought to exist in liquid vanadium pentafluoride, is preserved in the formation of the polymeric V\(_4\)F\(_8\) complexes and that a vanadium-fluorine bond that is not involved in bridging is broken. However there is no apparent reason why a bridge bond, which would probably be a weaker bond than a non-bridging bond, should be preserved in the reaction. Muettterties has suggested that 'strong' fluorine bridge bonds are formed in solid TeF\(_4\) (9) to account for its extremely high lattice energy. It is therefore possible that the bonds involved in reactions
of vanadium pentafluoride could be 'strong' fluorine bridge bonds, however in view of the lack of information about the strength and nature of the fluorine bridge bond it is not possible to make any predictions about its behaviour.

The lack of solvolysis of the fluorides expresses a difference in bond type and bond energy between fluorides and chlorides. Because of the complex nature of the factors involved in the energy requirements of a reaction it is not possible to attribute the lack of solvolysis to a definite cause. Further study of the reactions is necessary to obtain a more complete understanding of the factors involved in the fluorine bond formation and its influence on the structure and properties of the fluorides.
In recent years structural studies of the simple fluorides have been greatly aided by the use of nuclear magnetic resonance spectroscopy. It has been possible in some cases to resolve the spectrum sufficiently to enable interpretation of the resonance peaks in terms of a definite structural model. Sulphur tetrafluoride thus has been shown to have a trigonal bipyramid structure (with a lone pair occupying a trigonal planar position) on the basis of its NMR spectrum (9). Structural determinations using other techniques have verified this result.

It has not been possible to resolve the spectrum of all simple fluorides although many attempts have been made to do so. Muettretties and Phillips (9) have investigated many simple fluorides and have obtained resolved spectra in many cases. They also report a number of chemical shift values for the fluorides studied. The broad, unresolved $^19F$ resonance lines obtained have been attributed to the presence of a rapid exchange process involving association through the formation of fluorine bridge bonds and perhaps, in addition, a self-dissociation into ionic species. These processes have been discussed in earlier chapters.
The nuclear magnetic resonance study of vanadium pentafluoride was undertaken with a view to obtaining more information about its structure and mode of association. The preliminary results reported here have not yet realized this aim and further study is necessary. The resonance spectrum obtained with vanadium pentafluoride was a very broad, unresolved peak from which only the chemical shift could be obtained. This broadening can be attributed to two sources.

Vanadium has a nuclear spin of $7/2$, and associated with it an electric quadrupole moment. The presence of a quadrupole moment is known to broaden a nuclear resonance signal and in some cases the nuclear quadrupole broadening makes the resonance signal disappear completely. The spectrum can sometimes be resolved by cooling the sample to a low temperature which reduces the rate of quadrupole relaxation of the nuclear resonance signal sufficient to obtain a spectrum in which the orientation of the magnetic states of the nuclear quadrupole is effectively constant. The $^{19}\text{F}$ resonance spectrum resolved by this method would consist of $(2J+1)$ lines, where $J$ is the nuclear spin of the central atom, for each set of equivalent $^{19}\text{F}$ nuclei. In the case where the central atom is vanadium with $J = 7/2$, a total of 8 lines per set of equivalent $^{19}\text{F}$ nuclei would be obtained.

It was mentioned earlier that vanadium pentafluoride is probably associated through the formation of fluorine
bridge bonds and in addition self-ionisation is also thought to occur. The effect of these processes is the transfer of fluorine from one vanadium nucleus to another resulting in exchange broadening of the nuclear resonance signal. The spectrum can be resolved in some cases by decreasing the rate of exchange through cooling of the sample.

In analogy with the nuclear resonance spectrum of antimony pentafluoride (8), vanadium pentafluoride would probably have at least three sets of equivalent nuclei. Each of these sets could be split into eight components by the nuclear spin of vanadium. Thus if the nuclear resonance spectrum of vanadium pentafluoride can be resolved it will probably be quite complicated. Resolution may be possible at low temperatures where both the quadrupole and exchange broadening can be removed but in order to work at low temperatures, that is about -100°C, it will be necessary to find a solvent for vanadium pentafluoride because its melting point is 19.5°C.

The chemical shift is defined by the relation:

\[ \delta = \frac{H_s - H_r}{H_r} \times 10^6 \]  

(at constant frequency)

where: \( \delta \) = the chemical shift in ppm  
\( H_s \) = the resonant field strength for the sample  
\( H_r \) = the resonant field strength for the reference

The chemical shift is a function of the electron density around the nucleus and thus will be dependent on
the type of bond formed, the relative electronegativity values of the atoms involved and other parameters. Because the relationships are complex and not fully understood, the factors influencing the chemical shift will not be discussed here. The chemical shift of vanadium pentfluoride has been found to be -335 ppm relative to a trifluoroacetic acid reference. This value is in agreement with the chemical shifts of hexafluorides of neighboring elements. The chemical shift values of molybdenum and tungsten hexafluorides are -355 and -242 ppm, respectively, relative to trifluoroacetic acid (9). The values for niobium and tantalum pentafluorides are not known.
CHAPTER 8: EXPERIMENTAL

(i) General Techniques:

Early investigators often reported that many fluorides, in particular volatile fluorides, attacked glass thus prohibiting the use of glass apparatus in studies of fluorides. Recent workers (27) have shown that volatile transition metal fluorides can be manipulated in glass vacuum systems without etching provided that hydrogen fluoride and traces of moisture are absent. Traces of hydrogen fluoride, a common impurity in the preparation of fluorides, can be removed by passing or collecting the fluoride over carefully dried sodium fluoride, where the hydrogen fluoride is absorbed, forming stable sodium bifluoride.

The marked susceptibility of volatile fluorides to moisture is due to the autocatalytic nature of the hydrolysis reaction.

\[
\text{MF}_n + \text{H}_2\text{O} \rightarrow \text{MOF}_{n-2} + 2\text{HF} \\
4\text{HF} + \text{SiO}_2 \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \\
\text{MF}_n + \text{H}_2\text{O} \rightarrow \text{etc.}
\]

Thus minute traces of moisture in glass apparatus can completely decompose the fluoride.

Reactive volatile transition metal fluorides have been found to attack vacuum grease, even the fluorinated greases. Hence glass taps and ground joints which require vacuum grease can not be used in the apparatus.
Purification and general manipulation of a volatile transition metal fluoride, such as vanadium pentafluoride, can be done in simple all-glass distillation systems which have been described by many earlier workers. A typical system consisted of three or four traps connected via capillary constrictions. Each trap was fitted with a glass break seal. After thoroughly flaming the system in vacuo, the capillary leading to the vacuum manifold was sealed off leaving an all-glass, grease and moisture free distillation line. After distillation of volatile materials, the interconnecting capillaries were sealed off and the contents of the trap could be transferred, by connecting the trap through its break seal, to another similar system. This technique, while making possible the study of the chemical properties of the reactive transition metal fluorides, necessitates the continual, rather laborious, assembly of such distillation systems.

The susceptibility of the fluorides to hydrolysis requires, in addition to vigorously dried apparatus, that all the reagents placed in contact with the fluoride be perfectly free of traces of moisture. Before reaction with the fluoride all the materials used in this study were distilled several times from drying agents in all-glass, grease and moisture free systems that have just been described.

The volatile products of the nitrogen base reactions were identified principally by the use of infrared
spectroscopy. All spectra were measured on a Perkin-Elmer "model 21" or "Infracord" recording spectrophotometers equipped with sodium chloride optics. Gaseous materials were contained in a 10 cm. cell. The liquid materials were generally prepared as thin films between sodium chloride plates. Solids were prepared as mulls or potassium bromide pellets.

X-ray powder photographs of the solid products were taken on a General Electric source with Copper radiation and nickel filters. The camera, supplied by General Electric, was of a conventional design having a circumference of 45 cm. Some of the X-ray photographs were kindly taken by Dr. R. M. Thompson of the Geology Dept. of this University. The samples were sealed in thin walled 0.5 mm diameter capillaries to prevent hydrolysis of the sample during the photographing.

Magnetic susceptibilities of the solids were measured on a Gouy balance. A Varian G004 magnet with 2 inch tapered pole faces supplied a magnetic field of approximately 15,000 gauss. The magnetic moment was calculated from the weight gain of the unknown solid on application of the magnetic field and the weight gain of an equal volume of a reference solid, (mercuric cobaltitetrathiocyanate, HgCo(SCN)$_4$) of known susceptibility, in the same tube and with the same field strength. All susceptibilities were measured at room temperature.
The dissociation pressure of an easily hydrolyzed solid can be readily determined with an all-glass spiral gauge which has been described previously (27).

The apparatus consisted of a Pyrex spiral attached to a small sample-containing bulb. The spiral was encased in a glass envelope with an optical face opposite the point where a mirror was attached to the spiral. Deflections of the spiral caused by pressure differences could be detected with a suitable optical system. The spiral gauge was not calibrated but rather was used as a null-point instrument in conjunction with a mercury manometer.

The sample bulb was connected via a side arm to the vacuum manifold so that both sides of the spiral gauge could be evacuated. The side arm was constricted close to the sample bulb to facilitate sealing off. A B-10 socket was joined to the side arm, above the capillary constriction, through which the sample could be introduced.

The solid sample was placed in a bent tube in a dry-box and connected to the dissociation pressure apparatus via the B-10 joint. Sealing of the joint was accomplished with a Teflon sleeve, the upper edge of which was lightly smeared with vacuum grease. The system was evacuated, the Pyrex spiral flushed with dry air several times and the small bulb at the base of the spiral was flamed. When the apparatus was dry the bent tube was twisted through 180° and the sample poured through the capillary into the
bulb. The capillary was sealed off leaving the sample in an all glass system. The dissociation pressure of the solid could then be measured with a minimum of hydrolysis.
(ii) **ANALYTICAL METHODS:**

The compositions of the solid products obtained in the reactions of nitrogen bases with the pentafluorides were determined by quantitative analysis of the elements present. In all cases, standard methods were used. All microanalyses for carbon and hydrogen were done by Dr. Alfred Bernhardt, Mulheim, Germany.

(a) **Vanadium:**

A dilute (1%) sulphuric acid solution of the sample was oxidized to the pentavalent state with excess permanganate. The vanadium was then reduced to the tetravalent state by bubbling sulphur dioxide into the solution for 10 to 15 minutes. Excess sulphur dioxide was removed by boiling the solution. Tetravalent vanadium was then oxidized to pentavalent vanadium by titration with standard (0.01N) potassium permanganate until the permanganate color became visible. In compounds where lower valency states of vanadium were suspected, the sample was titrated with 0.01N permanganate immediately after dissolving in dilute sulphuric acid solution and then the above procedure was repeated. In this way the presence of trivalent or tetravalent vanadium in the product could be detected.

(b) **Niobium:**

The sample was dissolved in water and the solution made alkaline with ammonium hydroxide. The resultant precipitate of hydrated niobium oxide was ignited to niobium pentoxide and weighed.
Interference by ethylenediamine in the estimations of niobium and vanadium was prevented by digestion of the sample with concentrated sulphuric acid and mercuric oxide (as in the Kjeldahl method for nitrogen) which destroyed the ethylene diamine. The sample was then diluted with water and the metal estimated as above. In the vanadium estimation mercury, which precipitated during the reduction with sulphur dioxide, was filtered off before titration with standard permanganate.

(c) Fluorine:

It was found to be quite difficult to obtain reproducible fluorine analyses, especially in the vanadium compounds. Several different gravimetric methods were investigated; namely precipitation of fluorine as calcium fluoride, triphenyltin fluoride or lead chlorofluoride. The most convenient and most reliable gravimetric method was found to be precipitation as lead chlorofluoride. Triphenyltin fluoride precipitation did not give good results. Calcium fluoride precipitation requires a coprecipitation step with calcium carbonate and offers no advantage over lead chlorofluoride. The simplicity of lead chlorofluoride precipitation and the large conversion factor of lead chlorofluoride make this a more suitable method than calcium fluoride precipitation.

Volumetric determination of fluoride with thorium nitrate solution is supposed to be reliable however the
difficulty of observing the endpoint of the titration requires much practice with the method before reliable results can be obtained. This method is not suitable for occasional fluorine analyses.

Regardless of the method of precipitation used, a preliminary separation of fluorine from interfering ions is necessary. Distillation of fluoride as fluorosilicic acid from a constant boiling (135°C) mixture of sulphuric acid quantitatively separates fluoride from all other cations and anions (33). The distillate contains only silicon and fluorine (presumably as SiF$_6^{2-}$) and fluoride can be determined by any of the methods discussed previously. This separation has the widest applicability as well as being the most reliable. Precipitation of interfering metal ions with specific analytical precipitants was not as satisfactory as distillation.

Fluorine analyses were done according to the following method. A weighed sample was dropped into 75 ml. of 33% sulphuric acid solution in a 250 ml. distilling flask equipped with a thermometer, a dropping funnel and a condenser. The solution was brought to the boil and the boiling liquid was maintained between 130 and 135°C by adding water slowly from the dropping funnel. The distillation was continued until 250 ml. of distillate was collected. The distillate was neutralized with dilute sodium hydroxide, using bromphenol blue indicator, and one ml. of concentrated hydrochloric
acid added. The distillate was then heated and 5 gm. of lead nitrate dissolved in the water when it reached 70°. Five gm. of sodium acetate were added when the solution was about 95°C. The solution was kept hot for one hour and allowed to cool overnight. The precipitate of lead chlorofluoride was filtered in a glass crucible, washed with saturated lead chlorofluoride solution, dried at 140°C and weighed.

(d) Nitrogen:

Nitrogen was determined in pyridine and ethylenediamine derivatives by digesting the sample with conc. sulphuric acid, potassium sulphate and mercuric oxide followed by steam distillation of ammonia from conc. alkali into boric acid solution. The evolved ammonia was titrated with standard (0.01N) hydrochloric acid using methylene blue-methyl red indicator. The digestion step was omitted in the ammonia derivatives; the sample being added to conc. alkali and steam distilled as in the standard procedure. Microanalyses on some of the samples by Dr. Bernhardt provided a check on the method.
(iii) **FLUORINE SUPPLY:**

Fluorine was supplied by the Allied Chemical Co. in a steel gas cylinder containing six pounds of fluorine at 400 p.s.i. The cylinder was installed in an upright position in a walk-in fume hood and shielded with a brick screen to minimize the spreading of any violent reaction which might occur upon entry of high pressure fluorine into the regulating system. Reduction of the gas pressure was achieved with two stainless steel needle valves (Hoke type 316 No. Y343H) in series. The high pressure gas line was constructed from $\frac{1}{2}$-inch stainless steel pressure tube, threaded and silver soldered at all joints.

On the low pressure side of the needle valves $\frac{1}{8}$" copper tubing, connected with brass compression fittings, was used. In the low pressure line, directly after the reducing needle valves was a blow-off consisting of silver soldered T-joint of $\frac{1}{2}$" copper tubing with outlet dipping into a test-tube of Fluorolube oil (Hooker Chemical Co.; FS-5). The blow-off, originally intended as a safety device to prevent a dangerous buildup of pressure in the copper line, eventually served as a crude flow meter when the original flowmeter failed to function. The flow was roughly estimated by counting the bubbles emerging through the blow-off when the top at the exit of the low pressure line was closed.

Next to the blow-off was an 8" copper tube, $\frac{1}{2}$" in diameter, containing sodium fluoride pellets to remove traces
of hydrogen fluoride. A differential manometer flow meter followed the hydrogen fluoride absorber. The flow meter consisted of a glass U-tube filled with Fluorolube oil (Hooker Chemical Co.; FS-5) and connected via Teflon tubing to \( \frac{1}{8} \)" copper tube sidearms joined with a silver soldered T-joint to the gas flow line. The sidearms had expansion chambers (1" diameter and 2" long) with sufficient volume to contain all the manometric fluid in case it was displaced by sudden application of a high pressure. The pressure difference was created with a Teflon diaphragm, punctured with a small hole, placed in the flow line between the two arms of the manometer. A nickel by-pass valve was connected in parallel with the diaphragm so that once the flow rate had been determined the pressure could be equalized and the flowmeter bypassed. This bypass valve also permitted passage of fluorine in the event of blockage in the flow-meter. A brass needle valve (Hoke no. 431) followed the flowmeter permitting the fluorine supply to be turned off at this point.

A brass T-joint was next in the line to permit mixing dry nitrogen with the fluorine. A brass needle valve (Hoke no. 431) was included in the nitrogen inlet. The mixed gases then were passed from the T-joint through a brass needle valve (Hoke no. 431) into the reaction systems which were connected to the fluorine regulating system at this point with brass compression fittings.
(iv) PREPARATION OF VANADIUM AND NIOBiUM PENTAFLUORIDES

Vanadium and niobium pentafluorides were prepared by fluorination of the powdered metals at 300 - 325°C as described previously (14). Fluorinations were done in a nickel reactor tube 12 ins. long and 1 in. diameter with one end open and flanged to permit the entry of nickel boats containing the powdered metal. The large opening was sealed by bolting a nickel plate, with a ½" exit tube silver soldered to it, to the flange, compressing a lead washer to make a gas tight seal. The ½" exit tube in the faceplate was connected to the collection system with a brass compression fitting. The other end of the nickel tube was silver soldered to a length of ½ in. nickel tubing which could be connected to the fluorine supply line with a ⅛ in. compression fitting.

The fluorides were collected in glass traplines, the design of which depended on the fluoride being prepared. Vanadium pentafluoride was collected in a simple distillation line of four traps, the two following the reactor being equipped with capillary constrictions in each arm and a breakseal. The remaining two traps served to prevent back diffusion of moisture into the traps collecting vanadium pentafluoride. Niobium pentafluoride, being less volatile was collected in a similar trapline but with the breakseals omitted as the fluoride was transferred to small bulbs in a dry box immediately before performing a reaction, instead
of by distillation.

To prepare the fluoride, about ten grams of the powdered metal was placed in a nickel boat (6 in. long, 3/4 in. wide) which was then placed in the nickel reactor tube. The flange was bolted into place and then the nickel tube was placed in a tube furnace and connected to the fluorine/nitrogen supply line, with a brass compression fitting. The reactor was heated to 300°C and nitrogen passed for two hours to remove all traces of moisture from the metal and reactor. A glass trapline was then connected to the exit of the nickel reactor with a compression fitting and dry nitrogen was passed for several hours (generally overnight). The glass trapline was periodically flamed with a hand torch and the nickel tube was maintained at 200 - 300°C during the passage of nitrogen to ensure the complete removal of moisture. The glass traps were then chilled with dry ice - alcohol baths, the metal heated to 325 - 350°C and fluorine gas, diluted with dry nitrogen, passed into the reactor and the products were collected in the first two traps. The best yields of the pentafluoride were obtained when the fluorine concentration was sufficiently high to ignite the metal. On completion of the fluorination, dry nitrogen was passed for one hour to remove unreacted fluorine from the system and the glass traps sealed off under vacuum.

Niobium pentafluoride obtained in this manner was
analyzed without further purification. Found: Nb, 49.3. Calc. for NbF₅: Nb, 49.4%. It was stored in sealed traps until required and then transferred to reaction tubes in a dry box. The lower rate of hydrolysis and the much lower volatility of niobium pentafluoride relative to vanadium pentafluoride made this procedure possible.

Vanadium pentafluoride prepared in this manner was distilled under vacuum onto carefully dried sodium fluoride and then into glass traps equipped with breakseals. It was found to be a white solid melting about 20°C to a pale straw coloured liquid as previously reported (4). A sample of the product was analysed according to the methods previously described.

Found: V, 35.3; F, 64.1%.
Calc. for VF₅: V, 34.9; F, 65.1%.
THE REACTION OF VANADIUM PENTAFLUORIDE WITH AMMONIA

Gaseous ammonia (Matheson Co.) was carefully dried by condensing it onto metallic sodium in a carefully dried, all-glass distillation system. An excess was then distilled from sodium onto vanadium pentafluoride and allowed to melt. A reddish brown solid along with traces of orange and yellow solids was formed on contact of gaseous ammonia with vanadium pentafluoride. In liquid ammonia a reddish-brown solid was formed which did not appear to be soluble in an excess of liquid ammonia. The ammonia was kept liquid at approximately \(-50^\circ C\) for several hours to allow reaction to take place and then the volatile products were fractionated through a series of traps cooled to \(0^\circ C\), \(-78^\circ C\) and \(-196^\circ C\) in ice, alcohol \(-CO_2\) and liquid nitrogen baths respectively. Volatile fractions, condensing at \(-196^\circ C\) and \(-78^\circ C\) were identified spectroscopically as ammonia. No material was found to condense at \(0^\circ C\).

The solid remaining after removal of the volatile materials was a dry, powdery, reddish-brown solid which lost ammonia readily, building up a pressure of \(NH_3\) when sealed in tubes. This reddish-brown solid was "pumped" for 20 hours while at room temperature and the volatile products condensed in a liquid nitrogen trap. The only volatile product obtained was ammonia. The reddish solid, when subjected to this treatment, became a buff-coloured solid which did not lose ammonia on standing. An X-ray powder
The photograph of the latter solid indicated the presence of ammonium fluoride in the product.

The buff solid, which could be exposed to the atmosphere for short periods without appreciable hydrolysis, was placed in a bulb, heated to 100°C with an oil bath and "pumped" for 120 hours. The volatile products were again condensed in a liquid nitrogen trap. The original buff solid decreased in weight approximately 20% and slowly became darker in colour. A white crystalline solid which collected in the outlet of the bulb and the liquid nitrogen trap, was identified as ammonium fluoride.

An X-ray photograph of the remaining brown solid showed only faint lines in the positions corresponding to ammonium fluoride. Quantitative analysis of the product indicated a composition $\text{VF}_4(\text{NH}_3)$ with a small amount of ammonium fluoride remaining.

Found: $V, 34.7\%; F, 45.8\%; \text{NH}_3, 12.5\%$
Calc. $\text{VF}_4(\text{NH}_3)$: $V, 35.4\%; F, 52.8\%; \text{NH}_3, 11.8\%$
Calc. $\text{VF}_4(\text{NH}_3)$ (0.08 mole) $\text{V}, 34.7\%; F, 53.1\%; \text{NH}_3, 12.2\%$

The magnetic susceptibility of the solid showed that it was paramagnetic and the magnetic moment, on the basis of the above composition, was calculated as 2.1 Bohr magnetons. The presence of lower valency states of vanadium was confirmed by dissolving the compound in dilute sulphuric acid (1%) and titrating directly with potassium permanganate. The titre corresponded to 44% vanadium, indicating that about 8% of the vanadium was present in the tervalent state. It
was not possible to account for this in the overall composition of the product.

The infrared spectrum of the solid, in a KBr pellet, showed the following absorptions (in cm^{-1}): 3250 & 3100 (strong and broad but resolved); shoulder at 2850; 1650 (weak and broad); 1425 (strong); 980 (strong). A possible weak absorption occurred at 1075 but was not resolved.

The solubility of amminotetrafluorovanadium IV, (NH₃)VF₄, was investigated in various solvents. The solvents used were dried with crushed potassium hydroxide (except ethanol) before the compound was added. It was found to be insoluble in benzene, carbon tetrachloride, ethanol (100%), ether, nitrobenzene and pyridine. It dissolved in water giving green coloured solution which turned blue when acidified. The product appeared to be inhomogeneous because the major portion of a sample dissolved immediately in water leaving traces of a black, difficultly soluble material which eventually went into solution.

When amminotetrafluorovanadium IV was heated in a dry, sealed tube decomposition occurred about 250°C accompanied by severe attack of the glass. A lustrous black powdery material was formed which was not identified.
Ammonia was carefully dried with sodium metal as before and an excess was distilled onto niobium pentafluoride. A reaction occurred immediately on melting the ammonia to form a yellow solid, apparently insoluble in excess liquid ammonia. The volatile contents were distilled through two traps cooled to -78° and -196°C. The solid material was "pumped" 4 to 5 hours through these same traps. The final product obtained was identified as diamminopentafluoroniobium V, \((\text{NH}_3)_2\text{NbF}_5\), by analysis.

\[
\text{Found:} \quad \text{Nb, 41.9; F, 41.5; NH}_3, 15.3\% \\
\text{Calc.} \quad (\text{NH}_3)_2\text{NbF}_5: \quad \text{Nb, 41.9; F, 42.8; NH}_3, 15.3\%
\]

The product dissolved quickly in water and was hydrolyzed slowly in moist air. Magnetic susceptibility measurements showed the solid was diamagnetic, indicating pentavalent niobium. An X-ray powder photograph did not show any lines that could be attributed to ammonium fluoride.

The infrared spectrum of \((\text{NH}_3)_2\text{NbF}_5\), prepared as a KBr pellet, showed the following absorptions (in cm\(^{-1}\)):

- A broad, strong band with a maximum at 3250 and a shoulder at 2850; 1650 (very, weak, broad); 1420 (strong); 1055 (very weak); 937 and 913 (strong, partially resolved doublet); 800 (weak, broad)

When heated in a dry, sealed tube, \((\text{NH}_3)_2\text{NbF}_5\) melted about 300 - 310°C. This melting point is not reliable because considerable attack of the glass tube occurred upon melting which obscured the appearance of the sample. Melting was
presumably accompanied by some decomposition.

The dissociation pressure of \((\text{NH}_3)_2\text{NbF}_5\) was measured in the all-glass spiral Bourdon gauge apparatus described earlier. The following results were obtained.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>(\frac{1}{T} \times 10^3)</th>
<th>P(mm)</th>
<th>(\log_{10} P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318.1</td>
<td>3.144</td>
<td>1.5</td>
<td>0.176</td>
</tr>
<tr>
<td>232.2</td>
<td>3.094</td>
<td>2.0</td>
<td>0.301</td>
</tr>
<tr>
<td>327.7</td>
<td>3.051</td>
<td>2.5</td>
<td>0.398</td>
</tr>
<tr>
<td>332.8</td>
<td>3.005</td>
<td>2.9</td>
<td>0.462</td>
</tr>
<tr>
<td>337.7</td>
<td>2.966</td>
<td>3.3</td>
<td>0.519</td>
</tr>
<tr>
<td>342.6</td>
<td>2.919</td>
<td>3.9</td>
<td>0.591</td>
</tr>
<tr>
<td>348.0</td>
<td>2.874</td>
<td>4.9</td>
<td>0.690</td>
</tr>
<tr>
<td>352.3</td>
<td>2.840</td>
<td>5.5</td>
<td>0.740</td>
</tr>
<tr>
<td>357.7</td>
<td>2.795</td>
<td>6.4</td>
<td>0.806</td>
</tr>
<tr>
<td>362.7</td>
<td>2.757</td>
<td>7.5</td>
<td>0.875</td>
</tr>
<tr>
<td>367.2</td>
<td>2.723</td>
<td>8.9</td>
<td>0.949</td>
</tr>
<tr>
<td>373.2</td>
<td>2.677</td>
<td>10.7</td>
<td>1.029</td>
</tr>
</tbody>
</table>

From these values the plot of \(\log p\) vs. \(1/T\) is linear, and obeys the relation:

\[
\log_{10} P(\text{mm}) = 5.62 - \frac{1720}{T}
\]

Also using the relation:

\[
\log_{10} \frac{P_2}{P_1} = -\frac{\Delta H}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\(\Delta H = 7870\) cal/mole.
Reagent grade pyridine (Eastman Kodak) was dried by distilling from crushed potassium hydroxide in a dry, all-glass system. An excess of dry pyridine was distilled onto vanadium pentafluoride. Immediate reaction occurred forming a dark brown solid which was insoluble in excess pyridine. The volatile materials present were distilled from the reaction trap and separated into arbitrary fractions condensation at -196°, -78° and -23°C by cooling a series of traps with liquid nitrogen, dry-ice and alcohol and carbon tetrachloride slush baths respectively.

The dark brown solid remaining in the trap was not appreciably hygroscopic and could be handled in air without noticeable decomposition. It was identified as pyridinetetrafluorovanadium IV, (Py)VF$_4$, by quantitative analysis.

Found: V, 24.6; F, 35.0; N, 6.2; C, 30.3; H, 3.5%
Calc. for (Py)VF$_4$: V, 24.7; F, 36.9; N, 6.8; C, 29.2; H, 2.4%

Magnetic susceptibility measurements indicated a paramagnetic solid and the magnetic moment calculated for (Py)VF$_4$ was 1.67 Bohr magnetons, close to the expected value of 1.73 for tetravalent vanadium. Titration with standard (0.01N) potassium permanganate immediately after dissolving the sample in dilute sulphuric acid indicated that all the vanadium was present in the tetravalent state.
No volatile materials were found in the -196°C fraction. The liquid found in both -78°C and -23°C fractions was identified spectroscopically as pyridine. No infrared evidence was found for fluorinated pyridines. A reactive fluoride, which bleached a zirconium nitrate-alizarin test paper, was found in the -23°C fraction of pyridine and slight etching of the glass trap was observed when the trap contents were distilled under non-anhydrous conditions. It was not possible to identify the reactive fluoride present. No trace of fluoride was found in the -78°C pyridine fraction.

In a second reaction vanadium pentafluoride was sublimed onto the walls of a large diameter tube and frozen with dry-ice. Pyridine vapour was passed over the solid VF₅ with the same result as before. A dark brown solid was formed on immediate contact of pyridine with vanadium pentafluoride which was identified as (Py)VF₄ (found V, 24.4%)

When heated in a sealed tube, pyridinetetrafluoro-
vanadium IV did not melt but rather decomposed about 150°C yielding a brown liquid and a greenish coloured solid.

The infrared spectrum of pyridinetetrafluoro-
vanadium IV showed many peaks identical to those found in the pyridine spectrum: The following absorption peaks (incm⁻¹) were observed: 3100(vs), 2800(s), 2150(w), 1850(w), 1685(shoulder), 1625(s), 1540(m), 1475(s),
1325(w), 1260(m), 1245(m), 1200(m), 1175(m), 1100(shoulder),
1060(shoulder), 1050(shoulder), 980(broad), 855(vw),
780(s), 755(s).
Reagent grade ethylenediamine (Eastman-Kodak) was carefully dried with crushed potassium hydroxide and distilled, in an all-glass vacuum system, onto vanadium pentafluoride. A reaction occurred immediately on melting the ethylenediamine and a brown solid, insoluble in excess ethylenediamine was formed. Volatile materials were distilled from the reaction trap through a series of traps arbitrarily cooled to -196°C, -78°C and -23°C with liquid nitrogen, alcohol CO₂ and a carbon tetrachloride slush respectively.

The volatile materials were readily removed leaving a dark brown powdery solid found to have the composition VF₄(en)₃

**Found:** V, 16.9; F, 24.9; N, 24.1; C, 23.7; H, 7.3%.

**Calc. for VF₄(en)₃:** V, 16.7; F, 24.8; N, 27.1; C, 23.4; H, 7.9%

Magnetic susceptibility measurements indicated a paramagnetic solid and the magnetic moment, calculated for the composition VF₄(en)₃, was 2.0 Bohr magnetons. It was not possible to confirm the tetravalency of vanadium indicated by the magnetic measurements with a direct titration because of the interference of ethylenediamine with the permanganate titration. It was found necessary to remove ethylenediamine with strong oxidizing conditions before reliable vanadium estimations could be obtained and so the lower valence state of vanadium
could not be preserved while removing ethylenediamine.

The volatile materials collected in -23°C and -78°C traps were identified spectroscopically as ethylenediamine. No trace of a reactive fluoride was found in the liquid fractions. The infrared spectra of the liquid fractions indicated that no fluorinated ethylenediamine was present. No reaction product was found in the -196°C trap.

The infrared spectrum of tris(ethylenediamine) tetrafluorovanadium IV, \([V(en)_3]F_4\), was complex, resembling the spectrum of pure ethylenediamine. The following absorption peaks (in cm\(^{-1}\)), with indicated relative intensity, were observed: 3200(s), 3110(s), 2490(s), 2340(shoulder), 2140(w), 1595(m), 1463(m), 1330(m), 1285(m), 1130(s), 1050(s), 965(s), 725(broad). There were no absorption peaks that could be assigned to C-F vibration frequencies indicating that the ethylenediamine in the solid was not fluorinated in the reaction.

When heated in a sealed tube the compound did not melt but decomposed above 160°C yielding a mixture of liquid and solid products which were not identified. The original reaction product, tris(ethylenediamine) tetrafluorovanadium IV was found to be insoluble in benzene, ether, ethanol (100%), carbon tetrachloride, nitrobenzene and pyridine. It dissolved quickly in water when slightly acidified with sulphuric acid. It was not markedly hygroscopic and could be handled in air without noticeable decomposition.
Reagent grade ethylenediamine (Eastman-Kodak) was carefully dried over crushed potassium hydroxide and distilled in vacuum in an all-glass apparatus. An excess was then condensed, in vacuum, onto niobium pentafluoride (0.503 gm, 2.6 millimoles) and melted. Reaction occurred slowly and the ethylenediamine slowly turned yellow. On standing at room temperature for several hours, a dark brown viscous syrup formed from which ethylenediamine could only be removed with difficulty. The syrupy brown contents of the reaction trap were heated to 90 - 95°C and "pumped" for a total of 12 hours which removed all but 0.257 gm (4.3 millimoles) of ethylenediamine. During removal of ethylenediamine, the dark brown syrup was seen to slowly solidify and become a glassy, light brown material which could be easily crushed. The gain in weight of 0.257 gm corresponds to the formation of a product with the overall composition NbF$_5$(en)$_{1.6}$. This composition was confirmed by analysis.

Found: Nb, 32.6; F, 33.4%
Calc. for NbF$_5$(en)$_{1.6}$: Nb, 32.7; F, 33.4%

The only volatile material removed from the brown syrup was ethylenediamine which was identified spectroscopically.

The solid product, NbF$_5$(en)$_{1.6}$, was readily soluble in water. It was not appreciably hygroscopic and could
be handled in air without noticeable decomposition. On heating in a sealed tube decomposition occurred about 240°C yielding a mixture of unidentified solids and liquids. Owing to the indefinite nature of the product, no further information could be obtained.
Vanadium pentafluoride was distilled twice in vacuum from carefully dried sodium fluoride and thence into a 4 m.m. pyrex tube which was then sealed off. The tube containing vanadium pentafluoride was then placed inside a 5 mm pyrex tube. A few drops of reagent trifluoroacetic acid was placed in the 5 mm tube and frozen and the external, 5 mm tube was then sealed off under vacuum.

The fluorine resonance spectrum of vanadium pentafluoride was measured at room temperature with a Varian model 4300-B high-resolution nuclear magnetic resonance spectrometer equipped with a twelve inch electromagnet, and a 40 megacycle radio frequency oscillator. A magnetic field strength of approximately 9000 gauss was used. The sample tube was spun for increased resolution.

The chemical shift of vanadium pentafluoride was calculated from the linear displacement of the F\textsuperscript{19} signal in VF\textsubscript{5} relative to the F\textsuperscript{19} signal of the trifluoroacetic acid external reference. On the assumption that the field sweep was linear, the chemical shift measured was - 335 ppm.

Only a broad resonance peak having a width at half-height of approximately 75 cps was obtained for vanadium pentafluoride. No attempts to resolve the
spectrum, by lowering the sample temperature, were made because pure vanadium pentafluoride freezes at 19.5°C. A low melting, non-reacting solvent for vanadium pentafluoride has not yet been found.
REFERENCES