

Transition Metal Fluoride Derivatives  
With Nitrogen-Containing  
Ligands

*A Thesis presented for the degree of  
Doctor of Philosophy  
in the  
Faculty of Science  
by  
G. A. Griffith*

*June 1988*

UMI Number: U527041

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI U527041

Published by ProQuest LLC 2015. Copyright in the Dissertation held by the Author.  
Microform Edition © ProQuest LLC.

All rights reserved. This work is protected against  
unauthorized copying under Title 17, United States Code.



ProQuest LLC  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106-1346

x75149780x

*Families, when a son is born,  
Want him to be intelligent.  
I, through intelligence,  
Having wrecked my whole life,  
Only hope the child will prove  
Ignorant and stupid.  
Then he will crown a tranquil life  
By becoming a Cabinet Minister.*

*Su Shih*

### Statement

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester between October 1983 and October 1986, except when otherwise stated. The work has not been submitted, and is not currently being submitted, for any other degree at this or any other university.

A handwritten signature in black ink, appearing to be 'C. Griffiths', written over a horizontal line.

June 1988

Parts of this work have been published or are being submitted for publication as follows:

" The reaction between tungsten hexafluoride and pentafluoroaniline"

J.Fawcett , G.A.Griffith , R.D.Peacock and D.R.Russell

*Polyhedron* (1988) \*

\* article submitted for publication ( May 1988 )

### Acknowledgements:

I wish to express my thanks to the following, without whom much or all of this thesis would not have been possible:

The University of Leicester for providing a Research Scholarship

My supervisor Prof. R.D.Peacock.

Prof. J.H.Holloway for much helpful discussion.

Dr. D.Russell for help with X-ray crystallography.

Dr. J.Fawcett for much practical advice, X-ray crystallographic work, bonhomie and a great line in barbecues.

Drs. D.L.Turner and W.Dukat for copious assistance with, and running of,  $^{19}\text{F}$  nmr spectra.

The Technical staff of the Chemistry Department who made many things possible.

The Leicester University American Football team - a nicer bunch of psychopaths you couldn't hope to meet in a dark alley.

Several people for putting up with me, notably Andy Mackie and Carl Edwards.

The music of The The, New Model Army, Half-man Half-biscuit, Shriekback and Tangerine Dream.

The Final Frontier comic shop, for provision of an alternative consciousness

### List of abbreviations

Kel-F	Polytrifluorochloroethylene
F.E.P.	Tetrafluoroethylene/perfluoropropylene copolymer
P.T.F.E.	Polytetrafluoroethylene
LN	Liquid nitrogen
TFA	Trifluoroacetic acid
ppm	Parts per million
o.d.	Outside diameter
i.d.	Inside diameter
IR	Infra-red
nmr	Nuclear magnetic resonance
TTSH	Tetrakis-trimethylsilylhydrazine , $(\text{Me}_3\text{Si})_2\text{N}-\text{N}(\text{SiMe}_3)_2$
Me	Methyl , $-\text{CH}_3$
MeCN	Acetonitrile , $\text{CH}_3\text{CN}$
Genetron-113	1,1,2-Trichloro-trifluoroethane
soln.	Solution
T.M.	Transition metal
TMS	Trimethylsilyl
eqn.	equation
H.F.	High frequency
vas	IR asymmetric stretching mode ( $\nu_{\text{as}}$ )
vs	IR symmetric stretching mode ( $\nu_{\text{s}}$ )

## List of Figures.

2.1	The Basic Vacuum Manifold.....	10
2.2	Apparatus for sorting single crystals.....	12
3.1	IR spectrum of the yellow solid from (WF <sub>6</sub> + C <sub>6</sub> F <sub>5</sub> NH <sub>2</sub> ).....	20
3.2	Mass spectrum of the solid "[WF <sub>5</sub> NC <sub>6</sub> F <sub>5</sub> ] <sup>-</sup> [C <sub>6</sub> F <sub>5</sub> NH <sub>3</sub> ] <sup>+</sup> ".....	21
3.3	19F nmr spectrum of the MeCN soln. of the yellow solid from (WF <sub>6</sub> + C <sub>6</sub> F <sub>5</sub> NH <sub>2</sub> ).....	24
3.4	19F nmr of MeCN soln.; expansion of the region 50-68ppm...	25
3.5	19F nmr: expansion of [WOF <sub>5</sub> ] <sup>-</sup> and [W <sub>2</sub> F <sub>9</sub> (NC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ] <sup>-</sup> multiplets.....	26
3.6	19F nmr: expansion of the C <sub>6</sub> F <sub>5</sub> N region of the MeCN soln.....	27
3.7	19F nmr spectrum of the TFA soln. of the yellow solid from (WF <sub>6</sub> + C <sub>6</sub> F <sub>5</sub> NH <sub>2</sub> ).....	29
3.8	IR spectrum of the solid recrystallised from TFA.....	30
3.9	IR spectrum of the solid from (MoF <sub>6</sub> + C <sub>6</sub> F <sub>5</sub> NH <sub>2</sub> ).....	32
3.10	IR spectrum of the solid from (ReF <sub>6</sub> + C <sub>6</sub> F <sub>5</sub> NH <sub>2</sub> ).....	34
3.11	Mass spectrum (170°C) of the solid from (C <sub>6</sub> F <sub>5</sub> NH <sub>2</sub> + ReF <sub>6</sub> )..	35
3.12	Stacked plots of the 19F - 19F COSY nmr spectrum of the 'C <sub>6</sub> F <sub>5</sub> N-' region : MeCN solution containing [WF <sub>5</sub> NC <sub>6</sub> F <sub>5</sub> ] <sup>-</sup> [C <sub>6</sub> F <sub>5</sub> NH <sub>3</sub> ] <sup>+</sup> .....	42
3.13	The Crystal structure of [ C <sub>6</sub> F <sub>5</sub> N=WF <sub>4</sub> -F-WF <sub>4</sub> =NC <sub>6</sub> F <sub>5</sub> ] <sup>-</sup> [C <sub>6</sub> F <sub>5</sub> NH <sub>3</sub> ] <sup>+</sup> .....	47
3.14	Re-orientation of the [C <sub>6</sub> F <sub>5</sub> N=WF <sub>4</sub> -F-WF <sub>4</sub> =NC <sub>6</sub> F <sub>5</sub> ] <sup>-</sup> [C <sub>6</sub> F <sub>5</sub> NH <sub>3</sub> ] <sup>+</sup> unit cell.....	49
4.1	IR spectrum of WF <sub>5</sub> -NCO.....	57
4.2	IR spectrum of the volatile products from (WF <sub>5</sub> -NCO + TFA).	59
4.3	IR spectrum of "WF <sub>5</sub> NHC(O)CF <sub>3</sub> " ( from WF <sub>5</sub> -NCO + TFA ).....	60
4.4	IR spectrum of MoF <sub>5</sub> -NCO (Nujol mull).....	63
4.5	IR spectrum of MoF <sub>4</sub> NH.....	65
4.6	IR spectrum of MoF <sub>4</sub> NH.MeCN.....	67
4.7	IR spectrum of the solid from (MoF <sub>4</sub> NH + ClF <sub>3</sub> ).....	69
4.8	Proposed structure of MoF <sub>4</sub> NH.....	74
5.1	Mass spectrum of WOF <sub>3</sub> -NCO.....	79
5.2	IR spectrum of WOF <sub>3</sub> -NCO.....	80
6.1	Apparatus for the preparation of TTSH.....	90



6.2	Separation of precipitates: filtration under N <sub>2</sub> TTSH prepn.....	91
6.3	Sublimation purification of TTSH.....	92
6.4	IR spectrum of MoF <sub>5</sub> (from MoF <sub>6</sub> + TTSH).....	95
6.5	IR spectrum of ReF <sub>5</sub> (from ReF <sub>6</sub> + TTSH).....	99
6.6	IR spectrum of the tan solid from WF <sub>6</sub> + TTSH.....	102
6.7	IR spectrum of the solid ([WNF <sub>4</sub> ] <sub>2</sub> ) recrystallised from MeCN.....	103
6.8	Mass spectrum (90°C) of the solid ([WNF <sub>4</sub> ] <sub>2</sub> ) recrystallised from MeCN.....	104

## List of Tables

3.1	Selected d-spacings from the X-ray powder pattern of the yellow solid " $[\text{WF}_5\text{NC}_6\text{F}_5]^-[\text{C}_6\text{F}_5\text{NH}_3]^+$ ".....	23
3.2	Chemical shifts (ppm) and coupling constants(Hz) for $^{19}\text{F}$ nmr of MeCN solutions of the product from $(\text{WF}_6 + \text{C}_6\text{F}_5\text{NH}_2)$ .....	39
3.3	Estimation of dilution effects $\delta\text{F}(\text{ppm})$ in $[\text{C}_6\text{F}_5\text{NH}_3]^+$ ...	44
3.4	Chemical shifts (ppm) and coupling constants(Hz) for the $^{19}\text{F}$ nmr of the TFA solution of the product from $(\text{WF}_6 + \text{C}_6\text{F}_5\text{NH}_2)$ .....	45
3.5	Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ).....	48
3.6	Comparison of W=N bond lengths ( $\text{\AA}$ ).....	50
3.7	Defined planes enclosing designated , numbered atoms...	52
4.1	X-ray powder pattern of the white solid formed from $\text{MoF}_4\text{NH} + \text{ClF}_3$ .....	70
6.1	The mass spectrum of $\text{MoF}_5$ .....	96
6.2	Comparison of the powder pattern of the dark solid from " $\text{ReF}_6 + \text{TTSH}$ " with Re metal.....	100
6.3	Comparison of the X-ray powder patterns of " $[\text{WNF}_4]_2$ " and $\text{WF}_5$ .....	105

## Appendix      Crystallography Tables

7.1	Fractional atomic coordinates for $[\text{C}_6\text{F}_5\text{NH}_3]^+$ $[(\text{C}_6\text{F}_5)\text{NWF}_4-\text{F}-\text{WF}_4\text{N}(\text{C}_6\text{F}_5)]^-$ .....	111
7.2	Atomic thermal parameters ( $\times 10^4$ ) for $[\text{C}_6\text{F}_5\text{NH}_3]^+$ $[(\text{C}_6\text{F}_5)\text{NWF}_4-\text{F}-\text{WF}_4\text{N}(\text{C}_6\text{F}_5)]^-$ .....	113
7.3	Bond lengths ( $\text{\AA}$ ) for $[(\text{C}_6\text{F}_5)\text{NWF}_4-\text{F}-\text{WF}_4\text{N}(\text{C}_6\text{F}_5)]^-$ $[\text{C}_6\text{F}_5\text{NH}_3]^+$ .....	115
7.4	Bond angles ( $^\circ$ ) for $[(\text{C}_6\text{F}_5)\text{NWF}_4-\text{F}-\text{WF}_4\text{N}(\text{C}_6\text{F}_5)]^-$ $[\text{C}_6\text{F}_5\text{NH}_3]^+$ .....	116
7.5	Non-bonded contacts ( $\text{\AA}$ ) for $[(\text{C}_6\text{F}_5)\text{NWF}_4-\text{F}-\text{WF}_4\text{N}(\text{C}_6\text{F}_5)]^-$ $[\text{C}_6\text{F}_5\text{NH}_3]^+$ .....	118
7.6	Observed and calculated structure factors for $[(\text{C}_6\text{F}_5)\text{NWF}_4-\text{F}-\text{WF}_4\text{N}(\text{C}_6\text{F}_5)]^-[\text{C}_6\text{F}_5\text{NH}_3]^+$ .....	120

<u>Contents</u>	<u>Page</u>
Statement.....	i
Acknowledgements .....	ii
List of abbreviations.....	iii
List of Figures.....	iv
List of Tables.....	vi
Contents.....	vii
 Chapter 1.....	 1
1.1 Introduction.....	2
 Chapter 2.....	 7
2.1 General Preparative Techniques.....	8
2.2 Vacuum Systems.....	9
2.3 Preliminary Treatment of Crystals.....	12
2.4 Characterisation of Products.....	13
2.5 Starting Materials and Solvents.....	14
 Chapter 3.....	 17
3.1 Introduction.....	18
3.2 Experimental.....	19
3.2.1 Reaction of Pentafluoroaniline with $WF_6$ .....	19
3.2.2 Reaction of Pentafluoroaniline with $MoF_6$ .....	31
3.2.3 Reaction of Pentafluoroaniline with $ReF_6$ .....	33
3.3 Discussion.....	36
 Chapter 4.....	 54
4.1 Introduction.....	55
4.2 Experimental.....	56
4.2.1 The Preparation of Pentafluorotungsten(VI)iso-	
cyanate.....	56
4.2.2 Reaction of Pentafluorotungsten(VI)isocyanate	
with TFA.....	58
4.2.3 The Preparation of Pentafluoromolybdenum(VI)iso-	
cyanate.....	61
4.2.4 The Reaction of $MoF_5NCO$ with Anhydrous Hydrogen	
Fluoride.....	62

4.2.5	The Preparation of N-imidomolybdenum(VI)tetra- Fluoride.....	64
4.2.6	The Preparation of the Acetonitrile Adduct MoF <sub>4</sub> NH.MeCN.....	66
4.2.7	The Reaction of MoF <sub>4</sub> NH with Chlorine Trifluoride	66
4.3	Discussion.....	68
Chapter 5.....		75
5.1	Introduction.....	76
5.2	Experimental.....	77
5.2.1	The Reaction of Trimethylsilylisocyanate with WOF <sub>4</sub> .....	77
5.2.1	The Reaction of Trimethylsilylazide with Tungsten Oxyfluoride.....	81
5.3	Discussion.....	82
Chapter 6.....		86
6.1	Introduction.....	87
6.2	Experimental.....	89
6.2.1	The Preparation of Tetrakis-trimethylsilyl- hydrazine.....	89
6.2.2	The Reaction of Molybdenum Hexafluoride with TTSH.....	93
6.2.3	The Reaction of Rhenium Hexafluoride with TTSH..	97
6.2.4	The Reaction of Tungsten Hexafluoride with TTSH.	98
6.3	Discussion.....	107
Appendix.....		110
Table 7.1	Fractional atomic co-ordinates.....	111
Table 7.2	Atomic thermal parameters ( x10 <sup>4</sup> ).....	113
Table 7.3	Bond lengths ( Å ).....	115
Table 7.4	Bond angles.....	116
Table 7.5	Non-bonded contacts ( Å ).....	118
Table 7.6	Observed and calculated structure factors for [(C <sub>6</sub> F <sub>5</sub> )NWF <sub>4</sub> -F-WF <sub>4</sub> N(C <sub>6</sub> F <sub>5</sub> )] <sup>-</sup> [C <sub>6</sub> F <sub>5</sub> NH <sub>3</sub> ] <sup>+</sup> ...	120
References.....		132

# Chapter One

## Introduction

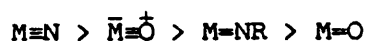
## 1.1 Introduction

The existence of many types of compound possessing a nitrogen-containing moiety bonded directly to the transition metal in a transition metal complex has been known for some time. Griffith <sup>(1)</sup> and , more recently , Nugent and Haymore <sup>(2)</sup> have reviewed the chemistry of many of these derivatives. The nitrogen-containing compounds can be broadly categorised into three types:-

- 1) Those containing a transition metal ( T.M. ) to nitrogen single ( amido ) bond ( M-N ).
- 2) Those containing a T.M. to nitrogen double ( imido ) bond ( M=N ).
- 3) Those containing a T.M. to nitrogen triple ( nitrido ) bond ( M≡N ).

Most compounds fall into the latter two categories , ( M=N ) imido and ( M≡N ) nitrido compounds. However , examples of compounds containing two types of T.M. to nitrogen bond exist , such as  $[\text{AsPh}_4]_2^+[\text{ReN}(\text{NCS})_5]^{2-}$  <sup>(3)</sup> and  $[\text{OsN}(\text{NCS})_5]^{2-}$  <sup>(4)</sup> which contain both nitrido and amido groups bonded to the same T.M. centre. As expected the imido and nitrido bonds possess strong  $\pi$ -bonding character , best explained in terms of the nitrogen adopting  $sp$ - hybridisation with overlap with the  $d_{z^2}$  orbital of the metal to form a  $\sigma$  bond , and overlap of  $p_x$  or  $p_y$  orbitals with the metal  $d_{xz}$  or  $d_{yz}$  orbitals to form  $\pi$  bonds <sup>(1)</sup> respectively. The order of T.M. to nitrogen bond strengths and the isoelectronic T.M. to oxygen bond strengths have been estimated and compared by several workers using various criteria such as bond length measurements , resistance to reduction <sup>(1,2)</sup>,  $^{19}\text{F}$

nmr chemical shifts <sup>(5,6)</sup> and spectroscopic force constant data <sup>(7,8)</sup> and found to decrease from M=N bonds in the order:-



The greater strengths of the T.M. to nitrogen bonds compared with those of the isoelectronic oxo-compounds has been explained as a result of the lower electronegativity of nitrogen allowing greater donation of electron density to the metal atom. Another recurrent feature of amido, imido and nitrido compounds is the preference for the formation of multiple M-N bonds, such that compounds formally ascribed as containing an imido (M=N) bond, tend to show features indicative of a bond order slightly greater than two.

The examination of T.M. halide derivatives has centred almost entirely on chlorides. Not surprisingly, the high-oxidation-state stabilisation brought about by the attachment of nitrido ligands favours formation of chlorides with the heavier second- and third-row elements. However, some first-row transition metal chloride azides,  $TiCl_3N_3$  and  $VOCl_2N_3$  are known<sup>(9)</sup>. The neutral nitrido chlorides  $Cl_3M=N$  (M= Mo, W)<sup>(10)</sup> have been synthesised, and the crystal structure of one,  $Cl_3Mo=N$ , has been determined<sup>(11)</sup>. Several salts of  $[MNC_4]^-$  anions have been studied and identified by IR spectroscopy (M= Mo<sup>(14)</sup>, Os<sup>(15)</sup>, Ru<sup>(16)</sup>) and possess the expected square-based pyramidal ( $C_{4v}$ ) structure. The neutral  $ReNCl_4$ <sup>(17)</sup> adopts a  $C_{4v}$  geometry about Re but packs as a chain structure with alternating Re=N-Re bonds in the unit cell. The crystal structures of the other T.M. nitrido and imido chlorides,  $[Cl_5WNC_2Cl_5]^-$ <sup>(18)</sup>,  $Cl_3PO(Cl_4)MN-C_2Cl_5$  (M= Re<sup>(19)</sup>, Mo<sup>(20)</sup>), have also been determined. The imido-chloride  $[Cl_4WNC_2Cl_5]_2$ <sup>(21)</sup> adopts chlorine bridges and, unusually,

a dimeric N-N bonded structure has been proposed for  $[\text{MoNCl}_4]_2^{(22)}$ . Some imido chlorides possess unusual alkyl substituents, such as the organoimido molybdenum complex  $(p\text{-TolylN})\text{MoCl}_4(\text{thf})^{(27)}$  and  $[\text{WCl}_2(\text{NPh})_2(\text{bipy})]^{(28)}$ , and there is also an example of a mixed chloro-, fluoro-trinuclear nitrido salt,  $[\text{CPh}_3]^+[\text{Ph}_3\text{CNWCl}_4-(\mu\text{-F})\text{WNCl}_2(\mu\text{-F})\text{Cl}_4\text{WNCPh}_3]^{-(29)}$ .

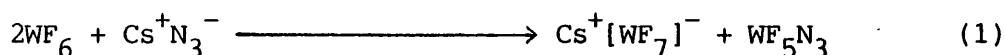
The chemistry of transition metal imido, nitrido and amido fluorides is not as well documented as that of the chlorides. The earliest attempt to form a T.M. fluoride complex with a nitrogen-containing group was in 1905 when Eisner and Ruff<sup>(23)</sup> treated tungsten hexafluoride ( $\text{WF}_6$ ) with gaseous and liquid ammonia ( $\text{NH}_3$ ). They isolated a white and an orange-brown solid, which were not fully identified. Clark and Emeleus<sup>(24)</sup> repeated the reaction and isolated an orange-brown solid with the composition  $(\text{NH}_3)_4.\text{WF}_6$ . Later work using  $^{19}\text{F}$  nmr spectroscopy by Winfield et al<sup>(5,25)</sup> showed the reaction of  $\text{WF}_6$  with amines to proceed via iminolysis. A  $^{19}\text{F}$  nmr study of the reaction between  $\text{WF}_6$  and  $\text{NH}_3$ <sup>(6)</sup> also showed iminolysis to occur. From this it seems highly likely that Eisner and Ruff prepared the first transition metal imido fluoride salt - but did not possess the analytical tools necessary to recognise it as such. Reaction of  $\text{MoF}_6$  with  $\text{NH}_3$  has been reported to yield a mixture of ammonium fluoride and  $\text{MoF}_5.4\text{NH}_3$ <sup>(26)</sup>, again it seems likely that in this case too, iminolysis has occurred.

The reactions of  $\text{MoF}_6$  and  $\text{WF}_6$  with  $\text{NH}_3$  are representative of one of the two most used methods to prepare T.M. imido fluorides. The first method is by treating the metal hexafluoride with a primary amine ( $\text{RNH}_2$ ), which produces the anionic fluoro-imide salt,  $[\text{MF}_5\text{NR}]^- [\text{NRH}_3]^+$ , and the corresponding amine fluoride salt  $[\text{NRH}_3]^+\text{F}^-$ . So far



several primary amines have been treated with  $\text{WF}_6$ <sup>(5,6,25)</sup> and all the products identified by  $^{19}\text{F}$  nmr spectroscopy , but not by X-ray crystallography.

The increased usage of trimethylsilyl (TMS) compounds in preparative chemistry , and the accompanying diversity of substituted TMS derivatives available , paved the way for the second method of preparing T.M. imido fluorides. Substituted TMS compounds (  $\text{Me}_3\text{Si-X}$  ) can be treated with the T.M. hexafluoride in relatively clean , one-step reactions to form  $\text{MF}_5\text{X}$  and  $\text{Me}_3\text{Si-F}$ . This preparative route has yielded nitrogen-containing metal fluorides that have had structures determined crystallographically , such as  $\text{WF}_5\text{N}_3$ <sup>(30)</sup> and  $\text{WF}_4^-(\text{N=PPh}_3)_2$ <sup>(31)</sup>. The reaction of TMS derivatives with T.M. hexafluorides is believed to occur via straight exchange of fluoride ion for the nitrogen-containing substituent. In a similar preparation of  $\text{WF}_5\text{N}_3$  using the reaction  $\text{WF}_6$  with  $\text{CsN}_3$  , Brownstein<sup>(32)</sup> has proposed a reaction scheme (eqn.1) involving the azide ion :-



This reaction does not appear to occur in systems using TMS derivatives , although Winfield<sup>(5)</sup> has proposed the existence of a TMS-containing intermediate species ,  $\text{WF}_5\text{N(H)SiMe}_3$ .

Formation of imido fluorides from the corresponding chloro-derivatives has , so far , proved of limited value , with only two compounds having been prepared in this fashion ;  $\text{ReNF}_4.\text{ReF}_5(\text{NCl})$  by direct fluorination of  $\text{ReNCl}_4$  with  $\text{F}_2$ <sup>(33)</sup> and , more recently ,  $\text{WF}_4\text{NPh}$  by adding  $\text{HF}$  to  $\text{WCl}_4\text{NPh}$ <sup>(34)</sup>.

The paucity of examples of T.M. fluorides with nitrogen-containing substituents bonded to the metal atom in comparison with the T.M. chlorides prompted the work described in this thesis. The aim was to obtain new crystalline derivatives of T.M. imido fluorides of tungsten, molybdenum and rhenium, using either the reaction of the hexafluorides with a primary amine or reaction with a TMS derivative. Chapter 2 details the practical techniques and analytical methods employed throughout the research.

In Chapter 3 the reactions of  $\text{MF}_6$  (  $\text{M} = \text{Mo}, \text{W}, \text{Re}$  ) with the bulky primary amine  $\text{C}_6\text{F}_5\text{NH}_2$  are examined; and the crystal structure determination of the imido tungsten fluoride salt  $[\text{C}_6\text{F}_5\text{NH}_3]^+$   $[\text{C}_6\text{F}_5\text{NWF}_4-\text{F}-\text{WF}_4\text{NC}_6\text{F}_5]^-$  and the formation of the mixed oxo-imido anion  $[\text{O}=\text{WF}_4-\text{F}-\text{WF}_4\text{NC}_6\text{F}_5]^-$  in acetonitrile solutions are reported.

The preparative route using a TMS derivative is examined in Chapter 4 where the reactions of  $\text{MF}_6$  (  $\text{M} = \text{Mo}, \text{W}$  ) with  $\text{TMS-NCO}$  and of  $\text{MoF}_6$  with  $(\text{Me}_3\text{Si})_2\text{NH}$  are detailed. Monomeric, pseudo-octahedral (  $\text{C}_{4v}$  ) structures are proposed for the compounds  $\text{MF}_5\text{NCO}$  (  $\text{M} = \text{Mo}, \text{W}$  ) and  $\text{MoF}_4\text{NH} \cdot \text{MeCN}$ , and a cis-fluorine bridged, polymeric chain structure for  $\text{MoF}_4\text{NH}$ .

The reaction of  $\text{WOF}_4$  with  $\text{TMS-NCO}$  and  $-\text{N}_3$  is reported in Chapter 5, the isocyanate product being identified by its mass spectrum as  $\text{WOF}_3\text{NCO}$ . Finally, the reaction of  $\text{MF}_6$  (  $\text{M} = \text{Mo}, \text{W}, \text{Re}$  ) with tetrakis-trimethylsilylhydrazine (TTSH) is detailed in Chapter 6. With  $\text{MoF}_6$  and  $\text{ReF}_6$  as reactants there is reduction of the hexafluoride to the pentafluoride in approximately 50% yield,  $\text{WF}_6$  is believed to react with formation of a nitrogen-bridged diimido fluoride species  $\text{WF}_4=\text{N}-\text{N}=\text{WF}_4$ .

# Chapter Two

Experimental |

## 2.1 General Preparative Techniques.

Most of the starting materials used and many of the compounds prepared are air or moisture sensitive , and need handling in an inert atmosphere or in vacuo to prevent decomposition. Metal , Pyrex glass or fluoroplastic containers were used for carrying out reactions and storage. Metal reactors were pumped to  $10^{-4}$  torr , hydrogenated , seasoned with fluorine and re-evacuated before use. All glass and fluoroplastic containers were pumped to  $10^{-5}$  torr with heating and seasoned with either fluorine or chlorine trifluoride before use.

Volatile compounds were manipulated in vacuum systems under either static or dynamic vacuum using conventional methods. Non-volatile compounds were manipulated under an inert atmosphere of dry nitrogen in auto-recirculating positive pressure dry boxes (Vacuum Atmospheres Company , model HE 42-2 Dri-Lab). Oxygen and water was removed from the nitrogen by columns of manganese oxide and molecular sieve within the drying unit (VAC HE-493 Dri-Train). Samples to be stored for later use were placed in seasoned Pyrex ampoules or Teflon FEP or Kel-F containers and sealed with fluoroplastic plugs. Samples for mass spectroscopy , melting point or X-ray powder analysis were placed in pre-seasoned Pyrex capillaries and sealed with dentistry wax ( Pinnacle Standard Wax , AD International Ltd. ) melted with a soldering iron ( Radio Spares ) to give a temporary seal. Once removed from the dry boxes the capillaries were sealed using a micro-torch ( model H164/1 Jencons , Hemel Hempstead , Herts. ).

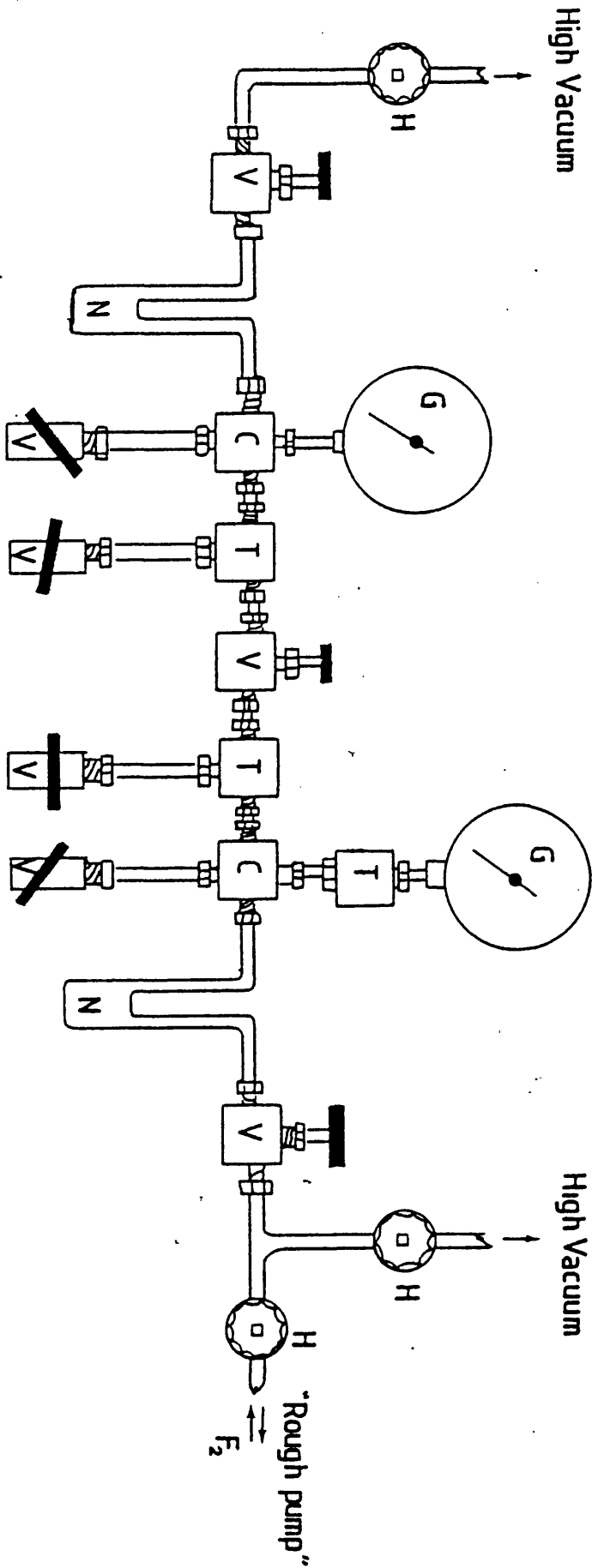
Static electricity acquired from the dry boxes made accurate weighings of fluoroplastic containers difficult. Once removed from the box , containers were wiped with iso-propanol to disperse the static and weighed on a laboratory balance ( Stanton Instruments Uni-matic CL41  $\pm$  0.1mg ).

## 2.2 Vacuum Systems.

Vacuum-line techniques were used to prepare all products. A metal manifold with high and low vacuum facilities (Fig.2.1) was constructed from 3/8" o.d. , 1/8" i.d. nickel tubing ( H.Wiggin & Co. , Hereford ), argon-arc welded U-traps (25cm<sup>3</sup> capacity) and AE-30VM series hard-drawn stainless steel needle valves , crosses and tees ( Autoclave Engineers Inc., Erie , Pennsylvania U.S.A.). The low-vacuum facility( 10<sup>-2</sup> torr ) was provided by a single-stage rotary pump ( type PSR2 , NGN Accrington , Lancs. ) fitted with an air admittance valve ( NGN vac.valve type P.V.1 ), connected to the manifold through a large metal trap filled with soda lime granules ( 5-10 mesh ). The low vacuum was used to remove fluorine and volatile fluorides removed from the manifold prior to using the high-vacuum facility. For convenience fluorine was contained in welded nickel cans ( 1 dm<sup>3</sup> capacity) fitted with AE-30VM stainless-steel needle valves attached to the metal manifold.

The main system (10<sup>-4</sup> torr) was provided by a double stage rotary pump ( Genevac , type GRD2 , General Engineering Co., Radcliffe , Lancs.) with a mercury diffusion pump and -196°C cold trap. The vacuum was monitored by a cold cathode Penning ionization gauge ( AEI Penning Gauge control VC 13 ). Manifold pressures ( 0-1500 torr $\pm$ 5

**FIGURE 2.1**  
The Basic Vacuum Manifold.



- |                           |                                  |
|---------------------------|----------------------------------|
| C = Stainless steel cross | H = Hoke (HOILE) valve           |
| T = Stainless steel 'tee' | V = Stainless steel needle valve |
| N = Nickel "U" trap       | G = Bourdon gauge                |

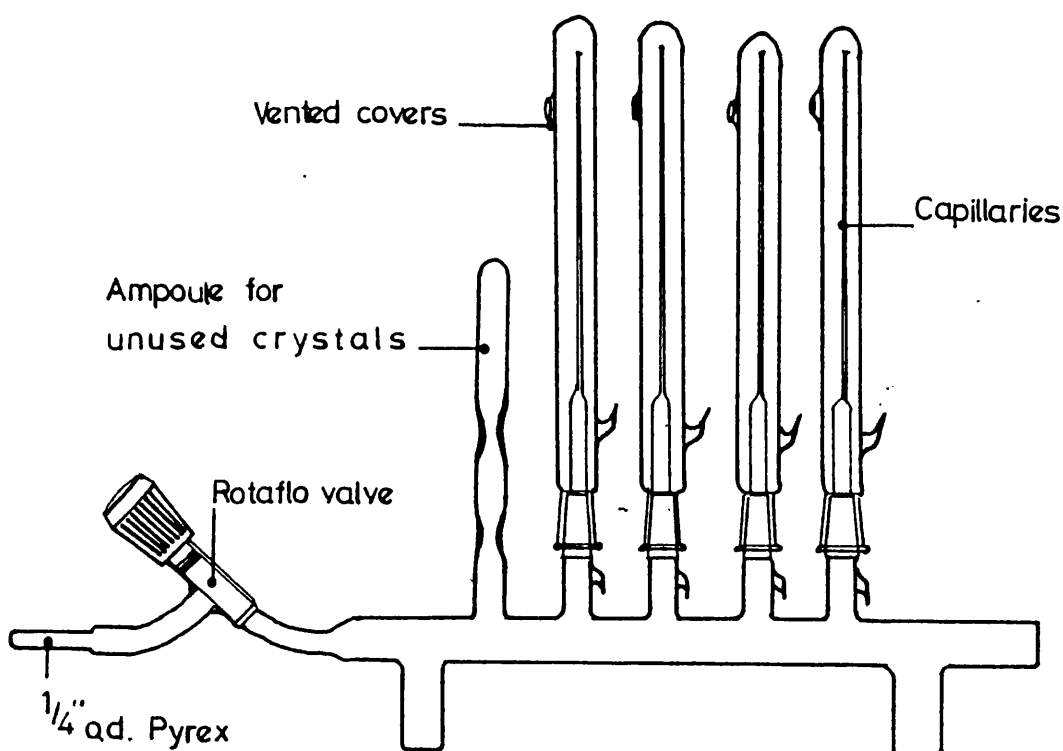
torr ) were measured using a Bourdon-type gauge ( IF/66 M , type 316 , Budenberg Gauge Co.Ltd., Broadheath , Greater Manchester ). Leaks in the metal manifold were detected by a Helium leak detector ( Edwards , model LT 104 mk II ). Leaks within the glass manifold were detected using a H.F. Tesla coil( Edwards High Vacuum Ltd., model ST 200K ).

A variety of metal or fluoroplastic reactors could be attached to the manifold. Pyrex glass apparatus was attached to the manifold by precision 1/4" o.d. glass fitting into Swagelock compression unions ( TFE-400-6 , Techmation Ltd., Edgware , Middlesex ). Where glass valves were required , usually for solvent containers , greaseless 'Rotaflo' valves ( Quickfit type TF2/13 or TF6/13 ) or 'Youngs' valves ( SPOR5 interchangeable 'O' ring stopcock ) with PTFE stems were used. Fluoroplastic apparatus was attached to the manifold through two types of valve. Chemcon PTFE needle valves ( type STD/UF-4/F Production Techniques Ltd., Fleet , Hants. ) were attached to the manifold or other apparatus through 1/4" o.d. compression seals. Kel-F valves were also used. Constructed to a design developed at the Argonne National Laboratory , Chicago , Illinois , U.S.A , the body and stem of the valves were fabricated from Kel-F block ( Pampus Fluoroplast Ltd , Stoke-on-Trent , Staffordshire ). A PTFE packing disc formed a seal between the stem and body which was enclosed in a supporting aluminium case. Small fluoroplastic reactors were fabricated by heating and moulding 6mm o.d. Kel-F tubing ( Voltalef-Paris ) or 1/4" o.d. FEP tubing ( Trimflex Division , Teleflex Inc., Dover New Jersey , U.S.A ). Larger reactors made from 3/4" o.d. Kel-F with approximately 30 cm<sup>3</sup> volume were also used ( Argonne National Laboratory ).

### 2.3 Preliminary Treatment of Crystals.

Single crystals were grown from solution of either anhydrous solvent or excess of starting material. The compounds studied were moisture sensitive , and having been prepared under rigorously dry conditions , it was necessary to isolate and mount suitable crystals in an inert atmosphere. A Pyrex capillary apparatus (Fig.2.2) was designed which , after evacuation to  $10^{-5}$  torr and treatment with chlorine trifluoride , could be charged with a sample in a nitrogen atmosphere dry box. The sealed apparatus was then manipulated under a microscope until single crystals were isolated and wedged in the capillaries. The capillaries were then sealed using a microtorch.

Figure 2.2 Apparatus for sorting single crystals





## 2.4 Characterisation of Products.

Products were characterised , where possible , by 4 methods; X-ray powder photography , mass spectrometry and Infra-red and  $^{19}\text{F}$  nmr spectroscopy.

For X-ray powder diffraction , samples were first ground in a dry box , then loaded into pre-seasoned , thin-walled Pyrex capillaries. The photographs were taken by the Straumanis method using nickel filtered  $\text{Cu-K}\alpha$  radiation using an 11.64 cm diameter Philips' Debye-Scherrer camera ( type PW.1026 ) loaded with 35mm Kodak DEF-392 film ( Kodak Ltd.).

Mass spectra were recorded using a V.G.Micromass 16B ( V.G. Micromass Ltd., Winsford ) equipped with a Datermass MM16 digital interface ( Leicester University , Chemistry Department ) and Gould 6320 Colorwriter plotter. To minimise decomposition of the sample during passage through the mass spectrometer , the ionization chamber was seasoned with small amounts of fluorine prior to use. Samples in glass capillaries were mounted on the end of a stainless steel probe. Once mounted the capillary was broken open and the whole assemblage inserted into the ionization chamber as quickly as possible.

A Perkin Elmer 580 spectrometer was used to obtain infra-red spectra. Solid samples were ground in a dry box , and the fine powder spread between KBr plates( $4000\text{--}350\text{ cm}^{-1}$ ). The KBr plates were then clamped in place within the plate holder and the spectrum of the dry powder ( or Nujol mull ) obtained. Exclusion of atmospheric moisture from the sample was difficult , the sample often hydrolysing from the

edge inward towards the central portion. Gas-phase spectra were obtained using a 10 cm path length copper cell with AgCl windows (4000-400  $\text{cm}^{-1}$ ). PTFE gaskets were used as an air-tight seal between the windows and the cell body. The cell was attached to the manifold through a Hoke diaphragm valve ( type 4171 M2B Hoke International Ltd., Barnet , Herts. ) and was pumped to  $10^{-4}$  torr before the sample was admitted , typically at about 15 torr pressure.

$^{19}\text{F}$  nmr samples were placed into 5 mm i.d. FEP or Kel-F reactor tubes connected to the manifold through Chemcon needle valves. After distilling the required volume of anhydrous solvent onto the sample , the reactor was cooled to  $-196^{\circ}\text{C}$  and sealed under dynamic vacuum using an electrically heated metal coil to collapse the fluoroplastic wall. Kel-F sample tubes were placed inside a 5mm i.d. nmr tube and spun in the probe. Spectra were recorded on a Bruker AM 300 280MHz nmr spectrometer , with an external reference , usually  $\text{CClF}_3$ .

Melting points were determined by placing capillaries loaded with sample on a hot-stage melting point apparatus ( C.Reichert Optische Werke , AG , Vienna , Austria ).

## 2.5 Starting Materials and Solvents.

Fluorine ; for reactions on the manifold fluorine was taken from a 1/2 lb cylinder ( Matheson Gas Products ) and transferred , without purification , to welded nickel cans ( 1  $\text{dm}^3$  capacity ).

Tungsten hexafluoride ( Allied Chemicals Ltd ); was vacuum distilled from the cylinder into a 1/4" o.d. FEP tube containing

sodium fluoride to remove hydrogen fluoride.

Molybdenum hexafluoride ( Ozark Mahoning Ltd ); was vacuum distilled into a 1/4" o.d. FEP tube containing sodium fluoride to remove hydrogen fluoride.

Genetron 113 ( Fluorochem Ltd ); was purified by vacuum distilling twice from phosphorus pentoxide and stored over phosphorus pentoxide.

Molecular sieves , type 4A ( BDH ); were activated by baking at approximately 400°C in a dynamic vacuum for 24 hours.

Acetonitrile , spectroscopic grade ( BDH ); was twice distilled from phosphorus pentoxide to remove traces of moisture and stored over activated molecular sieves ( type 4A ).

Chlorine trifluoride ( Ozark Mahoning Ltd ); was used as received.

Hexafluorobenzene ( Bristol Organics Ltd ); was degassed and stored over molecular sieves ( type 4A ).

1,1,1,3,3,3-Hexamethyldisilazane , trimethylsilylisocyanate ( Lancaster Synthesis ), trimethylsilylazide and 2,3,4,5,6,-Pentafluoroaniline ( Aldrich ); were stored in a dry box under nitrogen and used as received.

Anhydrous hydrazine ( Aldrich ), chlorotrimethylsilane and bromotrimethylsilane ( Lancaster Synthesis ); were used as received and stored in a refrigerator at approximately 3°C.

Trifluoroacetic acid ( Lancaster Synthesis ); was twice vacuum distilled from phosphorus pentoxide and stored in seasoned Pyrex containers.

Rhenium hexafluoride ; was prepared by heating rhenium metal powder ( Johnson Matthey Chemicals Ltd ) with fluorine in a nickel can. To avoid contamination with  $\text{ReF}_7$  , a slight excess of rhenium metal was used. The product was stored in the nickel can and used as required.

Tungsten oxide tetrafluoride ; was prepared by heating the metal powder ( BDH ) in a stream of fluorine and oxygen ( 4:1 ). The product was then resublimed in vacuo to give colourless crystals.

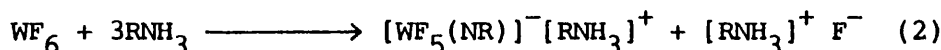
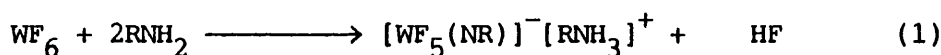
Anhydrous hydrogen fluoride ( ICI Ltd ); was distilled from the cylinder into nickel storage cans and fluorine gas added to dry the liquid. The anhydrous hydrogen fluoride was then distilled into 3/4" o.d. Kel-F reactors.

# Chapter Three

The reaction of Pentafluoroaniline  
with  $\text{MoF}_6$  ,  $\text{WF}_6$  and  $\text{ReF}_6$

### 3.1 Introduction.

Several imido derivatives of transition metal halides have been characterised <sup>(1,2,35)</sup>, however, fluoro-derivatives are not as numerous. The reaction of amines, specifically primary amines, with  $WF_6$  has been used to produce several imido-tungsten fluoride species of the type  $[WF_5(NR)]^-$  <sup>(5,6)</sup> (eqns.1 and 2) and the neutral species  $WF_4(NR).MeCN$  ( $R = H, Bu^n$  <sup>(6)</sup>;  $R = Me$  <sup>(5)</sup>).



The combination of  $WF_4(NMe)$  and  $[WF_5(NMe)]^-$  to form the fluorine bridged, dimeric anion  $[W_2F_9(NMe)_2]^-$  has also been observed <sup>(5)</sup>. Although crystalline chloro derivative salts, such as  $[WCl_5(NC_2Cl_5)]^- [AsPh_4]^+$  <sup>(18)</sup>, have been characterised, all the alkyl-imido fluoride compounds prepared to date have been identified by  $^{19}F$  nmr spectroscopy, and have not been studied crystallographically.

The reaction of  $WF_6$  with the bulky primary amine, pentafluoroaniline,  $(C_6F_5NH_2)$  was found to proceed via iminolysis, to produce a mixture of both  $[WF_5(NC_6F_5)]^-$  and  $[W_2F_9(NC_6F_5)_2]^-$  salts, from which the fluorine bridged salt  $[(C_6F_5N)WF_4-F-WF_4(NC_6F_5)]^- [C_6F_5NH_3]^+$  was separated using TFA, and its crystal structure determined. The pentafluoroanilinium  $\mu$ -fluorobis [N-pentafluorophenylimidotetrafluorotungstate(VI)] crystallised in the triclinic,  $P\bar{1}$ , space group with two formula units of the salt in the unit cell.

Evidence for the formation of the dimeric , mixed pentafluorophenylimido oxyfluoride  $[\text{O}=\text{WF}_4-\text{F}-\text{WF}_4(\text{NC}_6\text{F}_5)]^-$ , similar to the chalcogenide oxyfluorotungstate  $[\text{O}=\text{WF}_4-\text{F}-\text{WF}_4=\text{S}]^-$  <sup>(36)</sup> was found in the  $^{19}\text{F}$  nmr spectra of the acetonitrile solutions of the tungsten imido salt mixture.

Reaction of  $\text{C}_6\text{F}_5\text{NH}_2$  with  $\text{MF}_6$  (  $\text{M} = \text{Mo}, \text{Re}$  ) gave products believed to be the result of iminolysis , although complete characterisation of the products has not yet been possible.

### 3.2 Experimental.

#### 3.2.1 Reaction of Pentafluoroaniline with $\text{WF}_6$

(A) An excess of  $\text{WF}_6$  (2.15mmoles) was distilled onto a Genetron solution of pentafluoroaniline (0.59mmoles) and allowed to warm slowly to room temperature. A lemon yellow precipitate was formed immediately and without gas evolution. The yellow solid and excess of  $\text{WF}_6$ /Genetron mixture was then gently warmed for approximately 15 minutes and left to stand for two hours to allow the reaction to reach completion. The excess of  $\text{WF}_6$  and Genetron was distilled from the reaction tube and the remaining , non-volatile , lemon solid warmed to  $45^\circ\text{C}$  under dynamic vacuum to ensure removal of any unreacted amine. The same yellow solid was produced if  $\text{WF}_6$  was used as both solvent and reactant.

The yellow solid (m.pt.  $\sim 140^\circ\text{C}$ ) is believed to be a mixture containing  $[\text{WF}_5(\text{NC}_6\text{F}_5)]^- [\text{C}_6\text{F}_5\text{NH}_3]^+$  ,  $[\text{C}_6\text{F}_5\text{NH}_3]^+ \text{F}^-$  and  $[\text{W}_2\text{F}_9(\text{NC}_6\text{F}_5)_2]^-$  and has a complicated IR spectrum (Fig.3.1) containing bands which

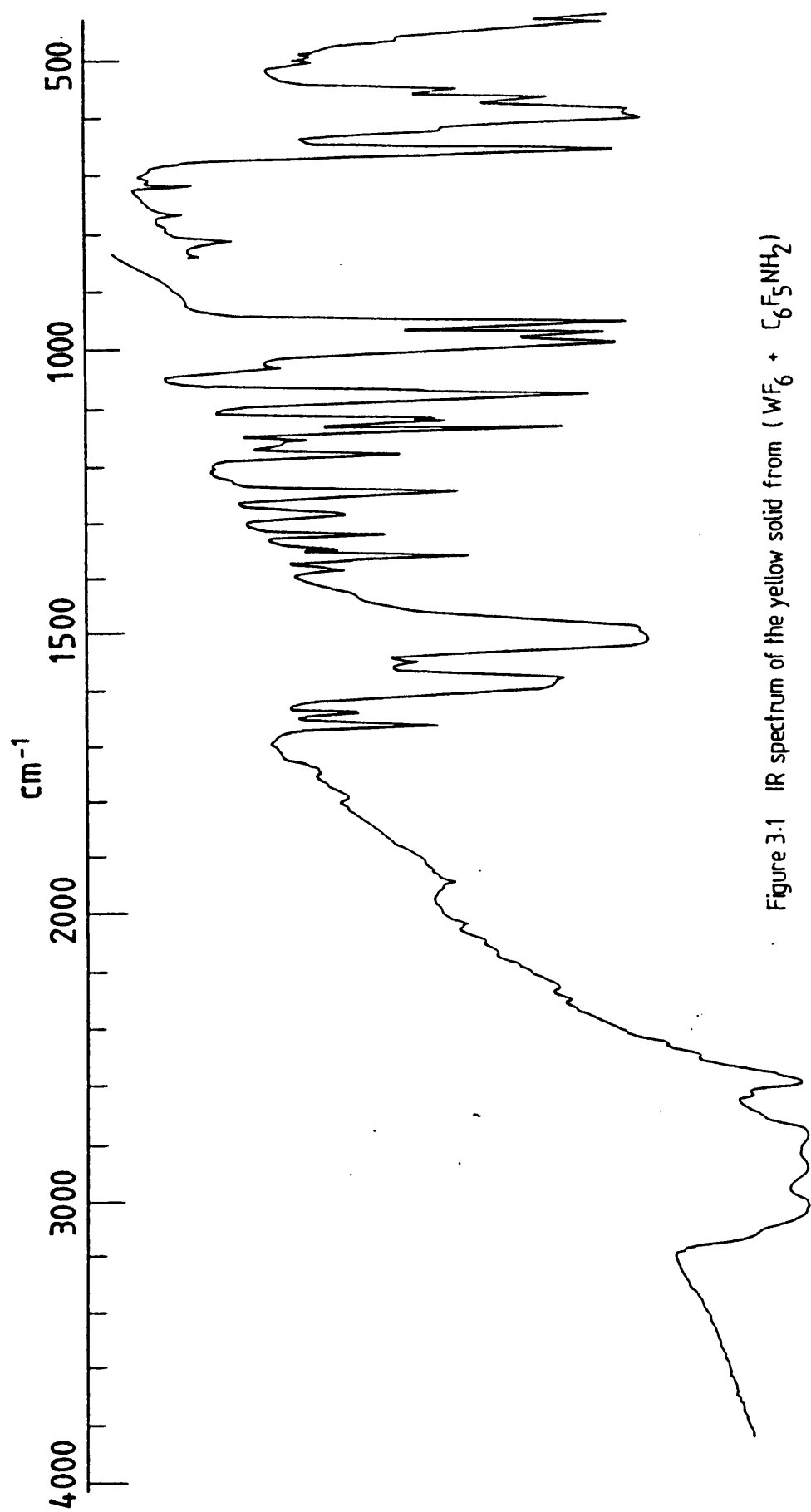
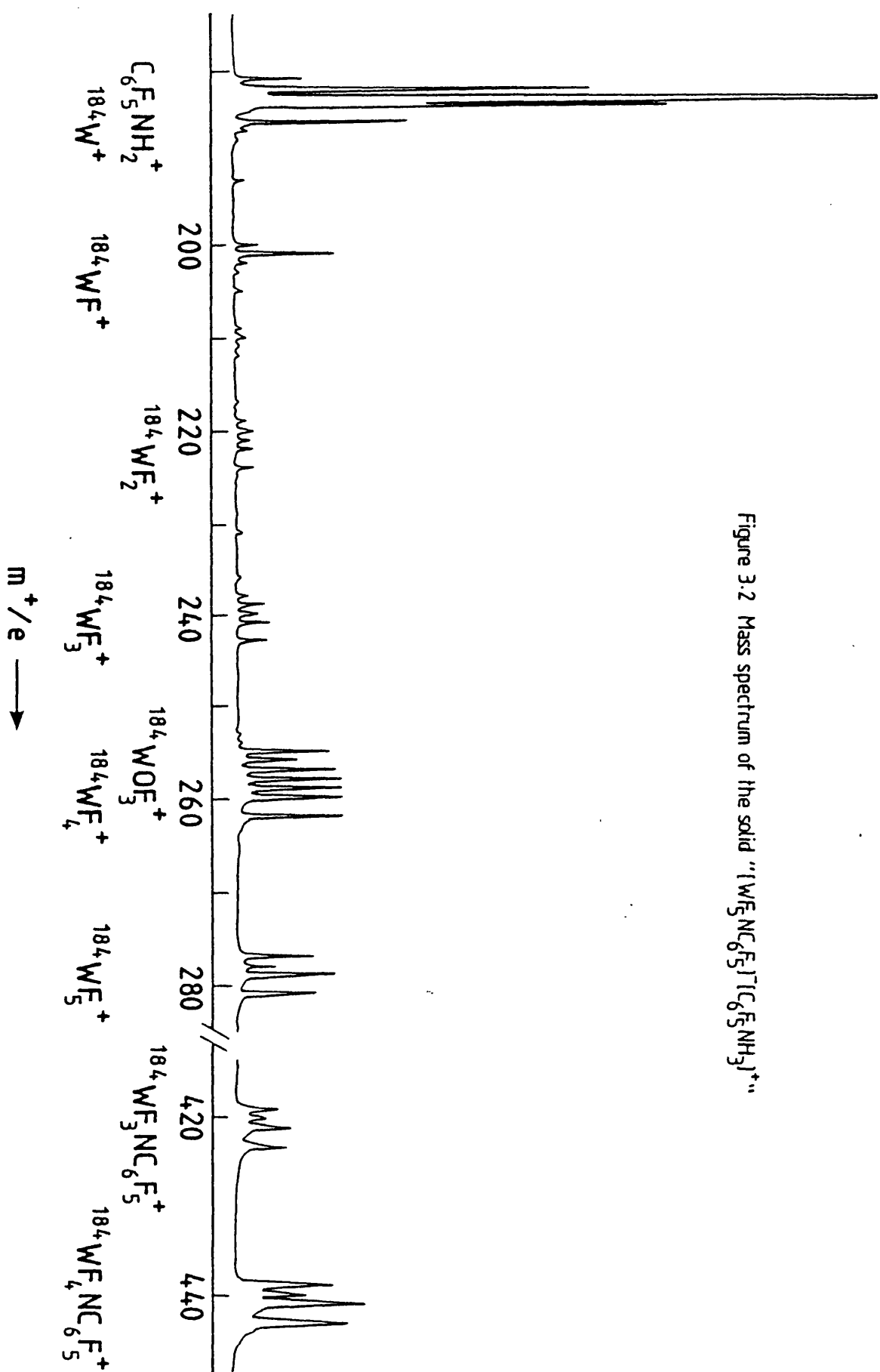


Figure 3.1 IR spectrum of the yellow solid from (  $\text{WF}_6$  +  $\text{C}_6\text{F}_5\text{NH}_2$  )



Figure 3.2 Mass spectrum of the solid "[W<sub>5</sub>NC<sub>6</sub>F<sub>5</sub>][C<sub>6</sub>F<sub>5</sub>NH<sub>3</sub>]<sup>+</sup>"



can be assigned to  $\nu(\text{N-H})$  ,  $\nu(\text{W-F})$  ,  $\nu(\text{W=N})$  ,  $\nu(\text{C-F})$  and  $\nu(\text{C-C})$ . The mass spectrum of the solid (Fig.3.2) did not show the parent ions of any of the species enumerated , but a tungsten abundance pattern at  $m^+/e$  values corresponding to the  $[\text{WF}_4(\text{NC}_6\text{F}_5)]^+$  species , and further fragmentation species down to  $\text{W}^+$  and  $\text{C}_6\text{F}_5\text{NH}_2^+$  were observed. The X-ray powder pattern (Table 3.1) of the solid was extremely complicated. The yellow solid is insoluble in Genetron and excess of  $\text{WF}_6$  , but dissolves readily in acetonitrile to give a yellow solution. An  $^{19}\text{F}$  nmr spectrum of acetonitrile solutions (Figs.3.3 - 3.6) showed several species to be present in solution , including both the monomeric and dimeric anions , the  $[\text{C}_6\text{F}_5\text{NH}_3]^+$  cation ,  $\text{WOF}_4$  ,  $\text{WOF}_5^-$  and the unique mixed oxo-species  $[\text{O}=\text{WF}_4-\text{F}-\text{WF}_4=\text{NC}_6\text{F}_5]^-$ . The ' $\text{C}_6\text{F}_5\text{N}$ ' region of the spectrum was complicated (Fig.3.6).

(B) Isolation of the dimeric salt  $[\text{W}_2\text{F}_9(\text{NC}_6\text{F}_5)_2]^- [\text{C}_6\text{F}_5\text{NH}_3]^+$

An orange solid was recrystallised from a trifluoroacetic acid (TFA) solution of the yellow ' $[\text{WF}_5(\text{NC}_6\text{F}_5)]^- [\text{C}_6\text{F}_5\text{NH}_3]^+$ ' mixture. The  $^{19}\text{F}$  nmr of the solution (Fig.3.7) showed the presence of the dimeric salt and fluorinated species only. The IR spectrum (Fig.3.8) of the solid was considerably simpler than the spectrum recorded for the original yellow solid. The orange solid possessed fewer bands in the regions associated with  $\nu(\text{C-C})$  and  $\nu(\text{C-F})$  , as well as a more pronounced band at  $500\text{cm}^{-1}$ , assigned to the bridging fluorine atom stretching frequency. The mass spectrum of the orange solid was identical to that of the original yellow solid. A crystal grown from the TFA solution proved suitable for an X-ray crystallographic study , and was identified as the dimeric anion salt  $[\text{C}_6\text{F}_5\text{NH}_3]^+ [\text{C}_6\text{F}_5\text{N}=\text{WF}_4-\text{F}-\text{WF}_4=\text{NC}_6\text{F}_5]^-$ .

**Table 3.1** Selected d-spacings from the X-ray powder pattern  
of the yellow solid  $[\text{WF}_5\text{NC}_6\text{F}_5]^- [\text{C}_6\text{F}_5\text{NH}_3]^+$ ,

$\sin^2\theta$	d (Å)	I/I <sup>0</sup>
0.0032	13.71	40
0.0038	12.60	70
0.0050	10.89	80
0.0062	9.76	30
0.0086	8.32	10
0.0096	7.85	80
0.0119	7.05	25
0.0168	5.95	70
0.0192	5.57	55
0.0220	5.20	30
0.0238	5.00	30
0.0258	4.80	25
0.0325	4.28	65
0.0342	4.17	100
0.0380	3.95	10
0.0407	3.82	10
0.0445	3.65	60
0.0484	3.51	10
0.0540	3.32	45

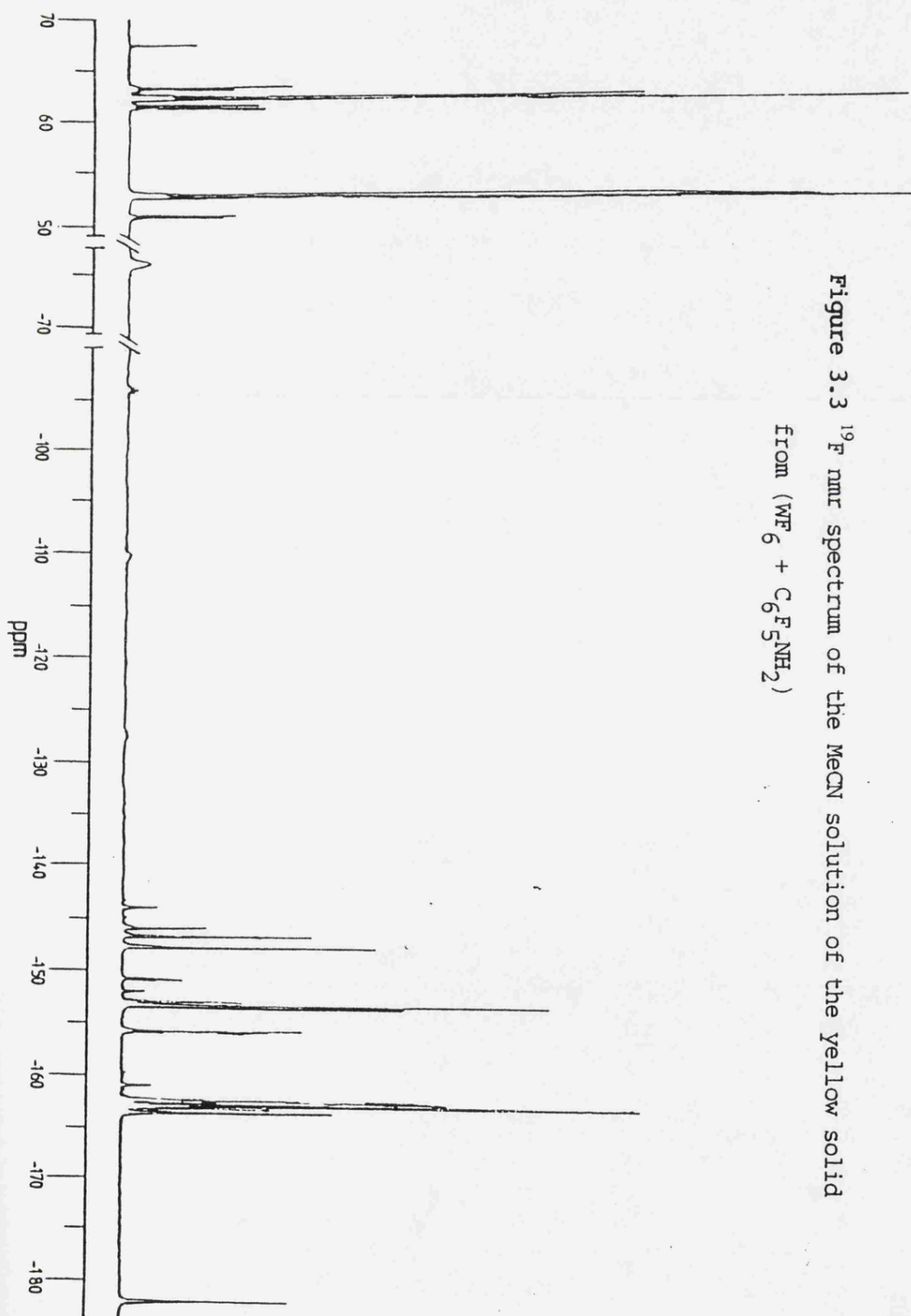


Figure 3.3  $^{19}\text{F}$  nmr spectrum of the MeCN solution of the yellow solid  
from ( $\text{WF}_6 + \text{C}_6\text{F}_5\text{NH}_2$ )

Figure 3.4  $^{19}\text{F}$  nmr of MeCN soln.; Expansion of the region 50–68 ppm

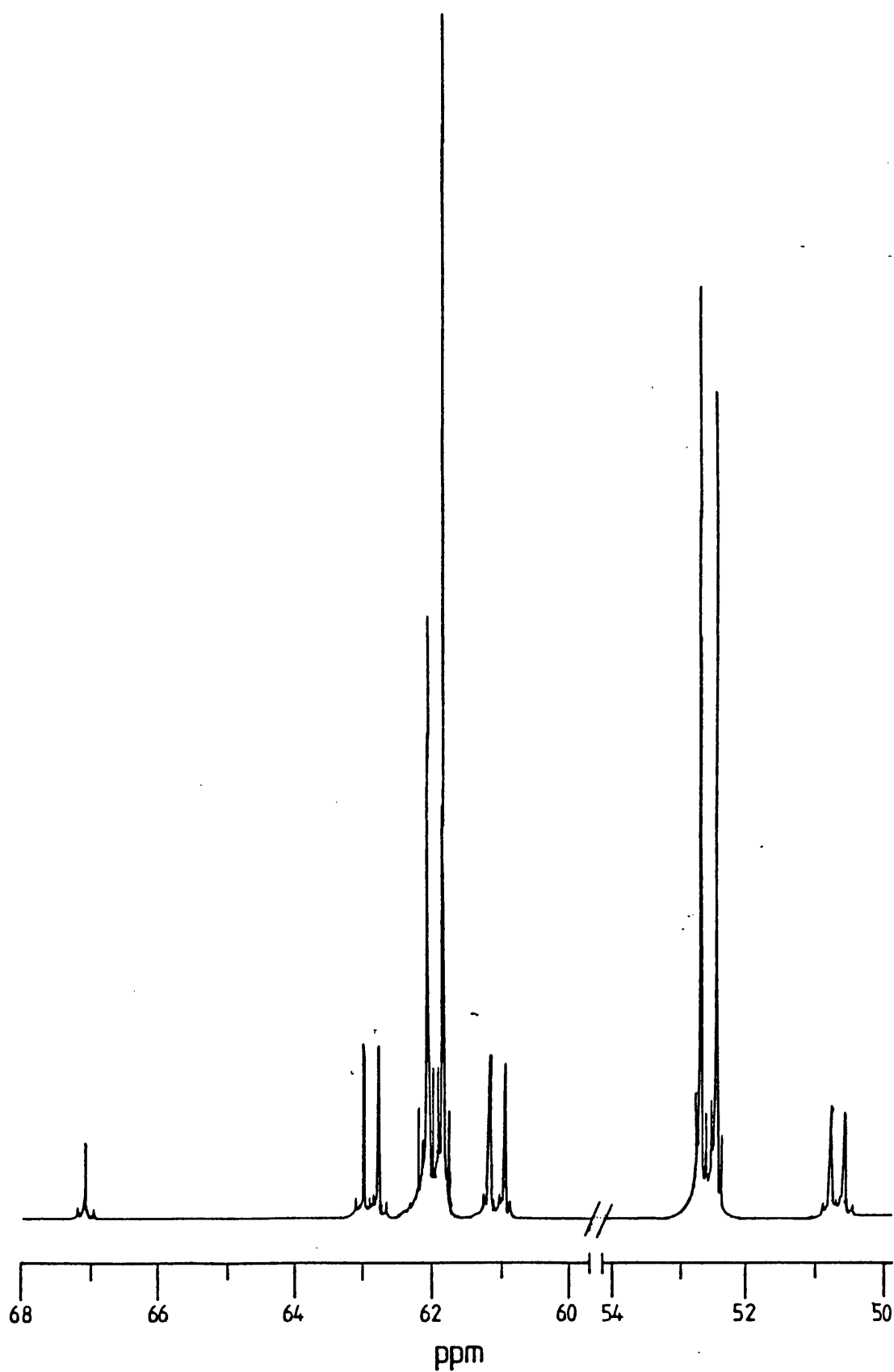


Figure 3.5  $^{19}\text{F}$ nmr : Expansion of  $[\text{WOF}_5]^-$  and  $[\text{W}_2\text{F}_9(\text{C}_6\text{F}_5\text{N})_2]^-$  multiplets

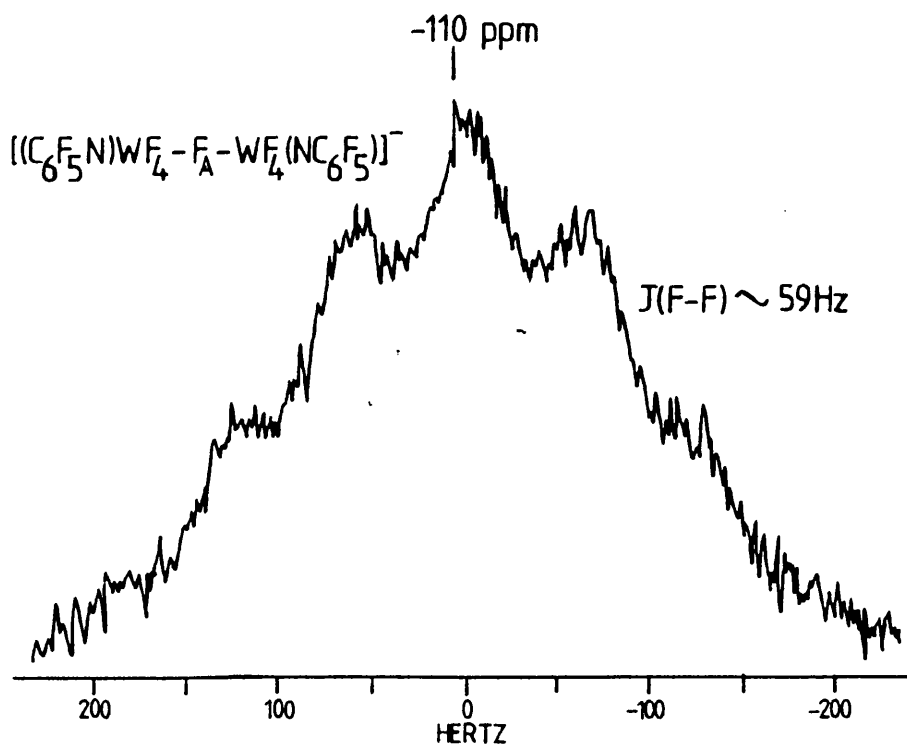
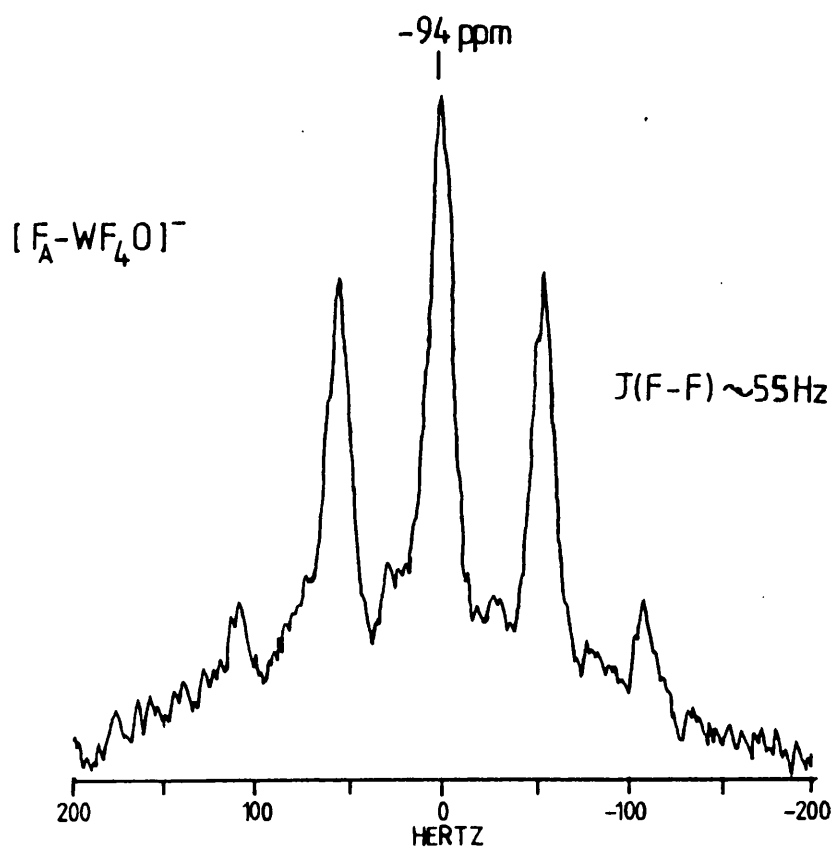
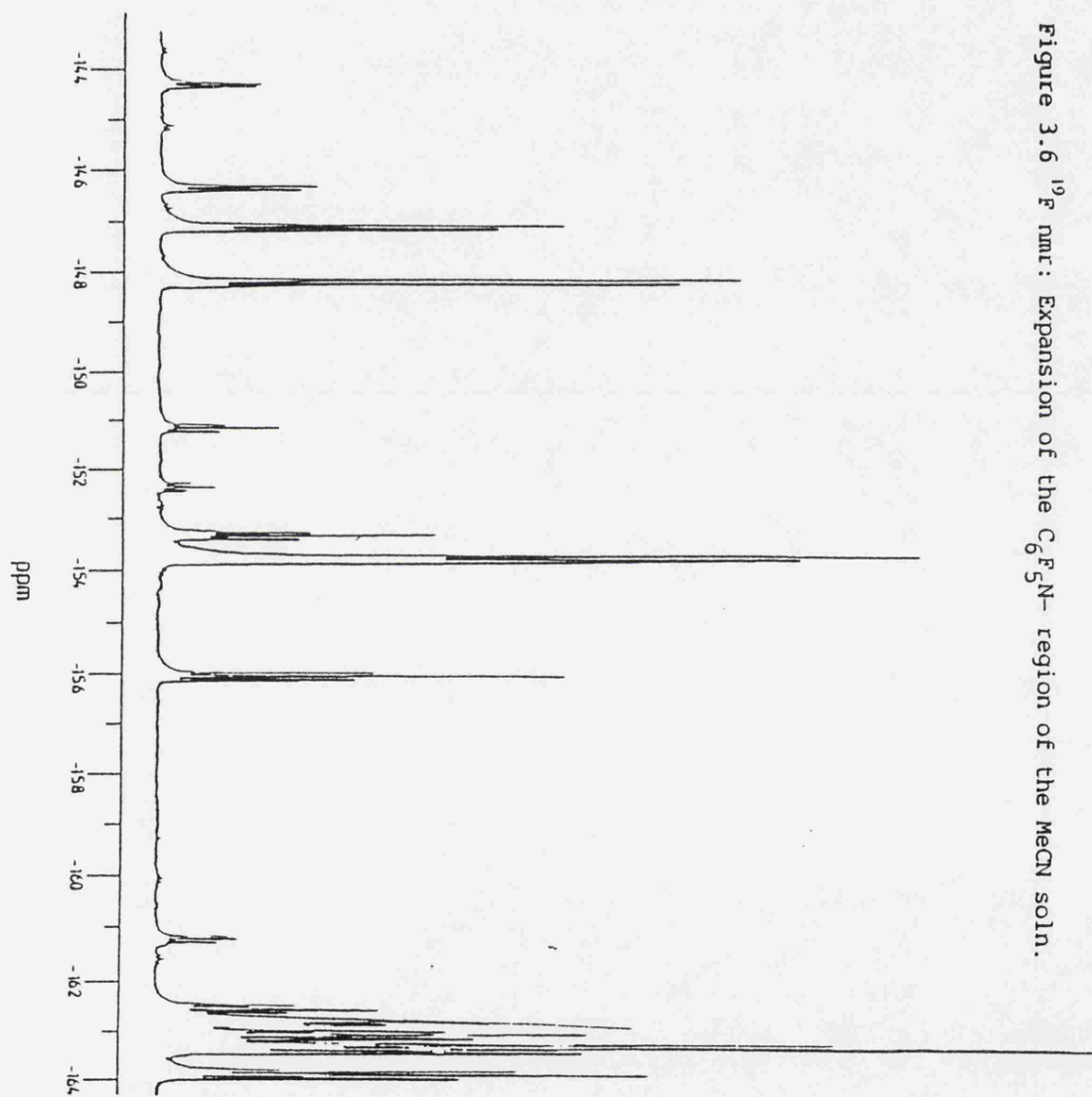


Figure 3.6  $^{19}\text{F}$  nmr: Expansion of the  $\text{C}_6\text{F}_5\text{N}$ - region of the MeCN soln.



Crystal Data :  $W_4C_{36}H_6F_{48}N_6$  ,  $M = 2169.79$  , Triclinic  $P\bar{1}$  ,

$a = 15.393(41)$  ,  $b = 17.723(27)$  ,  $c = 11.375(50)$  Å ,

$\alpha = 78.6(2)$  ,  $\beta = 98.0(2)$  ,  $\gamma = 111.3(1)^\circ$  ,

$U = 2827.2$  Å<sup>3</sup> ,  $Z = 2$  ,  $\lambda(Mo-K_\alpha) = 0.7107$  Å ,

$\mu = 79.35$  cm<sup>-1</sup> ,  $F(000) = 1983.6$  ,  $d_x = 2.548$  g cm<sup>-3</sup>

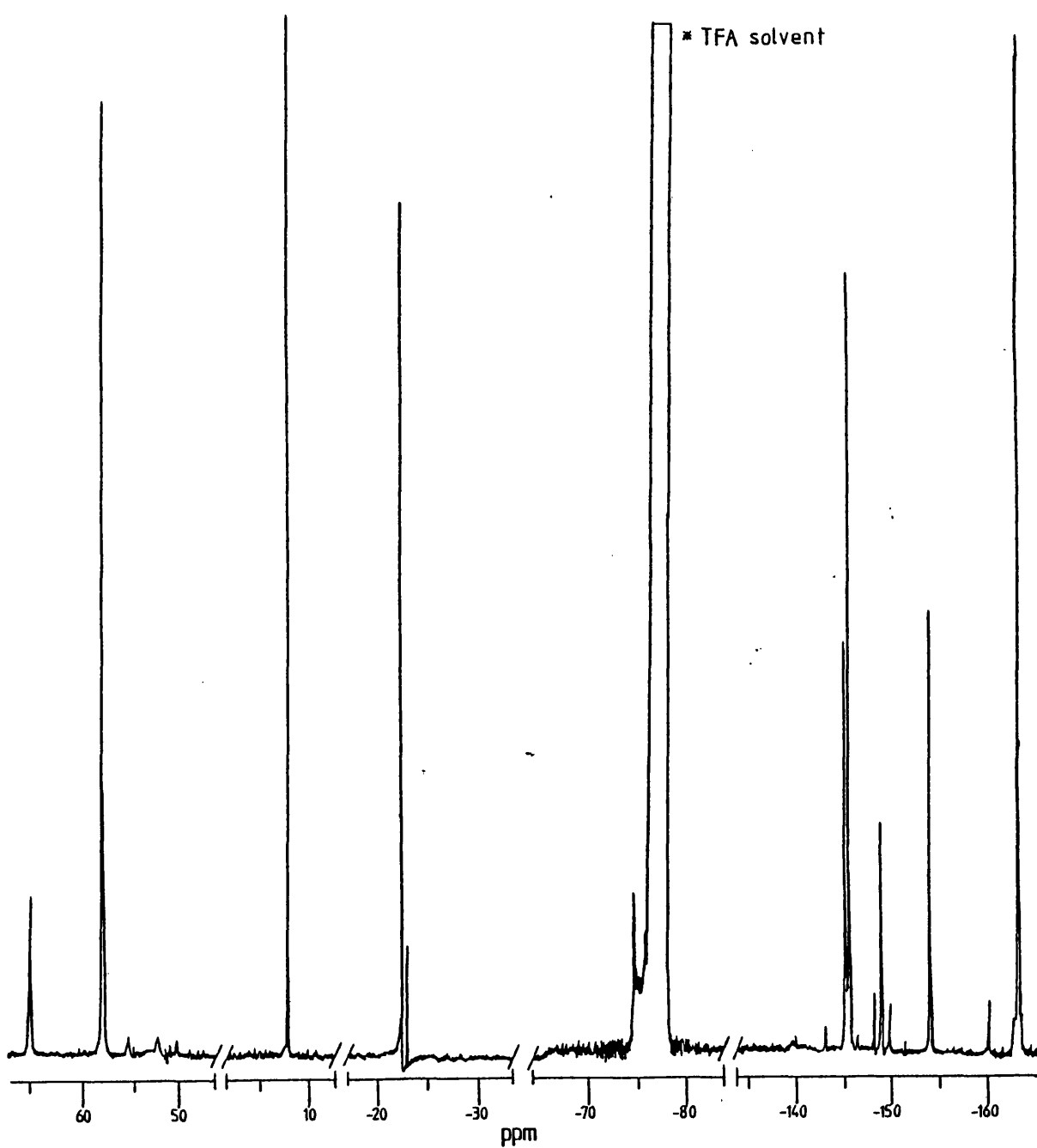
The crystal used for data collection was yellow , wedge shaped , with approximate dimensions of 0.46 x 0.12 x 0.09 mm. The intensities of 8730 unique reflections with  $2\theta < 50^\circ$  and ( $\pm h$  ,  $\pm k$  , 0-12 l) were measured on a Stadi-2 Weissenberg diffractometer , with graphite monochromated Mo-K $\alpha$  radiation using an omega-scan technique. The data were corrected for Lorentz and polarisation effects to yield 3046 reflections with  $|Fo| > 5\sigma(|Fo|)$ .

The tungsten atoms were located using the Patterson option of SHELXS 84. All subsequent calculations were carried out using the computer program SHELX<sup>(37)</sup>. Cycles of least squares refinement with the tungsten atoms included gave an R factor of 0.38 and located the carbon , fluorine and nitrogen atoms. An absorption correction was applied to the data with the maximum and minimum transmission factors of 0.533 and 0.328 respectively. Due to program constraints on the number of independant variables it was not possible to refine all atoms with anisotropic thermal parameters. All tungsten and nitrogen atoms were refined anisotropically. In addition fifty-one of the carbon and fluorine atoms were refined with anisotropic thermal parameters.

Final cycles of refinement employed a weighing parameter  $g(.00081)$  {  $w = [1/(\sigma^2(F) + g(F)^2)]$  } and gave the final residual indices  $R\{ = \Sigma (|Fo| - |Fc|) / \Sigma |Fo| \} = 0.0879$  and  $R_w\{ = \Sigma w[ (|Fo| - |Fc|)^2 / w|Fo|^2 ]^{1/2} \} = 0.0878$ . The remaining difference Fourier



Figure 3.7  $^{19}\text{F}$  nmr spectrum of the TFA soln. of the yellow solid from  
( $\text{WF}_6 + \text{C}_6\text{F}_5\text{NH}_2$ )



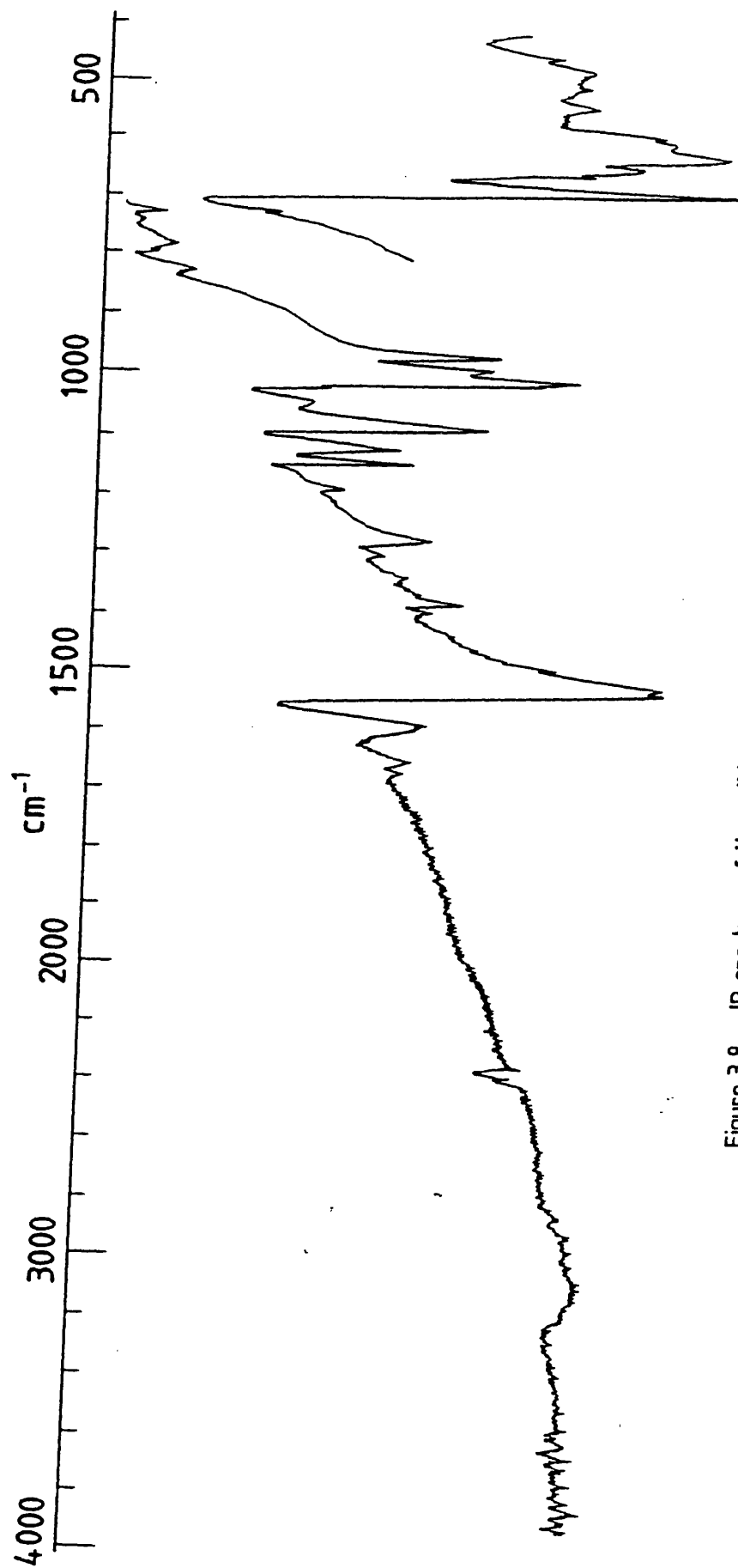


Figure 3.8 . IR spectrum of the solid recrystallised from TFA

map revealed  $\leq 1.7$  e peaks ( and  $\geq -3$ e troughs ) around the tungsten-fluorine region , though an analysis of the weighting scheme over  $|F_o|$  and  $\sin\theta/\lambda$  was satisfactory.

Tables of fractional atomic coordinates; atomic thermal parameters ; bond lengths and angles ; non-bonded contacts and structure factors are located in the Appendix.

### 3.2.2 The reaction of Pentafluoroaniline with MoF<sub>6</sub>

An excess of molybdenum hexafluoride (0.78 mmoles) was distilled onto a Genetron solution of pentafluoroaniline (0.29 mmoles) and allowed to warm to room temperature. A dark , maroon solid was formed immediately with effervescence of the solution and a slight staining of the reaction tube wall. The mixture was quenched with liquid nitrogen (LN) and re-warmed to room temperature. The insoluble maroon solid settled out from the orange Genetron solution , and showed no solubility in the Genetron when warmed. An IR spectrum of the volatile components showed the presence of Genetron and MoF<sub>6</sub> only. The reaction mixture was left to stand overnight at room temperature before removing the volatile compounds from the reaction tube by distillation.

An IR spectrum of the non-volatile , air-sensitive, dark solid (Fig.3.9) showed similar features to that of the product of the reaction with WF<sub>6</sub>. The solid did not produce an X-ray powder pattern and a mass spectrum yielded fragmentation patterns of oxyfluorides only. The solid dissolves very readily in acetonitrile , but attempts to grow crystals suitable for crystallographic study were not successful. The solid is believed to contain  $[\text{C}_6\text{F}_5\text{NH}_3]^+[\text{MoF}_5(\text{NC}_6\text{F}_5)]^-$ .

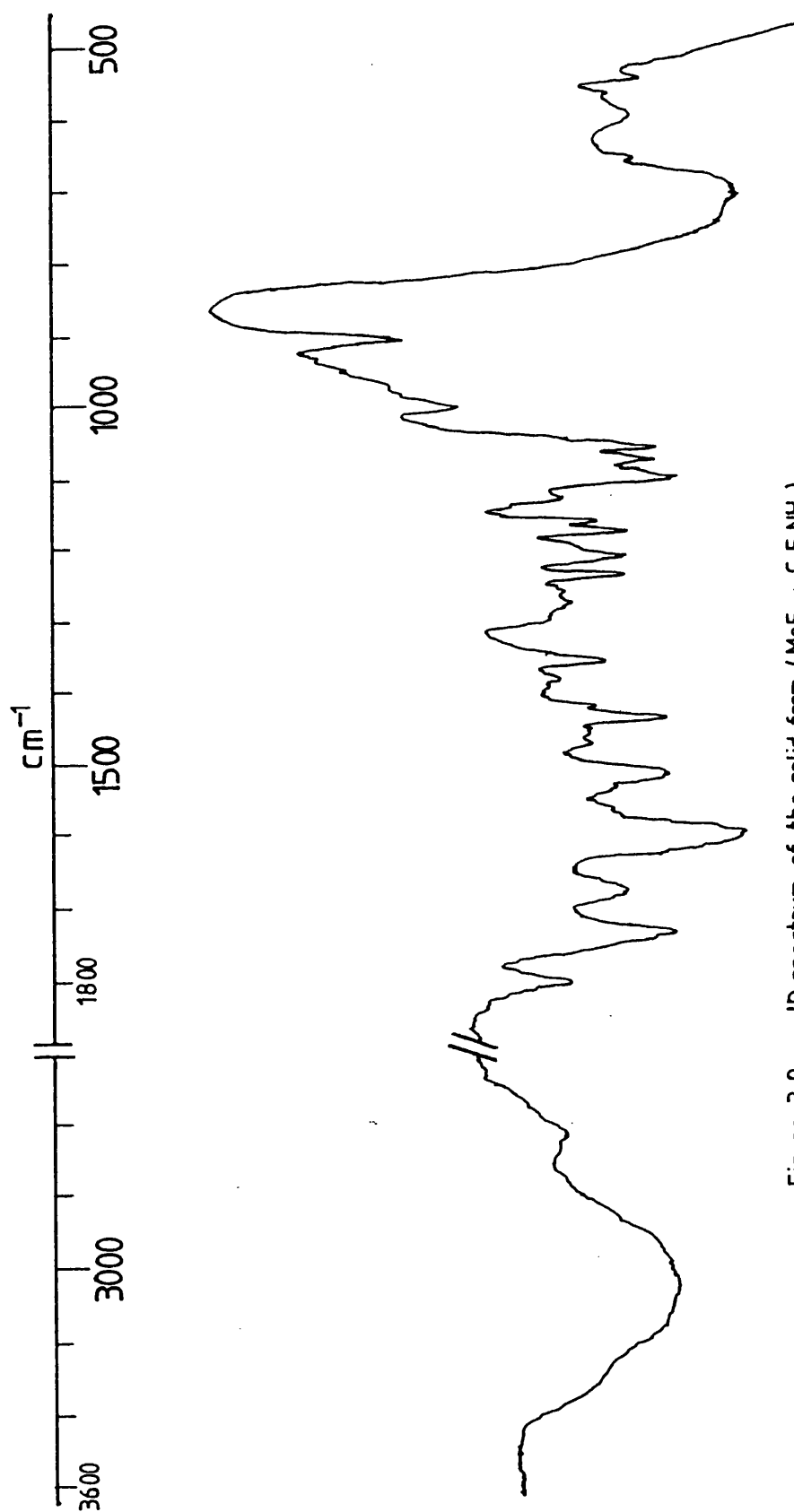


Figure 3.9 IR spectrum of the solid from ( $\text{MoF}_6 + \text{C}_6\text{F}_5\text{NH}_2$ )

### 3.2.3 The Reaction of Pentafluoroaniline with $\text{ReF}_6$

(A) An excess of rhenium hexafluoride (1.23 mmoles) was distilled onto a Genetron solution of pentafluoroaniline (0.59 mmoles) and allowed to warm slowly to room temperature. There was formation of a dark solid at the liquid-liquid junction with purple staining of the reaction tube wall, and the solution subsequently became dark with effervescence. The mixture was allowed to stand at room temperature overnight to allow the dark solid to settle out from the light-red coloured Genetron solution.

The volatile components distilled from the reaction vessel showed a slight colouring from unreacted  $\text{ReF}_6$ . The non-volatile, air-sensitive dark solid has an IR spectrum (Fig.3.10) similar to that of  $[\text{C}_6\text{F}_5\text{NH}_3]^+[\text{WF}_5\text{NC}_6\text{F}_5]^-$ , however, the  $\nu(\text{N-H})$  band expected in the  $3000\text{cm}^{-1}$  region is not visible, and the pattern of peaks in the region associated with  $\nu(\text{Re-F})$  is simpler than expected. The mass spectrum of the solid (Fig.3.11) shows patterns associated with rhenium oxyfluorides,  $\text{ReF}_3\text{N}$  and  $\text{C}_6\text{F}_5\text{NH}_2$  only. The dark solid is believed to be a mixture containing the neutral compound  $\text{ReF}_4(\text{NC}_6\text{F}_5)$  and  $[\text{C}_6\text{F}_5\text{NH}_3]^+\text{F}^-$ .

### (B) The Reaction of ' $\text{ReF}_4(\text{NC}_6\text{F}_5)$ ' with Chlorine Trifluoride

**CAUTION:** Chlorine trifluoride was added to the dark solid (22 mg) believed to be  $\text{ReF}_4(\text{NC}_6\text{F}_5)$  initially as 40 mmHg aliquots of the gas. After three additions with subsequent removal of volatiles, a 150 mmHg aliquot was admitted to the reaction tube. There was slight sparking and formation of an orange oil. The volatiles were removed

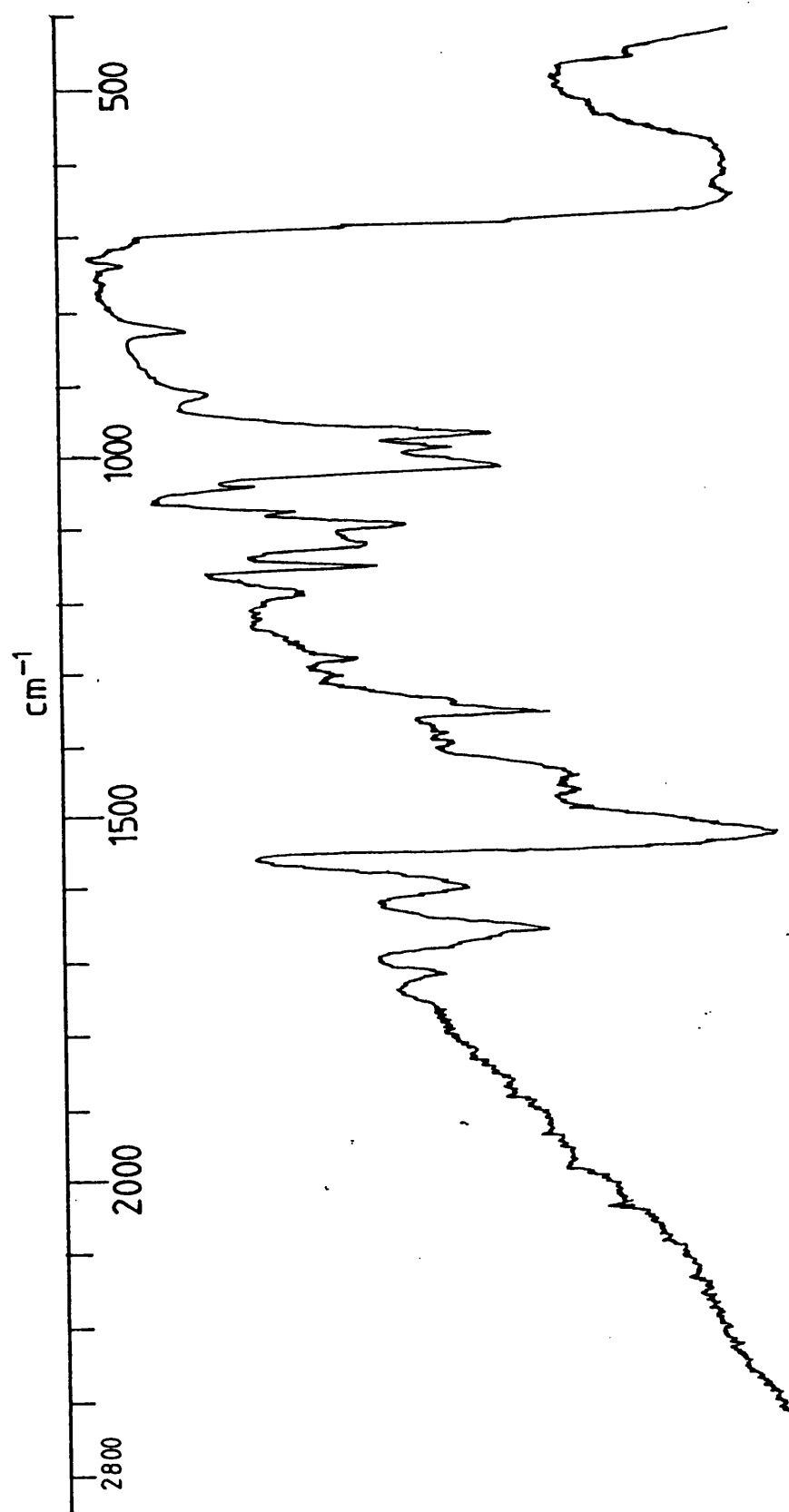


Figure 3.10 IR spectrum of the solid from (  $\text{ReF}_6$  +  $\text{C}_6\text{F}_5\text{NH}_2$  )

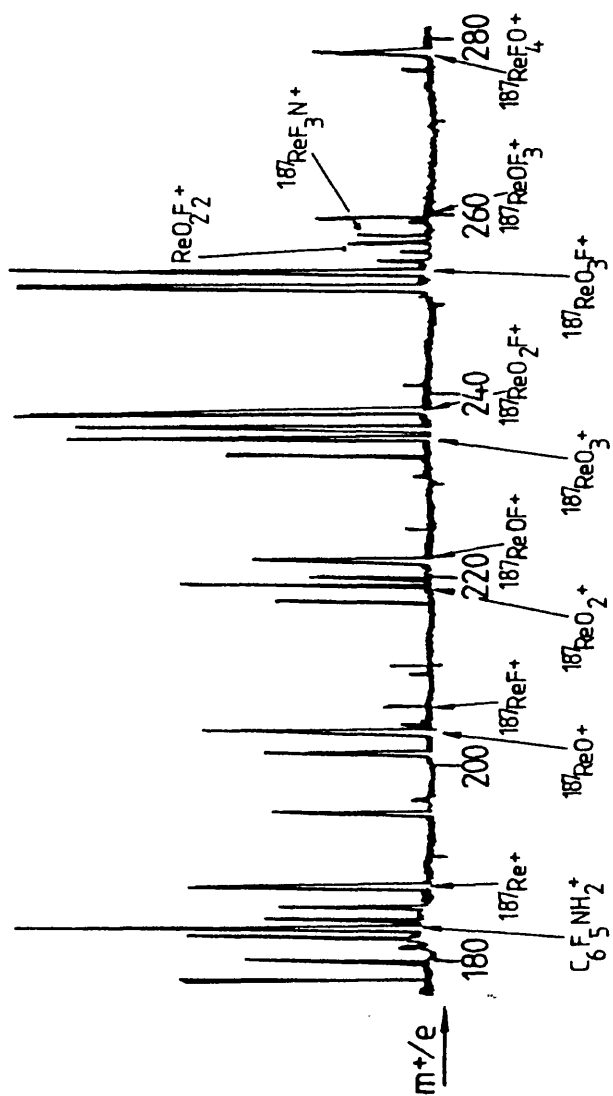


Figure 3.11 Mass spectrum ( $170^\circ C$ ) of the solid from  $(C_6F_5NH_2 + ReF_6)$

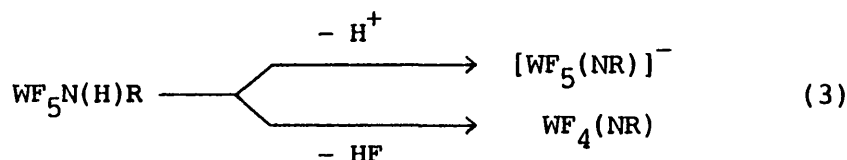
from the reaction vessel and 30 mmHg of  $\text{ClF}_3$  was condensed (LN) into the tube, forming more of the orange oil. The volatile compounds were again removed and two 50 mmHg aliquots of  $\text{ClF}_3$  were condensed onto the remaining solid/oil mixture. Gas was liberated and the reaction vessel was quenched with LN before adding a final 100 mmHg aliquot of  $\text{ClF}_3$ . As the mixture warmed to room temperature gas evolution continued. The orange oil was left to stand at room temperature overnight and the excess of volatiles then distilled from the reaction vessel.

The remaining oil was heated to approximately  $65^\circ\text{C}$  under a dynamic vacuum. A small amount of purple solid and larger amount of orange solid sublimed on to the cooler sections of the tube wall, leaving a non-volatile pale yellow solid. The purple solid is believed to be  $\text{ReF}_5\text{NCl}$  <sup>(30)</sup> and the orange solid  $\text{ReF}_5\text{NF}$ . A mass spectrum of the yellow solid, believed to be  $\text{ReO}_3\text{F}$ , showed a large amount of the  $\text{ReO}_3\text{F}^+$  ion present. The oxyfluoride is believed to be formed as a result of oxide fluoride impurities in both the  $\text{ClF}_3$  and  $\text{ReF}_4(\text{NC}_6\text{F}_5)$  (chiefly  $\text{ClO}_2\text{F}$  in the former).

### 3.3 Discussion

The aminolysis reactions of  $\text{WF}_6$  with  $\text{RNH}_2$  compounds are thought to proceed by first forming a 1:1  $\text{WF}_6:\text{RNH}_2$  complex, which then loses HF to produce an intermediate species,  $\text{WF}_5\text{N}^{(s)}(\text{H})\text{R}$ . Loss of either  $\text{H}^+$  or HF (equation 3) will form either  $[\text{WF}_5(\text{NR})]^-$  or the neutral  $\text{WF}_4(\text{NR})$  compound.





The identity and molar ratios of products formed in aminolysis reactions are dependant to a large extent upon solvent and stoichiometry. The reaction of  $\text{C}_6\text{F}_5\text{NH}_2$  with  $\text{WF}_6$  proceeds via aminolysis to produce a mixture of imido compounds.

The IR spectrum (Fig.3.1) of the original yellow product is very complicated. Several sharp peaks are observed in the region  $1650 - 1000\text{cm}^{-1}$ , a region covering the ranges of aromatic  $\nu(\text{C-C})$  ( $1600 - 1450\text{cm}^{-1}$ ) and  $\nu(\text{C-F})$  ( $1400 - 1000\text{cm}^{-1}$ ) stretching frequencies. Coupling of the C-C vibrations with the C-F vibrations can cause bands to be strong within this range. Hornig<sup>(51)</sup> has assigned the  $\nu_3$  and  $\nu_4$  modes of  $\text{NH}_4^+$  (in  $\text{NH}_4\text{F}$ ) to the bands at  $2815$  and  $1494\text{cm}^{-1}$  respectively, and so strong bands in the IR spectrum at  $\sim 2800$  and  $1500\text{cm}^{-1}$  are assigned to  $\nu(\text{N-H})$  of the  $\text{C}_6\text{F}_5\text{NH}_3^+$  cation. Similarly, Cabana and Sandorfy<sup>(52)</sup> analysed the IR spectrum of  $\text{CH}_3\text{NH}_3^+\text{F}^-$  and identified (N-H)  $\nu_7$  and  $\nu_4$  modes at  $2660$ ,  $2573$  and  $1574\text{cm}^{-1}$ . Bands occurring at  $2660$  and  $1600\text{cm}^{-1}$  in the yellow solid compare well and are attributed to  $\text{C}_6\text{F}_5\text{NH}_3^+\text{F}^-$ . Assignments of  $\nu(\text{M=N})$  in several chloro-anions  $[\text{MnCl}_4]^{-(12)}$  ( $\text{M=W}$ ,  $1030\text{cm}^{-1}$ ;  $\text{M=Mo}$ ,  $1055\text{cm}^{-1}$ ) and  $[\text{MnCl}_5]^{-(54)}$  ( $\text{M=Mo}$   $1059$ ,  $1023\text{cm}^{-1}$ ;  $\text{M=W}$   $1035$ ,  $1025\text{cm}^{-1}$ ), chloride nitrides,  $\text{MnCl}_3$  ( $\text{M=Mo}$   $1045\text{cm}^{-1}$ ;  $\text{M=W}$   $1084$ ,  $1068\text{cm}^{-1}$ )<sup>(10)</sup> and alkoxynitrides,  $(\text{RO})_3\text{M=N}$  <sup>(47,53)</sup> ( $\text{M=Mo}$   $1020\text{cm}^{-1}$ ;  $\text{M=W}$   $1010\text{cm}^{-1}$ ) suggest that the intense band at  $1000\text{cm}^{-1}$  is the  $\nu(\text{W=N})$  vibration of  $[\text{WF}_5(\text{NC}_6\text{F}_5)]^-$ . Peaks occurring in the  $600\text{cm}^{-1}$  region are assigned to  $\nu(\text{W-F})$ . The yellow solid produced is a mixture containing at least  $[\text{C}_6\text{F}_5\text{NH}_3]^+\text{F}^-$  and  $[\text{C}_6\text{F}_5\text{NH}_3]^+[\text{WF}_5(\text{NC}_6\text{F}_5)]^-$ .

The IR spectrum of the solid recrystallised from TFA (Fig.3.8) is considerably simplified, the absence of bands at 2600 and  $1600\text{cm}^{-1}$  indicating that the solid is free of  $[\text{C}_6\text{F}_5\text{NH}_3]^+\text{F}^-$ . The bands at 1500, 1000, 600 and  $500\text{cm}^{-1}$  are assigned to the  $\nu(\text{N-H})$ ,  $\nu(\text{W=N})$ ,  $\nu(\text{W-F})$  and  $\nu(\text{W-F-W})$  stretching frequencies of the dimeric anion salt  $[\text{C}_6\text{F}_5\text{NH}_3]^+[\text{C}_6\text{F}_5\text{N=WF}_4\text{-F-WF}_4\text{=NC}_6\text{F}_5]^-$ .

The  $^{19}\text{F}$  nmr spectra of acetonitrile and TFA solutions of the yellow solid (Tables 3.2 and 3.4) showed that the MeCN solutions contained the expected tungsten imido fluoride salts and oxyfluorides, as well as the mixed imido-oxyfluoride anion  $[\text{OWF}_4\text{-F-WF}_4(\text{NC}_6\text{F}_5)]^-$ . The TFA solution showed the presence of the dimeric  $[\text{W}_2\text{F}_9(\text{NC}_6\text{F}_5)_2]^-$  ion,  $\text{WOF}_4$  and fluorination products only. Signals associated with  $\text{WOF}_4$  and  $\text{WOF}_5^-$  compared favourably with literature values <sup>(38,39)</sup>.

The tungsten compounds containing the  $-\text{NC}_6\text{F}_5$  moiety possess chemical shifts downfield from those of related imido compounds not containing  $\text{C}_6\text{F}_5\text{N-}$  e.g.  $\delta\text{F}_x$  in  $[\text{WF}_5(\text{NC}_6\text{F}_5)]^-$  is at 52.5ppm, compared with  $\delta\text{F}_x$  in  $[\text{WF}_5(\text{NR})]^-$  ( $\text{R} = \text{Me}, \text{H}$ ) <sup>(5,6)</sup> at 28 and 33.4 ppm. The deshielding of the fluorine nuclei associated with the tungsten atoms can be attributed to the magnetic anisotropy and electron withdrawing ability of the aromatic  $\text{C}_6\text{F}_5\text{N-}$  group.

Both the mono- and dimeric anion species are present in the MeCN  $^{19}\text{F}$  nmr spectra, the monomeric ion  $[\text{WF}_5(\text{NC}_6\text{F}_5)]^-$  being the major species, producing an  $\text{AX}_4$  type spectrum with  $^{183}\text{W}$  satellites associated with the  $\text{X}_4$  doublet {  $\delta\text{F}_x = 52.5 \text{ ppm}$ ;  $\text{J}(\text{F}_a\text{-F}_x) = 64.7 \text{ Hz}$ ;  $\text{J}(\text{F}_x\text{-}^{183}\text{W}) = 41.8 \text{ Hz}$  } and a broad, unresolved multiplet associated with A {  $\delta\text{F}_a = -63 \text{ ppm}$  }. The dimeric ion  $[\text{W}_2\text{F}_9(\text{NC}_6\text{F}_5)_2]^-$  produces a well resolved doublet associated with the eight equivalent  $\text{F}_x$  nuclei

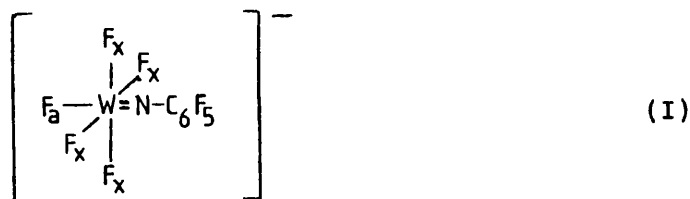
Table 3.2  $^{19}\text{F}$  n.m.r. Chemical Shifts and Coupling Constants for the MeCN Solutions of the Product from  $(\text{WF}_6 + \text{C}_6\text{F}_5\text{Mn}_2)$ .

ASSIGNMENT	Spectral Form	Chem. shift (rel. to $\text{CFCl}_3$ ), ppm					Spin-spin coupling constants, Hz					Approx. relative molar ratio
		$\delta F_X$	$\delta F_A$	$\delta F_O$	$\delta F_m$	$\delta F_p$	$J_{F_A-F_X}$	$J_{F_X-^{183}\text{W}}$	$J_{F_O-F_m}$	$J_{F_p-F_m}$		
$\text{WOF}_4$	$X_4$	67.1	-	-	-	-	-	68.9	-	-	10	
$(\text{WOF}_4-\text{F}_A-\text{WF}_4\text{R})^-$	$\text{AX}_4^*$	62.8	-127	-	-	-	58	70.9	-	-	51	
$(\text{WOF}_4-\text{F}_A-\text{WF}_4\text{R})^-$	$\text{AX}_4^*$	61	-127	-	-	-	64.7	40.9	-	-		
$(\text{WOF}_4-\text{F}_A-\text{WF}_4\text{R})^-$	-	-	-	-144.32	-161.26	-152.34	-	-	$\sim 14$	$\sim 20$		
$(\text{RWF}_4-\text{F}_A-\text{WF}_4\text{R})^-$	$\text{AX}_4$	61.9	-110	-	-	-	64.7	39	-	-	126	
$(\text{RWF}_4-\text{F}_A-\text{WF}_4\text{R})^-$	-	-	-	-147.1	-163.7	-153.31	-	-	$\sim 14$	$\sim 20$		
$(\text{F}_A-\text{WF}_4\text{R})^-$	$\text{AX}_4$	52.5	-63	-	-	-	64.7	41.8	-	-	250	
$(\text{F}_A-\text{WF}_4\text{R})^-$	-	-	-	-148.20	-163.9	-156.08	-	-	$\sim 14$	$\sim 20$		
$(\text{WOF}_4-\text{F}_A)^-$	$\text{AX}_4$	50.6	-94.2	-	-	-	53.6	71.3	-	-	41	
$(\text{WF}_4\text{R}(\text{?}))^\dagger$	-	-	-	-146.36	-162.63	-151.14	-	-	$\sim 14$	$\sim 20$	50	
$(\text{C}_6\text{F}_5\text{Mn}_3)^\dagger$	-	-	-	-153.77	-163.4	-162.87	-	-	$\sim 20$	$\sim 20$	426	
$\text{HfF}(\text{impure})$	-	-102.4	-	-	-	-	-	-	-	-	-	

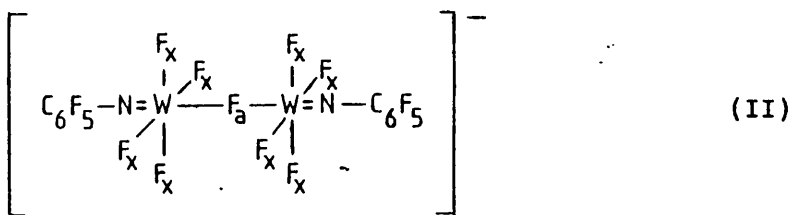
\* = quintet broad with further unresolved coupling; R =  $-\text{NC}_6\text{F}_5$ ;  $^\dagger$  = dubious assignment, no singlet associated with W-F observed.

{  $\delta F_x = 61.9$  ppm ;  $J(F_a - F_x) = 64.7$  Hz ;  $J(F_x - {}^{183}\text{W}) = 39$  Hz } , the decrease in electron density at the tungsten centres , as a result of fluorine bridging , decreases the shielding of the  $F_x$  nuclei , with a resulting shift to lower field. The expected nonet of  $F_a$  coupled to eight equivalent fluorine atoms was not clearly resolved , and the broad , poorly resolved signal at -110 ppm (Fig.3.5) is tentatively assigned to  $F_a$ . In the TFA solution (Table 3.4) the signal associated with  $F_x$  (  $\delta F = 58.6$  ppm ) could not be resolved and the  $F_a$  multiplet was not observed.

In solution the  $[\text{WF}_5(\text{NC}_6\text{F}_5)]^-$  ion is believed to adopt the pseudo-octahedral structure (I) proposed for  $\text{WF}_5(\text{NR})^-$  ions <sup>(5,6)</sup>, with a linear  $F_a\text{-W-N-C}$  skeleton.

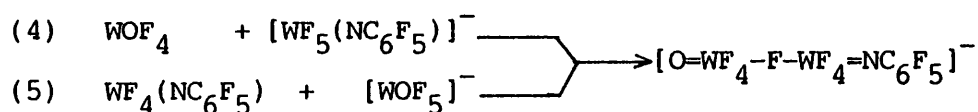


The dimeric anion  $[\text{W}_2\text{F}_9(\text{NC}_6\text{F}_5)_2]^-$  is also believed to adopt a linear ,  $\text{C-N-W-F}_a\text{-W-N-C}$  , skeleton (II) when in solution.



The formation of the dimeric anion most likely results from the combination of  $[\text{WF}_5(\text{NC}_6\text{F}_5)]^-$  and the neutral species  $\text{WF}_4(\text{NC}_6\text{F}_5)$ . The singlet expected from the  $\text{WF}_4$  fragment of the neutral compound was not observed. However , signals thought to be associated with the aromatic fluorine nuclei of the compound have been tentatively assigned {  $\delta F_o = -146.6$  ,  $\delta F_m = -162.6$  ,  $\delta F_p = -151.1$  ppm }.

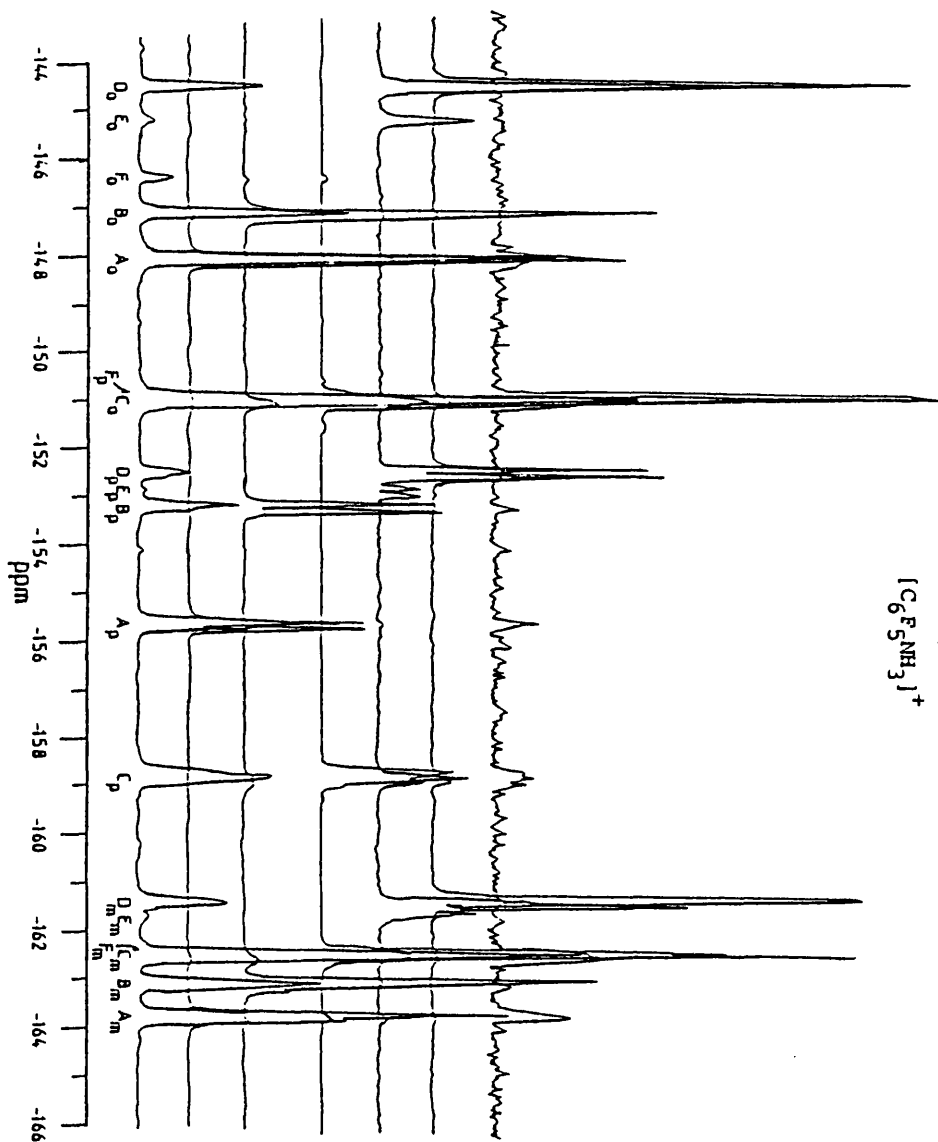
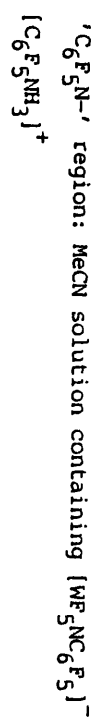
The mixed oxy-imido species observed in the MeCN solutions is believed to be produced in the same manner as the non-mixed dimer , but by two indistinguishable pathways , the first via combination of  $\text{WOF}_4$  and  $[\text{WF}_5(\text{NC}_6\text{F}_5)]^-$  (4) , and the second via combination of  $[\text{WOF}_5]^-$  and  $\text{WF}_4(\text{NC}_6\text{F}_5)$  (5) :-



The two doublets associated with equatorial ( $F_x$ ) nuclei on  $\text{W}=\text{O}$  ( $F_x(o)$ ) and  $\text{W}=\text{NC}_6\text{F}_5$  ( $F_x(n)$ ) show  $^{183}\text{W}$  satellites and can be distinguished by their differing spin-spin coupling constants. Because of the  $\text{NC}_6\text{F}_5$  groups' slightly greater electron withdrawing ability, the  $F_x(o)$  doublet is shifted to slightly lower field ( 62.8 ppm) than that of the  $F_x$  nuclei in  $[\text{W}_2\text{O}_2\text{F}_9]^{-(38,40)}$  ( 62 ppm ). Similarly , the  $F_x(n)$  nuclei are more shielded , and at higher field ( 61 ppm ) than the non-mixed dimer ( 61.9 ppm ). The broad , unresolved , low intensity peak at -127ppm is believed to be the  $F_a$  signal.

The analysis of the region of the  $^{19}\text{F}$  nmr spectra associated with the  $\text{C}_6\text{F}_5\text{N}-$  moieties was achieved by using 2D-nmr (COSY) techniques (Fig.3.12) to match the various ortho- , meta- and para-fluorine nuclei signals. Assignments were made on the basis of comparison of peak integrals and the differing shielding effects of the imido compounds. Using these considerations the o- , m- and p-fluorines of  $[\text{WF}_5(\text{NC}_6\text{F}_5)]^-$  and  $[\text{W}_2\text{F}_9(\text{NC}_6\text{F}_5)_2]^-$  in MeCN were assigned as {  $\delta F_o = -148.2$  ;  $\delta F_m = -163.9$  ;  $\delta F_p = -156.1$  ppm } and {  $\delta F_o = -147.1$  ;  $\delta F_m = -163.7$  ;  $\delta F_p = -153.3$  ppm } respectively. The most intense

Figure 3.12 Stacked plots of the  $^{19}\text{F}$ - $^{19}\text{F}$  COSY nmr spectrum of the



Assignments

- A =  $[\text{C}_6\text{F}_5\text{NW}_5\text{F}_5]^-$
  - B =  $[(\text{C}_6\text{F}_5\text{NH}_2\text{WF}_5\text{F}_5)]^-$
  - C =  $[\text{C}_6\text{F}_5\text{NH}_3]^+$
  - D =  $[\text{C}_6\text{F}_5\text{NW}_5\text{F}_5-\text{F}-\text{WF}_5\text{O}]^-$
  - E = ?
  - F =  $\text{C}_6\text{F}_5\text{N}=\text{WF}_5$  (?)
- O = ortho, P = para, m = meta

signals in the aromatic fluorine region of the spectra were assigned to the  $[\text{C}_6\text{F}_5\text{NH}_3]^+$  cation. The high susceptibility of the cation to solvent effects and acidity is evident in the chemical shifts of the o-, m- and p- fluorine nuclei. Cohen et al<sup>(41)</sup> measured chemical shifts of  $[\text{C}_6\text{F}_5\text{NH}_3]^+$  in 12M HCl of  $\delta\text{F}_o = -150$  ;  $\delta\text{F}_m = -162.4$  ;  $\delta\text{F}_p = -155$  , whereas in MeCN solutions made mildly acidic by the presence of HF , chemical shifts of  $\delta\text{F}_o = -153.8$  ;  $\delta\text{F}_m = -163.4$  ;  $\delta\text{F}_p = -162.9$  ppm (Table 3.2) were recorded. By comparing  $\delta\text{F}_o$  of the cation in strong acid with the values obtained in dilute acid (i.e. HF in MeCN) and  $\delta\text{F}_o$  of the non-protonated amine <sup>(41,42)</sup>, estimations of the remaining chemical shifts can be made and compared with observed values. The results obtained (Table 3.3) are consistent with a dilution effect causing movement of the fluorine nuclei signals of the  $[\text{C}_6\text{F}_5\text{NH}_3]^+$  cation.

Unlike the MeCN solutions , the most intense signals in the aromatic C-F region of the  $^{19}\text{F}$  nmr spectrum of the TFA solution are tentatively assigned to a diacetamide species  $\text{C}_6\text{F}_5\text{N}(\text{COCF}_3)_2$ , produced by reaction of the TFA solvent with the cation. The diacetamide signals {  $\delta\text{F}_o = -146.1$  ;  $\delta\text{F}_m = -163.3$  ;  $\delta\text{F}_p = -154.4$  ppm } partially overlap the cation and dimeric anion signals at {  $\delta\text{F}_o = -148.2$  ;  $\delta\text{F}_m = -149.8$  ;  $\delta\text{F}_p = -160.3$  ppm } and {  $\delta\text{F}_o = -145.8$  ;  $\delta\text{F}_m = -163.3$  ;  $\delta\text{F}_p = -149.3$  ppm }. The diacetamide can also be produced ( along with  $[\text{C}_6\text{F}_5\text{NH}_3]^+$  ) by adding TFA to  $\text{C}_6\text{F}_5\text{NH}_2$  - chemical shifts for the species matched those observed in the imido system spectra , and  $^1\text{H}$  nmr confirmed the absence of an N-H bond in the acetamide. Other fluorination products were also identified in the system. The intense signal at  $\delta\text{F} = 13.6$  ppm was expanded and found to be a quartet (  $J(\text{F}-\text{F}) = 6$  Hz ) , in good agreement with the values reported for  $\text{CF}_3\text{COF}$  <sup>(43)</sup>, and the signal at  $\delta\text{F} = -22.3$  ppm was assigned to

Table 3.3 Estimation of dilution effects on  $\delta F(\text{ppm})^*$  in  $[\text{C}_6\text{F}_5\text{NH}_3]^+$

Nucleus	$\delta F \text{ C}_6\text{F}_5\text{NH}_2$		$\delta F \text{ C}_6\text{F}_5\text{NH}_3^+ / \text{dil. HF}$		$\delta F \text{ C}_6\text{F}_5\text{NH}_3^+ / 12\text{M HCl}^{(41)}$
	A	B	Calculated		
			A	B	
Forlho	-163.6	-165.2	—	—	-150
Fineu	-165.7	-168.4	-162.7	-163.9	-162.4
Fpara	-174.1	-178.1	-160.3	-160.8	-155
				Observed	

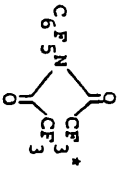
\* relative to  $\text{CFCl}_3$  .

A Lawrenson <sup>(42)</sup>

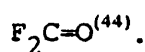
B Cohen <sup>(41)</sup>



Table 3.4 <sup>19</sup>F nmr Chemical Shifts and Coupling Constants for the TFA Solution of the product from (WF<sub>6</sub> + C<sub>6</sub>F<sub>5</sub>NH<sub>2</sub>)

ASSIGNMENT	Spectral Form	Chem. shift (rel. to CFCl <sub>3</sub> ), ppm					Spin-spin Coupling Constants, Hz				Approx. relative molar ratio
		δF <sub>X</sub>	δF <sub>A</sub>	δF <sub>O</sub>	δF <sub>M</sub>	δF <sub>P</sub>	J <sub>F<sub>A</sub>-F<sub>X</sub></sub>	J <sub>F<sub>X</sub>-183<sub>W</sub></sub>	J <sub>F<sub>O</sub>-F<sub>M</sub></sub>	J <sub>F<sub>P</sub>-F<sub>M</sub></sub>	
WOF <sub>4</sub>	X <sub>4</sub>	65.9	-	-	-	-	-	n.o.	-	-	21
( <u>WF<sub>4</sub></u> -F <sub>A</sub> - <u>WF<sub>4</sub></u> R) <sup>⊖</sup> ( <u>WF<sub>4</sub></u> -F <sub>A</sub> - <u>WF<sub>4</sub></u> R) <sup>⊖</sup>	AX <sub>4</sub>	58.6	n.o.	-	-	-	n.o.	n.o.	-	-	39
CF <sub>3</sub> COF <sub>X</sub>	quartet	13.6	-	-	-	-	6.1	-	-	-	150
CF <sub>3</sub> COF <sub>X</sub>	doublet	-75	-	-	-	-	6.1	-	-	-	
F <sub>2</sub> C=O	singlet	-22.3	-	-	-	-	-	-	-	-	114
[C <sub>6</sub> F <sub>5</sub> NH <sub>3</sub> ] <sup>⊕</sup>		-	-	-148.2	-160.3	-149.8	-	-	n.o.	n.o.	7
		-	-	-146.1	-163.3	-154.4	-	-	n.o.	n.o.	112

n.o. = not observed; R = -NC<sub>6</sub>F<sub>5</sub>; \* = Tentative assignment.



The nmr evidence illustrates that whilst TFA can be used to isolate the dimeric salt  $[\text{W}_2\text{F}_9(\text{NC}_6\text{F}_5)_2]^- [\text{C}_6\text{F}_5\text{NH}_3]^+$ , prolonged standing will result in progressively larger amounts of fluorination products forming at the expense of the imido compound.

The dimeric anion salt crystallised from TFA has two formula units within the triclinic unit cell (Fig.3.13 and Table 3.5 ). Unlike the linear structure proposed for the anion in solution, the anion in the solid state has near linear C-N-W fragments, but with distorted and slightly differing geometries about the two bridging fluorine atoms ( F(1) , F(31) ). The difference between the two bridging angles,  $150.8^\circ$  and  $170.4^\circ$  is clearly observable if the unit cell is reorientated and the  $[\text{C}_6\text{F}_5\text{NH}_3]^+$  cations removed for clarity ( Fig. 3.14 ). Dehnicke and co-workers <sup>(33)</sup> have prepared a fluorine bridged nitrido-nitreno rhenium fluoride,  $\text{ReNF}_4 \cdot \text{ReF}_5(\text{NCl})$ , possessing a similar bent geometry at the fluorine bridge (  $\text{Re-F-Re} = 168^\circ$  ) <sup>(33)</sup>, and the trinuclear nitrido nitrene complex  $[\text{Ph}_3\text{C-NWCl}_4\text{-F-WNCl}_2\text{-F-WCl}_4\text{N-CPh}_3]^-$  <sup>(29)</sup> has  $\text{W-F-W} = 163^\circ$ .

The average equatorial fluorine to tungsten bond length of  $1.917 \text{ \AA}$  ( $\sigma = 0.057$ ) is greater than the W-F bond lengths of  $\text{WF}_6$  <sup>(45)</sup> {  $1.832 \text{ \AA}$  },  $\text{WClF}_5$  <sup>(46)</sup> {  $1.836 \text{ \AA}$  },  $\text{WF}_5\text{N}_3$  <sup>(30)</sup> {  $1.836 \text{ \AA}$  } and  $\text{WF}_4(\text{N=PPh}_3)_2$  <sup>(31)</sup> {  $1.891 \text{ \AA}$  } consistent with greater withdrawal of electron density from the metal atom. The imido group exerts a noticeable trans effect on the trans W-F bonds [ average  $\text{W-F}_{\text{trans}} = 2.124 \text{ \AA}$  ( $\sigma = 0.041$ ) compared with  $\text{WF}_5\text{N}_3$  <sup>(30)</sup> {  $1.89 \text{ \AA}$  } and  $\text{WF}_4(\text{N=PPh}_3)_2$  <sup>(31)</sup> {  $1.935 \text{ \AA}$  }]. All equatorial W-F bonds are bent approximately  $10^\circ$  away from the perpendicular to the imido groups ( average  $\text{N-W-F}_{\text{eq}} = 99.1^\circ$

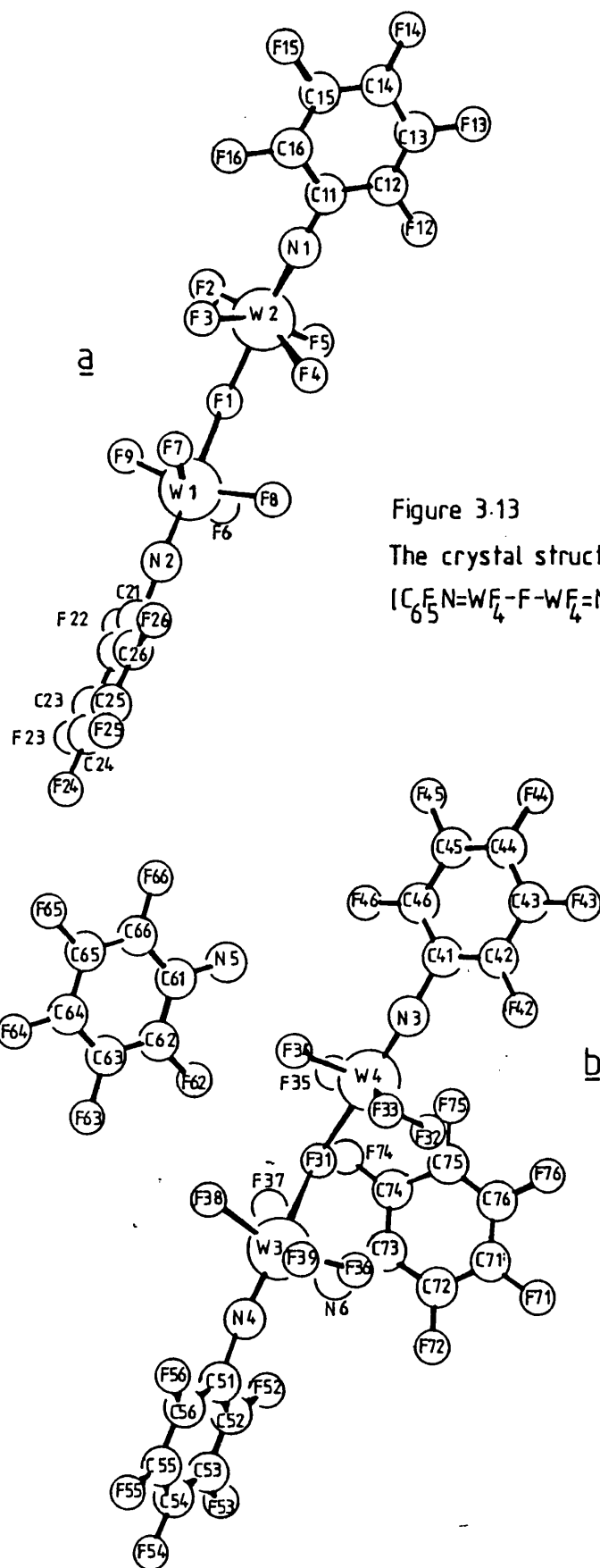


Figure 3.13

The crystal structure of

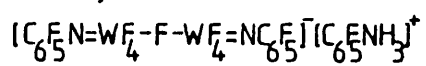


Table 3.5      Selected bond lengths(Å) and angles(°)  
with estimated standard deviations in parentheses

Bond	Length(Å)	Atoms	Angles(°)
F(1)-W(1)	2.159(29)	W(1)-F(1)-W(2)	150.8(12)
F(1)-W(2)	2.117(25)	W(3)-F(31)-W(4)	170.4(19)
F(31)-W(3)	2.16(3)	N(2)-W(1)-F(6)	98.5(12)
F(31)-W(4)	2.06(4)	N(2)-W(1)-F(7)	101.3(13)
F(6)-W(1)	1.893(21)	N(2)-W(1)-F(8)	97.5(13)
F(7)-W(1)	1.935(22)	N(2)-W(1)-F(9)	98.5(13)
F(8)-W(1)	1.904(20)	N(1)-W(2)-F(2)	100.3(14)
F(9)-W(1)	1.867(25)	N(1)-W(2)-F(3)	94.7(15)
F(2)-W(2)	1.926(22)	N(1)-W(2)-F(4)	97.0(13)
F(3)-W(2)	1.875(24)	N(1)-W(2)-F(5)	104.3(16)
F(4)-W(2)	1.976(24)	N(4)-W(3)-F(36)	100.9(14)
F(5)-W(2)	1.840(26)	N(4)-W(3)-F(37)	101.2(14)
F(36)-W(3)	1.907(25)	N(4)-W(3)-F(38)	96.4(15)
F(37)-W(3)	1.985(26)	N(4)-W(3)-F(39)	98.8(13)
F(38)-W(3)	1.843(24)	N(3)-W(4)-F(32)	97.4(14)
F(39)-W(3)	1.998(26)	N(3)-W(4)-F(33)	102.0(14)
F(32)-W(4)	1.864(22)	N(3)-W(4)-F(34)	101.2(14)
F(33)-W(4)	2.026(21)	N(3)-W(4)-F(35)	95.8(14)
F(34)-W(4)	1.867(26)	W(1)-N(2)-C(21)	175.3(22)
F(35)-W(4)	1.968(25)	W(2)-N(1)-C(11)	179.0(30)
W(1)-N(2)	1.80(4)	W(3)-N(4)-C(51)	172.1(22)
W(2)-N(1)	1.78(4)	W(4)-N(3)-C(41)	179.6(15)
W(3)-N(4)	1.69(4)		
W(4)-N(3)	1.68(3)		
N(1)-C(11)	1.39(5)		
N(2)-C(21)	1.40(5)		
N(3)-C(41)	1.49(4)		
N(4)-C(51)	1.52(4)		

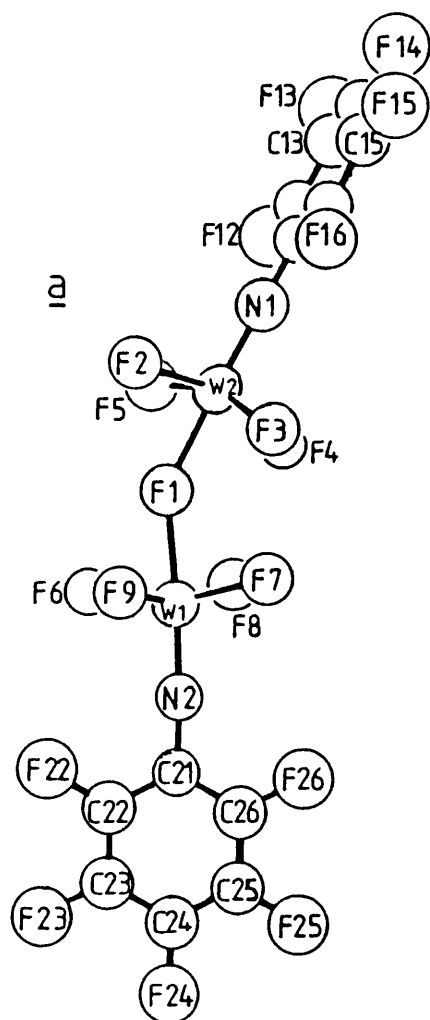
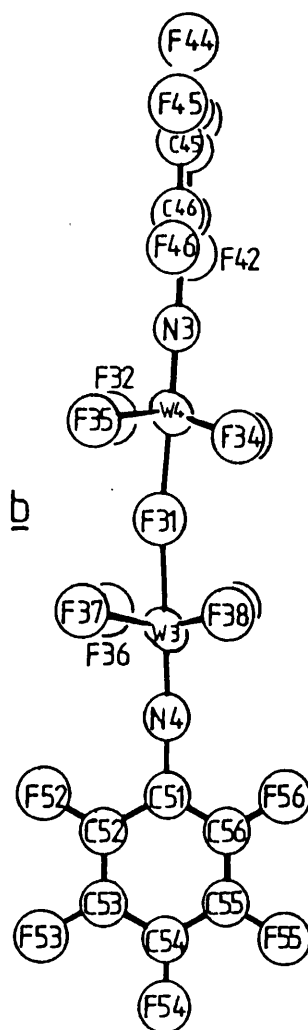


Figure 3.14

Re-orientation of the  
 $[\text{C}_6\text{F}_5\text{N}=\text{WF}_4-\text{F}-\text{WF}_4=\text{NC}_6\text{F}_5][\text{C}_6\text{F}_5\text{NH}_3]^+$   
 unit cell



). In the tungsten chloroimido ion  $[\text{WCl}_5(\text{NC}_2\text{Cl}_5)]^-$  <sup>(18)</sup> the equatorial chlorine atoms are bent  $5^\circ$  towards the axial chlorine atom (  $\text{Cl}_a\text{-W-Cl}_e = 85^\circ$  ), the effect is more pronounced in  $\text{ReNF}_4\text{-ReF}_5(\text{NCl})$  (  $\text{N-Re-F} = 98^\circ$  ) <sup>(33)</sup>. The movement of the equatorial fluorines away from the imido group can be explained as the repulsion of the W-F bonds away from the greater electron density of the W=N bond.

The W=N bond ( average  $1.74 \text{ \AA}$  ), although formally assigned as a double bond , possesses a bond order of greater than two (Table 3.6 ) attributed to  $d_\pi\text{-p}_\pi$  overlap to form  $\text{M}\equiv\text{N-R}$ .

TABLE 3.6 Comparison of W=N bond lengths ( $\text{\AA}$ )

Compound	W-N ( $\text{\AA}$ )	Ref.
$[\text{W}_2\text{F}_9(\text{NC}_6\text{F}_5)_2]^- [\text{C}_6\text{F}_5\text{NH}_3]^+$	1.74	This work
$[\text{WCl}_5(\text{NC}_2\text{Cl}_5)]^- [\text{AsPh}_4]^+$	1.648	(18)
$[\text{Cl}_4\text{W=N-C}_2\text{Cl}_5]_2$	1.71	(21)
$(\text{BuO})_3\text{W}\equiv\text{N}$	1.74	(47)
$\text{W}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2$	1.742	(48)
$\text{W}(\text{NPh})\text{Cl}_2(\text{PPh}_3)_3$	1.755	(48)
$\text{WCl}_2(\text{NSO}_2\text{Ph})_2(\text{MeCN})_2$	1.766	(49)
$\text{WCl}_2(\text{NPh})_2(\text{bipy})$	1.789	(28)
$\text{WF}_4(\text{N=PPh}_3)_2$	1.825	(31)
$\text{WF}_5\text{N}_3$	1.85	(30)

Torsional angles between  $\text{WF}_4$  groups in the anions were approximated by excluding the bridging fluorine atoms ( F(1) , F(31) ), thus measuring torsion angles between F-W-W-F. In the less distorted anion ,b, (Fig.3.14) the torsion angle was found to be  $2.6^\circ \pm 1.5$  i.e. both  $\text{WF}_4$  segments eclipsing. The larger bridging angle of the second anion ,a, causes the  $\text{WF}_4$  segments to adopt slightly staggered alignments to avoid steric interactions , which is seen in the aver-

age torsion angle of  $19.7^\circ \pm 1.3$ .

Planes involving three or four atoms were defined within the  $\text{NC}_6\text{F}_5$  and  $\text{WF}_4\text{-F-WF}_4$  fragments (Table 3.7) for both anions in the unit cell, and angles between the planes calculated in order to determine the orientation of the  $\text{-NC}_6\text{F}_5$  and  $\text{WF}_4$  groups with respect to each other. Planes involving four or more atoms are 'best calculated' planes; in the examples used (Table 3.7) the maximum deviation from the calculated plane was 0.05 Å.

The angles between  $\text{-NC}_6\text{F}_5$  and  $\text{-WF}_4$  groups in anion b (between Planes 1 and 2 and Planes 3 and 4 [Table 3.7]) are  $47.9^\circ$  and  $49.8^\circ$  respectively. The  $\text{-NC}_6\text{F}_5$  groups 'bisect' the F-W-F angle of the neighbouring  $\text{-WF}_4$  group, and are orientated close to right angles ( $86.2^\circ$ ) to each other (Planes 2 and 4). The adoption of a staggered geometry by the  $\text{-WF}_4$  groups in the anion a, and the greater bridging angle is evident in the change in angles between the  $\text{-NC}_6\text{F}_5$  and  $\text{-WF}_4$  groups (between Planes 5 and 6 and Planes 7 and 8) to  $64.4^\circ$  and  $57.1^\circ$  respectively. Similarly the orientation of the two fluorophenyl groups (Planes 6 and 8) is altered to  $76.6^\circ$ . The distortion of the anion a, is ascribed to packing considerations within the triclinic crystal lattice of the  $[\text{W}_2\text{F}_9(\text{NC}_6\text{F}_5)_2]^- [\text{C}_6\text{F}_5\text{NH}_3]^+$  salt.

Reaction of pentafluoroaniline with  $\text{MoF}_6$  is also believed to result in iminolysis to produce the salts  $[\text{MoF}_5(\text{NC}_6\text{F}_5)]^- [\text{C}_6\text{F}_5\text{NH}_3]^+$  and  $[\text{C}_6\text{F}_5\text{NH}_3]^+\text{F}^-$ . The IR spectrum (Fig.3.9) of the solid produced possesses the same salient features found in the tungsten product, including peaks at  $2640$  and  $1600\text{cm}^{-1}$  attributable to  $[\text{C}_6\text{F}_5\text{NH}_3]^+\text{F}^-$ . The  $\nu(\text{Mo}=\text{N})$  stretch is believed to be at  $1000\text{cm}^{-1}$ .

Table 3.7 Defined planes enclosing designated , numbered atoms.

Plane No.	Boundary atoms	Equation ( w.r.t. frac. coords. )	R.M.S. Deviation <sup>+</sup>
		Deviations(Å) of atoms from defined plane n <sup>+</sup>	
1	W4 F31 F33 F35	$7.5224 \cdot X - 1.8656 \cdot Y + 9.0327 \cdot Z = 9.8460$	0.017
		W4= 0.025 F31= 0.005 F33= -0.015 F35= -0.015	
2	C42 C44 C46	$-4.7994 \cdot X - 9.9788 \cdot Y - 7.6430 \cdot Z = -8.4414$	—
3	W3 F31 F36 F38	$-0.2002 \cdot X + 16.5975 \cdot Y + 1.6399 \cdot Z = 2.1685$	0.030
		W3= -0.046 F31= -0.007 F36= 0.026 F38= 0.027	
4	C52 C54 C56	$-3.1618 \cdot X + 11.7285 \cdot Y - 6.8640 \cdot Z = -4.3028$	—
5	W2 F1 F2 F4	$-2.2559 \cdot X - 8.0880 \cdot Y - 9.9241 \cdot Z = -6.7246$	0.022
		W2= -0.033 F1= -0.005 F2= 0.019 F4= 0.019	
6	C12 C14 C16	$-3.9708 \cdot X + 17.5759 \cdot Y + 1.3867 \cdot Z = 9.7312$	—
7	W1 F1 F8 F9	$-7.1265 \cdot X - 9.5754 \cdot Y - 5.7193 \cdot Z = -5.8481$	0.020
		W1= -0.031 F1= -0.004 F8= 0.017 F9= 0.018	
8	C22 C24 C26	$-5.9291 \cdot X + 3.6775 \cdot Y - 9.4910 \cdot Z = -0.5026$	—

<sup>+</sup> applicable to planes involving four or more boundary atoms.



The reaction of  $\text{ReF}_6$  with pentafluoroaniline produces a solid the IR spectrum of which (Fig.3.10) is slightly simpler than that of the molybdenum and tungsten derivatives. The absence of a band at  $2600\text{cm}^{-1}$  places some doubt as to presence of  $[\text{C}_6\text{F}_5\text{NH}_3]^+\text{F}^-$  in the solid, even though  $\nu(\text{N-H})$  associated with the anilinium cation is present at  $1500\text{cm}^{-1}$ . The  $\nu(\text{Re=N})$  band has variously been assigned at  $1102\text{cm}^{-1(33)}$  and at  $1011$  and  $995\text{cm}^{-1(17)}$ , the presence of bands at both these regions means that an unambiguous assignment of  $\nu(\text{Re=N})$  is not possible due to overlap with  $\nu(\text{C-C})$  and  $\nu(\text{C-F})$  vibrational modes. The peaks in the  $600\text{cm}^{-1}$  region are assigned to  $\nu(\text{Re-F})$ . The solid is believed to be a mixture containing the neutral species,  $\text{ReF}_4(\text{NC}_6\text{F}_5)$ . The isolation of  $\text{ReF}_5(\text{NCl})^{(50)}$  as a product of the fluorination of the mixture by  $\text{ClF}_3$  is further chemical evidence to support the presence of a rhenium imido fluoride species.

# Chapter Four

The reaction of N-containing  
Trimethylsilyl derivatives with  
 $\text{MoF}_6$  and  $\text{WF}_6$

#### 4.1 Introduction

The fission of the element-silicon bond in trimethyl-silyl derivatives of the type  $\text{Me}_3\text{Si-X}$  ( $\text{X} = \text{non-metal}$ ), represents a useful method of preparing substituted tungsten fluoride derivatives of the type  $\text{WF}_{(6-n)}\text{X}_n$ , where  $\text{X} = \text{Cl}^{(55)}$ ,  $\text{OMe}^{(56)}$ ,  $\text{OPh}^{(56)}$  or  $\text{OC}_6\text{F}_5^{(57)}$ , resulting, as it does, in the exchange of a fluorine atom for X. The formation of the thermodynamically stable trimethylsilylfluoride,  $\text{Me}_3\text{SiF}$  ( $\Delta H_f = -527 \text{ kJ mol}^{-1}$ )<sup>(58)</sup> as a by-product is believed to be a driving force for these reactions.

By using a nitrogen containing group, X, it is possible to make nitrogen-containing tungsten fluoride derivatives;  $\text{WF}_5\text{NET}_2^{(60)}$ ,  $\text{WF}_4(\text{NET}_2)_2^{(57)}$ ,  $\text{WF}_2(\text{NET}_2)_4^{(57)}$  using  $\text{X} = \text{NET}_2$  and  $\text{WF}_4(\text{NMe})\text{L}$  ( $\text{L} = \text{MeCN}$ ,  $\text{Py}$ )<sup>(5,6)</sup> using  $(\text{Me}_3\text{Si})_2\text{NMe}$ . The majority of work on these compounds has involved  $^{19}\text{F}$  nmr spectroscopy, but recently crystal structures of the derivatives  $\text{WF}_5\text{N}_3^{(30)}$  and  $\text{WF}_4(\text{N=PPh}_3)_2^{(31)}$  have been determined. The reaction of  $\text{Me}_3\text{Si-N}_3$  and  $-\text{NCO}$  with rhenium hexafluoride is believed to yield, at low temperatures, initially  $\text{ReF}_5\text{X}$  ( $\text{X} = \text{N}_3$ ,  $\text{NCO}$ )<sup>(50)</sup>, and there is good evidence to support the formation of the isothiocyanate,  $\text{WF}_5\text{SCN}$ , from the reaction between  $\text{WF}_6$  and  $\text{Me}_3\text{Si-NCS}^{(72)}$ , and the formation of  $\text{OsF}_5\text{NCO}^{(74)}$  from  $\text{OsF}_6$  and  $\text{Me}_3\text{SiNCO}$ . Also the reaction of bis(trimethylsilyl)carbodiimide with  $\text{WF}_6^{(71)}$  is believed to form the carbodiimide species  $\text{WF}_5\text{-NCN-WF}_5$ .

The reactions of  $\text{WF}_6$  and  $\text{MoF}_6$  with trimethylsilylisocyanate ( $\text{Me}_3\text{SiNCO}$ ) were carried out to try to obtain the novel fluoro-isocyanates  $\text{MF}_5\text{NCO}$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ). Although fluoro-isocyanates of non-

transition elements , such as  $\text{SF}_5\text{NCO}^{(62)}$  and  $\text{TeF}_5\text{NCO}^{(63,64)}$  as well as the fluoro anion ,  $[\text{SbF}_5\text{NCO}]^{-(73)}$  , are known, transition metal fluoro-isocyanates are relatively unknown , so that  $\text{WF}_5\text{NCO}$  and  $\text{MoF}_5\text{NCO}$  represent new examples of this group of compounds. The reaction between  $\text{MoF}_6$  and hexamethyldisilazane ,  $(\text{Me}_3\text{Si})_2\text{NH}$  , was also carried out with a view to obtaining a sample of  $\text{MoF}_4(\text{NH})$  suitable for crystallography.

## 4.2 Experimental

### 4.2.1. The Preparation of Pentafluorotungsten(VI)isocyanate.

An excess of tungsten hexafluoride (3.68mmoles) was distilled onto a Genetron solution of trimethylsilylisocyanate (2.23mmoles). The mixture was allowed to warm to room temperature with agitation to ensure complete mixing of the reagents. The clear solution became cloudy and small amounts of fine , pale yellow solid slowly precipitated from the mixture. On leaving to stand for several hours the solid darkened to a bright lemon colour with slow gas evolution. The amount of solid formed after the reaction mixture had been left to stand for a day was less than would be expected for a 1:1 reaction. Gas phase IR spectra showed the presence of the Genetron solvent ,  $\text{Me}_3\text{SiF}^{(59)}$  and unreacted  $\text{Me}_3\text{SiNCO}$  and  $\text{WF}_6$ . The condensed volatiles distilled from the reaction tube were initially clear , but became cloudy after a short while as more yellow solid precipitated from the mixture. The remaining yellow solid is non-volatile and decomposes at approximately  $124^\circ\text{C}$ . The IR spectrum of the  $\text{WF}_5\text{NCO}$  solid ( Fig.4.1 ) is complicated , with bands attributable to  $\nu(\text{NCO})$  ( 2240 , 2160  $\text{cm}^{-1}$ ),  $\nu(\text{NCO})$  ( 1415  $\text{cm}^{-1}$ ) and  $\nu(\text{W-F})$  ( 760 , 625 , 600 , 535  $\text{cm}^{-1}$ ).

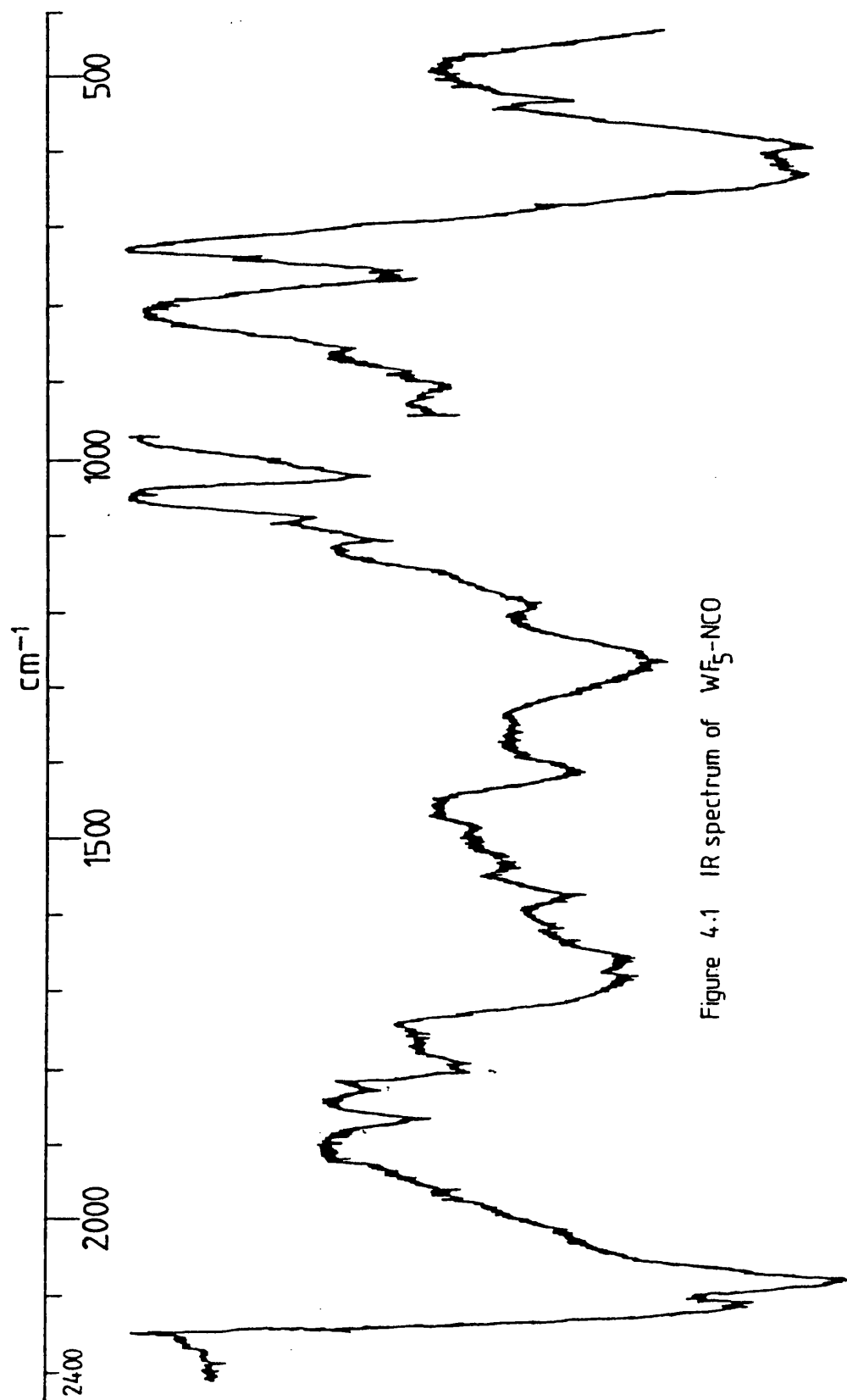


Figure 4.1 IR spectrum of W/E<sub>5</sub>-NCO

The yellow  $\text{WF}_5\text{NCO}$  , which rapidly hydrolyses in air , is insoluble in excess of  $\text{Me}_3\text{SiNCO}$  and  $\text{WF}_6$  , Genetron , acetonitrile , liquid  $\text{SO}_2$  ,  $\text{CH}_2\text{Cl}_2$  and diethylether. Addition of tetrahydrofuran (thf) completely dissolves the  $\text{WF}_5\text{NCO}$  to give a yellow solution , which then polymerizes to give a very thick , yellow oil.

X-ray powder photographs of the powdered solid showed no lines after a maximum exposure time of ten hours. Mass spectroscopy showed only hydrolysis products , the  $\text{WF}_5\text{NCO}$  not possessing sufficient volatility to allow detection.

#### 4.2.2. Reaction of Pentafluorotungsten(VI)isocyanate with TFA.

To a small amount of  $\text{WF}_5\text{NCO}$  (0.37mmoles) a very large excess of trifluoroacetic acid(TFA) was added. There was no sign of solution or immediate reaction , so the mixture was left to stand at room temperature for approximately  $1\frac{1}{2}$  days. The TFA became slightly cloudy and off-white in colour , whilst the yellow  $\text{WF}_5\text{NCO}$  was replaced by a small amount of a white , partially soluble solid. A gas-phase IR spectrum of the volatiles (Fig.4.2) showed mostly peaks from the TFA and two peaks at 2350 and 670  $\text{cm}^{-1}$  assigned to the  $\nu_3$  and  $\nu_2$  modes of  $\text{CO}_2$  <sup>(61)</sup>. Comparison of the spectrum with a blank reference scan ruled out the presence of  $\text{CO}_2$  as a result of an inefficient purge unit within the IR spectrometer. The excess TFA and other volatile products were distilled from the reaction vessel to leave behind the white solid , which could be sublimed under vacuum to produce opaque white crystals with a melting point of approximately  $160^\circ\text{C}$ . Several attempts to obtain crystals suitable for a structural determination , from solution and sublimation , did not succeed.

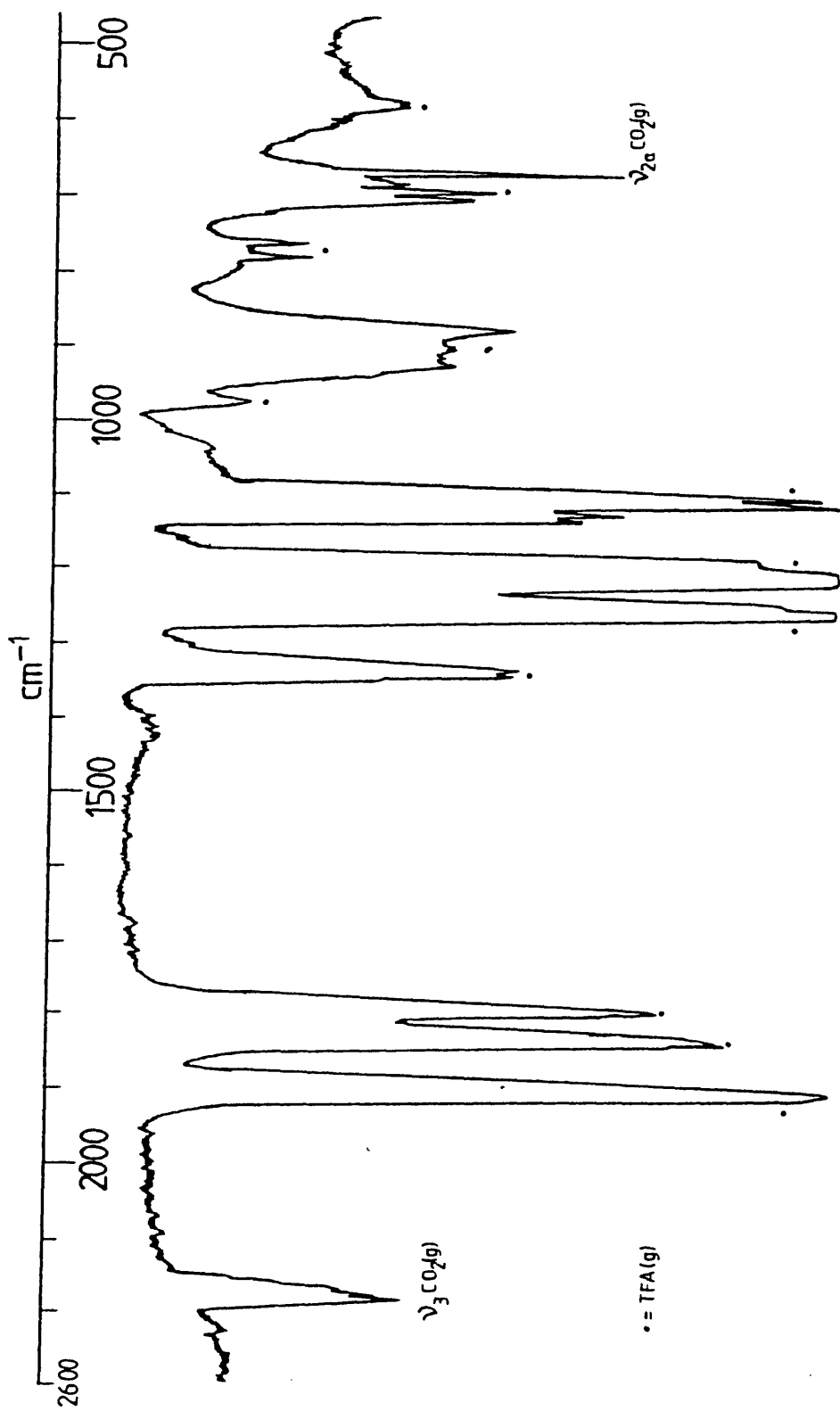


Figure 4.2 IR spectrum of the volatile products from  $\text{W}_5\text{-NCO} + \text{TFA}$

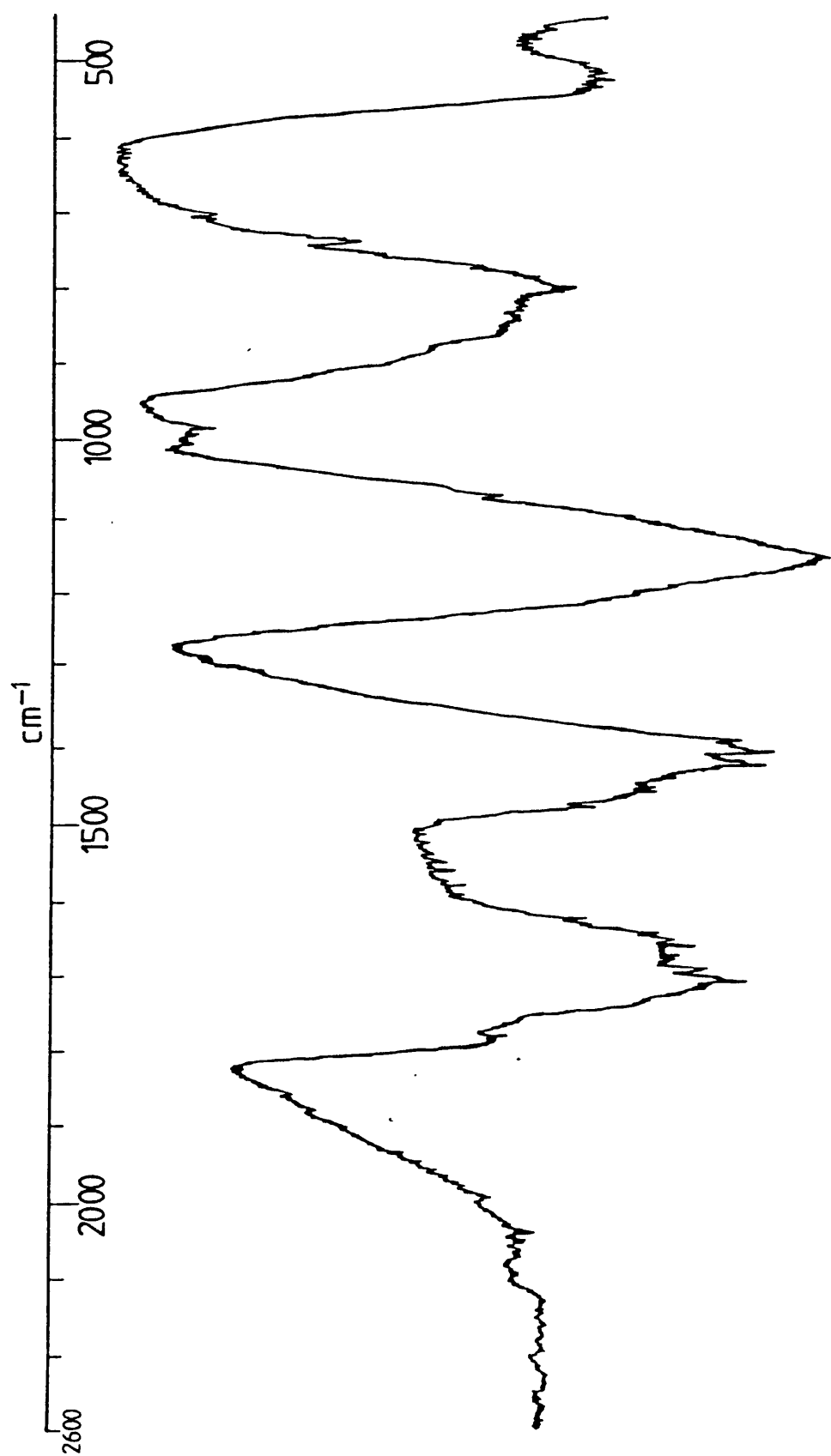


Figure 4.3 IR spectrum of " $\text{W}_5\text{NH}(\text{O})\text{CF}_3$ " ( from  $\text{W}_5\text{-NCO} + \text{TFA}$  )



The IR spectrum of the white solid (Fig.4.3) showed bands at 1700 and 1420  $\text{cm}^{-1}$  attributable to  $\nu(\text{C=O})$  and  $\nu(\text{N-H})$  amide stretching frequencies , as well as bands at 1150  $\text{cm}^{-1}$   $\nu(\text{C-F})$  and 800 and 530  $\text{cm}^{-1}$   $\nu(\text{W-F})$ . The IR data , and the liberation of  $\text{CO}_2$  , indicated that the white solid could be the N-pentafluorotungstentrifluoroacetamide  $\text{F}_5\text{WNHC(O)CF}_3$ .

The white solid showed no tungsten abundance pattern species in the mass spectrum , and only four very weak lines were visible on the X-ray powder photograph :-

d-spacing( $\text{\AA}$ ) [ $I/I^0$ ] : 8.91[5.0],6.90[9.0],4.49[3.5],2.30[10]

#### 4.2.3. The Preparation of Pentafluoromolybdenum(VI)isocyanate.

Trimethylsilylisocyanate (0.68mmoles) was distilled on to a Genetron solution containing an excess of molybdenum hexafluoride (1.14 mmoles) , and washed down the reaction tube walls by a small amount of Genetron. The mixture was allowed to warm to room temperature , forming a pale yellow solution with gas evolution. At room temperature the rate of gas evolution rapidly increased and the solution darkened as a deep orange coloured solid formed. The reaction mixture was left overnight at room temperature to reach completion , whereupon a red solid settled out of a yellow Genetron solution. A gas IR spectrum of the volatile products showed the presence of Genetron and  $\text{Me}_3\text{SiF}$ . The solvent and volatile products were distilled from the reaction vessel to leave behind a non-volatile , light brown solid. The volatiles removed retained the yellow colouration , believed to be  $\text{MoF}_5$  formed as a by-product.

The light brown , air sensitive , solid believed to be  $\text{MoF}_5\text{NCO}$  , begins to decompose at approximately  $55^\circ\text{C}$  and showed no molybdenum fragmentation patterns in its mass spectrum. The solid did not produce an X-ray powder diffraction pattern after 8 hours exposure. The  $\text{MoF}_5\text{NCO}$  is totally insoluble in Genetron ,  $\text{SO}_2\text{ClF}$  and diethyl-ether. The IR spectrum of the solid as a Nujol mull (Fig.4.4) is similar to the tungsten analogue ,  $\text{WF}_5\text{NCO}$  , showing the vas NCO stretching mode at 2220 , 2150  $\text{cm}^{-1}$  and  $\nu(\text{Mo-F})$  modes at 770 , 670 and 610  $\text{cm}^{-1}$ . The spectrum shows traces of moisture to be present , presumably from the Nujol , which explains the presence of the  $\nu(\text{Mo=O})$  peak at approximately 1020  $\text{cm}^{-1}$ . The remainder of the spectrum is complicated and was not assigned.

The percentage yield of formation of  $\text{MoF}_5\text{NCO}$  is ~ 53%.

#### 4.2.4. The Reaction of $\text{MoF}_5\text{NCO}$ with Anhydrous Hydrogen Fluoride.

In an attempt to solvate  $\text{MoF}_5\text{NCO}$  , anhydrous hydrogen fluoride (AHF) was added to a small amount of the light brown solid. At room temperature there was slight yellowing of the AHF which then became clear as the solid at the bottom of the reaction vessel coagulated , followed by slow gas evolution from the surface of the red , oily coagulant. A gas-phase IR of the volatile components (~30mmHg at room temperature) showed broad , intense peaks centred at 1935 and 1230  $\text{cm}^{-1}$  , a medium strength peak at 1025  $\text{cm}^{-1}$  and weak peaks at 815 and 770  $\text{cm}^{-1}$ . The gas liberated by the reaction has not been characterised .

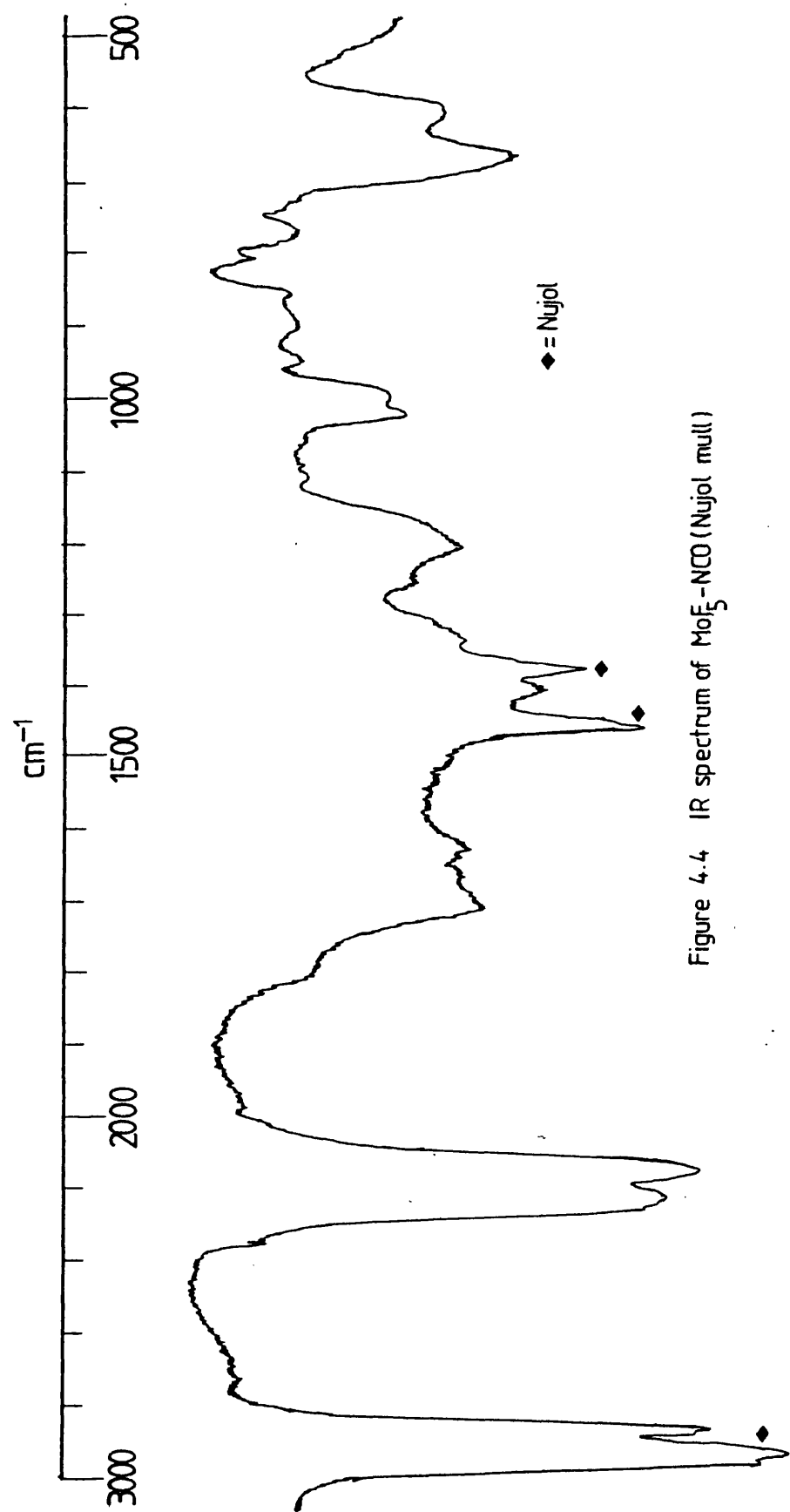


Figure 4.4 IR spectrum of  $\text{MoF}_5\text{-NCO}$  (Nujol mull)

The excess of AHF solvent was distilled from the reaction tube, leaving a small amount of non-volatile , red oil behind. The oil did not solidify on standing and has not been characterised .

#### 4.2.5. The Preparation of N-Imidomolybdenum(VI)tetrafluoride.

A slight excess of molybdenum hexafluoride (2.22mmoles) was distilled onto a Genetron solution of 1,1,1,3,3,3-hexamethyldisilazane (1.92 mmoles) , and the mixture allowed to warm to  $-10^{\circ}\text{C}$ . The initially yellow-coloured solution darkened , with rapid gas formation causing solid to be thrown up onto the reaction tube wall. The reaction mixture was quenched several times with LN and then left to warm up to room temperature. A large amount of fine , brown solid settled out from the pale yellow Genetron solution , and after standing at room temperature for two hours there was still a slow release of gas from the reaction mixture. Gas phase IR spectra of the volatiles showed the presence of the Genetron solvent and  $\text{Me}_3\text{SiF}$  only. The reaction mixture was left to stand a further two days before distilling the volatile components from the non-volatile brown solid. The volatiles removed retained the yellow colouration , attributable to  $\text{MoF}_5$  , and turned blue immediately the solution was exposed to air.

The brown  $\text{MoF}_4\text{NH}$  could not be obtained analytically pure because of encapsulation of traces of  $\text{Me}_3\text{SiF}$  within the solid. The IR spectrum of  $\text{MoF}_4\text{NH}$  (Fig.4.5) showed bands that can be assigned to  $\nu(\text{N-H})$  ,  $\nu(\text{Mo=N})$  and  $\nu(\text{Mo-F})$  terminal and bridging at 1423 , 1015 , 650 and  $495\text{ cm}^{-1}$  , plus peaks attributable to  $\text{Me}_3\text{SiF}$ . The brown  $\text{MoF}_4\text{NH}$  exhibits neither a mass spectrum pattern nor an X-ray powder dif-

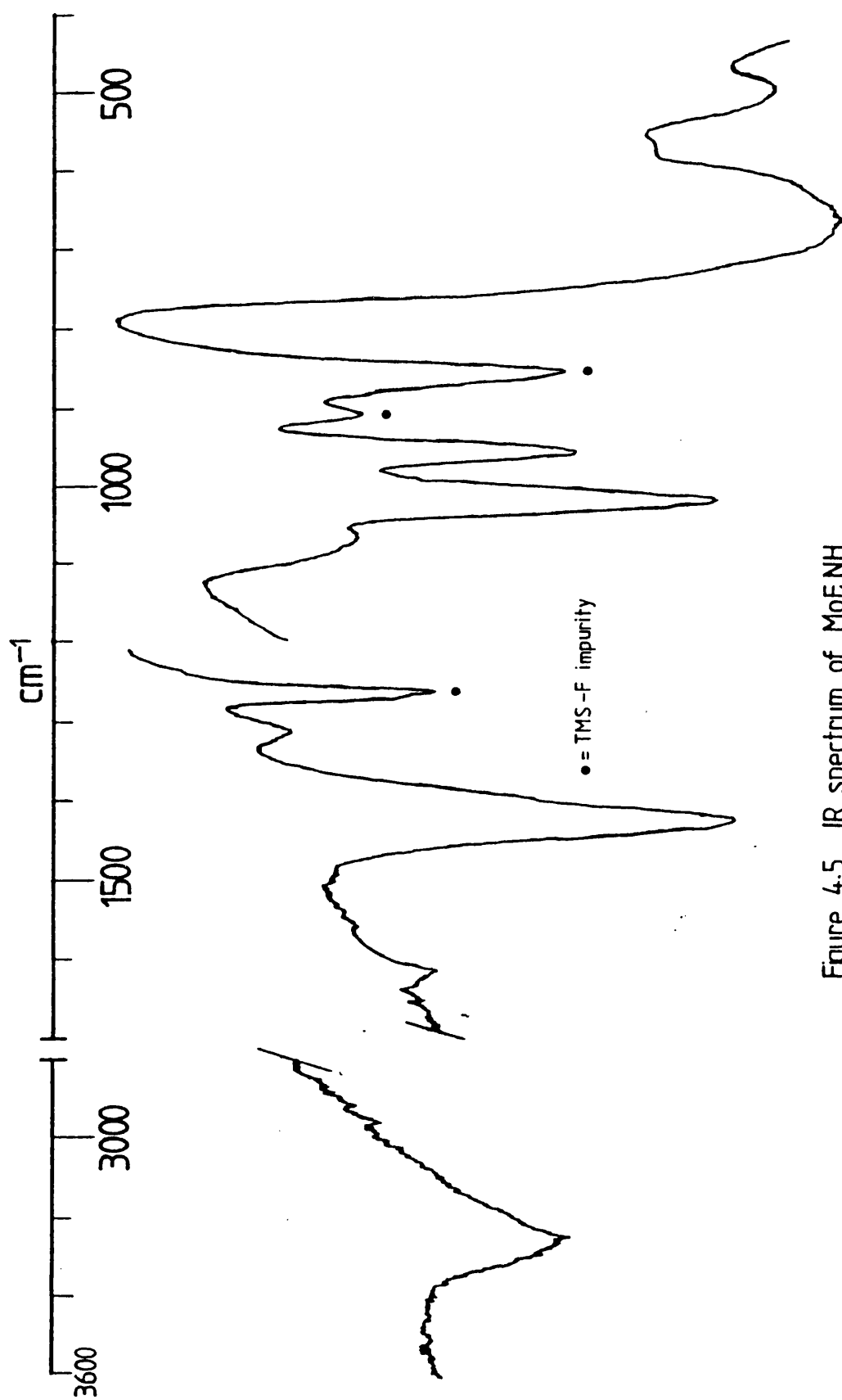


Figure 4.5 IR spectrum of  $\text{MoF}_4\text{NH}$

fraction pattern.

#### 4.2.6. The Preparation of the Acetonitrile Adduct $\text{MoF}_4\text{NH} \cdot \text{MeCN}$ .

A large volume of acetonitrile (MeCN) was distilled onto  $\text{MoF}_4\text{NH}$  and allowed to warm up to room temperature, gas being liberated as it did so. The mixture was left to stand until all gas evolution had ceased. The IR spectrum of the gas showed  $\text{Me}_3\text{SiF}$  only. Warming the solution resulted in only sparse solubility to form a pale red solution and an insoluble brick-red solid, lighter in colour than the original  $\text{MoF}_4\text{NH}$ . The excess of solvent was distilled from the non-volatile solid. The IR spectrum of the solid (Fig.4.6) showed peaks assignable to coordinated MeCN,  $\nu(\text{N-H})$ ,  $\nu(\text{Mo=N})$  and a single band in the  $\nu(\text{Mo-F})$  region. The solid is believed to be a monomeric 1:1 adduct with MeCN, possessing  $C_{4v}$  symmetry about the metal centre. The adduct did not show appreciable scattering of X-rays to yield a powder pattern.

#### 4.2.7. The Reaction of $\text{MoF}_4\text{NH}$ with Chlorine Trifluoride.

**CAUTION:** To reduce the risk of detonations, chlorine trifluoride ( $\text{ClF}_3$ ) was added as 50mmHg aliquots then allowed to stand at room temperature for five minutes. The volatiles were then removed with dynamic vacuum before charging the FEP tube with a fresh aliquot. After five such additions, 50mmHg of  $\text{ClF}_3$  had been condensed into the tube and allowed to warm to room temperature. On contact with brown solid on the tube wall red droplets formed. Adding 100mmHg

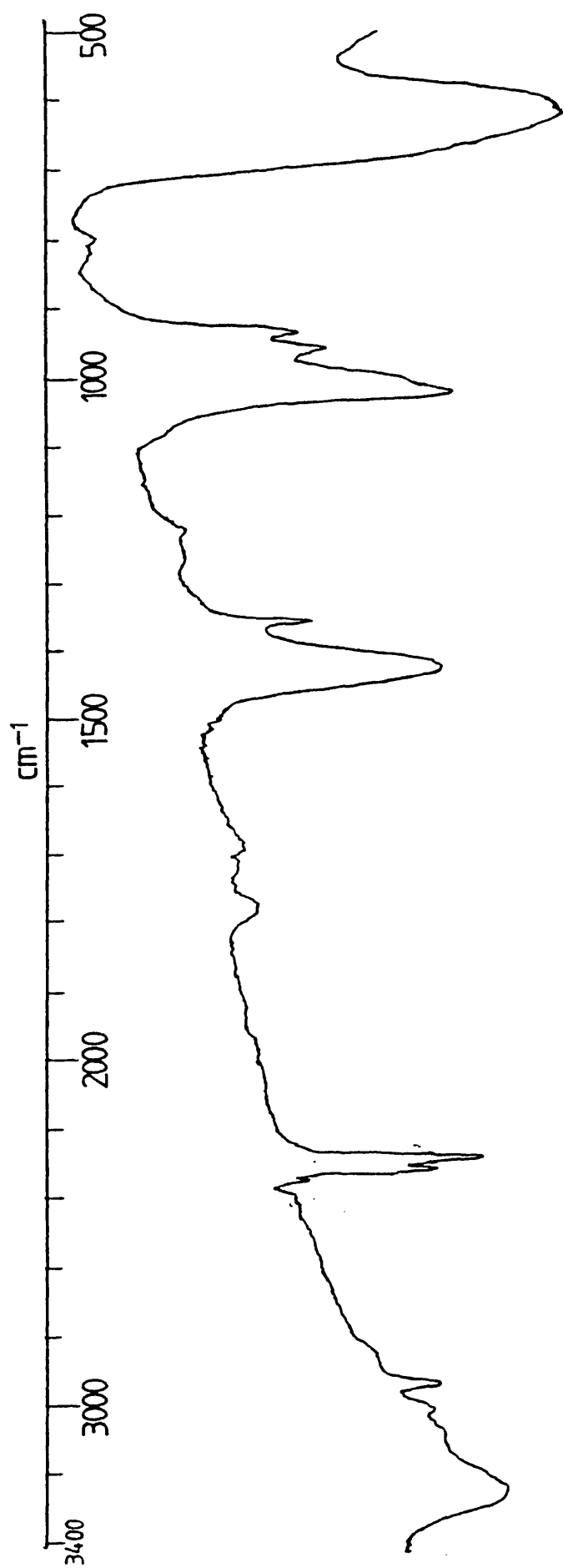


Figure 4.6 IR spectrum of  $\text{MoF}_4 \cdot \text{NH}_3 \cdot \text{MeCN}$

of  $\text{ClF}_3$  gave the same result. When approximately 200 mmHg of  $\text{ClF}_3$  had been condensed into the reaction tube there was a mild detonation as the reaction mixture warmed. The tube walls were not damaged so the volatiles were removed and 150mmHg of  $\text{ClF}_3$  was condensed onto the solid and left to stand at room temperature overnight, forming an orange oil. Removal of the volatile components left behind a non-volatile, white solid. IR spectra of the volatiles showed  $\text{MoF}_6$  and  $\text{ClF}_3$  to be present.

The IR spectrum of the white solid (Fig.4.7) is very simple, showing only 4 well defined bands, assignable to  $\nu(\text{N-H})$ ,  $\nu(\text{Mo=N})$  and  $\nu(\text{Mo-F})$  at 3290, 1417, 1020 and 645  $\text{cm}^{-1}$ . The solid has a melting point of  $\sim 165^\circ\text{C}$  and produces an X-ray powder pattern (Table 4.1) that is different from that of  $\text{MoOF}_4$ , which is frequently formed if traces of moisture get into reaction tubes. Despite the solid's relatively low melting point, it does not possess a volatility suitable for a mass spectrum to be obtained. The white solid is air sensitive becoming yellow as exposure time increases. The solid is slightly soluble in AHF. However, crystals grown from a saturated solution were either too small or twinned, and proved unsatisfactory for X-ray diffraction study.

#### 4.3 Discussion

A major practical difficulty, preventing full characterisation of the products  $\text{MF}_5\text{NCO}$  ( $\text{M} = \text{Mo}, \text{W}$ ) and  $\text{MoF}_4\text{NH}$ , was the encapsulation of  $\text{Me}_3\text{SiF}$  within the solid products. Encapsulation of  $\text{Me}_3\text{SiF}$  in  $\text{WF}_4\text{NH}$  was previously reported by Winfield et al<sup>(5)</sup> and was observed in the formation of  $\text{MoF}_4\text{NH}$ . Similarly, samples of  $\text{MF}_5\text{NCO}$  ( $\text{M} = \text{Mo}, \text{W}$ ) we sent for analysis were found to have traces of  $\text{Me}_3\text{SiF}$  present, producing inconsistent results for several batches.



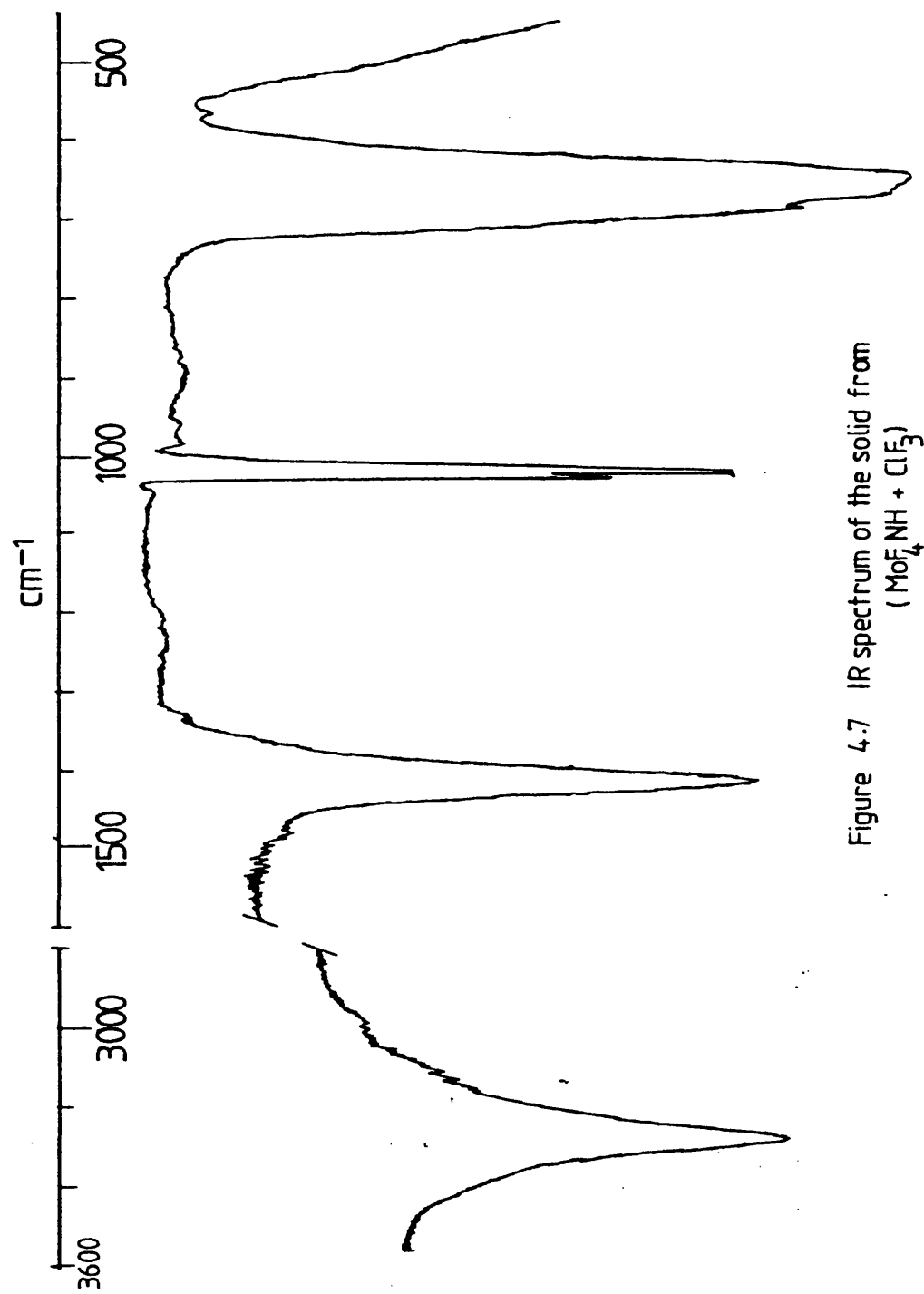
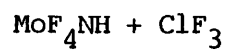


Figure 4.7 IR spectrum of the solid from  
( $\text{MoF}_4$ )<sub>4</sub>NH +  $\text{ClF}_3$

Table 4.1 X-ray powder pattern of the white solid formed from



$\sin^2\theta$	d (Å)	I/I <sup>0</sup>
0.0205	5.39	55
0.0228	5.11	50
0.0241	4.97	80
0.0324	4.28	5
0.0398	3.87	100
0.0448	3.64	40
0.0467	3.57	40
0.0750	2.82	20
0.0792	2.74	30
0.0845	2.65	10
0.0901	2.57	10
0.0958	2.49	10
0.1015	2.42	10
0.1121	2.30	35
0.1229	2.20	25
0.1291	2.15	27
0.1486	2.00	25
0.1592	1.93	37
0.1649	1.90	10
0.1808	1.81	10
0.1891	1.77	15
0.1942	1.75	15
0.2094	1.69	17
0.2153	1.66	10
0.2300	1.61	9
0.2491	1.55	17
0.2571	1.52	10
0.2648	1.50	5
0.2735	1.47	5
0.2806	1.46	5

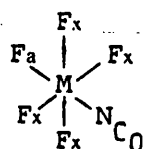
The formation of the pentafluoroisocyanates  $\text{MF}_5\text{NCO}$  ( $\text{M} = \text{Mo}, \text{W}$ ) can only be inferred from the IR spectra of the two solids. Both compounds were insoluble in a wide range of solvents and possess no appreciable volatility, thus preventing characterisation at present by mass and  $^{19}\text{F}$  nmr spectroscopy, and of obtaining crystal structures. The IR spectra of both  $\text{MoF}_5\text{NCO}$  and  $\text{WF}_5\text{NCO}$  are similar, showing intense  $\nu_{\text{as NCO}}$  bands at 2220, 2150  $\text{cm}^{-1}$  and 2240, 2160  $\text{cm}^{-1}$  respectively, lower in strength than the  $\nu_{\text{as}}$  bands found in  $\text{SF}_5\text{NCO}$  (2276  $\text{cm}^{-1}$ )<sup>(62)</sup> and  $\text{TeF}_5\text{NCO}$  (2295  $\text{cm}^{-1}$ )<sup>(63)</sup> as a result of  $d_{\pi}-p_{\pi}$  overlap between the metal and nitrogen of the  $-\text{NCO}$  group. Peaks at 1415 and 1405  $\text{cm}^{-1}$  are tentatively assigned to the  $\nu_{\text{s NCO}}$  modes for  $\text{WF}_5\text{NCO}$  and  $\text{MoF}_5\text{NCO}$ . In the M-F stretching region the Mo-F stretches are at slightly higher frequencies than the W-F stretch modes:

$\nu(\text{Mo-F})$ [ $\text{MoF}_5\text{NCO}$ ]	770, 670 and 610 $\text{cm}^{-1}$
$\nu(\text{W-F})$ [ $\text{WF}_5\text{NCO}$ ]	760, 635, 600 and 535 $\text{cm}^{-1}$

The remaining bands are unassigned excepting the medium strength bands at approximately 1025  $\text{cm}^{-1}$  in both compounds, which were assigned to  $\nu(\text{M=O})$  of oxyfluoride impurities resulting from the onset of hydrolysis.

Neither of the spectra exhibit bands associated with bridging fluorine-atom stretches, indicating that in the solid state both compounds exist as monomeric systems. Both  $\text{MoF}_5\text{NCO}$  and  $\text{WF}_5\text{NCO}$  are believed to adopt a pseudo-octahedral geometry with  $C_{4v}$  symmetry about the central metal atom. The isocyanato group would be expected to exert a trans influence upon the apical fluorine atom ( $\text{F}_a$ ), such that an  $\text{AX}_4$  type spectrum would be observed in a  $^{19}\text{F}$  nmr spectrum. Simil-

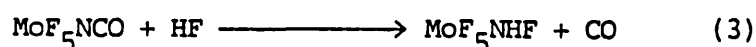
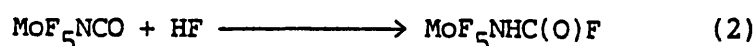
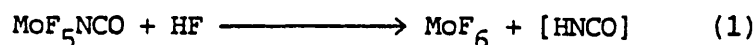
arly , in the solid state the bond lengths of  $F_a-M$  should be longer than the terminal ,  $F_x-M$  , bonds.

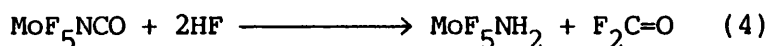


$M = Mo, W$

The reactivity of  $WF_5NCO$  towards trifluoroacetic acid was examined. Clifford et al<sup>(65)</sup> has treated  $SF_5NCO$  with certain carboxylic acids to form the corresponding N-pentafluorosulphur amides with loss of  $CO_2$ . The reaction of  $WF_5NCO$  with TFA proceeds slowly to form a white solid and  $CO_2$ . However , the reaction is not reproducible. The IR spectrum of the solid matches some of the features expected for  $WF_5NHC(O)CF_3$ ; the  $\nu(C=O)$  and  $\nu(N-H)$  amide stretching frequencies at  $1700$  and  $1420\text{ cm}^{-1}$ , and the  $\nu(CF_3)$  mode at  $1160\text{ cm}^{-1}$  are shifted to frequencies slightly lower than those measured for 2,2,2-tri-fluoroacetamide. However , the absence of  $\nu(N-H)$  in the  $3200-3000\text{ cm}^{-1}$  region and the presence of a  $\nu(W-F)$  band at  $810\text{ cm}^{-1}$ , higher in energy than expected for a terminal fluorine bond , place some doubt on the identity of the product. The absence of the  $\nu(N-H)$  band in a T.M. imido compound has been observed for the species  $[MoCl_2(NH)O(EtPh_2PO)_2]^{(75)}$ , indicating that  $WF_5NHC(O)CF_3$  is the most likely product of the reaction. The lack of further corroborating evidence does not rule out an impure oxyfluoride as the product.

Reacting  $MoF_5NCO$  with AHF presents several plausible reaction schemes :-



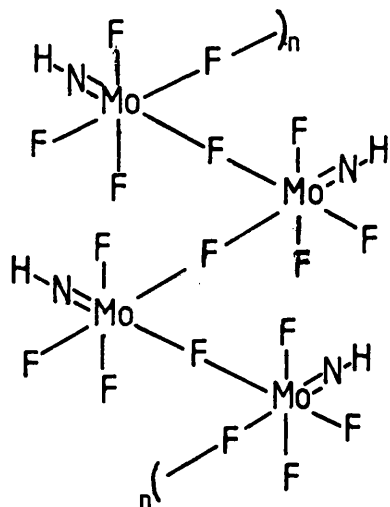


Scheme (2) can be eliminated as it produces no volatile compounds, whereas the observed reaction produces gas with an IR spectrum showing peaks at 1935, 1230, 1025, 815 and  $770\text{cm}^{-1}$ . The IR spectrum of  $\text{HNCO}^{(66)}$  has two bands assigned to  $\nu(\text{NCO})$  at 1922 and  $487\text{cm}^{-1}$ . The absence of a band at  $487\text{cm}^{-1}$  and of evidence of  $\text{MoF}_6$  eliminates scheme (1). Similarly, the absence of the  $\nu(\text{CO})$  stretch of CO, reported at  $2138\text{cm}^{-1(67)}$ , eliminates scheme (3). The IR spectrum of  $\text{F}_2\text{C=O}$  has six IR active bands<sup>(68)</sup>: 1928, 1249, 965, 774, 626 and  $584\text{cm}^{-1}$ . Although agreement with the actual spectra is not identical, scheme (4) appears the most likely reaction pending full characterisation of both the gas and oil produced.

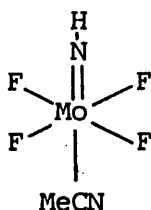
Unlike the reaction of  $\text{WF}_6$  with hexamethyldisilazane<sup>(5)</sup>, the reaction with  $\text{MoF}_6$  also produces a small quantity of  $\text{MoF}_5$  as well as the brown  $\text{MoF}_4\text{NH}$ . Several assignments of the  $\nu(\text{Mo=N})$  mode in IR spectra have been reported for  $[\text{MoNCl}_4]^-$  ions at  $1054\text{--}1060\text{cm}^{-1(12,14)}$  and for  $\text{MoF}_3\text{N}$  ( $1045\text{cm}^{-1(10)}$ ) and  $[\text{MoNCl}_4]_2$  ( $1022\text{cm}^{-1(22)}$ ). Therefore, assignment of  $\nu(\text{Mo=N})$  in  $\text{MoF}_4\text{NH}$  at  $1015\text{cm}^{-1}$  does not seem unreasonable.

The  $(=\text{NH})$  group is isoelectronic with  $(=\text{O})$ , so structural similarities are expected between  $\text{MoF}_4\text{NH}$  and  $\text{MoOF}_4$ . Fluorine bridging is observed in  $\text{MoF}_4\text{NH}$ , presumably this occurs as cis-fluorine bridged chains (Fig.4.8), similar to those reported for  $\text{MoOF}_4^{(69)}$ .

Figure 4.8 Proposed structure of  $\text{MoF}_4\text{NH}$



The bridging fluorine bond is sufficiently weak to allow breakage and formation of a pseudo-octahedral 1:1 acetonitrile adduct,  $\text{MoF}_4\text{NH} \cdot \text{MeCN}$ . The IR spectrum of the solid (Fig.4.6) shows peaks corresponding to coordinated MeCN<sup>(70)</sup> at 2320, 2280, 1355 and 955  $\text{cm}^{-1}$  assigned to  $(\nu_3 + \nu_4)$ ,  $\nu(\text{C}=\text{N})$ ,  $\nu_3$  and  $\nu_4$ . The disappearance of the bridging fluorine stretch and simplification of the band pattern in the  $\nu(\text{Mo}-\text{F})$  region are in agreement with a 1:1 adduct being formed:



The reaction of chlorine trifluoride with  $\text{MoF}_4\text{NH}$  is surprising in that the IR spectrum of the white solid formed indicates that the  $(=\text{NH})$  moiety has remained intact. The  $\text{Mo}=\text{N}$  stretching vibration, however, is shifted to a slightly lower frequency (1423-1417  $\text{cm}^{-1}$ ). The simplification of the spectrum in the  $\nu(\text{Mo}-\text{F})$  region indicates a  $C_{4v}$ , or lower, type symmetry about the central metal atom. From analysis of the X-ray powder pattern (Table 4.1) the white solid is believed to possess a monoclinic space group in the solid state. In the absence of more data the identity of the white solid remains unassigned.

# Chapter Five

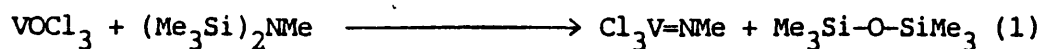
The reaction of  $\text{Me}_3\text{Si}(\text{NCO})$  and  
 $\text{Me}_3\text{Si}(\text{N}_3)$  with  $\text{WOF}_4$

## 5.1 Introduction

Major sources of impurities in inorganic fluorine systems are moisture and air , usually introduced via leaking apparatus. Whilst large volumes of moisture results in formation of hydrolysed species trace quantities of air or moisture can lead to the formation of oxy-fluoride species  $\text{MOF}_4$  (M= Mo,W).

It was decided to examine the reactivity of T.M. oxyfluorides towards trimethylsilyl reagents , to determine what end products could be expected with oxyfluoride impurities present in the hexa-fluoride systems. The reactions of several T.M. oxychlorides with both TMS derivatives and amines have been reported , and invariably result in the formation of a nitrogen-containing derivative.

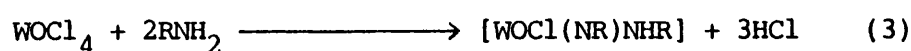
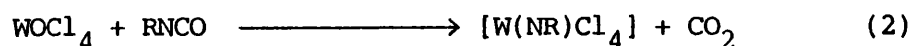
The reaction of a 1:1 mixture of  $\text{VOCl}_3$  and hexamethyldisilazane ,  $(\text{Me}_3\text{Si})_2\text{NH}$  , is reported to yield a 1:1 adduct species ,  $\text{VOCl}_3 : \text{HN}(\text{SiMe}_3)_2$  <sup>(76)</sup> whereas, if the  $(\text{Me}_3\text{Si})_2\text{NH}$  is added in excess, the silylated compound,  $(\text{Me}_3\text{SiO})_3\text{V}(\text{NSiMe}_3)$ , <sup>(77)</sup> is formed. When  $\text{VOCl}_3$  is allowed to react with the N-methyl disilazane ,  $(\text{Me}_3\text{Si})_2\text{NMe}$  , <sup>(78)</sup> there is formation of an imido chloride ,  $\text{Cl}_3\text{V}(\text{NMe})$  , (eqn.1) :-



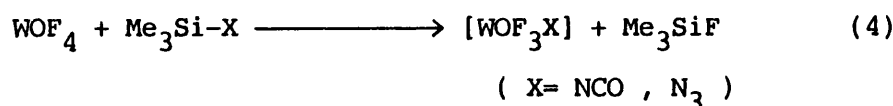
Dilworth et al <sup>(75)</sup> followed the reaction of  $\text{MoOCl}_3$  with TMS- $\text{N}_3$  with addition of a tertiary phosphine oxide and isolated the mixed oxo- , imido-chloride  $[\text{MoCl}_2(\text{NH})\text{O}(\text{EtPh}_2\text{PO})_2]$  , containing a non-linear Mo-N-H bond in the solid state.



The reaction of tungsten oxychloride ( $\text{WOCl}_4$ ) with non-TMS containing compounds such as  $\text{RNCO}$  (  $\text{R} = \text{Et, Ph}$  )<sup>(48)</sup> and  $\text{RNH}_2$  (  $\text{R} = \text{Me, Et}$  )<sup>(79)</sup> also results in the formation of imido chloride species (eqns. 2 and 3) :-



The reaction of tungsten oxyfluoride ( $\text{WOF}_4$ ) with  $\text{Me}_3\text{Si-X}$  (  $\text{X} = \text{NCO, N}_3$  ) is believed to occur according to the equation (4) below , to form a formal mixed oxo- , amido fluoride compound.



Whereas the reaction between  $\text{WF}_6$  and  $\text{TMS-N}_3$ <sup>(30)</sup> produces an explosive azide fluoride , surprisingly, the  $\text{WOF}_3\text{N}_3$  believed formed appears stable at low temperatures , decomposing at  $1^\circ\text{C}$  to form a non-explosive , uncharacterised species. The yellow  $\text{WOF}_3\text{NCO}$  produced using  $\text{TMS-NCO}$  has been characterised by its mass and IR spectra , and is found to decompose , with liberation of  $\text{CO}_2$  , in  $\text{MeCN}$ .

## 5.2 Experimental

### 5.2.1. The Reaction of Trimethylsilylisocyanate with $\text{WOF}_4$ :-

An equimolar quantity of trimethylsilylisocyanate ( 0.34 : mmoles ) was distilled on to a mixture of Genetron and  $\text{WOF}_4$  ( 0.34

mmoles ), and the reaction mixture allowed to warm to room temperature. There was gradual gas evolution and precipitation of a fine white solid. The solid progressively darkened until the solution became clear and faintly yellow , with an insoluble light yellow solid product. Gas IR spectra of the volatile components showed the presence of Genetron and  $\text{Me}_3\text{SiF}$ . After allowing the reaction mixture to stand at room temperature for four hours , with no sign of further reaction , the reaction tube was gently warmed without solvation of the yellow solid.

The excess reagents and solvent were distilled from the reaction vessel without retention of the yellow colouration , or subsequent precipitation of more solid , to leave the non-volatile yellow solid ,  $\text{WOF}_3\text{NCO}$ .

The pale solid begins to decompose at approximately  $95^\circ\text{C}$  and did not produce an X-ray powder pattern. The mass spectrum of the solid (Fig.5.1) shows a parent ion peak and fragmentation species expected for  $\text{WOF}_3\text{NCO}$ .

70 eV m+/e (184W,%):    299 ( $\text{WOF}_3\text{NCO}^+$ ,1.8%); 280 ( $\text{WOF}_2\text{NCO}^+$ ,1.9%);  
                               257 ( $\text{WOF}_3^+$ ,100%); 241 ( $\text{WF}_3^+$ ,5.1%);  
                               238 ( $\text{WOF}_2^+$ ,8.2%); 222 ( $\text{WF}_2^+$ ,6.9%);  
                               219 ( $\text{WOF}^+$ ,7.0%); 203 ( $\text{WF}^+$ ,8.5%);  
                               200 ( $\text{WO}^+$ ,1.9%); 184 ( $\text{W}^+$ ,4.1%);  
                               42 ( $\text{NCO}^+$ ,75.2%)

The IR spectrum of  $\text{WOF}_3\text{NCO}$  (Fig.5.2) shows peaks attributable to  $\nu_{\text{as NCO}}$  ,  $\nu(\text{W=O})$  and  $\nu(\text{W-F})$  in the 2200 , 1025 and 600  $\text{cm}^{-1}$  regions. Encapsulation of traces of  $\text{Me}_3\text{SiF}$  within the yellow solid

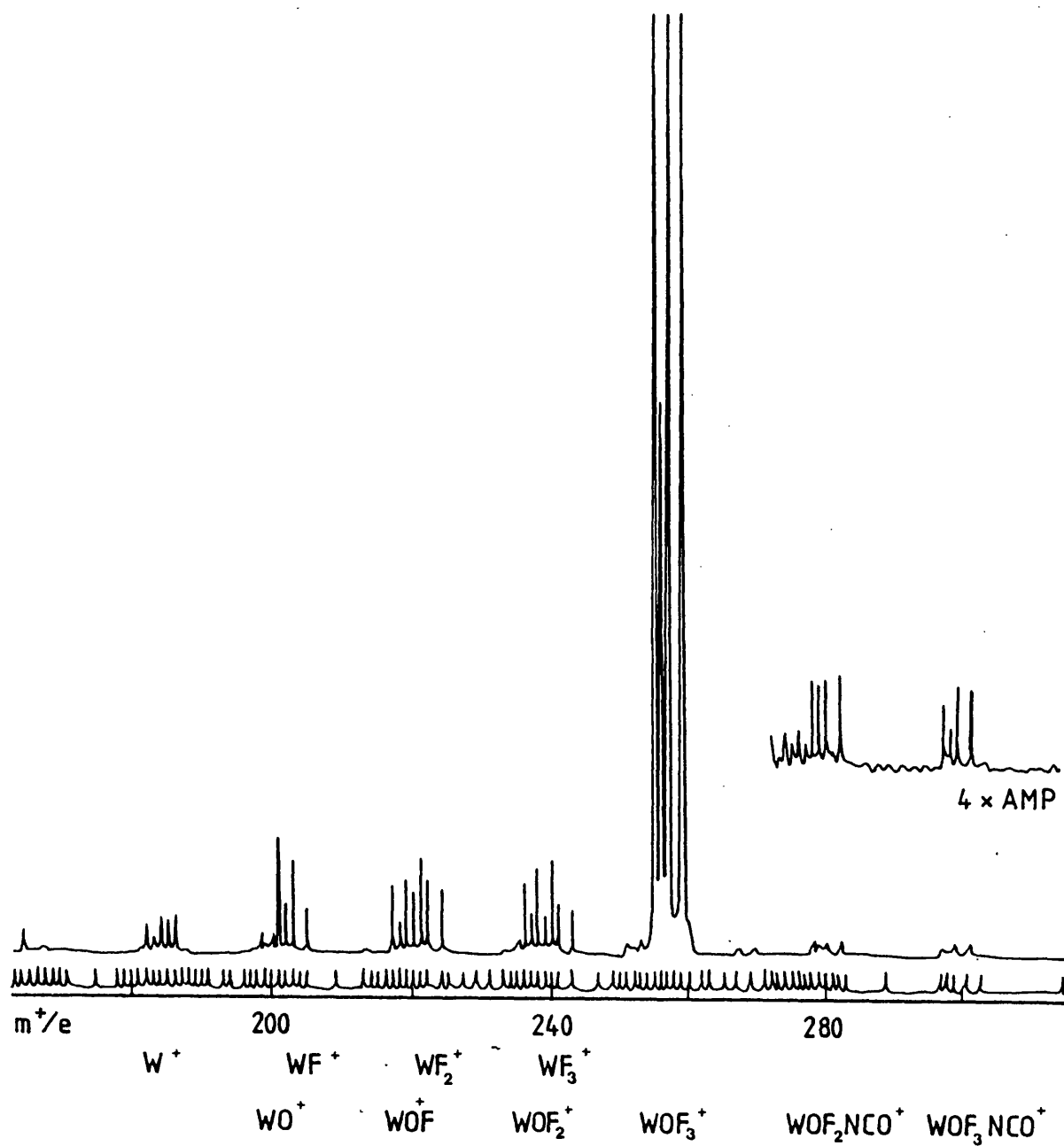


Figure 5.1 Mass spectrum of  $\text{WOF}_3\text{NCO}$

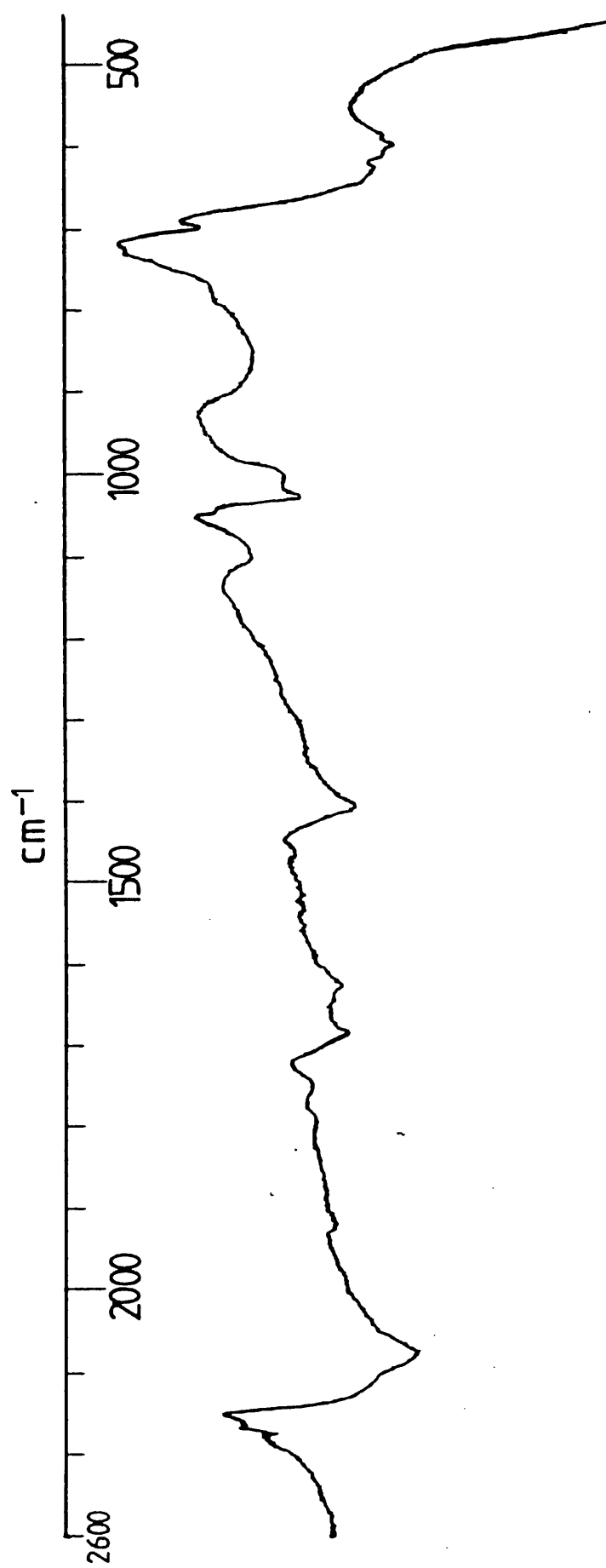


Figure 5.2 IR spectrum of  $\text{WOF}_3\text{-NCO}$

prevented both determination of elemental analysis and the percentage yield of the reaction , believed to be approximately 90%. Adding acetonitrile to the yellow  $\text{WOF}_3\text{NCO}$  results in decomposition with liberation of  $\text{CO}_2$  gas.

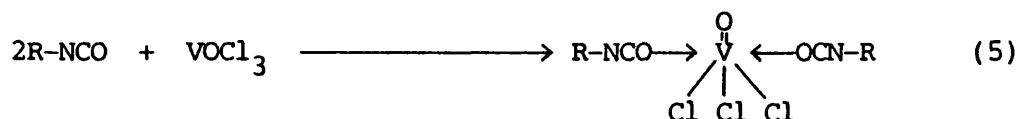
#### 5.2.2. The Reaction of Trimethylsilylazide with Tungsten Oxyfluoride.

Because of the risk of detonations the preparation was carried out on a small scale. Tetrafluorotungsten oxide ( $\text{WOF}_4$ ) is not soluble in Genetron , but Genetron was distilled onto  $\text{WOF}_4$  (0.48 mmoles) to act as a reaction moderator. A slight excess of trimethylsilylazide ,  $\text{Me}_3\text{SiN}_3$  ,(0.52 mmoles) was distilled on to the reaction mixture. There was formation of a yellow solution and solid. The solid darkened as the temperature was raised to become orange and gas was evolved. The whole mixture was frozen at  $-196^\circ\text{C}$  and then left overnight at  $-76^\circ\text{C}$ . The orange solid could be maintained at  $-25^\circ\text{C}$  without apparent decomposition. A gas IR spectrum of the volatiles at low temperature showed the presence of Genetron ,  $\text{Me}_3\text{SiN}_3$  and  $\text{Me}_3\text{SiF}$ . The solvent and volatile products were slowly distilled at  $-25^\circ\text{C}$  from the vessel , to leave the non-volatile orange solid behind. When warmed to  $1^\circ\text{C}$  , the orange solid decomposed to give a green solid. A gas-phase IR spectrum of the volatile components showed only traces of Genetron and  $\text{Me}_3\text{SiF}$ . The green solid begins decomposing further at approximately  $70^\circ\text{C}$  and has yet to be characterised.

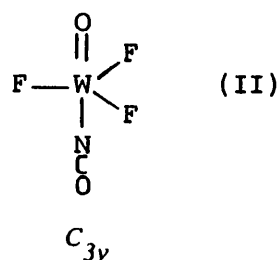
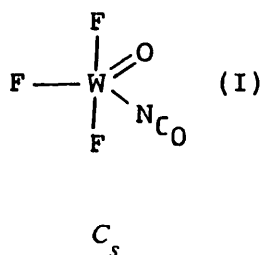
### 5.3 Discussion

The reaction of  $\text{Me}_3\text{SiN}_3$  and  $-\text{NCO}$  with  $\text{WOF}_4$  is believed to proceed in much the same way as the analogous reactions with the T.M. hexafluorides  $\text{MF}_6$  (  $\text{M} = \text{Mo}, \text{W}$  ), with exchange of a fluorine atom for the azido or isocyanato group.

The  $\text{WOF}_3\text{NCO}$  produced did not possess sufficient solubility in Genetron to obtain a  $^{19}\text{F}$  nmr spectrum. Unlike the reaction of  $\text{WOCl}_4$  with an isocyanate ( $\text{RNCO}$ ) (eqn.2)<sup>(48)</sup> and the reaction of  $\text{VOCl}_3$  with  $\text{PhNCO}$  <sup>(80)</sup>( with formation of a 2:1 adduct species bonded via the isocyanato oxygen (eqn.5) ) ,  $\text{WOF}_4$  reacts with  $\text{TMS-NCO}$  with coordination of the  $\text{NCO}$  group via the nitrogen atom to the T.M. centre and retention of the oxo-ligand. Liberation of  $\text{TMS-F}$  occurs.



The IR spectrum (Fig.5.2) of  $\text{WOF}_3\text{NCO}$  does not possess a band in the region associated with a bridging fluorine atom bonded to tungsten (  $500 \text{ cm}^{-1}$  ). This suggests that  $\text{WOF}_3\text{NCO}$  is monomeric in the solid state. Two plausible structures ( I,II ) for monomeric  $\text{WOF}_3\text{NCO}$  are shown below :-



In both cases the major assumption is that the W-N-C-O linkage is linear. Bearing this assumption in mind and treating the -NCO groups as one whole unit, the number of IR active bands for both I and II can be calculated using the equation (6):-

$$n(\gamma_i) = 1/h \sum_R g_R \cdot \chi(R) \cdot \chi'(R) \quad (6)$$

where

$n(\gamma_i)$  = the number of each type of symmetry species

$h$  = the order of the point group

$g_R$  = the number of operations in each class

$\chi'(R)$  = the characters of the irreducible representations

$\chi(R)$  = the character of the reducible representation

The values for  $h$ ,  $g_R$  and  $\chi'(R)$  for each symmetry point group can be obtained from Group Theory tables<sup>(81)</sup>. The reducible representation  $\chi(R)$ , can be calculated for Cartesian coordinates by multiplying the number of atoms unshifted by a symmetry operation by  $(+1 + 2\cos\theta)$ , and for internal coordinates by using the number of unshifted coordinates.

For structure I the Cartesian analysis produces the total number of vibrational bands ;-

$$\left[ 3n-6 = 8 A' + 4 A'' \right]$$

Both the  $A'$  and  $A''$  operations possess IR activity, so a total of 12 bands are expected in the IR spectrum. Using internal coordinates the number of W-F stretches can be calculated:-

$$\left[ \text{ind. (W-F)} = 2 A' + A'' \right]$$

Thus 3 W-F bands are expected to appear in the IR spectrum. The same treatments applied to structure II yield the expected total vibrational bands and W-F stretches:-

$$\Gamma_{3n-6} = 4 A' + 4 E$$

$$\Gamma_{\text{int. (W-F)}} = A' + E$$

Both  $A'$  and  $E$  operations are IR active, so that for structure II only two W-F stretching modes would be expected. The IR spectrum of  $\text{WOF}_3\text{NCO}$  has three bands in the  $\nu(\text{W-F})$  region at 705, 635 and  $600\text{ cm}^{-1}$  respectively, indicating structure I to be the most likely structure in the solid state.

The  $\nu_{\text{as NCO}}$  peak ( $2170\text{ cm}^{-1}$ ) is shifted by approximately  $100\text{ cm}^{-1}$  and the peak at  $1410\text{ cm}^{-1}$  is tentatively assigned to  $\nu_{\text{s NCO}}$ . The  $\text{W=O}$  stretching frequency at  $1020\text{ cm}^{-1}$  is split into a doublet, possibly as a result of solid state effects.

The weak band at  $1105\text{ cm}^{-1}$  is in the region usually associated with  $\nu(\text{W=N})$  and, although not emphatically assigned, could be the result of resonance between the two forms  $\text{M-N=C=O}$  and  $\text{M}^+=\text{N}^+=\text{C=O}$ , which could also explain the splitting of the  $\text{W=O}$  stretch. The two weak bands at  $1690$  and  $1635\text{ cm}^{-1}$  and the broad band centred at  $850\text{ cm}^{-1}$  remain unassigned.

The mass spectrum (Fig.5.1) of  $\text{WOF}_3\text{NCO}$  shows no sign of associated species, only the monomeric parent ion. This is further evidence of a non-fluorine bridged compound as the product. The



decomposition product formed upon addition of MeCN , with liberation of CO<sub>2</sub>, so far remains uncharacterised.

The reactions of T.M. chlorides with azides have been documented ; Chatt and Dilworth<sup>(82)</sup> carried out the reaction of MoCl<sub>4</sub>L<sub>n</sub> with TMS-N<sub>3</sub> (eqn.7) to form MoCl<sub>3</sub>NL.



Dehnicke <sup>(9)</sup> has prepared VOCl<sub>2</sub>N<sub>3</sub> from VOCl<sub>3</sub> using ClN<sub>3</sub>. The VOCl<sub>2</sub>N<sub>3</sub> can lose N<sub>2</sub> and Cl<sub>2</sub> to form VON.

At low temperatures the reaction between TMS-N<sub>3</sub> and WOF<sub>4</sub> is believed to occur in the same manner as the isocyanate reaction , with liberation of Me<sub>3</sub>SiF and formation of WOF<sub>3</sub>N<sub>3</sub>. The oxo- azide believed formed is stable against decomposition up to 1<sup>0</sup>C , whereupon it decomposes with liberation of a non-IR active gas to form an uncharacterised solid containing W-F bonds.

# Chapter Six

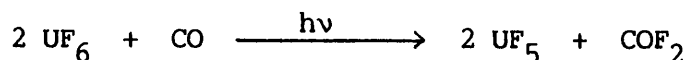
The reaction of Tetrakis-  
trimethylsilylhydrazine with  $\text{MoF}_6$  ,  
 $\text{WF}_6$  and  $\text{ReF}_6$

## 6.1 Introduction

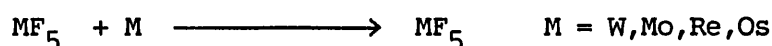
The preparation of the transition metal pentafluorides,  $\text{MF}_5$  ( $\text{M} = \text{Mo}, \text{Re}, \text{W}$ ), can be achieved by several methods. These may be separated into two broad categories; (i) the fluorination of the transition metal carbonyl and, more commonly, (ii) the reduction of the transition metal hexafluoride.

Peacock<sup>(83)</sup> used the flow fluorination of molybdenum hexacarbonyl at low temperatures to form a green solid of composition  $\text{Mo}_2\text{F}_9$ , from which the pentafluoride was sublimed to leave behind a non-volatile solid, with an analysis corresponding to  $\text{MoF}_4$ .

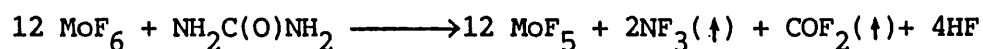
The reduction of a hexafluoride to give the pentafluoride is usually the cleaner reaction, and thus preferable for routine preparative work. Early methods involved reduction of the hexafluoride by the hexacarbonyl, or powdered metal, as in the reduction of molybdenum hexafluoride<sup>(84)</sup>. The reduction of  $\text{MoF}_6$  by phosphorus trifluoride ( $\text{PF}_3$ )<sup>(85)</sup> is a particularly clean method of preparing  $\text{MoF}_5$ , since both the  $\text{PF}_3$  and  $\text{PF}_5$  produced in the reaction are gaseous and can be easily removed from the reaction vessel. The reduction of the hexafluorides by powdered silicon metal in anhydrous hydrogen fluoride ( $\text{AHF}$ )<sup>(86)</sup> to yield the pentafluoride is also a clean reaction and works for several transition metal hexafluorides,  $\text{MF}_6$  ( $\text{M} = \text{Mo}, \text{Re}, \text{Os}, \text{U}$ ).  $\text{UF}_5$  can be produced by unique photolytic reductive elimination from  $\text{UF}_6$ <sup>(86)</sup>.



Falconer et al<sup>(87)</sup> used an electrically heated metal filament to produce the pentafluorides from the hexafluorides of several transition metals , the pentafluoride being deposited on the cooled reaction-vessel walls.



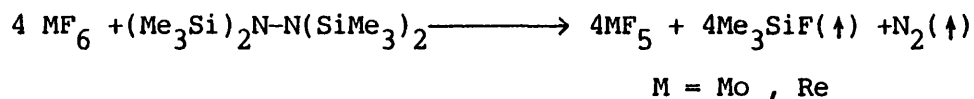
Recently the reduction of  $\text{MoF}_6$  with urea  $(\text{NH}_2\text{C}(\text{O})\text{NH}_2)^{(88)}$  has been used to prepare  $\text{MoF}_5$ . However , there is a difficulty with this method in that unless the ratio of hexafluoride to urea is greater than , or equal to , 12:1 , there is a high risk of forming partially fluorinated , unstable compounds.



Tetrakis trimethylsilylhydrazine  $((\text{Me}_3\text{Si})_2\text{N}-\text{N}(\text{SiMe}_3)_2)$  has been used as a reagent for the synthesis of  $\mu$ -dinitrogen complexes , or as a homogenous one-electron reducing agent<sup>(89)</sup>. When the tetrakis trimethylsilylhydrazine (TTSH) is allowed to react with  $\text{NbCl}_5$  and tetrahydrofuran (thf) in dichloromethane , the dinitrogen complex  $[\{\text{NbCl}_3(\text{thf})_2\}_2\text{N}_2]$  is formed. However , when TTSH and  $\text{MoCl}_4\text{L}_2$ ,  $\text{WCl}_6$  or  $\text{WOCl}_4$  are mixed in MeCN , there is a one-electron reduction to form  $[\text{MoCl}_3\text{L}_3]$  ,  $\text{WCl}_5$  or  $[\text{WOCl}_3(\text{MeCN})_2]$  (L= MeCN , thf ).

It was decided to carry out the reaction of TTSH with T.M. hexafluorides in an attempt to insert the  $(-\text{NSiMe}_3)$  moiety , to form an imido species. These reactions would be similar to that reported by Dilworth et al<sup>(89)</sup> for the reaction of  $\text{TaCl}_5$  with TTSH. This was not found to be the preferred reaction with the transition metal hexa-

fluorides,  $\text{MF}_6$  (  $\text{M} = \text{Mo, Re, W}$  ). Reaction of a fourfold , or greater , excess of  $\text{MF}_6$  (  $\text{M} = \text{Mo, Re}$  ) with tetrakis-trimethylsilylhydrazine yielded the pentafluoride in approximately 80% yield , together with dinitrogen , trimethylsilyl fluoride(  $\text{TMS-F}$  ) and a dark solid residue thought to consist of lower oxidation state metal fluorides and unreacted TTSH :-



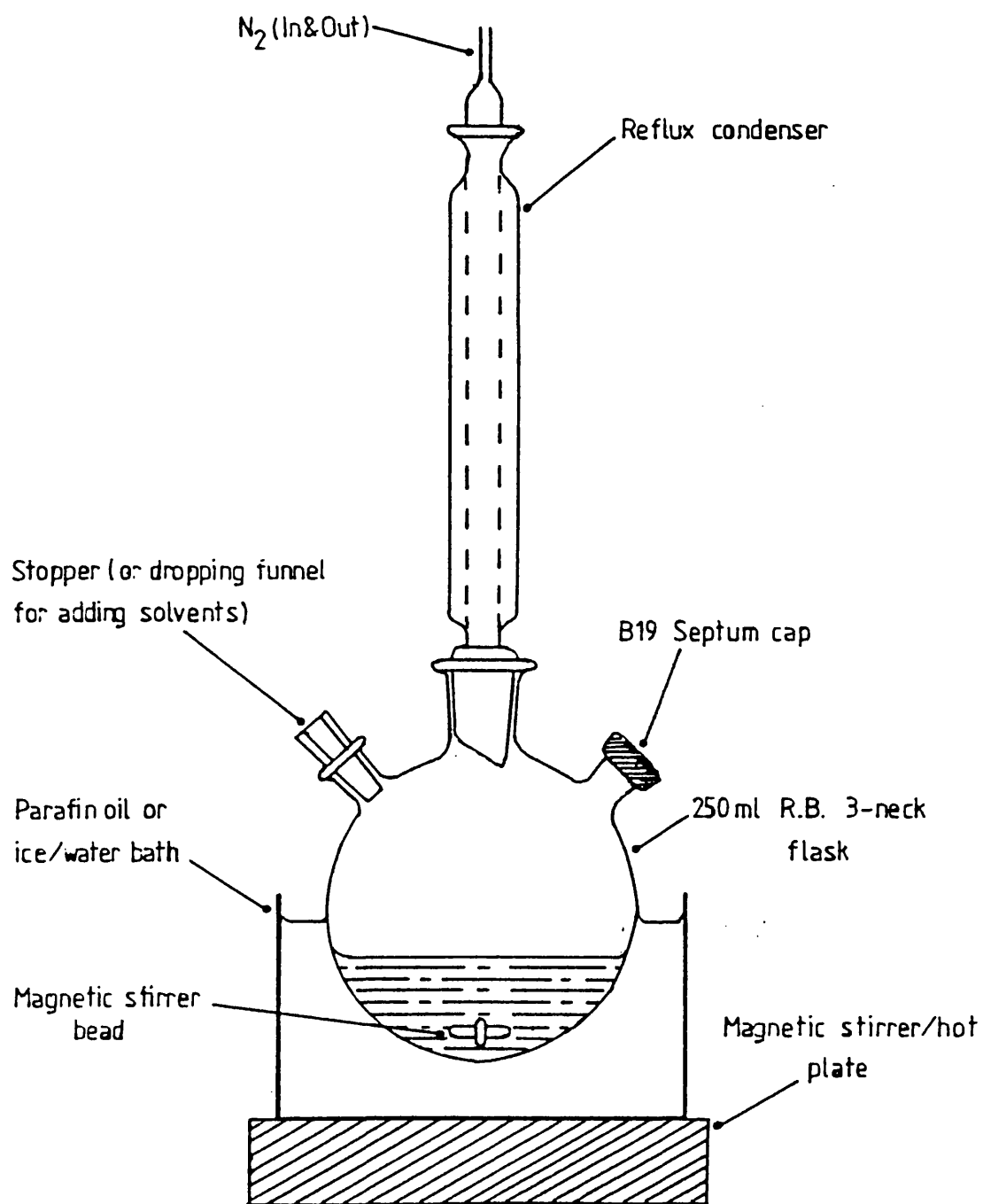
For both  $\text{MoF}_6$  and  $\text{ReF}_6$  the reaction is clean and simple , the pentafluoride being easily sublimed from the dark residue. When  $\text{WF}_6$  is allowed to react with TTSH , there is no reduction to the thermally unstable  $\text{WF}_5$  , but loss of  $\text{TMS-F}$  to form what is believed to be a nitrogen-bridged diazene tungsten fluoride species , bis (tetrafluorotungsten(VI))diazene ,  $[\text{WNF}_4]_2$ .

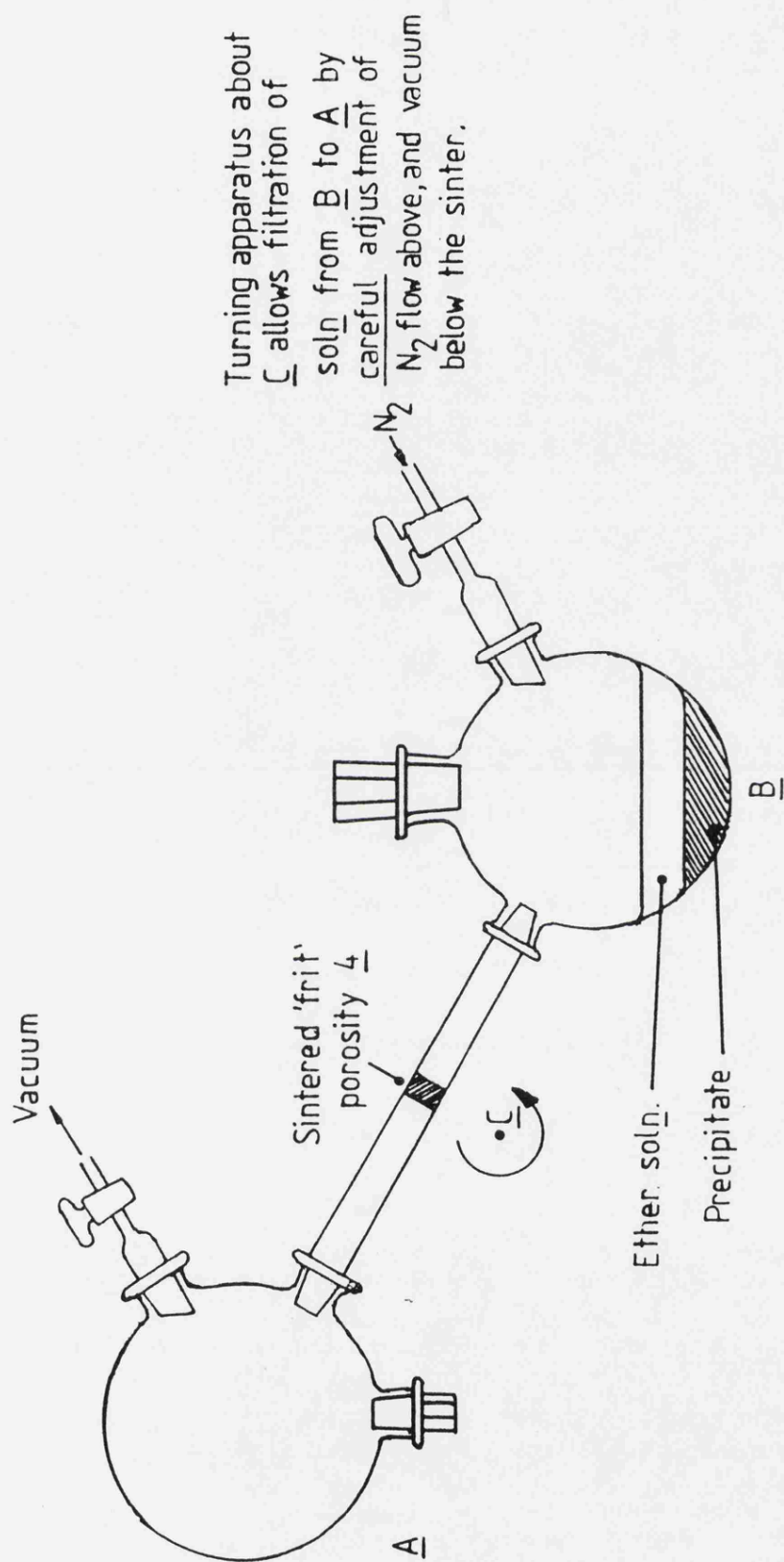
## 6.2 Experimental

### 6.2.1. The Preparation of Tetrakis-Trimethylsilylhydrazine.

Tetrakis-trimethylsilylhydrazine (TTSH) was prepared using a modified version of the method used by Seppelt and Sundermeyer<sup>(90)</sup>. The entire preparation was carried out at approximately 1/20th the scale of the original preparation. It was decided to keep the product of each step of the synthesis in solution , rather than separating products at each stage. This was felt necessary because of the extreme moisture sensitivity of the reagents. The preparation was carried out under nitrogen (Fig.6.1).

Figure 6.1      Apparatus for the preparation of T.T.S.H

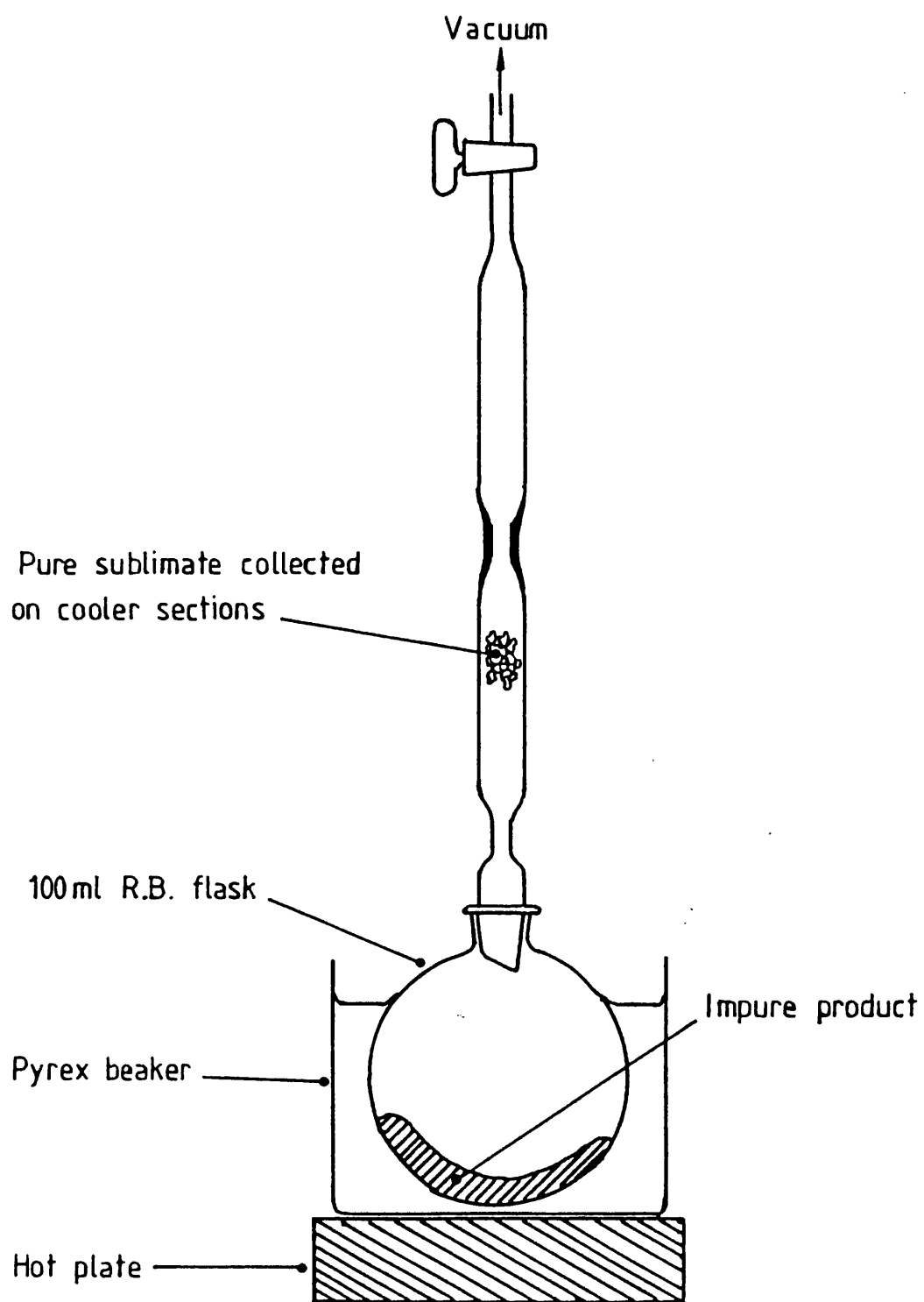




Turning apparatus about C allows filtration of soln from B to A by careful adjustment of  $N_2$  flow above, and vacuum below the sinter.

Figure 6.2 Separation of precipitates: filtration under  $N_2$  T.T.S.H. prep.

Figure 6.3 Sublimation purification of T.T.S.H





Anhydrous hydrazine(46.9 mmols) was added slowly to a stirred ethereal solution of chlorotrimethylsilane( $\text{ClSiMe}_3$ ) (78.5 mmols) and pyridine(92.5 mmols) , and refluxed for 2 days. N-Butyllithium (12.5 mmols) was added to the filtered solution and  $\text{ClSiMe}_3$ (12.5 mmols) was introduced with continued stirring. After 2 hours refluxing the mixture was allowed to cool , after which the  $\text{LiCl}$  formed was filtered (Fig.6.2) from the tris-trimethylsilylhydrazine solution.

$\text{N-BuLi}$ (12.5 mmols) was added to the solution to form the lithium-tris-trimethylsilyl hydrazide , and to this solution bromotrimethylsilane(37.8 mmols) was slowly added. After a 24 hour reflux the mixture was allowed to cool. The residual ether solution was deep yellow , indicative of unreacted  $\text{BuLi}$ . This was neutralised by adding a solution of ethanol in n-heptane , to form the ethoxide as a white precipitate. When all the precipitate had been removed by filtration , the solvent was removed by vacuum distillation to leave a viscous yellow oil. White , waxy crystals were sublimed from the oil with heating at approximately  $65^\circ\text{C}$  under dynamic vacuum (Fig.6.3). The IR and mass spectra of the white crystals agreed with the reported spectra.

#### 6.2.2. The Reaction of Molybdenum Hexafluoride with TTSH.

A large excess of  $\text{MoF}_6$  was distilled onto a solution of TTSH (0.17 mmols) dissolved in Genetron. The mixture was allowed to warm slowly to room temperature. Initially a bright yellow solution was formed , which darkened to an orange solution , with rapid effervescence. The reaction mixture was quenched twice with liquid nitro-

gen (LN) and allowed to warm to room temperature again , whereupon a dark solid precipitated out of the orange solution and settled at the bottom of the reaction vessel. After leaving the reaction mixture to stand at ambient temperature for approximately 1 hour all gas evolution ceased. An IR spectrum of the volatiles from the reaction showed peaks that were assigned to trimethylsilylfluoride ,  $\text{Me}_3\text{SiF}$  , and an unreacted excess of  $\text{MoF}_6$ .

The volatile components were slowly distilled from the reaction mixture to leave the dark solid and an orange oil behind. Careful removal of the volatiles did not result in complete separation of the adsorbed  $\text{MoF}_5$  from the solution of unreacted  $\text{MoF}_6$  ,  $\text{Me}_3\text{SiF}$  and Genetron. Several more distillations reduced the colour of the solution by only a small amount. The orange oil was warmed under dynamic vacuum until there was sublimation of yellow  $\text{MoF}_5$  as an oil further along the reaction tube wall. The dark solid was non-volatile and remained at the bottom of the reaction vessel. When there was no further sublimation the heating was stopped and the yellow oil left to cool under static vacuum. After standing at room temperature for 1 day the oil completely solidified to a lemon-yellow solid. The IR spectrum of this solid (Fig.6.4) showed a sharp peak at  $1035\text{cm}^{-1}$  and two strong bands centred at  $725\text{ cm}^{-1}$  and  $515\text{ cm}^{-1}$  respectively. The sharp peak at  $1035\text{cm}^{-1}$  was assigned to  $\nu(\text{Mo=O})$ , from oxyfluoride impurities in the hexafluoride and the onset of hydrolysis. The bands at  $725$  and  $515\text{cm}^{-1}$  were assigned to  $\nu(\text{Mo-F})$  terminal and  $\nu(\text{Mo-F})$  bridging. The spectrum compared favourably with the IR spectrum of  $\text{MoF}_5$  reported by Paine and Asprey<sup>(91)</sup>. The mass spectrum of the  $\text{MoF}_5$  (Table 6.1) showed molybdenum abundance patterns at  $m^+/e$  values corresponding to  $\text{MoF}_5^+$  , and further fragmentation products , plus doubly charged species. The total yield of  $\text{MoF}_5$  from the initial sublimation

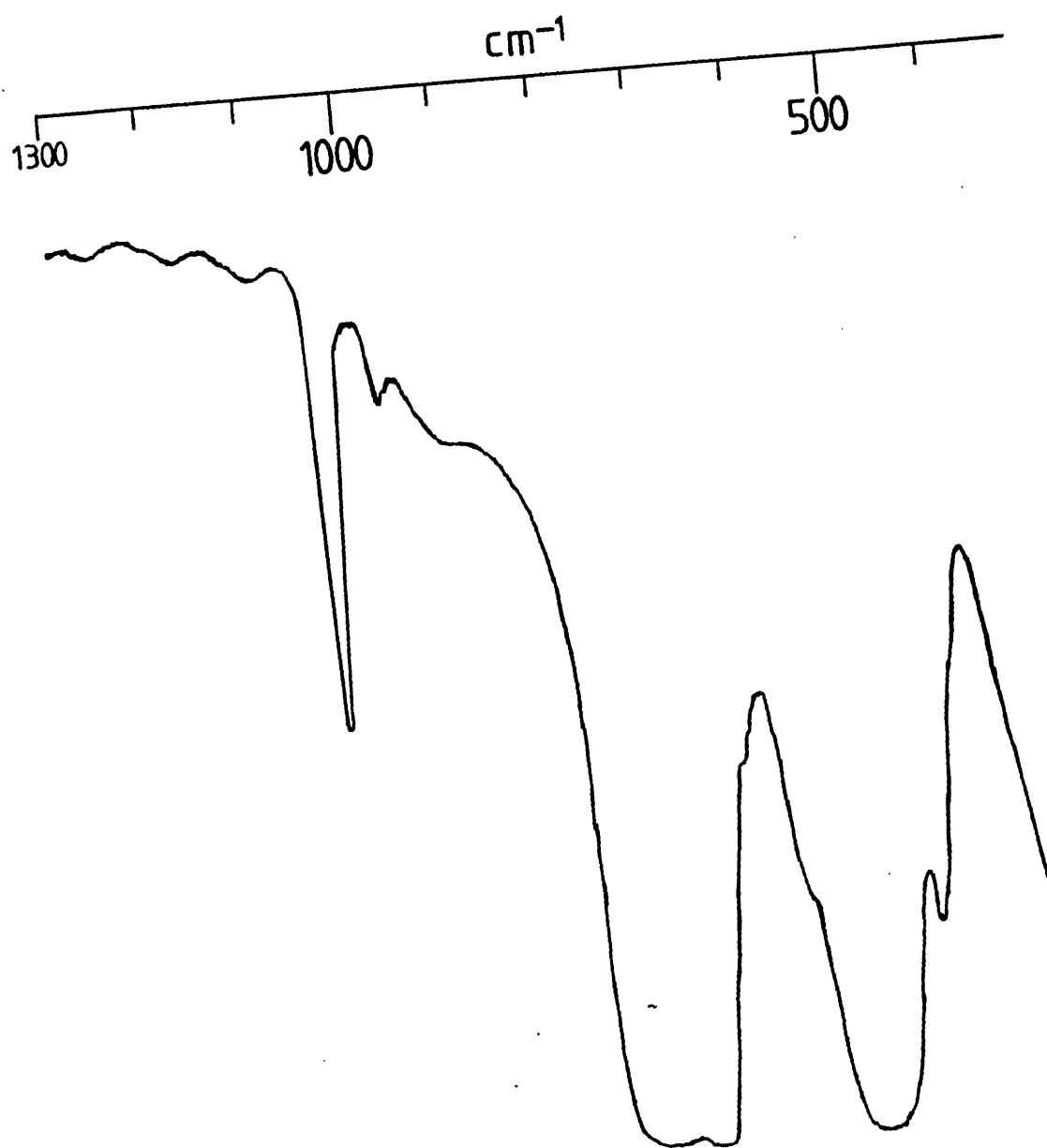


Figure 6.4 IR spectrum of  $\text{MoF}_5$  (from  $\text{MoF}_6$  + T.T.S.H.)

Table 6.1      The mass spectrum of  $\text{MoF}_5$  †

$M^+/e$	[Assignment]	Intensity(%)		
193	$[^{98}\text{MoF}_5^+]$	56		
174	$[^{98}\text{MoF}_4^+]$	100		
171	_____		$[^{98}\text{MoOF}_3^+]$	58
155	$[^{98}\text{MoF}_3^+]$	44		
152	_____		$[^{98}\text{MoOF}_2^+]$	47
136	$[^{98}\text{MoF}_2^+]$	38		
133	_____		$[^{98}\text{MoOF}^+]$	44
117	$[^{98}\text{MoF}^+]$	19		
98	$[^{98}\text{Mo}^+]$	31		
77.5	$[^{98}\text{MoF}_3^{2+}]$	36		

† Spectrum measured at  $80^\circ\text{C}$  and 70eV.

plus solid recovered from careful redistillations of the reaction volatile products was approximately 80%.

The dark solid remaining was a mixture of low fluorides and molybdenum metal. This can be explained as a result of non-uniform mixing of the reaction mixture as it warmed to room temperature. Thus, for a short while, some  $\text{MoF}_6$  was in contact with a much greater concentration of the TTSH than the bulk solution, resulting in reduction past the the  $\text{Mo}^V$  oxidation state to lower oxidation state fluorides and the metal itself.

#### 6.2.3. The Reaction of Rhenium Hexafluoride with TTSH.

A thirteen-fold excess of rhenium hexafluoride ( $\text{ReF}_6$ ) was distilled onto a Genetron solution containing 0.13 mmoles of TTSH. The mixture was left to stand overnight at  $-78^\circ\text{C}$ , resulting in the formation of a dark orange solution, and a small amount of solid at the bottom of the reaction tube. The solution was then allowed to warm to room temperature, and gas evolution took place as it did so. The gas-phase IR spectrum of the volatiles indicated the presence of TMS-F as well as the Genetron solvent. The volatile components were distilled from the dark orange solution to leave behind a dark oil and a non-volatile solid.

Warming the dark oil under dynamic vacuum conditions resulted in the sublimation of a green, viscous oil, and further along the tube walls a few fine, blue, needle-like crystals. As in the case of the  $\text{MoF}_6$  reaction, a small amount of dark non-volatile solid re-

maintained at the base of the tube. The blue crystals were shown to be  $\text{ReOF}_4$ , present as impurity in the original  $\text{ReF}_6$  reactant.

The IR spectrum of the green solid that crystallised from the green oil (Fig. 6.5) was in good agreement with the data reported for  $\text{ReF}_5$  <sup>(86,92)</sup>, showing strong, broad peaks at 750, 700 and 670  $\text{cm}^{-1}$ , assigned to  $\nu(\text{Re-F})$  and a band at 535  $\text{cm}^{-1}$  assigned to  $\nu(\text{Re-F})$  bridging. The small peak at 1070  $\text{cm}^{-1}$  was assigned to the metal oxide stretching frequency, attributed to traces of  $\text{ReOF}_4$  and hydrolysis products.

The X-Ray powder pattern of the dark solid showed a pattern indicative of rhenium metal which was confirmed by comparison with data in the JCPDS file (Table 6.2). This indicated that, as in the case of the  $\text{MoF}_6$  reaction, there had been some reduction of the rhenium hexafluoride past the  $\text{Re}^{\text{V}}$  oxidation state to the metal,  $\text{Re}^0$ , oxidation state, again due to non-uniform mixing of the reactants.

The yield of pentafluoride was approximately 70 %, which was slightly lower than the percentage yield of  $\text{MoF}_5$ .

#### 6.2.4. The Reaction of Tungsten Hexafluoride with TTSH.

(A)

A large excess of tungsten hexafluoride ( $\text{WF}_6$ ) was distilled onto TTSH (0.22 mmoles) and allowed to warm gradually. There was instant formation of a deep, red colouration at the interface between the warming  $\text{WF}_6$  and the solid TTSH. On further warming there was gas

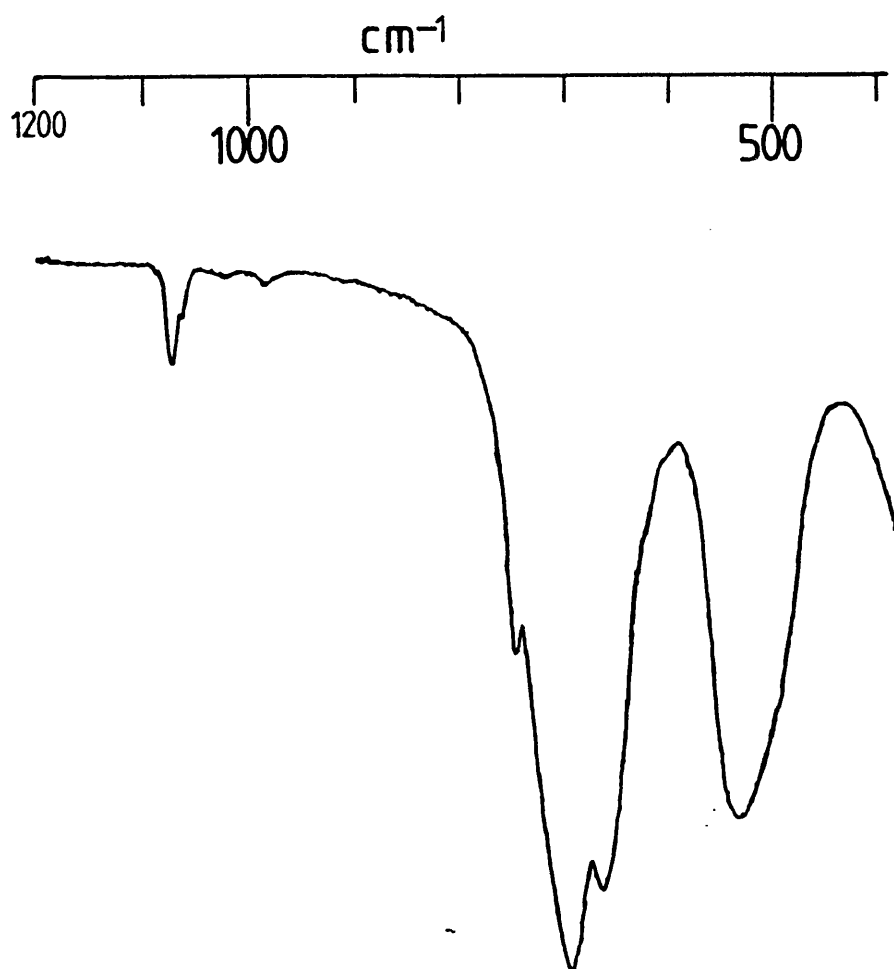


Figure 6.5 IR spectrum of  $\text{ReF}_5$  ( from  $\text{ReF}_6 + \text{TTSH}$  )

Table 6.2 Comparison of the powder pattern of the dark solid  
from "ReF<sub>6</sub> + TTSH" with Re metal.

'Dark solid'		Re metal*	
d (Å)	[I/I <sup>0</sup> ]	d (Å)	[I/I <sup>0</sup> ]
2.39	30	2.39	32
2.23	30	2.23	34
2.11	100	2.11	100
1.63	10	1.63	11
1.38	20	1.38	22
1.26	15	1.26	16
1.20	5	1.20	3
1.18	20	1.17	20
1.16	15	1.15	15
		1.11	2
		1.05	3
		1.01	2
		0.93	7
		0.90	3
		0.89	15
		0.87	8
		0.84	5
		0.82	8
		0.80	2

\* J.C.P.D.S. index card N° 5-702



evolution as the solution darkened to give a purple solution over a dark solid. Gas-phase IR of the volatiles showed the presence of TMS-F and unreacted  $\text{WF}_6$ . The reaction mixture was left at room temperature for an hour to allow it to reach completion, after which the excess of  $\text{WF}_6$ , used as both solvent and reactant, and trimethylsilylfluoride produced by the reaction, was distilled from the reaction tube. The volatiles that were removed were clear, and showed no sign of any product having distilled over with them. The remaining solid was tan coloured, and found to be insoluble in Genetron and carbon tetrachloride ( $\text{CCl}_4$ ).

If left to stand for several days the purple colour is discharged from the solution, leaving a slightly yellowed solution over an insoluble tan solid. The tan solid is presumed to be a mixture of  $[\text{WNF}_4]_2$  and unreacted TTSH.

Dry acetonitrile (MeCN) was added to the tan solid, resulting in the formation of a deep orange solution and fine, needle-like orange crystals, soluble in the MeCN solution. All attempts to obtain crystals suitable for a crystal structure to be determined were unsuccessful. From the IR spectra of the tan solid (Fig.6.6) and the solid recrystallised from MeCN (Fig.6.7) it seems reasonable to assume that the orange crystals are of the neutral species  $\text{F}_4\text{W}=\text{N}-\text{N}=\text{WF}_4$ . The solid begins to decompose at approximately  $90^\circ\text{C}$ , and its mass spectrum (Fig.6.8) shows a trace of  $\text{WF}_4^+$  and oxyfluorides of tungsten, but no peaks attributable to a parent ion or  $\text{WF}_4\text{N}^+$ , the expected main fragmentation product. The X-ray powder pattern of the orange solid (Table 6.3) is not that of  $\text{WF}_5$ .

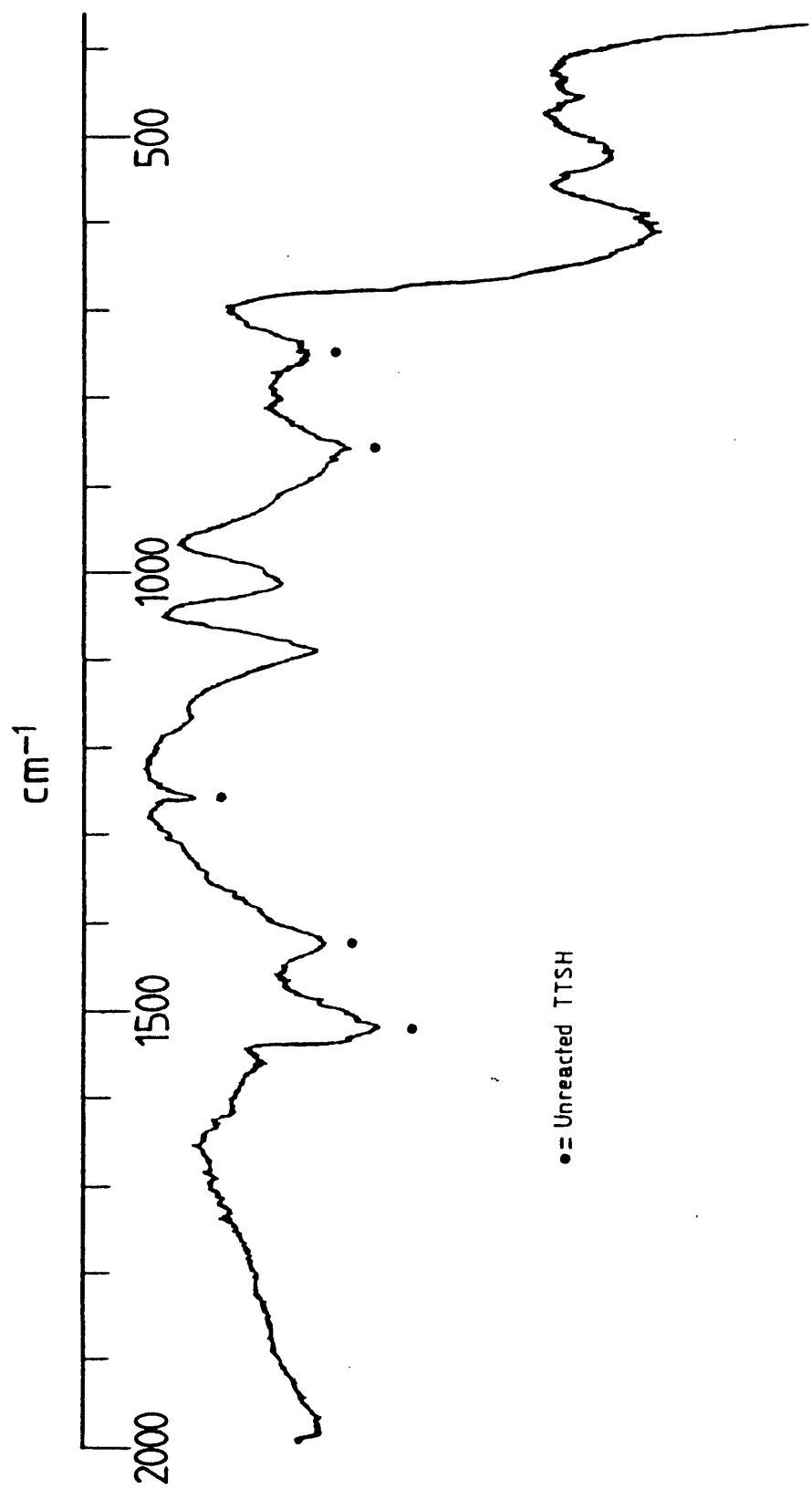


Figure 6.6 IR spectrum of the tan solid from  $\text{WF}_6 + \text{TTSH}$

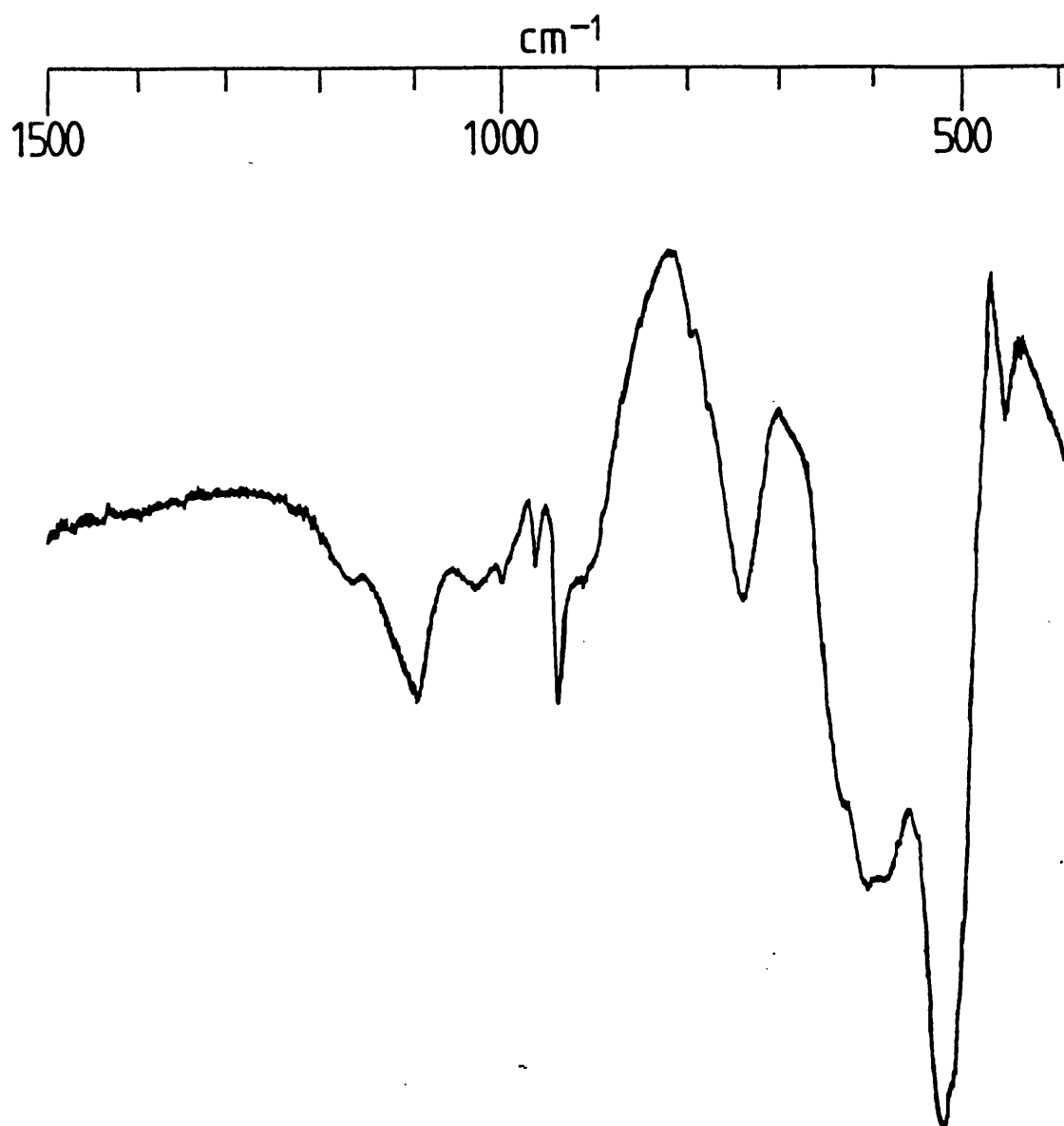


Figure 6.7 IR spectrum of the solid ( $[\text{WNF}_4]_2$ )  
recrystallised from MeCN

Figure 6.8 Mass spectrum (90°C) of the solid  $(WF_4N)_2$  recrystallised from MeCN

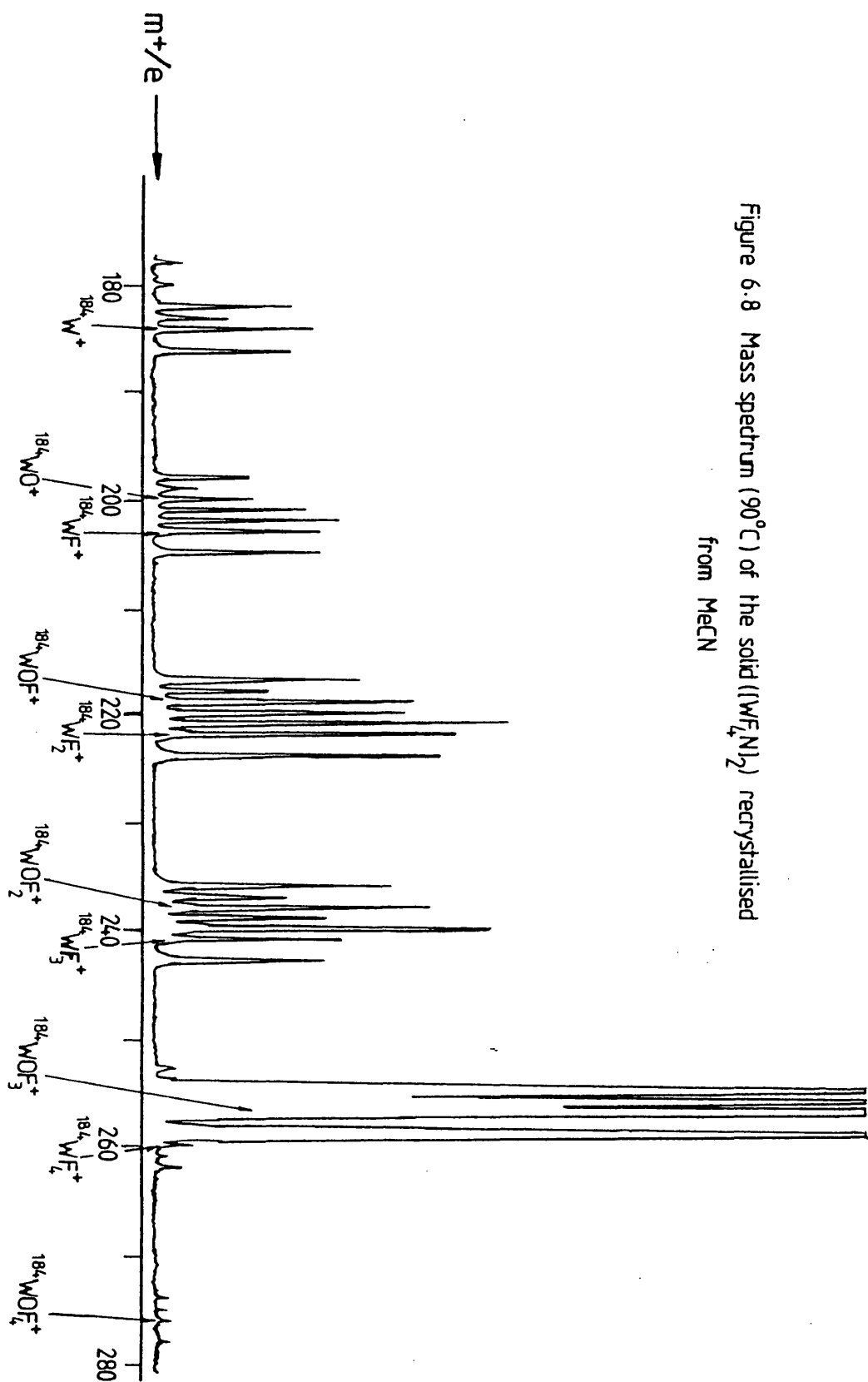


Table 6.3 Comparison of the X-ray powder patterns of

" $[\text{WF}_4\text{N}]_2$ " and  $\text{WF}_5$ .

$[\text{WF}_4\text{N}]_2$		$\text{WF}_5^*$	
d (Å)	[I/I°]	d (Å)	[I/I°]
7.62	25	7.86	20
6.92	60	7.12	10
6.22	30	5.21	60
5.64	100	4.49	30
5.52	40	4.21	100
5.04	5	3.96	80
4.61	15	3.68	20
4.24	15	3.56	50
4.09	100	3.35	80
3.90	60	3.26	30
3.79	5	3.11	10
3.37	40	3.06	100
3.20	10	2.94	10
2.47	15	2.86	20
2.42	10	2.77	80
2.26	5	2.73	80
		2.65	10
		2.58	10

\* J.C.P.D.S. index card N° 23-1447

(B)

Using Hexafluorobenzene as Reaction Solvent.

Hexafluorobenzene( $C_6F_6$ ) was distilled onto TTSH(0.13 mmoles) and allowed to warm. The TTSH proved to be highly soluble in the hexafluorobenzene , completely dissolving to give a clear solution. A nine-fold excess of  $WF_6$  was added to the solution , and a small amount of  $C_6F_6$  was distilled over to wash the  $WF_6$  down into the reaction mixture. The whole mixture was allowed to warm slowly from  $-193^{\circ}C$  to approximately  $-3^{\circ}C$  , whereupon the solution slowly developed a yellow colouration , which darkened with gas evolution , to a red solution. Allowing the solution to warm further to  $4^{\circ}C$  resulted in little change in the colour but , after leaving to stand for 2 hours , solid had settled out at the bottom of the reaction tube. Solvent and volatile products were distilled from the reaction mixture , still maintained at  $4^{\circ}C$  , to leave a tan non-volatile product as in the original preparation. The volatile components removed formed a yellow-green solution. The colour is a result of the formation of a 1:1 adduct between the  $C_6F_6$  solvent and unreacted  $WF_6$ <sup>(93)</sup>.

MeCN was added to the tan solid to form an orange solution above an insoluble dark solid. Repeated warming and cooling cycles prompted no further solubility of the solid , or crystallisation from the orange solution. After leaving the mixture to stand for several days the solution was heated for a slightly longer duration , resulting in the discharging of the orange colour to give a clear solution and a dark insoluble solid. On cooling to room temperature , fine white crystals precipitated from the solution. All the solvent was distilled from the tube and the dark solid heated under dynamic vacuum. This resulted in sublimation of the white solid as crystals

to the cooler sections of the tube wall. Comparison of the mass spectrum of the white sublimate with the pure starting material , TTSH , showed that the white sublimate was unreacted tetrakis(trimethylsilyl)hydrazine. The non-volatile dark solid was presumed to be  $WF_4$  resulting from the thermal decomposition of the orange  $[WNF_4]_2$ .

### 6.3 Discussion

Although less vigorous a reducing agent than hydrazine , the reaction of TTSH , when allowed to combine with 2nd and 3rd row T.M. hexafluorides , results in the fission of the Si-N bonds to form TMS-F and reduce the hexafluoride to the pentafluoride , rather than fission of the N-N bond required to form  $-N(SiMe_3)$  derivatives.

For both molybdenum and rhenium hexafluoride the reaction with TTSH gives quantitative yields of the pentafluoride in a one-step reaction , useful for small scale preparations.

When TTSH is treated with tungsten hexafluoride , the least oxidising of the hexafluorides , the reaction is not a simple reduction. The purple coloured solution formed during the reaction could be attributed to a soluble intermediate species. The fact that the colour is discharged from the solution after several days , to leave the same tan solid , supports this conclusion. A similar coloured intermediate species , believed to be  $WF_5N(Me)SiMe_3$  , was reported by Winfield et al<sup>(5)</sup> in the reaction between  $WF_6$  and  $(Me_3Si)_2NMe$ . A similar intermediate species  $WF_5N(SiMe_3)-N(SiMe_3)WF_5$  could be formed as the first step in the formation of  $[F_4WN]_2$ .

The IR spectrum of the tan solid (Fig.6.6) shows that there is still unreacted TTSH present , with peaks at 1520 , 1420 , 1260 , 860 and 780  $\text{cm}^{-1}$  attributable to TTSH , plus peaks at 610 and 520  $\text{cm}^{-1}$  assigned to  $\nu(\text{W-F})$  but obscured by TTSH peaks. By comparison with the orange solid recrystallised from MeCN (Fig.6.7) , the unreacted TTSH has remained in solution , and the pure product separated out for the IR spectrum. The absence of any  $\nu(\text{C-H})$  or  $\nu(\text{C=N})$  stretches rules out the possibility of the product being an acetonitrile adduct or an  $\text{N-SiMe}_3$  species. However , the strong band at  $1100\text{cm}^{-1}$  can be assigned to  $\nu(\text{W=N})$ . A nitrogen bridged molybdenum diazene ,  $[\text{MoCl}_4\text{N}]_2$ , has been reported by Dehnicke<sup>(22)</sup> and is thus useful for comparison. The geometry of the chlorine atoms about the molybdenum was assigned as  $C_{4v}$ , and its IR spectrum showed peaks assigned to  $\nu(\text{Mo=N})$ ,  $\nu(\text{MoCl}_4)$   $\delta(\text{MoCl}_4)$  and  $\delta(\text{MoN})$ .

It seems reasonable to assume that the  $\text{WF}_4=\text{N-N}=\text{WF}_4$  also adopts a  $C_{4v}$  symmetry about the metal atoms. Group theory analysis using Cartesian coordinates yields the following vibrational modes for  $C_{4v}$  symmetry (eqn.1):-

$$3N-6 = 3A_1 + B_1 + 2B_2 + 3E \quad (1)$$

Using internal coordinates for the  $\text{W=N}$  and  $\text{W-F}$  stretches only , the following modes can be obtained (eqns.2 and 3):-

$$\text{Int.Coord. : } \quad \text{W=N} \quad A_1 \quad (2)$$

$$\quad \quad \text{W-F} \quad A_1 + B_1 + E \quad (3)$$

Subtraction of the internal coordinate modes from the total  $3N-6$  modes leaves the bending and flapping modes (eqn.4):-

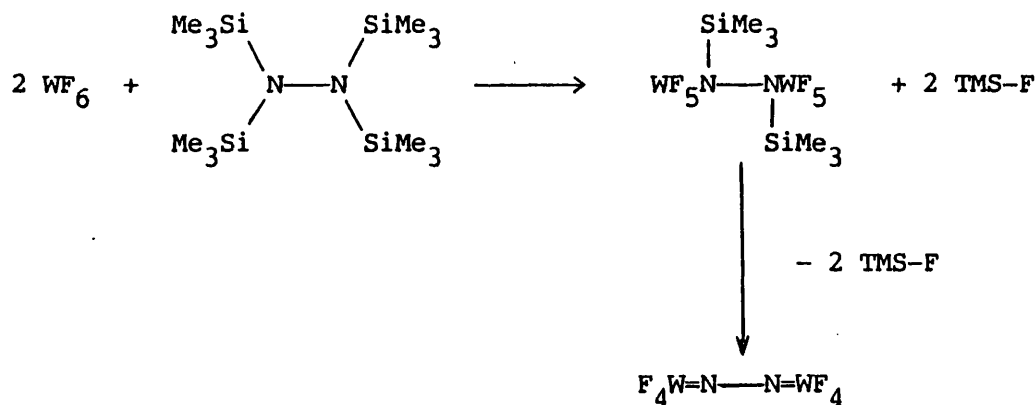


$$(3N-6)\text{-Int.} = A_1 + 2B_2 + 2E \quad (4)$$

The  $B_1$  and  $B_2$  modes are purely Raman active, whereas the  $A_1$  and  $E$  modes are both Raman and IR active. Thus, in the IR spectrum of bis(tetrafluorotungsten(VI))diazene, assuming that the compound has  $C_{4v}$  symmetry, there should be a total of six IR active bands. The band at  $1100\text{cm}^{-1}$  is assigned to  $\nu(\text{W}=\text{N})$ , the bands at 740, 610, 595 and  $520\text{cm}^{-1}$  to  $\nu(\text{W}-\text{F})$  and  $\delta(\text{W}-\text{F})$ , and the peak at  $460\text{cm}^{-1}$  to  $\delta(\text{W}=\text{N})$ . The peak at  $1025\text{cm}^{-1}$  can be accounted for as the  $\nu(\text{W}=\text{O})$  stretch of oxyfluoride impurities. The peaks in the region  $915\text{--}960\text{cm}^{-1}$  are believed to be overtones and combination bands.

A proposed reaction scheme for the formation of  $[\text{WF}_4\text{N}]_2$  is shown below (Scheme 5).

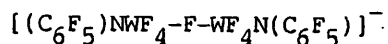
Scheme 5



# Appendix

Crystallography Tables

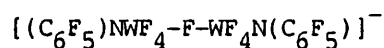
Table 7.1 Fractional atomic coordinates for  $[\text{C}_6\text{F}_5\text{NH}_3]^+$



Atom	x	y	z
W(1)	0.01039(14)	0.47803(12)	0.21461(14)
W(2)	-0.22801(14)	0.47951(12)	0.34191(15)
W(3)	0.89809(14)	0.09908(12)	0.40092(16)
W(4)	0.66189(14)	0.08817(12)	0.55981(16)
F(1)	-0.0930(16)	0.5107(14)	0.2828(22)
F(2)	-0.2198(15)	0.5852(14)	0.2498(20)
F(3)	-0.2674(19)	0.4296(15)	0.2037(19)
F(4)	-0.2006(15)	0.3788(13)	0.4138(19)
F(5)	-0.1509(21)	0.5314(17)	0.4621(23)
F(6)	0.0892(15)	0.5605(13)	0.3033(19)
F(7)	-0.1020(16)	0.3958(15)	0.1594(25)
F(8)	-0.0052(18)	0.4000(14)	0.3587(18)
F(9)	-0.0010(19)	0.5603(16)	0.0892(20)
F(31)	0.7709(18)	0.0929(18)	0.468(4)
F(32)	0.6105(19)	0.1037(15)	0.4025(19)
F(33)	0.7303(16)	0.2107(14)	0.5216(21)
F(34)	0.7508(19)	0.0874(15)	0.6893(23)
F(35)	0.6233(17)	-0.0308(14)	0.5622(22)
F(36)	0.8227(18)	0.1169(17)	0.2577(22)
F(37)	0.8285(19)	-0.0206(17)	0.4145(25)
F(38)	0.9431(22)	0.0891(15)	0.5599(21)
F(39)	0.9260(16)	0.2177(15)	0.4054(22)
C(11)	-0.4311(11)	0.4220(10)	0.4347(14)
C(12)	-0.4403(11)	0.4102(10)	0.5575(14)
C(13)	-0.5282(11)	0.3870(10)	0.6000(14)
C(14)	-0.6069(11)	0.3758(10)	0.5196(14)
C(15)	-0.5977(11)	0.3877(10)	0.3969(14)
C(16)	-0.5098(11)	0.4108(10)	0.3544(14)
F(12)	-0.3644(11)	0.4209(10)	0.6349(14)
F(13)	-0.5371(11)	0.3756(10)	0.7183(14)
F(14)	-0.6916(11)	0.3535(10)	0.5606(14)
F(15)	-0.6735(11)	0.3769(10)	0.3194(14)
F(16)	-0.5009(11)	0.4223(10)	0.2360(14)
C(21)	0.1738(9)	0.4418(9)	0.1161(14)
C(22)	0.2558(9)	0.5073(9)	0.0901(14)
C(23)	0.3270(9)	0.4955(9)	0.0413(14)
C(24)	0.3162(9)	0.4183(9)	0.0185(14)
C(25)	0.2343(9)	0.3528(9)	0.0445(14)
C(26)	0.1631(9)	0.3645(9)	0.0933(14)
F(22)	0.2661(9)	0.5817(9)	0.1120(14)
F(23)	0.4060(9)	0.5587(9)	0.0162(14)
F(24)	0.3849(9)	0.4070(9)	-0.0285(14)
F(25)	0.2239(9)	0.2784(9)	0.0226(14)
F(26)	0.0841(9)	0.3014(9)	0.1184(14)
C(41)	0.4901(9)	0.0804(8)	0.6920(11)
C(42)	0.4422(9)	0.1347(8)	0.6506(11)
C(43)	0.3650(9)	0.1281(8)	0.7077(11)
C(44)	0.3356(9)	0.0672(8)	0.8062(11)
C(45)	0.3835(9)	0.0128(8)	0.8475(11)
C(46)	0.4608(9)	0.0194(8)	0.7905(11)
F(42)	0.4705(9)	0.1935(8)	0.5557(11)
F(43)	0.3188(9)	0.1805(8)	0.6679(11)
F(44)	0.2612(9)	0.0608(8)	0.8612(11)
F(45)	0.3552(9)	-0.0459(8)	0.9421(11)

F(46)	0.5069(9)	-0.0330(8)	0.8303(11)
C(51)	1.0853(8)	0.1033(8)	0.3032(12)
C(52)	1.0771(8)	0.0525(8)	0.2206(12)
C(53)	1.1569(8)	0.0499(8)	0.1797(12)
C(54)	1.2448(8)	0.0981(8)	0.2216(12)
C(55)	1.2530(8)	0.1489(8)	0.3042(12)
C(56)	1.1732(8)	0.1515(8)	0.3451(12)
F(52)	0.9924(8)	0.0061(8)	0.1802(12)
F(53)	1.1490(8)	0.0009(8)	0.1000(12)
F(54)	1.3217(8)	0.0956(8)	0.1822(12)
F(55)	1.3377(8)	0.1954(8)	0.3446(12)
F(56)	1.1811(8)	0.2005(8)	0.4248(12)
C(61)	1.0431(10)	0.2560(9)	0.6730(11)
C(62)	0.9616(10)	0.2713(9)	0.6795(11)
C(63)	0.9139(10)	0.2416(9)	0.7836(11)
C(64)	0.9478(10)	0.1966(9)	0.8814(11)
C(65)	1.0293(10)	0.1813(9)	0.8749(11)
C(66)	1.0769(10)	0.2110(9)	0.7708(11)
F(62)	0.9289(10)	0.3147(9)	0.5853(11)
F(63)	0.8354(10)	0.2564(9)	0.7899(11)
F(64)	0.9018(10)	0.1680(9)	0.9818(11)
F(65)	1.0619(10)	0.1379(9)	0.9691(11)
F(66)	1.1554(10)	0.1962(9)	0.7646(11)
C(71)	0.5176(9)	0.2413(7)	-0.0029(12)
C(72)	0.5128(9)	0.2538(7)	0.1125(12)
C(73)	0.5879(9)	0.2577(7)	0.1973(12)
C(74)	0.6677(9)	0.2490(7)	0.1668(12)
C(75)	0.6725(9)	0.2365(7)	0.0514(12)
C(76)	0.5974(9)	0.2326(7)	-0.0335(12)
F(71)	0.4452(9)	0.2376(7)	-0.0847(12)
F(72)	0.4358(9)	0.2622(7)	0.1419(12)
F(74)	0.7401(9)	0.2527(7)	0.2486(12)
F(75)	0.7495(9)	0.2281(7)	0.0219(12)
F(76)	0.6020(9)	0.2205(7)	-0.1447(12)
N(1)	-0.3425(29)	0.4471(19)	0.392(4)
N(2)	0.0992(25)	0.4543(18)	0.1577(26)
N(3)	0.5707(19)	0.0839(20)	0.6295(27)
N(4)	0.9967(22)	0.1068(19)	0.343(3)
N(5)	1.0908(16)	0.2819(14)	0.5767(24)
N(6)	0.5805(17)	0.2701(15)	0.3021(22)

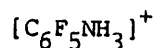
Table 7.2 Atomic thermal parameters ( $\times 10^4$ ) for  $[\text{C}_6\text{F}_5\text{NH}_3]^+$



Atom	U or U11	U22	U33	U23	U13	U12
W(1)	983(17)	783(16)	494(10)	-65(9)	98(10)	273(13)
W(2)	1014(18)	781(16)	584(11)	-89(10)	45(10)	376(13)
W(3)	973(17)	720(15)	724(12)	-134(10)	178(11)	324(13)
W(4)	928(17)	737(16)	728(12)	-125(10)	157(11)	291(13)
F(1)	955(192)	847(182)	1123(192)	-153(144)	220(148)	300(152)
F(2)	857(69)					
F(3)	1592(244)	1252(225)	575(141)	-244(133)	-112(140)	695(192)
F(4)	798(66)					
F(5)	1742(284)	1340(244)	872(182)	-244(162)	9(172)	661(214)
F(6)	781(169)	810(174)	872(156)	-409(128)	29(124)	62(138)
F(7)	743(178)	1122(213)	1537(234)	-931(181)	-529(160)	227(161)
F(8)	1650(249)	849(184)	553(132)	-35(118)	297(138)	316(171)
F(9)	1572(253)	1318(231)	665(151)	299(146)	171(148)	767(200)
F(31)	751(203)	1425(270)	2765(432)	-645(259)	376(222)	411(191)
F(32)	1756(265)	1129(214)	509(134)	-202(127)	-37(142)	474(192)
F(33)	913(73)					
F(34)	1501(246)	980(205)	1005(189)	-143(151)	-174(167)	523(184)
F(35)	1015(80)					
F(36)	1348(236)	1625(257)	955(183)	-598(169)	-343(159)	957(207)
F(37)	1220(94)					
F(38)	2193(325)	1008(215)	673(160)	-167(139)	169(174)	277(208)
F(39)	990(78)					
C(11)	1773(516)	540(309)	683(288)	-172(229)	125(293)	710(328)
C(12)	1555(610)	980(434)	1217(483)	-565(350)	8(390)	646(426)
C(13)	505(363)	1572(521)	1079(402)	-314(347)	26(305)	368(370)
C(14)	432(346)	722(365)	2341(652)	217(399)	859(399)	115(293)
C(15)	1548(610)	1190(472)	750(359)	64(322)	-124(360)	824(457)
C(16)	918(420)	1293(463)	826(348)	-568(314)	81(289)	280(363)
F(12)	1916(353)	1661(309)	910(218)	5(200)	175(202)	352(264)
F(13)	2825(455)	1781(330)	871(221)	-42(207)	487(241)	461(297)
F(14)	1713(314)	1073(244)	2146(366)	-35(217)	1110(277)	461(229)
F(15)	1119(265)	1624(304)	1954(360)	254(255)	-90(223)	632(232)
F(16)	1612(290)	2261(362)	831(200)	-388(199)	94(176)	803(257)
C(21)	581(103)					
C(22)	1146(181)					
C(23)	514(330)	1019(431)	748(275)	19(277)	-39(238)	-435(304)
C(24)	1191(453)	565(337)	862(319)	32(257)	-55(286)	449(341)
C(25)	864(137)					
C(26)	822(134)					
F(22)	1545(265)	997(216)	1256(224)	-65(165)	349(186)	434(189)
F(23)	895(209)	1258(250)	1443(246)	67(188)	250(177)	410(185)
F(24)	1195(232)	1396(255)	1332(229)	-185(179)	389(176)	732(203)
F(25)	2147(334)	978(224)	1753(304)	-612(200)	361(239)	581(221)
F(26)	1571(265)	962(214)	1165(217)	-176(163)	119(183)	208(191)
C(41)	467(264)	543(283)	1025(302)	-112(228)	-119(225)	278(225)
C(42)	822(132)					
C(43)	1170(426)	1057(424)	797(310)	-163(276)	33(275)	758(356)
C(44)	1335(496)	1141(458)	1328(468)	-459(355)	521(385)	333(396)
C(45)	862(141)					
C(46)	915(142)					
F(42)	1258(226)	1045(210)	1251(217)	-69(161)	428(172)	481(177)
F(43)	1389(269)	1161(248)	1623(283)	-104(198)	439(212)	628(210)
F(44)	1841(323)	1474(288)	1807(327)	-217(224)	962(258)	635(246)
F(45)	1574(278)	1596(276)	1182(226)	173(189)	763(199)	600(221)

F(46)	1508(239)	979(191)	957(178)	237(142)	444(162)	806(179)
C(51)	604(105)					
C(52)	595(107)					
C(53)	524(307)	1229(423)	640(254)	-193(251)	-75(222)	458(302)
C(54)	431(287)	1088(385)	992(322)	-181(267)	200(244)	444(282)
C(55)	917(146)					
C(56)	935(144)					
F(52)	933(188)	886(183)	1236(199)	-292(149)	122(149)	343(152)
F(53)	1509(251)	909(201)	1176(213)	-427(158)	250(174)	510(179)
F(54)	1393(256)	1171(232)	1404(245)	91(176)	686(197)	642(200)
F(55)	978(212)	1307(237)	1517(250)	-697(195)	-90(173)	341(182)
F(56)	1176(220)	1192(220)	1234(212)	-642(171)	146(163)	376(178)
C(61)	896(138)					
C(62)	504(94)					
C(63)	794(128)					
C(64)	855(133)					
C(65)	943(145)					
C(66)	938(143)					
F(62)	1456(111)					
F(63)	1253(219)	1108(204)	1015(181)	50(146)	497(155)	620(172)
F(64)	2260(328)	1226(240)	792(176)	397(156)	786(188)	571(224)
F(65)	2851(417)	1244(265)	1019(216)	68(179)	-449(231)	891(270)
F(66)	1560(117)					
C(71)	1010(149)					
C(72)	971(150)					
C(73)	654(110)					
C(74)	867(140)					
C(75)	691(113)					
C(76)	1064(156)					
F(71)	1478(111)					
F(72)	1429(263)	1087(229)	1865(305)	16(199)	91(215)	700(200)
F(74)	2452(402)	1914(358)	1468(313)	-392(250)	526(281)	594(302)
F(75)	1924(287)	1262(237)	1022(197)	-26(161)	565(183)	766(214)
F(76)	1654(121)					
N(1)	1750(402)	428(237)	1532(370)	313(224)	935(311)	401(245)
N(2)	1531(335)	587(230)	559(186)	-47(158)	-63(192)	600(228)
N(3)	513(219)	1005(274)	827(219)	-217(190)	84(168)	322(199)
N(4)	850(260)	715(256)	943(248)	4(191)	59(197)	346(212)
N(5)	239(167)	210(171)	876(196)	-182(142)	266(144)	-102(135)
N(6)	440(188)	460(196)	533(160)	28(137)	268(136)	111(156)

Table 7.3 Bond lengths (Å) for  $[(C_6F_5)NWF_4-F-WF_4N(C_6F_5)]^-$



F(1)-W(1)	2.159(29)	F(6)-W(1)	1.893(21)
F(7)-W(1)	1.935(22)	F(8)-W(1)	1.904(20)
F(9)-W(1)	1.867(25)	N(2)-W(1)	1.80(4)
F(1)-W(2)	2.117(25)	F(2)-W(2)	1.926(22)
F(3)-W(2)	1.875(24)	F(4)-W(2)	1.976(24)
F(5)-W(2)	1.840(26)	N(1)-W(2)	1.78(4)
F(31)-W(3)	2.16(3)	F(36)-W(3)	1.907(25)
F(37)-W(3)	1.985(26)	F(38)-W(3)	1.843(24)
F(39)-W(3)	1.998(26)	N(4)-W(3)	1.69(4)
F(31)-W(4)	2.06(4)	F(32)-W(4)	1.864(22)
F(33)-W(4)	2.026(21)	F(34)-W(4)	1.867(26)
F(35)-W(4)	1.968(25)	N(3)-W(4)	1.68(3)
C(12)-C(11)	1.390(23)	C(16)-C(11)	1.390(21)
N(1)-C(11)	1.39(5)	C(13)-C(12)	1.390(23)
F(12)-C(12)	1.340(21)	C(14)-C(13)	1.390(21)
F(13)-C(13)	1.340(23)	C(15)-C(14)	1.390(23)
F(14)-C(14)	1.340(23)	C(16)-C(15)	1.390(23)
F(15)-C(15)	1.340(21)	F(16)-C(16)	1.340(23)
C(22)-C(21)	1.390(17)	C(26)-C(21)	1.390(23)
N(2)-C(21)	1.40(5)	C(23)-C(22)	1.390(25)
F(22)-C(22)	1.340(23)	C(24)-C(23)	1.390(23)
F(23)-C(23)	1.340(17)	C(25)-C(24)	1.390(17)
F(24)-C(24)	1.340(25)	C(26)-C(25)	1.390(25)
F(25)-C(25)	1.340(23)	F(26)-C(26)	1.340(17)
C(42)-C(41)	1.390(22)	C(46)-C(41)	1.390(17)
N(3)-C(41)	1.49(4)	C(43)-C(42)	1.390(21)
F(42)-C(42)	1.340(17)	C(44)-C(43)	1.390(17)
F(43)-C(43)	1.340(22)	C(45)-C(44)	1.390(22)
F(44)-C(44)	1.340(21)	C(46)-C(45)	1.390(21)
F(45)-C(45)	1.340(17)	F(46)-C(46)	1.340(22)
C(52)-C(51)	1.390(22)	C(56)-C(51)	1.390(15)
N(4)-C(51)	1.52(4)	C(53)-C(52)	1.390(21)
F(52)-C(52)	1.340(15)	C(54)-C(53)	1.390(15)
F(53)-C(53)	1.340(22)	C(55)-C(54)	1.390(22)
F(54)-C(54)	1.340(21)	C(56)-C(55)	1.390(21)
F(55)-C(55)	1.340(15)	F(56)-C(56)	1.340(22)
C(62)-C(61)	1.390(24)	C(66)-C(61)	1.390(19)
N(5)-C(61)	1.32(3)	C(63)-C(62)	1.390(18)
F(62)-C(62)	1.340(19)	C(64)-C(63)	1.390(19)
F(63)-C(63)	1.340(24)	C(65)-C(64)	1.390(24)
F(64)-C(64)	1.340(18)	C(66)-C(65)	1.390(18)
F(65)-C(65)	1.340(19)	F(66)-C(66)	1.340(24)
C(72)-C(71)	1.390(21)	C(76)-C(71)	1.390(22)
F(71)-C(71)	1.340(18)	C(73)-C(72)	1.390(18)
F(72)-C(72)	1.340(22)	C(74)-C(73)	1.390(22)
N(6)-C(73)	1.28(3)	C(75)-C(74)	1.390(21)
F(74)-C(74)	1.340(18)	C(76)-C(75)	1.390(18)
F(75)-C(75)	1.340(22)	F(76)-C(76)	1.340(21)

Table 7.4 Bond angles ( $^{\circ}$ ) for  $[(C_6F_5)NWF_4-F-WF_4N(C_6F_5)]^{-}$

$[C_6F_5NH_3]^{+}$

F(6)-W(1)-F(1)	79.9(10)	F(7)-W(1)-F(1)	80.4(11)
F(7)-W(1)-F(6)	159.5(12)	F(8)-W(1)-F(1)	83.5(11)
F(8)-W(1)-F(6)	89.5(9)	F(8)-W(1)-F(7)	82.5(10)
F(9)-W(1)-F(1)	80.6(12)	F(9)-W(1)-F(6)	88.8(10)
F(9)-W(1)-F(7)	93.7(10)	F(9)-W(1)-F(8)	164.0(14)
N(2)-W(1)-F(1)	178.1(10)	N(2)-W(1)-F(6)	98.5(12)
N(2)-W(1)-F(7)	101.3(13)	N(2)-W(1)-F(8)	97.5(13)
N(2)-W(1)-F(9)	98.5(13)	F(2)-W(2)-F(1)	82.7(10)
F(3)-W(2)-F(1)	83.7(11)	F(3)-W(2)-F(2)	91.5(10)
F(4)-W(2)-F(1)	79.9(9)	F(4)-W(2)-F(2)	162.5(10)
F(4)-W(2)-F(3)	84.5(11)	F(5)-W(2)-F(1)	77.1(12)
F(5)-W(2)-F(2)	89.1(11)	F(5)-W(2)-F(3)	160.5(14)
F(5)-W(2)-F(4)	89.1(11)	N(1)-W(2)-F(1)	176.6(14)
N(1)-W(2)-F(2)	100.3(14)	N(1)-W(2)-F(3)	94.7(15)
N(1)-W(2)-F(4)	97.0(13)	N(1)-W(2)-F(5)	104.3(16)
F(36)-W(3)-F(31)	76.9(13)	F(37)-W(3)-F(31)	80.1(13)
F(37)-W(3)-F(36)	89.6(11)	F(38)-W(3)-F(31)	85.7(15)
F(38)-W(3)-F(36)	162.0(15)	F(38)-W(3)-F(37)	92.1(11)
F(39)-W(3)-F(31)	79.8(11)	F(39)-W(3)-F(36)	84.8(11)
F(39)-W(3)-F(37)	159.9(12)	F(39)-W(3)-F(38)	87.5(11)
N(4)-W(3)-F(31)	177.5(14)	N(4)-W(3)-F(36)	100.9(14)
N(4)-W(3)-F(37)	101.2(14)	N(4)-W(3)-F(38)	96.4(15)
N(4)-W(3)-F(39)	98.8(13)	F(32)-W(4)-F(31)	80.5(14)
F(33)-W(4)-F(31)	78.4(12)	F(33)-W(4)-F(32)	82.7(10)
F(34)-W(4)-F(31)	80.9(14)	F(34)-W(4)-F(32)	160.2(12)
F(34)-W(4)-F(33)	87.0(10)	F(35)-W(4)-F(31)	83.7(12)
F(35)-W(4)-F(32)	91.6(11)	F(35)-W(4)-F(33)	161.8(11)
F(35)-W(4)-F(34)	93.1(11)	N(3)-W(4)-F(31)	177.8(14)
N(3)-W(4)-F(32)	97.4(14)	N(3)-W(4)-F(33)	102.0(14)
N(3)-W(4)-F(34)	101.2(14)	N(3)-W(4)-F(35)	95.8(14)
W(2)-F(1)-W(1)	150.8(12)	W(4)-F(31)-W(3)	170.4(19)
C(16)-C(11)-C(12)	120.0(15)	N(1)-C(11)-C(12)	119.7(21)
N(1)-C(11)-C(16)	120.3(21)	C(13)-C(12)-C(11)	120.0(14)
F(12)-C(12)-C(11)	120.0(15)	F(12)-C(12)-C(13)	120.0(15)
C(14)-C(13)-C(12)	120.0(15)	F(13)-C(13)-C(12)	120.0(14)
F(13)-C(13)-C(14)	120.0(15)	C(15)-C(14)-C(13)	120.0(15)
F(14)-C(14)-C(13)	120.0(15)	F(14)-C(14)-C(15)	120.0(14)
C(16)-C(15)-C(14)	120.0(14)	F(15)-C(15)-C(14)	120.0(15)
F(15)-C(15)-C(16)	120.0(15)	C(15)-C(16)-C(11)	120.0(15)
F(16)-C(16)-C(11)	120.0(15)	F(16)-C(16)-C(15)	120.0(14)
C(26)-C(21)-C(22)	120.0(16)	N(2)-C(21)-C(22)	120.3(18)
N(2)-C(21)-C(26)	119.6(15)	C(23)-C(22)-C(21)	120.0(15)
F(22)-C(22)-C(21)	120.0(16)	F(22)-C(22)-C(23)	120.0(12)
C(24)-C(23)-C(22)	120.0(12)	F(23)-C(23)-C(22)	120.0(15)
F(23)-C(23)-C(24)	120.0(16)	C(25)-C(24)-C(23)	120.0(16)
F(24)-C(24)-C(23)	120.0(12)	F(24)-C(24)-C(25)	120.0(15)
C(26)-C(25)-C(24)	120.0(15)	F(25)-C(25)-C(24)	120.0(16)
F(25)-C(25)-C(26)	120.0(12)	C(25)-C(26)-C(21)	120.0(12)
F(26)-C(26)-C(21)	120.0(16)	F(26)-C(26)-C(25)	120.0(15)
C(46)-C(41)-C(42)	120.0(13)	N(3)-C(41)-C(42)	121.1(16)
N(3)-C(41)-C(46)	118.8(18)	C(43)-C(42)-C(41)	120.0(11)
F(42)-C(42)-C(41)	120.0(14)	F(42)-C(42)-C(43)	120.0(14)
C(44)-C(43)-C(42)	120.0(14)	F(43)-C(43)-C(42)	120.0(12)
F(43)-C(43)-C(44)	120.0(14)	C(45)-C(44)-C(43)	120.0(13)
F(44)-C(44)-C(43)	120.0(14)	F(44)-C(44)-C(45)	120.0(12)
C(46)-C(45)-C(44)	120.0(11)	F(45)-C(45)-C(44)	120.0(14)



F(45)-C(45)-C(46)	120.0(14)	C(45)-C(46)-C(41)	120.0(14)
F(46)-C(46)-C(41)	120.0(14)	F(46)-C(46)-C(45)	120.0(12)
C(56)-C(51)-C(52)	120.0(13)	N(4)-C(51)-C(52)	118.6(15)
N(4)-C(51)-C(56)	121.3(17)	C(53)-C(52)-C(51)	120.0(11)
F(52)-C(52)-C(51)	120.0(14)	F(52)-C(52)-C(53)	120.0(14)
C(54)-C(53)-C(52)	120.0(14)	F(53)-C(53)-C(52)	120.0(11)
F(53)-C(53)-C(54)	120.0(13)	C(55)-C(54)-C(53)	120.0(13)
F(54)-C(54)-C(53)	120.0(14)	F(54)-C(54)-C(55)	120.0(11)
C(56)-C(55)-C(54)	120.0(11)	F(55)-C(55)-C(54)	120.0(14)
F(55)-C(55)-C(56)	120.0(14)	C(55)-C(56)-C(51)	120.0(14)
F(56)-C(56)-C(51)	120.0(13)	F(56)-C(56)-C(55)	120.0(11)
C(66)-C(61)-C(62)	120.0(12)	N(5)-C(61)-C(62)	122.8(16)
N(5)-C(61)-C(66)	117.2(18)	C(63)-C(62)-C(61)	120.0(13)
F(62)-C(62)-C(61)	120.0(13)	F(62)-C(62)-C(63)	120.0(15)
C(64)-C(63)-C(62)	120.0(15)	F(63)-C(63)-C(62)	120.0(13)
F(63)-C(63)-C(64)	120.0(12)	C(65)-C(64)-C(63)	120.0(12)
F(64)-C(64)-C(63)	120.0(15)	F(64)-C(64)-C(65)	120.0(13)
C(66)-C(65)-C(64)	120.0(13)	F(65)-C(65)-C(64)	120.0(13)
F(65)-C(65)-C(66)	120.0(15)	C(65)-C(66)-C(61)	120.0(15)
F(66)-C(66)-C(61)	120.0(12)	F(66)-C(66)-C(65)	120.0(13)
C(76)-C(71)-C(72)	120.0(12)	F(71)-C(71)-C(72)	120.0(15)
F(71)-C(71)-C(76)	120.0(14)	C(73)-C(72)-C(71)	120.0(14)
F(72)-C(72)-C(71)	120.0(12)	F(72)-C(72)-C(73)	120.0(14)
C(74)-C(73)-C(72)	120.0(14)	N(6)-C(73)-C(72)	117.7(18)
N(6)-C(73)-C(74)	122.3(17)	C(75)-C(74)-C(73)	120.0(12)
F(74)-C(74)-C(73)	120.0(14)	F(74)-C(74)-C(75)	120.0(15)
C(76)-C(75)-C(74)	120.0(14)	F(75)-C(75)-C(74)	120.0(12)
F(75)-C(75)-C(76)	120.0(14)	C(75)-C(76)-C(71)	120.0(14)
F(76)-C(76)-C(71)	120.0(13)	F(76)-C(76)-C(75)	120.0(15)
C(11)-N(1)-W(2)	179(3)	C(21)-N(2)-W(1)	175.3(22)
C(41)-N(3)-W(4)	179.6(15)	C(51)-N(4)-W(3)	172.1(22)

Table 7.5 Non-bonded contacts (Å) for  $[(C_6F_5)NWF_4-F-WF_4N(C_6F_5)]^-$

$[C_6F_5NH_3]^+$

W(2)...W(1)	4.138	C(21)...W(1)	3.200
C(11)...W(2)	3.179	C(51)...W(3)	3.201
C(41)...W(4)	3.167	F(2)...F(1)	2.675
F(3)...F(1)	2.669	F(4)...F(1)	2.631
F(5)...F(1)	2.475	F(6)...F(1)	2.609
F(7)...F(1)	2.648	F(9)...F(1)	2.612
F(5)...F(2)	2.642	F(4)...F(3)	2.592
N(1)...F(3)	2.693	F(5)...F(4)	2.679
F(8)...F(6)	2.673	F(9)...F(6)	2.631
F(8)...F(7)	2.533	F(32)...F(31)	2.543
F(33)...F(31)	2.584	F(34)...F(31)	2.556
F(35)...F(31)	2.691	F(36)...F(31)	2.535
F(37)...F(31)	2.670	F(39)...F(31)	2.669
F(33)...F(32)	2.573	N(3)...F(32)	2.662
F(34)...F(33)	2.682	N(3)...F(34)	2.741
N(3)...F(35)	2.712	F(39)...F(36)	2.634
F(39)...F(38)	2.659	N(4)...F(38)	2.633
C(13)...C(11)	2.407	C(14)...C(11)	2.780
C(15)...C(11)	2.407	F(12)...C(11)	2.364
F(16)...C(11)	2.364	C(14)...C(12)	2.408
C(15)...C(12)	2.780	C(16)...C(12)	2.407
F(13)...C(12)	2.365	N(1)...C(12)	2.408
C(15)...C(13)	2.407	C(16)...C(13)	2.780
F(12)...C(13)	2.364	F(14)...C(13)	2.364
C(16)...C(14)	2.408	F(13)...C(14)	2.364
F(15)...C(14)	2.364	F(14)...C(15)	2.364
F(16)...C(15)	2.364	F(15)...C(16)	2.364
N(1)...C(16)	2.415	C(23)...C(21)	2.408
C(24)...C(21)	2.780	C(25)...C(21)	2.407
F(22)...C(21)	2.365	F(26)...C(21)	2.364
C(24)...C(22)	2.408	C(25)...C(22)	2.780
C(26)...C(22)	2.408	F(23)...C(22)	2.364
N(2)...C(22)	2.422	C(25)...C(23)	2.408
C(26)...C(23)	2.780	F(22)...C(23)	2.365
F(24)...C(23)	2.364	C(26)...C(24)	2.408
F(23)...C(24)	2.364	F(25)...C(24)	2.365
F(24)...C(25)	2.365	F(26)...C(25)	2.364
F(25)...C(26)	2.364	N(2)...C(26)	2.414
C(43)...C(41)	2.408	C(44)...C(41)	2.780
C(45)...C(41)	2.407	F(42)...C(41)	2.364
F(46)...C(41)	2.365	C(44)...C(42)	2.408
C(45)...C(42)	2.780	C(46)...C(42)	2.408
F(43)...C(42)	2.364	N(3)...C(42)	2.509
C(45)...C(43)	2.408	C(46)...C(43)	2.780
F(42)...C(43)	2.364	F(44)...C(43)	2.364
C(46)...C(44)	2.407	F(43)...C(44)	2.364
F(45)...C(44)	2.364	F(44)...C(45)	2.364
F(46)...C(45)	2.364	F(45)...C(46)	2.364
N(3)...C(46)	2.480	C(53)...C(51)	2.407
C(54)...C(51)	2.780	C(55)...C(51)	2.407
F(52)...C(51)	2.364	F(56)...C(51)	2.364
C(54)...C(52)	2.408	C(55)...C(52)	2.780
C(56)...C(52)	2.407	F(53)...C(52)	2.364
N(4)...C(52)	2.505	C(55)...C(53)	2.408
C(56)...C(53)	2.780	F(52)...C(53)	2.365
F(54)...C(53)	2.365	C(56)...C(54)	2.407
F(53)...C(54)	2.364	F(55)...C(54)	2.364

F(54)...C(55)	2.365	F(56)...C(55)	2.364
F(55)...C(56)	2.364	N(4)...C(56)	2.539
C(63)...C(61)	2.408	C(64)...C(61)	2.780
C(65)...C(61)	2.408	F(62)...C(61)	2.364
F(66)...C(61)	2.364	C(64)...C(62)	2.408
C(65)...C(62)	2.780	C(66)...C(62)	2.408
F(63)...C(62)	2.364	N(5)...C(62)	2.376
C(65)...C(63)	2.408	C(66)...C(63)	2.780
F(62)...C(63)	2.364	F(64)...C(63)	2.364
C(66)...C(64)	2.408	F(63)...C(64)	2.364
F(65)...C(64)	2.365	F(64)...C(65)	2.365
F(66)...C(65)	2.364	F(65)...C(66)	2.364
N(5)...C(66)	2.310	N(5)...F(66)	2.662
C(73)...C(71)	2.408	C(74)...C(71)	2.780
C(75)...C(71)	2.408	F(72)...C(71)	2.364
F(76)...C(71)	2.364	C(74)...C(72)	2.408
C(75)...C(72)	2.780	C(76)...C(72)	2.408
F(71)...C(72)	2.364	N(6)...C(72)	2.287
C(75)...C(73)	2.408	C(76)...C(73)	2.780
F(72)...C(73)	2.364	F(74)...C(73)	2.364
C(76)...C(74)	2.408	F(75)...C(74)	2.364
N(6)...C(74)	2.342	F(74)...C(75)	2.364
F(76)...C(75)	2.364	F(71)...C(76)	2.365
F(75)...C(76)	2.364	N(6)...F(72)	2.655
N(6)...F(74)	2.747		

Table 7.6 Observed and calculated structure factors for  $[(C_6F_5)_4NWF_4(C_6F_5)]^+[(C_6F_5NH_3)]^+$  PAGE 1

3	0	0	147	155	-7	3	0	0	45	54	7	5	0	20	22	-5	8	0	99	89	0	11	0	117	111
4	0	0	30	34	-6	3	0	0	20	35	9	5	0	104	-74	-4	9	0	102	95	1	11	0	58	47
5	0	0	19	11	-5	3	0	0	25	31	9	5	0	150	-111	-3	8	0	24	-32	2	11	0	37	39
7	0	0	57	-100	-4	3	0	0	217	-231	11	5	0	24	-23	-2	8	0	23	22	4	11	0	85	-72
8	0	0	55	34	-3	3	0	0	159	-156	12	5	0	42	-44	-1	8	0	294	281	7	11	0	48	-39
9	0	0	45	175	-2	3	0	0	70	-19	-13	5	0	43	26	0	8	0	104	-97	8	11	0	33	-19
10	0	0	43	45	-1	3	0	0	290	-392	-13	5	0	94	69	3	8	0	155	-145	-13	12	0	45	-39
11	0	0	43	19	0	3	0	0	34	-347	-12	5	0	84	-76	3	8	0	32	-25	-12	12	0	45	-39
12	0	0	110	33	1	3	0	0	29	-36	-11	5	0	25	-21	5	8	0	79	61	-11	12	0	43	-38
16	0	0	33	-17	2	3	0	0	43	-43	-9	6	0	45	-42	8	8	0	69	55	-9	12	0	68	58
-11	1	0	36	33	4	3	0	0	119	-114	-9	6	0	41	-42	9	8	0	37	30	-6	12	0	68	58
-10	1	0	75	-59	5	3	0	0	154	-47	-7	6	0	30	30	-14	9	0	30	-25	-4	12	0	120	-104
-5	1	0	27	-24	8	3	0	0	222	-180	-6	6	0	35	37	-13	9	0	33	14	-2	12	0	81	-73
-2	1	0	30	27	9	3	0	0	127	-99	-5	6	0	149	155	-12	9	0	133	97	0	12	0	49	-42
-5	1	0	213	-234	9	3	0	0	55	43	-4	6	0	69	-65	-10	9	0	34	28	1	12	0	105	-27
-4	1	0	267	-429	-12	4	0	0	55	-46	-3	6	0	28	-20	-6	9	0	74	-66	4	12	0	39	26
-3	1	0	53	-59	-11	4	0	0	35	-24	-2	6	0	69	-65	-10	9	0	32	23	3	12	0	35	-32
3	1	0	47	54	-10	4	0	0	44	-49	-1	6	0	305	303	-5	9	0	164	-141	5	12	0	35	-32
4	1	0	230	-224	-8	4	0	0	105	103	0	6	0	235	-229	-3	9	0	190	171	-17	13	0	39	-23
5	1	0	232	-234	-7	4	0	0	35	-37	2	6	0	26	26	0	9	0	70	65	-10	13	0	48	-45
6	1	0	33	32	-5	4	0	0	351	364	4	6	0	169	140	1	9	0	33	-23	-8	13	0	43	-39
7	1	0	150	-130	-4	4	0	0	157	157	5	6	0	24	24	2	9	0	35	30	-7	13	0	52	44
9	1	0	123	-109	-3	4	0	0	157	-154	6	6	0	97	78	3	9	0	127	-104	-6	13	0	48	40
9	1	0	25	-39	-2	4	0	0	46	46	7	6	0	77	78	4	9	0	187	-149	-5	13	0	30	17
10	1	0	23	-21	0	4	0	0	59	61	9	6	0	41	24	4	9	0	32	-25	-3	13	0	38	32
12	1	0	33	26	0	4	0	0	82	73	13	6	0	30	9	7	9	0	41	-18	-2	13	0	43	-41
13	1	0	58	-31	1	4	0	0	122	125	-13	7	0	69	53	12	10	0	33	-14	-1	13	0	104	-97
14	1	0	48	-29	2	4	0	0	34	37	-13	7	0	54	43	-16	10	0	41	-14	-1	13	0	78	77
-17	2	0	23	19	3	4	0	0	101	102	-12	7	0	35	34	-13	10	0	36	-30	-13	14	0	48	-31
-14	2	0	22	19	4	4	0	0	277	267	-11	7	0	125	-116	-9	10	0	75	70	-12	14	0	46	-50
-9	2	0	22	146	5	4	0	0	121	114	-9	7	0	135	-37	-9	10	0	121	102	-10	14	0	47	-43
-5	2	0	236	235	7	4	0	0	30	30	-7	7	0	115	111	-8	10	0	87	-69	-9	14	0	38	-31
-6	2	0	117	121	10	4	0	0	29	-12	-5	7	0	89	-97	-6	10	0	45	41	-4	14	0	67	-69
-5	2	0	159	235	11	4	0	0	29	-12	-5	7	0	71	77	-5	10	0	78	-70	-3	14	0	64	-59
-3	2	0	22	-23	12	4	0	0	44	31	-5	7	0	71	77	-5	10	0	91	-85	-1	14	0	51	-55
3	2	0	26	-31	13	4	0	0	32	23	-2	7	0	150	152	-4	10	0	153	137	2	14	0	31	-24
3	2	0	223	230	-12	5	0	0	40	40	-2	7	0	104	100	-1	10	0	187	166	3	14	0	44	44
4	2	0	23	27	-11	5	0	0	67	37	-1	7	0	104	100	0	10	0	86	74	4	14	0	44	43
5	2	0	24	54	-10	5	0	0	43	-56	1	7	0	205	-191	2	10	0	74	76	-14	15	0	35	26
6	2	0	24	-26	-9	5	0	0	215	-201	1	7	0	140	-133	4	10	0	28	-5	-10	15	0	40	-48
7	2	0	48	41	-7	5	0	0	124	122	3	7	0	231	-204	7	10	0	26	43	-8	15	0	43	49
9	2	0	123	103	-6	5	0	0	124	25	4	7	0	120	-115	8	10	0	64	43	-10	15	0	63	40
10	2	0	70	57	-5	5	0	0	24	10	5	7	0	75	69	9	10	0	44	34	-7	15	0	39	41
12	2	0	64	47	-3	5	0	0	56	-54	9	7	0	70	-45	-14	11	0	71	-31	-5	15	0	64	64
13	2	0	47	12	-2	5	0	0	132	186	12	7	0	34	-41	-14	11	0	42	56	-4	15	0	50	56
-17	3	0	37	12	-1	5	0	0	395	-400	13	7	0	34	-41	-14	11	0	71	-31	-12	15	0	43	-40
-13	3	0	55	-33	0	5	0	0	252	-249	-15	8	0	35	-12	-8	11	0	58	55	-9	16	0	30	-30
-12	3	0	97	-77	1	5	0	0	16	-16	-13	8	0	47	-38	-7	11	0	60	55	-9	16	0	50	-60
-11	3	0	29	19	2	5	0	0	81	-61	-11	8	0	35	-26	-5	11	0	119	-112	-8	16	0	42	-53
-10	3	0	59	-34	3	5	0	0	145	-152	-10	8	0	82	-69	-4	11	0	64	-57	-5	16	0	35	39
-9	3	0	90	-37	3	5	0	0	33	32	-9	8	0	154	-136	-3	11	0	131	109	-4	17	0	39	67
-2	3	0	101	105	6	5	0	0	33	23	-7	8	0	75	-72	-2	11	0	73	-66	-9	17	0	36	35

4-13	H	K	L	FO	FC	H	K	L	EC	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
10-13			1	50	69	-3	-7	1	156	176	8	-4	1	159	-145	-9	1	1	95	-91	0	4	1	317	324	4	4	1	317	324
-1-12			1	35	91	-1	-7	1	123	142	10	-4	1	76	84	-8	1	1	174	-167	1	4	1	112	-122	1	4	1	112	-122
0-12			1	30	-41	0	-7	1	226	248	11	-4	1	37	-40	-7	1	1	57	-45	2	4	1	24	-31	2	4	1	24	-31
1-12			1	64	-36	2	-7	1	141	-143	-7	-3	1	89	-95	-6	1	1	51	45	3	4	1	56	-57	4	4	1	56	-57
5-12			1	74	-35	5	-7	1	163	152	-6	-3	1	106	-85	-5	1	1	102	124	4	4	1	46	-49	5	4	1	46	-49
6-12			1	109	-106	6	-7	1	151	127	-4	-3	1	72	-72	-4	1	1	91	100	6	4	1	85	79	6	4	1	85	79
9-12			1	64	-98	9	-7	1	133	124	-3	-3	1	122	-117	3	1	1	38	37	9	4	1	32	29	9	4	1	32	29
1-11			1	53	65	5	-7	1	133	124	-2	-3	1	38	-238	5	1	1	108	118	8	4	1	44	66	8	4	1	44	66
2-11			1	112	113	-7	-6	1	33	-59	-1	-3	1	65	53	6	1	1	74	-35	-7	5	1	141	-138	-7	5	1	141	-138
4-11			1	104	103	-6	-6	1	53	30	0	-3	1	235	242	7	1	1	50	44	-6	5	1	87	-93	-6	5	1	87	-93
5-11			1	187	183	-5	-6	1	112	-106	1	-3	1	272	369	8	1	1	94	90	-5	5	1	133	-131	-5	5	1	133	-131
7-11			1	37	-33	-3	-6	1	175	165	2	-3	1	121	-124	9	1	1	54	-60	-4	5	1	304	-300	-4	5	1	304	-300
8-11			1	42	44	-2	-6	1	98	102	5	-3	1	102	-115	-15	1	1	31	30	-2	5	1	77	-76	-2	5	1	77	-76
-3-10			1	57	-74	-1	-6	1	35	53	7	-3	1	26	25	-12	1	1	48	61	0	5	1	123	126	-1	5	1	123	126
-2-10			1	93	-102	0	-6	1	46	-53	8	-3	1	34	35	-9	1	1	36	-47	-1	5	1	181	183	-1	5	1	181	183
0-10			1	227	-219	1	-6	1	75	-69	9	-3	1	78	72	-7	1	1	147	155	1	5	1	147	155	1	5	1	147	155
1-10			1	148	-135	2	-6	1	27	15	10	-3	1	81	81	-6	1	1	31	29	2	5	1	122	-114	2	5	1	122	-114
2-10			1	119	111	3	-6	1	37	-34	-8	-2	1	131	125	-5	1	1	35	-33	3	5	1	153	-128	3	5	1	153	-128
3-10			1	62	63	4	-6	1	239	-294	-7	-2	1	169	155	-4	1	1	37	400	4	5	1	135	-152	4	5	1	135	-152
4-10			1	59	-57	5	-6	1	179	-173	-4	-2	1	38	-40	-3	1	1	31	356	5	5	1	135	-128	5	5	1	135	-128
5-10			1	48	-43	6	-6	1	59	69	-4	-2	1	111	-101	2	1	1	143	151	6	5	1	33	-35	6	5	1	33	-35
6-10			1	43	-33	7	-6	1	33	-30	-2	-2	1	46	46	3	1	1	56	-54	6	5	1	37	45	6	5	1	37	45
3-10			1	36	-44	10	-6	1	44	-47	5	-2	1	25	-27	4	1	1	110	-120	-12	6	1	70	86	-12	6	1	70	86
9-10			1	167	-182	-7	-5	1	133	-128	6	-2	1	74	-76	5	1	1	125	127	-11	6	1	155	148	-11	6	1	155	148
10-10			1	87	-100	-6	-5	1	25	-19	6	-2	1	31	-44	7	1	1	27	33	-9	6	1	194	195	-9	6	1	194	195
-4-9			1	148	164	-4	-5	1	41	-35	8	-2	1	152	-153	9	1	1	35	-35	-6	6	1	39	-50	-6	6	1	39	-50
-3-9			1	69	59	-3	-5	1	77	-71	9	-2	1	101	-94	7	1	1	67	73	-4	6	1	139	131	-4	6	1	139	131
-2-9			1	88	-82	-2	-5	1	61	96	10	-2	1	70	72	-8	1	1	251	-254	-3	6	1	179	162	-3	6	1	179	162
-1-9			1	68	-69	-1	-5	1	101	66	-11	-1	1	41	-52	-7	1	1	128	-128	-2	6	1	139	131	-2	6	1	139	131
0-9			1	87	88	0	-3	1	37	39	-11	-1	1	39	-38	-5	1	1	74	-91	0	6	1	305	307	0	6	1	305	307
1-9			1	104	-104	1	-5	1	347	337	-5	-1	1	100	-89	-4	1	1	60	69	-12	6	1	317	308	-12	6	1	317	308
2-9			1	39	46	2	-9	1	102	96	-5	-1	1	138	-148	3	1	1	82	-80	3	6	1	317	308	3	6	1	317	308
4-9			1	126	119	4	-5	1	105	-103	-3	-1	1	353	-374	1	1	1	564	-231	2	6	1	317	308	2	6	1	317	308
5-9			1	309	279	3	-5	1	71	74	-2	-1	1	138	-148	3	1	1	227	-231	3	6	1	317	308	3	6	1	317	308
6-9			1	84	79	4	-5	1	32	84	3	-1	1	72	80	4	1	1	60	-63	3	6	1	317	308	3	6	1	317	308
8-9			1	104	106	7	-5	1	72	66	4	-1	1	243	281	5	1	1	41	-34	-12	6	1	43	-63	-12	6	1	43	-63
9-9			1	30	57	8	-5	1	107	99	5	-1	1	48	49	6	1	1	35	-34	-8	7	1	53	-50	-8	7	1	53	-50
-6-8			1	30	42	9	-5	1	130	179	9	-1	1	95	-91	8	1	1	125	123	-5	7	1	62	-50	-5	7	1	62	-50
-5-8			1	79	-84	10	-5	1	51	61	8	-1	1	45	44	6	1	1	39	-84	-8	7	1	120	-115	-8	7	1	120	-115
-3-8			1	33	-29	11	-5	1	32	-44	9	-1	1	26	-23	10	1	1	49	47	-5	7	1	185	-177	-5	7	1	185	-177
-1-8			1	81	-83	-8	-4	1	70	65	-9	0	1	70	-65	-12	1	1	98	117	-3	7	1	186	-177	-3	7	1	186	-177
0-8			1	134	-123	-5	-4	1	97	-94	-7	0	1	114	117	-9	1	1	49	47	-4	7	1	186	-177	-4	7	1	186	-177
1-8			1	307	-286	-4	-4	1	215	-212	-8	0	1	249	248	-9	1	1	97	97	-3	7	1	186	-177	-3	7	1	186	-177
4-8			1	222	-196	-3	-4	1	57	67	-4	0	1	212	231	-8	1	1	35	29	-2	7	1	186	-177	-2	7	1	186	-177
5-8			1	55	-46	-2	-4	1	203	194	-3	0	1	37	45	-6	1	1	41	42	0	7	1	186	-177	0	7	1	186	-177
6-8			1	92	-91	-1	-4	1	250	-254	-3	0	1	56	-61	-7	1	1	53	60	-4	7	1	186	-177	-4	7	1	186	-177
8-8			1	32	-23	0	-4	1	179	179	5	0	1	159	165	-5	1	1	67	-68	1	7	1	186	-177	1	7	1	186	-177
9-8			1	101	-111	1	-4	1	175	179	9	0	1	90	-75	-4	1	1	162	-68	2	7	1	186	-177	2	7	1	186	-177
10-8			1	107	-113	3	-4	1	59	-72	9	0	1	117	-118	-3	1	1	398	168	3	7	1	186	-177	3	7	1	186	-177
-7-7			1	36	-53	4	-4	1	139	-159	-12	1	1	38	-78	-2	1	1	157	159	4	7	1	186	-177	4	7	1	186	-177
-4-7			1	108	104	5	-4	1	126	-141	-11	1	1	92	-108	-1	1	1	28	-25	5	7	1	186	-177	5	7	1	186	-177

[illegible]

0	13	1	50	-87	10	-7	2	115	130	16	-4	2	31	4	-7	1	2	102	-106	7	4	2	27
-3	13	1	60	-61	8	-7	2	56	-56	9	-4	2	97	-99	-5	1	2	171	165	6	4	2	179
-3	13	1	110	-125	5	-7	2	51	-50	10	-4	2	122	-130	-5	1	2	122	138	6	4	2	138
-1	13	1	65	-32	3	-7	2	75	-35	8	-4	2	25	20	-11	1	2	72	60	3	4	2	54
-1	12	1	65	75	3	-7	2	97	-92	7	-4	2	110	-111	10	0	2	46	-53	1	4	2	42
-3	12	1	55	55	2	-7	2	270	260	5	-4	2	108	-106	5	0	2	225	-236	0	4	2	332
-4	12	1	180	159	1	-7	2	238	280	2	-4	2	108	-106	5	0	2	108	-106	0	4	2	332
-3	12	1	55	55	2	-7	2	270	260	5	-4	2	108	-106	5	0	2	225	-236	0	4	2	332
-3	11	1	170	-158	-7	-7	2	58	94	-3	-4	2	133	-124	-7	0	2	189	-187	-7	4	2	86
-3	11	1	52	52	8	-3	2	34	34	-4	-4	2	40	-38	-9	0	2	42	-42	-8	4	2	86
-7	11	1	49	45	5	-8	2	151	-150	-5	-4	2	78	73	-9	-1	2	136	138	-10	4	2	76
-3	11	1	103	-106	5	-8	2	151	-150	-5	-4	2	78	73	-9	-1	2	136	138	-10	4	2	76
-3	11	1	127	-132	4	-3	2	34	34	-4	-4	2	40	-38	-9	0	2	42	-42	-8	4	2	86
-3	11	1	65	93	3	-3	2	89	-82	13	-5	2	115	-120	8	-1	2	236	243	-12	4	2	60
4	10	1	58	62	2	-8	2	117	-108	11	-5	2	56	75	5	-1	2	78	74	9	3	2	47
2	10	1	153	141	-1	-8	2	64	55	10	-5	2	42	54	3	-1	2	39	-45	5	3	2	109
1	10	1	153	141	-1	-8	2	64	55	10	-5	2	42	54	3	-1	2	39	-45	5	3	2	109
0	10	1	60	-59	-3	-8	2	213	-204	9	-5	2	47	-52	-2	-1	2	142	146	4	3	2	167
-1	10	1	42	-41	-4	-8	2	115	-118	7	-5	2	83	-80	-3	-1	2	365	392	3	3	2	54
-2	10	1	75	-71	-6	-3	2	59	-91	5	-5	2	61	60	-4	-1	2	192	206	1	3	2	43
-3	10	1	38	37	10	-3	2	75	99	4	-5	2	195	185	-5	-1	2	99	-86	2	3	2	442
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-4	10	1	191	156	4	-3	2	77	66	3	-5	2	56	40	-9	-1	2	51	56	-3	3	2	49
-2	10	1	191	156	4	-3	2	77	66	3	-5	2	56	40	-9	-1	2	51	56	-3	3	2	49
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2	32	32	-7	-1	2	86	83	-3	3	2	82
-3	10	1	183	167	7	-3	2	120	120	3	-5	2											

8	4	2	40	-49	0	3	2	136	-139	-7	14	2	48	82	2	-7	3	134	-122	8	-4	3	44
-12	5	2	52	-73	4	5	2	251	-241	-2	14	2	45	59	3	-7	3	139	132	9	-4	3	84
-11	5	2	51	-93	4	5	2	76	-77	0	15	2	32	-42	5	-7	3	99	-65	10	-4	3	68
-7	5	2	121	130	4	5	2	40	55	5	13	3	35	-95	6	-7	3	39	32	-10	-3	3	50
-4	5	2	171	136	-10	5	2	32	-96	1	12	3	50	77	8	-7	3	50	-47	-8	-3	3	34
-5	5	2	149	-136	-2	5	2	62	-50	3	12	3	78	102	9	-7	3	62	-70	-7	-3	3	28
-4	5	2	130	134	-6	5	2	104	-98	3	12	3	54	-72	10	-7	3	88	-98	-6	-3	3	28
-3	5	2	133	-139	-5	5	2	33	-50	1	11	3	35	40	11	-7	3	40	-44	-5	-3	3	55
-2	5	2	134	-135	-4	5	2	95	91	5	11	3	59	-68	-3	-6	3	67	-78	-4	-3	3	58
-1	5	2	105	-93	-2	5	2	108	109	4	11	3	36	-35	-4	-6	3	36	33	-2	-3	3	240
2	5	2	105	-97	-2	5	2	108	109	4	11	3	36	-35	-4	-6	3	36	33	-2	-3	3	240
3	5	2	70	70	-1	5	2	45	-97	9	11	3	72	-75	0	-6	3	117	-108	0	-3	3	163
4	5	2	30	24	0	5	2	39	93	-2	10	3	52	-55	1	-6	3	70	72	2	-3	3	40
5	5	2	179	171	1	5	2	125	-157	0	10	3	60	68	2	-6	3	271	-245	3	-3	3	101
6	5	2	195	179	2	5	2	46	-114	1	10	3	43	65	3	-6	3	71	-63	4	-3	3	40
-9	5	2	55	-60	5	5	2	46	58	2	10	3	48	49	5	-6	3	61	60	5	-3	3	100
-10	5	2	46	47	-12	10	2	64	95	5	10	3	114	115	6	-6	3	88	84	6	-3	3	95
-8	5	2	97	-91	-8	10	2	63	-63	6	10	3	43	43	8	-6	3	45	-33	7	-3	3	146
-7	5	2	123	129	-6	10	2	37	-35	7	10	3	84	-91	10	-6	3	44	42	-6	-2	3	43
-6	5	2	65	67	-5	10	2	84	-81	-4	-9	3	34	-54	-7	-5	3	80	-86	-5	-2	3	43
-5	5	2	39	-40	-3	10	2	190	175	-3	-9	3	47	-54	-6	-5	3	69	63	-3	-2	3	290
-3	5	2	91	-37	-2	10	2	166	155	-2	-9	3	72	-78	-4	-5	3	69	56	-3	-2	3	158
-2	5	2	111	-112	0	10	2	55	60	1	-9	3	164	-154	-3	-5	3	69	56	-2	-2	3	89
-1	5	2	42	49	1	10	2	40	-40	2	-9	3	36	31	-2	-5	3	109	-109	4	-2	3	84
0	5	2	154	-159	4	10	2	74	-105	3	-9	3	138	129	-2	-5	3	93	92	6	-2	3	142
1	5	2	155	-156	-6	11	2	59	57	4	-9	3	62	-57	-3	-5	3	80	71	7	-2	3	38
2	5	2	154	-156	-7	11	2	44	-37	5	-9	3	102	-61	0	-5	3	97	-97	7	-2	3	41
3	5	2	30	14	-7	11	2	217	-197	7	-9	3	102	-102	1	-5	3	170	-161	8	-2	3	69
6	5	2	45	-42	-6	11	2	82	-76	9	-9	3	60	-71	2	-5	3	166	-151	10	-2	3	77
6	5	2	47	-48	-5	11	2	45	-36	10	-9	3	55	-83	3	-5	3	38	38	-11	-1	3	39
-11	7	2	133	-151	-4	11	2	115	-109	10	-9	3	64	-70	4	-5	3	31	-35	-11	-1	3	111
-10	7	2	56	-48	0	11	2	120	-126	-3	-8	3	112	112	5	-5	3	189	-188	-8	-1	3	51
-8	7	2	98	-45	2	11	2	99	-114	-2	-8	3	109	-99	6	-5	3	74	70	-7	-1	3	198
-5	7	2	40	-45	12	11	2	33	-37	0	-8	3	83	-137	7	-5	3	118	111	-6	-1	3	52
-4	7	2	166	159	-11	12	2	71	96	1	-8	3	76	69	8	-5	3	61	-55	-5	-1	3	61
-2	7	2	209	-204	-9	12	2	46	46	2	-8	3	76	77	9	-5	3	41	-40	-4	-1	3	84
0	7	2	36	-41	-5	12	2	92	86	3	-8	3	56	48	10	-5	3	39	-47	-3	-1	3	94
1	7	2	52	-38	-5	12	2	36	-32	4	-8	3	69	64	-8	-4	3	42	47	-2	-1	3	93
1	7	2	31	29	-4	12	2	131	-127	5	-8	3	82	83	-7	-4	3	124	-115	-2	-1	3	214
2	7	2	40	35	-3	12	2	54	55	4	-8	3	167	150	-6	-4	3	210	-186	3	-1	3	74
3	7	2	61	60	-2	12	2	145	144	5	-8	3	152	137	-5	-4	3	34	24	4	-1	3	54
4	7	2	152	144	-1	12	2	55	68	7	-8	3	49	-48	-4	-4	3	82	76	6	-1	3	82
5	7	2	154	156	-10	13	2	35	-22	8	-8	3	44	-43	-4	-4	3	21	11	-1	-1	3	69
-12	8	2	50	-50	-7	13	2	32	-89	9	-8	3	38	87	-2	-4	3	33	-29	11	-1	3	32
-3	8	2	53	-30	-6	13	2	61	-71	-5	-7	3	70	65	-1	-4	3	36	-37	-9	0	3	101
-7	8	2	56	51	-6	13	2	35	-108	-4	-7	3	67	-76	0	-4	3	33	31	-6	0	3	45
-6	8	2	47	190	-2	13	2	114	-128	-3	-7	3	70	59	1	-4	3	125	-120	-5	0	3	117
-5	8	2	117	114	-1	13	2	30	-13	-1	-7	3	51	-48	2	-4	3	148	-146	-3	0	3	186
-3	8	2	163	153	6	13	2	31	45	0	-7	3	62	-59	4	-4	3	74	63	4	0	3	43
-1	8	2	61	65	-1	14	2	76	90	1	-7	3	249	-232	7	-4	3	93	85	5	0	3	100



H	K	L	F0	FC	H	K	L	F0	FC
6	7	7	145	-159	-4	13	3	129	126
7	7	7	176	-157	-3	13	3	102	113
7	7	7	176	-157	-2	13	3	37	41
7	7	7	176	-157	-1	13	3	47	-52
7	7	7	176	-157	-1	13	3	78	-80
7	7	7	176	-157	-1	13	3	38	-36
7	7	7	176	-157	-1	13	3	62	73
7	7	7	176	-157	-1	13	3	35	-96
7	7	7	176	-157	-1	13	3	34	-53
7	7	7	176	-157	-1	13	3	48	104
7	7	7	176	-157	-1	13	3	55	-92
7	7	7	176	-157	-1	13	3	40	-44
7	7	7	176	-157	-1	13	3	58	-87
7	7	7	176	-157	-1	13	3	78	-58
7	7	7	176	-157	-1	13	3	66	-74
7	7	7	176	-157	-1	13	3	82	90
7	7	7	176	-157	-1	13	3	62	71
7	7	7	176	-157	-1	13	3	104	117
7	7	7	176	-157	-1	13	3	33	-86
7	7	7	176	-157	-1	13	3	45	-57
7	7	7	176	-157	-1	13	3	45	-57
7	7	7	176	-157	-1	13	3	52	-61
7	7	7	176	-157	-1	13	3	45	-51
7	7	7	176	-157	-1	13	3	181	-172
7	7	7	176	-157	-1	13	3	227	-205
7	7	7	176	-157	-1	13	3	64	58
7	7	7	176	-157	-1	13	3	51	-54
7	7	7	176	-157	-1	13	3	36	45
7	7	7	176	-157	-1	13	3	62	65
7	7	7	176	-157	-1	13	3	169	164
7	7	7	176	-157	-1	13	3	159	147
7	7	7	176	-157	-1	13	3	55	52
7	7	7	176	-157	-1	13	3	99	84
7	7	7	176	-157	-1	13	3	36	31
7	7	7	176	-157	-1	13	3	43	30
7	7	7	176	-157	-1	13	3	114	119
7	7	7	176	-157	-1	13	3	56	60
7	7	7	176	-157	-1	13	3	93	-116
7	7	7	176	-157	-1	13	3	58	-57
7	7	7	176	-157	-1	13	3	29	-32
7	7	7	176	-157	-1	13	3	95	-94
7	7	7	176	-157	-1	13	3	108	-96
7	7	7	176	-157	-1	13	3	47	46
7	7	7	176	-157	-1	13	3	106	-103
7	7	7	176	-157	-1	13	3	130	-119
7	7	7	176	-157	-1	13	3	225	-209
7	7	7	176	-157	-1	13	3	103	-91
7	7	7	176	-157	-1	13	3	174	-162
7	7	7	176	-157	-1	13	3	67	-67
7	7	7	176	-157	-1	13	3	34	35

PAGE 5

5	-3	4	97	-91	7	1	4	104	-122	7	5	4	50	-50	-3	10	4	120	108	2	-8	5	44	-49
10	-3	4	67	-95	4	1	4	32	-31	7	5	4	52	-51	-2	10	4	61	-60	3	-8	5	146	130
-10	-2	4	40	-47	5	1	4	92	-103	-11	5	4	62	-65	-1	10	4	198	-184	4	-8	5	67	53
-5	-2	4	41	-36	4	1	4	114	-112	-7	5	4	159	-153	1	10	4	45	-42	5	-8	5	58	-57
-5	-2	4	144	139	7	1	4	51	-57	-4	5	4	53	-55	2	10	4	125	-124	6	-8	5	41	-45
-4	-2	4	67	-53	-7	2	4	105	-39	-5	5	4	203	-208	3	10	4	50	-54	-4	-7	5	54	-51
-3	-2	4	139	135	-6	2	4	172	-20	-2	5	4	109	-116	-11	11	4	84	-86	-4	-7	5	69	-64
-2	-2	4	114	113	-5	2	4	52	-56	-1	5	4	42	-44	-5	11	4	77	-72	-3	-7	5	29	-29
-1	-2	4	63	-56	-3	2	4	60	-63	1	5	4	88	-89	-6	11	4	95	-94	-1	-7	5	42	-37
0	-2	4	20	-23	3	2	4	159	-164	2	5	4	163	152	-3	11	4	117	105	1	-7	5	81	75
2	-2	4	195	201	6	2	4	105	102	3	5	4	54	-51	-2	11	4	194	178	2	-7	5	65	61
3	-2	4	286	302	7	2	4	111	94	4	5	4	55	-51	-1	11	4	73	64	3	-7	5	104	90
4	-2	4	65	70	10	2	4	34	71	5	5	4	60	74	1	11	4	35	-37	6	-7	5	86	76
5	-2	4	260	138	-11	3	4	55	51	7	6	4	69	-80	-12	12	4	33	-37	8	-7	5	80	-84
6	-2	4	80	-79	-10	3	4	156	153	-11	7	4	72	-70	-10	12	4	54	-51	-5	-6	5	162	156
-10	-1	4	61	-68	-6	3	4	137	-148	-3	7	4	110	101	-7	12	4	174	-157	-3	-6	5	59	-53
-7	-1	4	155	-144	-5	3	4	58	63	-8	7	4	28	-27	-6	12	4	176	-160	-2	-6	5	28	20
-6	-1	4	38	32	-4	3	4	43	43	-7	7	4	103	105	-1	12	4	52	-53	-1	-6	5	26	18
-5	-1	4	149	156	-1	3	4	154	-160	-5	7	4	207	205	2	12	4	69	-83	3	-6	5	48	-42
-4	-1	4	58	-50	2	3	4	94	-82	-5	7	4	65	71	3	12	4	33	-61	4	-6	5	122	114
-3	-1	4	55	-57	3	3	4	104	-105	-3	7	4	27	-21	-11	13	4	74	78	5	-6	5	183	166
-2	-1	4	93	-98	5	3	4	114	-109	-2	7	4	40	-39	-10	13	4	71	73	4	-6	5	34	-32
-2	-1	4	311	-340	6	3	4	194	-172	-1	7	4	45	-48	-2	13	4	47	52	-9	-5	5	65	-62
3	-1	4	33	43	6	3	4	61	71	1	7	4	94	82	-8	13	4	40	42	-1	-5	5	205	-190
4	-1	4	141	150	-16	4	4	34	33	2	7	4	103	-96	-10	13	4	67	77	-6	-5	5	65	-62
5	-1	4	112	-113	-10	4	4	40	33	1	7	4	67	65	-8	14	4	40	42	-1	-5	5	142	-133
7	-1	4	48	-53	-9	4	4	38	-37	3	7	4	162	152	-6	14	4	43	-54	0	-5	5	61	61
8	-1	4	64	-72	-8	4	4	126	134	-11	8	4	143	-134	-3	14	4	61	-72	2	-5	5	37	-28
10	-1	4	65	-83	-7	4	4	149	-168	-6	8	4	56	68	-10	15	4	50	83	3	-5	5	86	-78
11	-1	4	33	-54	-6	4	4	172	-190	-5	8	4	114	-113	-7	15	4	68	87	4	-5	5	61	50
-11	0	4	32	37	-4	4	4	80	85	-3	8	4	39	47	-4	15	4	65	-97	5	-5	5	47	45
-10	0	4	68	-68	-4	4	4	172	-190	-2	8	4	200	-190	-2	10	5	32	-48	6	-5	5	69	63
-8	0	4	99	-95	0	4	4	33	-30	-3	8	4	169	-155	-1	10	5	77	91	-5	-4	5	38	35
-7	0	4	31	33	1	4	4	183	175	-1	8	4	93	86	0	-10	5	40	-37	-6	-4	5	187	170
-6	0	4	30	-31	2	4	4	151	-149	5	8	4	62	59	1	-10	5	70	91	-5	-4	5	38	35
-5	0	4	85	78	4	4	4	48	-49	6	8	4	32	48	4	-10	5	45	-58	-4	-4	5	118	107
-4	0	4	55	51	5	4	4	61	54	-9	9	4	41	36	6	-10	5	43	-54	-3	-4	5	51	-49
-3	0	4	117	130	-10	5	4	173	167	-9	9	4	39	-30	7	-10	5	45	-55	-2	-4	5	97	99
-2	0	4	89	-96	-7	5	4	76	80	-5	9	4	215	207	-4	-9	5	39	-66	-1	-4	5	120	115
2	0	4	78	99	-7	5	4	144	148	-4	9	4	119	111	-3	-9	5	31	43	0	-4	5	31	-28
4	0	4	49	44	-6	5	4	30	-29	-5	9	4	42	49	-1	-9	5	33	-40	1	-4	5	27	-29
5	0	4	185	182	-5	5	4	91	-95	-3	9	4	123	119	0	-9	5	50	47	2	-4	5	72	-67
6	0	4	132	130	-4	5	4	52	52	-2	9	4	92	87	1	-9	5	36	38	4	-4	5	44	41
7	0	4	28	-16	-3	5	4	119	-120	-1	9	4	29	-28	2	-9	5	78	77	5	-4	5	44	41
8	0	4	32	45	-1	5	4	187	189	1	9	4	90	-80	3	-9	5	92	91	6	-4	5	44	41
10	0	4	45	48	0	5	4	58	59	3	9	4	129	128	4	-9	5	44	-52	7	-4	5	89	82
-11	1	4	27	-30	1	5	4	78	-77	4	9	4	30	36	6	-9	5	50	48	8	-4	5	62	60
-9	1	4	169	-130	2	5	4	104	99	-10	10	4	167	-152	-4	-8	5	40	-39	-9	-3	5	85	-91
-7	1	4	52	-48	4	5	4	30	-26	-9	10	4	47	-42	-3	-8	5	31	-35	-8	-3	5	32	-36
-5	1	4	163	135	5	5	4	43	-47	-5	10	4	134	-128	0	-8	5	51	-48	-7	-3	5	30	-36
2	1	4	250	-284	6	5	4	152	-146	-5	10	4	43	-50	-2	-8	5	89	86	-6	-3	5	159	-146

M	K	L	FD	FC	M	K	L	FD	FC	M	K	L	FD	FC	M	K	L	FD	FC
-5	-3	5	91	-35	-7	1	5	32	-35	0	5	5	62	-62	-4	9	5	80	80
-4	-2	5	51	47	-6	1	5	49	-69	3	5	5	150	-147	-3	9	5	56	-50
-3	-2	5	23	14	-5	1	5	247	-252	4	5	5	41	44	-2	9	5	67	-64
-1	-3	5	35	-15	-4	1	5	113	-120	7	5	5	35	-25	2	9	5	47	-43
1	-3	5	154	-15	2	1	5	59	25	3	5	5	44	-67	3	9	5	142	-121
1	-3	5	50	-27	3	1	5	54	-65	-14	5	5	26	53	6	9	5	44	-67
3	-3	5	63	-54	4	1	5	195	-154	-11	5	5	75	70	-10	10	5	93	89
3	-3	5	273	-251	5	1	5	46	-44	-9	5	5	73	-76	-5	10	5	126	-109
5	-3	5	49	-44	4	1	5	36	-39	-6	5	5	124	129	-2	10	5	95	94
7	-3	5	83	93	7	1	5	134	-130	-4	5	5	156	159	-1	10	5	138	127
7	-3	5	30	33	8	1	5	58	-53	-4	5	5	79	78	1	10	5	48	39
10	-2	5	33	35	-10	2	5	51	41	-3	5	5	51	57	-2	10	5	124	113
-10	-2	5	85	34	-7	2	5	117	117	-2	5	5	258	247	-10	11	5	43	44
-9	-2	5	31	25	-7	2	5	35	102	-1	5	5	73	70	-9	11	5	140	136
-3	-2	5	52	-48	-4	2	5	260	280	0	5	5	124	-124	-8	11	5	46	45
-5	-2	5	122	118	-5	2	5	60	50	1	5	5	24	-13	-5	11	5	86	-80
-4	-2	5	157	153	-4	2	5	53	-68	2	5	5	80	77	-2	11	5	152	-137
-3	-2	5	77	75	-3	2	5	131	190	3	5	5	152	141	-1	11	5	62	54
-2	-2	5	136	134	2	2	5	308	319	4	5	5	152	141	0	11	5	70	66
-1	-2	5	219	220	3	2	5	54	53	6	5	5	67	72	1	11	5	30	-22
0	-2	5	61	68	5	2	5	40	-32	7	5	5	97	112	-16	12	5	35	35
1	-2	5	95	-97	6	2	5	54	52	-13	5	5	38	42	-13	12	5	34	-40
2	-2	5	100	102	6	2	5	75	75	-10	5	5	45	-39	-7	12	5	119	107
6	-2	5	46	-47	-11	3	5	122	-115	-9	5	5	81	-89	-6	12	5	86	82
8	-2	5	117	110	-9	3	5	47	42	-7	5	5	93	-97	-4	12	5	45	-33
9	-2	5	120	125	-7	3	5	46	46	-6	5	5	204	-207	-4	12	5	45	-33
-9	-1	5	42	-35	-7	3	5	59	-63	-4	5	5	97	95	-3	12	5	58	58
-8	-1	5	61	-59	-5	3	5	37	-40	-3	5	5	50	-48	2	12	5	58	75
-7	-1	5	43	-40	-4	3	5	39	-42	-2	5	5	69	-60	-3	12	5	39	52
-6	-1	5	175	-173	1	3	5	42	42	-1	5	5	70	-72	-11	13	5	44	-41
-5	-1	5	204	-204	2	3	5	123	-121	0	5	5	82	-79	-9	13	5	110	110
-4	-1	5	38	34	2	3	5	117	-111	1	5	5	81	-44	-6	13	5	63	64
-3	-1	5	27	45	3	3	5	47	-74	2	5	5	181	-172	-2	13	5	93	-98
-2	-1	5	123	-122	-11	4	5	42	39	3	5	5	236	-212	-10	14	5	59	64
-3	-1	5	174	-191	-7	4	5	53	60	6	5	5	38	-34	-6	14	5	61	64
4	-1	5	45	46	-6	4	5	270	307	4	5	5	81	81	-3	14	5	39	-41
5	-1	5	31	-34	-5	4	5	125	142	-11	8	5	93	85	-1	14	5	49	-39
7	-1	5	53	-53	-4	4	5	43	-50	-9	8	5	65	-64	-7	15	5	36	-38
-10	0	5	129	128	0	4	5	20	-10	-7	8	5	43	-44	-6	15	5	47	57
-8	0	5	117	110	2	4	5	103	107	-7	8	5	36	29	-5	15	5	71	84
-7	0	5	26	-19	3	4	5	271	269	-5	8	5	37	36	-10	16	5	44	-63
-6	0	5	36	27	4	4	5	145	149	-4	8	5	70	67	-9	16	5	42	-60
2	0	5	119	123	4	4	5	86	77	-3	8	5	84	81	-7	17	5	36	-42
2	0	5	140	157	7	4	5	55	60	-2	8	5	227	219	-7	17	5	47	68
3	0	5	124	147	-10	5	5	115	-107	-1	8	5	187	175	-4	11	6	62	90
4	0	5	27	-28	-7	5	5	84	-81	1	8	5	41	44	-1	10	6	56	-81
6	0	5	86	35	-5	5	5	115	-124	2	8	5	89	82	-1	10	6	78	-100
8	0	5	30	21	-5	5	5	78	-77	3	8	5	67	-65	-3	10	6	41	-43
12	0	5	29	24	-4	5	5	36	86	7	8	5	39	72	-1	9	6	54	57
-12	1	5	23	-22	-4	5	5	86	-93	-10	9	5	59	57	0	-9	6	36	-44
-11	1	5	43	-33	-3	5	5	34	-40	-7	9	5	34	-31	-2	-9	6	58	59
-9	1	5	54	-34	-2	5	5	240	-243	-5	9	5	74	-68	3	-9	6	46	57
															4	-9	6	76	76

2	-4	4	12	-11	-5	0	4	121	121	5	4	6	65	61	-9	9	6	37	-36	2	-9	7	38	-42
1	-4	4	91	-92	-3	0	4	58	58	6	4	6	34	-32	-8	9	6	53	53	-9	-9	7	35	44
3	-4	4	140	-132	-2	0	4	22	-23	9	4	6	44	-53	-5	9	6	84	-79	-3	-8	7	68	-91
4	-4	4	32	-30	2	0	4	72	-33	-14	5	6	33	-58	-4	9	6	140	-127	-3	-8	7	30	-31
7	-4	4	120	-124	3	0	4	136	143	-10	5	6	36	-32	-3	9	6	41	-37	-1	-8	7	34	-38
5	-4	4	37	-37	3	0	4	34	-33	-9	5	6	38	-32	-2	9	6	48	-49	-8	-7	7	33	-57
3	-3	4	37	-36	7	0	4	44	-38	-6	5	6	26	-5	0	9	6	68	-62	-5	-7	7	40	-16
-3	-3	4	103	-96	2	0	4	44	-34	-5	5	6	69	-71	3	9	6	42	-38	-3	-7	7	29	-23
-4	-3	4	112	-96	12	0	4	32	-34	-5	5	6	208	-228	-14	10	6	45	51	0	-7	7	93	-87
-2	-3	4	114	-114	-9	0	4	32	-34	-5	5	6	91	-87	-9	10	6	51	48	1	-7	7	131	-118
1	-3	4	142	-117	-5	0	4	56	-47	-4	5	6	101	-87	-8	10	6	114	63	4	-7	7	55	54
2	-3	4	81	-92	-7	0	4	57	-59	-3	5	6	34	105	-6	10	6	114	108	6	-7	7	41	-45
3	-3	4	115	-92	-5	0	4	53	-65	-2	5	6	26	-21	-5	10	6	223	201	-4	-6	7	90	-88
5	-3	4	119	-115	2	0	4	28	-32	0	5	6	47	-49	-4	10	6	49	42	-3	-6	7	33	-86
6	-3	4	47	-44	3	0	4	72	-84	1	5	6	38	-41	-3	10	6	27	22	-2	-6	7	85	-47
7	-3	4	79	-74	4	0	4	26	19	2	5	6	76	-80	-2	10	6	42	32	-1	-6	7	46	-47
11	-2	4	30	-3	1	0	4	59	71	3	5	6	30	-28	1	10	6	46	77	0	-6	7	93	-83
7	-3	4	31	-3	1	0	4	45	42	-12	6	6	38	-41	4	10	6	74	91	2	-6	7	49	-46
-3	-2	4	31	-35	6	0	4	90	-39	-9	6	6	91	-91	-12	11	6	38	-35	5	-6	7	32	-63
-7	-2	4	105	-39	5	0	4	37	-39	-7	6	6	170	-173	-10	11	6	86	-78	-8	-6	7	75	-34
-5	-2	4	50	-46	-10	0	4	51	-48	-6	6	6	48	-49	-9	11	6	117	-105	-5	-5	7	38	-54
-5	-2	4	25	-27	-5	0	4	71	-75	-6	6	6	60	-58	-7	11	6	35	-22	-7	-5	7	43	-55
-3	-2	4	74	-70	-4	0	4	93	-99	-4	6	6	86	-82	-6	11	6	65	-59	-5	-5	7	125	-113
-2	-2	4	97	-72	-4	0	4	227	-260	-2	6	6	65	-67	-1	11	6	140	-133	-4	-5	7	80	-78
-2	-2	4	173	-92	2	0	4	72	-70	-1	6	6	145	137	-14	12	6	125	-114	-3	-5	7	57	-51
0	-2	4	58	-56	4	0	4	155	-164	0	6	6	184	191	-14	12	6	35	51	-2	-5	7	28	-24
-1	-2	4	112	-107	5	0	4	75	-72	3	6	6	49	47	-10	12	6	38	42	0	-5	7	40	-38
2	-2	4	82	-35	4	0	4	62	-57	-13	7	6	51	-45	-9	12	6	46	-37	1	-5	7	96	-90
5	-2	4	56	-68	-9	0	4	138	-133	-8	7	6	34	-31	-5	12	6	181	160	4	-5	7	138	120
6	-2	4	47	-51	-5	0	4	108	-112	-5	7	6	198	-198	-2	12	6	92	80	5	-5	7	67	66
7	-2	4	105	-109	-6	0	4	59	-67	-4	7	6	168	-165	-2	12	6	86	79	-9	-4	7	44	43
8	-2	4	82	-26	-5	0	4	40	-42	-3	7	6	29	21	-1	12	6	63	61	-9	-4	7	53	-63
-3	-1	4	59	-49	-4	0	4	41	-38	-2	7	6	78	-69	-9	13	6	104	-104	-5	-4	7	42	42
-3	-1	4	82	-26	-4	0	4	114	-114	-1	7	6	104	-105	-7	13	6	36	-22	-4	-4	7	35	-32
-5	-1	4	82	-26	2	0	4	96	-78	1	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4	82	-26	3	0	4	96	-78	2	7	6	28	27	-6	13	6	126	-117	-4	-4	7	35	-32
-5	-1	4</																						

H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
4	-3	7	144	145	9	1	7	41	43	-1	6	7	154	-158	-8	11	7	120	-113
5	-3	7	114	114	-11	2	7	31	32	0	6	7	158	-158	-7	11	7	64	-60
5	-3	7	52	60	-7	2	7	52	-48	1	5	7	47	45	-5	11	7	58	-53
-3	-2	7	55	-93	-6	2	7	56	-48	2	6	7	31	22	-4	11	7	41	-38
-3	-2	7	115	-105	-5	2	7	151	-144	3	6	7	64	-60	-3	11	7	29	24
-5	-2	7	59	-97	-4	2	7	151	-152	3	6	7	32	-52	-1	11	7	84	76
-2	-2	7	72	-52	2	2	7	51	-58	-12	7	7	41	-39	0	11	7	50	48
-1	-2	7	54	-57	3	2	7	42	-43	-10	7	7	30	26	-1	11	7	48	-47
0	-2	7	154	-134	4	2	7	144	-144	-8	7	7	74	-83	-12	12	7	50	47
1	-2	7	152	-150	5	2	7	113	-107	-6	7	7	35	29	-9	12	7	86	80
3	-2	7	93	-33	7	2	7	41	-44	-5	7	7	105	112	-9	12	7	46	38
4	-2	7	157	-161	9	2	7	52	-51	-4	7	7	42	37	-5	12	7	70	-61
6	-2	7	42	38	-10	3	7	35	38	-3	7	7	69	-66	-3	12	7	38	-23
9	-2	7	33	-49	-10	3	7	103	107	-1	7	7	93	-94	-2	12	7	60	-56
-9	-1	7	53	51	-8	3	7	74	70	0	7	7	72	-75	0	12	7	73	73
-7	-1	7	33	-25	-6	3	7	54	60	-2	12	7	47	-42	1	12	7	33	28
-6	-1	7	79	63	-5	3	7	103	126	3	7	7	58	54	2	12	7	29	-15
-5	-1	7	79	81	-4	3	7	36	-95	5	7	7	89	31	-7	13	7	47	-58
-4	-1	7	170	170	1	3	7	30	90	-13	8	7	41	31	-7	13	7	41	-35
-3	-1	7	124	132	2	3	7	25	25	-13	8	7	59	54	-6	13	7	36	-31
-1	-1	7	172	171	2	3	7	134	140	-11	8	7	37	-32	-4	13	7	50	-41
0	-1	7	123	134	4	3	7	32	90	-9	8	7	34	-33	-9	14	7	110	-100
1	-1	7	75	-75	5	3	7	25	-25	-7	8	7	43	-34	-4	14	7	49	-56
2	-1	7	39	-43	-13	4	7	36	-39	-4	8	7	134	129	-13	15	7	86	-80
3	-1	7	50	59	-10	4	7	37	-39	-3	8	7	54	52	-12	15	7	36	-44
4	-1	7	70	74	-5	4	7	31	-27	-2	8	7	52	-45	-12	15	7	44	-45
5	-1	7	104	101	-8	4	7	59	110	-1	8	7	39	-40	-6	15	7	33	-28
6	-1	7	28	45	-6	4	7	50	-69	0	8	7	109	-107	-4	15	7	54	-63
9	-1	7	80	85	-4	4	7	31	-102	1	8	7	45	-47	-3	15	7	39	-50
-9	0	7	33	45	0	4	7	76	-79	5	8	7	36	28	-5	16	7	51	62
-8	0	7	107	-103	3	4	7	107	113	-13	9	7	33	28	-11	17	7	35	-1
-7	0	7	73	-71	4	4	7	30	-31	-11	9	7	37	-30	-9	17	7	43	-59
-6	0	7	82	-74	5	4	7	32	-58	-9	9	7	67	-61	-2	10	8	37	40
-5	0	7	167	-179	7	4	7	39	-34	-8	9	7	147	-148	0	-9	8	51	-60
-4	0	7	88	-92	8	4	7	54	-66	-7	9	7	33	-33	1	-9	8	31	-32
-3	0	7	53	62	-12	5	7	45	49	-6	9	7	32	34	4	-9	8	37	-46
1	0	7	107	-119	-8	5	7	45	49	-4	9	7	72	65	-4	-8	8	39	56
2	0	7	42	-48	-6	5	7	50	64	-3	9	7	56	53	3	-8	8	46	53
3	0	7	82	-91	-5	5	7	155	171	-3	9	7	28	-21	5	-8	8	46	67
4	0	7	151	-202	-3	5	7	136	-140	0	9	7	145	136	-1	-8	8	56	67
5	0	7	60	-60	-1	5	7	47	45	1	9	7	88	-79	-3	-7	8	37	-39
-11	1	7	34	25	2	5	7	29	34	-12	10	7	70	70	-1	-7	8	34	-36
-9	1	7	78	77	3	5	7	36	97	-8	10	7	47	-42	0	-7	8	59	-59
-8	1	7	52	46	4	5	7	35	37	-5	10	7	43	-49	1	-7	8	78	-71
-7	1	7	73	-77	7	5	7	35	-37	-5	10	7	105	-95	4	-7	8	46	-56
-6	1	7	49	53	-10	6	7	36	-32	-4	10	7	76	70	6	-7	8	50	50
-5	1	7	39	38	-9	6	7	46	-46	-4	10	7	65	54	-4	-6	8	36	27
3	1	7	53	107	-8	6	7	73	77	-2	10	7	29	-33	-3	-6	8	47	40
4	1	7	57	55	-6	6	7	72	79	0	10	7	30	35	-1	-6	8	64	57
6	1	7	37	37	-4	6	7	46	-51	3	10	7	46	35	0	-6	8	66	58
7	1	7	23	21	-3	6	7	45	-42	3	10	7	58	-54	1	-6	8	56	-53
8	1	7	59	61	-2	6	7	79	-35	4	10	7	59	-59	2	-6	8	37	-33



-3	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
-2				109	-107	-5	13	9	56	49	-6	1	10	29	32
-1				55	-37	-3	13	9	52	51	-5	1	10	54	50
0				55	35	-3	13	9	52	50	-3	1	10	102	-102
1				55	34	-7	14	9	51	-53	1	1	10	26	-19
2				55	34	-6	14	9	52	-25	6	1	10	57	-55
3				55	30	-4	14	9	52	-60	-11	2	10	21	2
4				55	30	-3	14	9	52	-48	-9	2	10	32	32
5				55	30	-3	14	9	52	54	-7	2	10	25	25
6				55	30	-7	15	9	52	32	-7	2	10	82	90
7				55	30	-8	15	9	52	54	-6	2	10	61	67
8				55	30	-3	15	9	52	-63	-4	2	10	45	43
9				55	30	-3	15	9	52	54	-6	2	10	39	44
10				55	30	0	17	9	52	36	1	2	10	78	87
11				55	30	1	-3	10	38	-32	2	2	10	42	37
12				55	30	-2	-7	10	37	-38	3	2	10	42	37
13				55	30	-1	-6	10	32	-31	-11	3	10	60	-62
14				55	30	0	-6	10	37	-33	-9	3	10	26	-40
15				55	30	3	-4	10	31	38	-6	3	10	25	26
16				55	30	-7	-5	10	42	-45	-7	4	10	74	83
17				55	30	4	-5	10	49	47	-6	4	10	82	101
18				55	30	-3	-4	10	45	36	3	4	10	27	33
19				55	30	-2	-4	10	58	63	5	4	10	30	38
20				55	30	0	-4	10	46	-44	6	4	10	47	33
21				55	30	7	-4	10	35	26	-11	5	10	33	33
22				55	30	-7	-3	10	53	-52	-10	5	10	39	-44
23				55	30	-6	-3	10	44	-43	-8	5	10	56	-65
24				55	30	-5	-3	10	30	30	-7	5	10	48	-60
25				55	30	-3	-3	10	31	-34	-6	5	10	27	29
26				55	30	-2	-3	10	44	-60	0	5	10	23	-31
27				55	30	-3	-2	10	84	42	1	5	10	72	-73
28				55	30	-2	-2	10	35	-42	2	5	10	64	-70
29				55	30	0	-2	10	35	-42	-12	6	10	44	40
30				55	30	1	-2	10	41	34	-9	6	10	27	-34
31				55	30	3	-2	10	30	-27	-10	6	10	37	-34
32				55	30	-7	-1	10	52	-49	-8	6	10	37	43
33				55	30	-6	-1	10	76	-74	-5	6	10	41	47
34				55	30	-3	-1	10	80	-73	-5	6	10	40	44
35				55	30	-1	-1	10	32	33	-4	6	10	51	49
36				55	30	2	-1	10	52	-46	-3	6	10	126	129
37				55	30	3	-1	10	61	-58	-2	6	10	43	62
38				55	30	6	-1	10	39	-46	-1	6	10	24	26
39				55	30	-10	0	10	35	45	0	6	10	26	21
40				55	30	-7	0	10	72	70	1	6	10	43	45
41				55	30	-5	0	10	35	-34	5	6	10	37	28
42				55	30	-2	0	10	58	61	6	6	10	51	58
43				55	30	1	0	10	57	61	-7	7	10	27	25
44				55	30	2	0	10	72	77	-4	7	10	58	-57
45				55	30	3	0	10	32	-19	-3	7	10	41	-41
46				55	30	4	0	10	31	-35	0	7	10	32	-32
47				55	30	1	1	10	35	-39	1	7	10	59	-60
48				55	30	-1	1	10	31	-26	2	7	10	89	-80
49				55	30	1	1	10	31	-26	5	7	10	37	-39
50				55	30	6	8	10	39	-35	-12	8	10	39	32
51				55	30	-11	8	10	50	50	-11	8	10	50	50
52				55	30	-8	8	10	48	53	-8	8	10	48	53
53				55	30	-4	8	10	40	-40	-4	8	10	40	-40
54				55	30	-3	8	10	67	67	-3	8	10	67	67
55				55	30	-2	8	10	84	83	-2	8	10	84	83
56				55	30	0	9	10	41	37	1	9	10	41	37
57				55	30	-1	9	10	65	65	-1	9	10	65	65
58				55	30	-7	9	10	33	31	-7	9	10	33	31
59				55	30	-4	9	10	53	-49	-4	9	10	49	-47
60				55	30	-6	9	10	60	-59	-6	9	10	60	-59
61				55	30	-3	9	10	76	-77	-3	9	10	76	-77
62				55	30	-2	9	10	27	27	-2	9	10	27	27
63				55	30	-6	9	10	27	-22	-6	9	10	27	-22
64				55	30	-3	9	10	29	-23	-3	9	10	29	-23
65				55	30	-1	9	10	37	-36	-1	9	10	37	-36
66				55	30	-8	10	10	60	58	-8	10	10	60	58
67				55	30	-7	10	10	39	36	-7	10	10	39	36
68				55	30	-6	10	10	55	-53	-6	10	10	55	-53
69				55	30	-2	10	10	32	27	-2	10	10	32	27
70				55	30	5	-1	11	35	25	5	-1	11	35	25
71				55	30	6	-1	11	38	41	6	-1	11	38	41
72				55	30	-6	0	11	43	40	-6	0	11	43	40
73				55	30	-5	0	11	43	39	-5	0	11	43	39
74				55	30	-3	0	11	34	-37	-3	0	11	34	-37
75				55	30	-8	1	11	57	-84	-8	1	11	57	-84
76				55	30	1	0	11	42	-33	1	0	11	42	-33
77				55	30	-7	12	10	55	-55	-7	12	10	55	-55
78				55	30	-4	12	10	34	34	-4	12	10	34	34
79				55	30	3	0	11	28	23	3	0	11	28	23
80				55	30	5	0	11	35	-22	5	0	11	35	-22
81				55	30	-9	1	11	26	-22	-9	1	11	26	-22
82				55	30	-5	1	11	36	-22	-5	1	11	36	-22
83				55	30	-3	1	11	39	41	-3	1	11	39	41
84				55	30	-12	1	11	44	45	-12	1	11	44	45
85				55	30	-10	1	11	31	30	-10	1	11	31	30
86				55	30	-4	1	11	42	45	-4	1	11	42	45
87				55	30	-5	2	11	50	-53	-5	2	11	50	-53
88				55	30	-2	2	11	32	-37	-2	2	11	32	-37
89				55	30	2	2	11	36	-33	2	2	11	36	-33
90				55	30	-9	3	11	37	-35	-9	3	11	37	-35
91				55	30	-6	3	11	48	-51	-6	3	11	48	-51
92				55	30	-3	3	11	36	-38	-3	3	11	36	-38
93				55	30	4	3	11	45	34	4	3	11	45	34
94				55	30	-10	4	11	27	-36	-10	4	11	27	-36
95				55	30	-6	5	11	56	-70	-6	5	11	56	-70
96				55	30	-5	5	11	41	-52	-5	5	11	41	-52
97				55	30	-1	5	11	29	24	-1	5	11	29	24
98				55	30	-11	6	11	57	58	-11	6	11	57	58
99				55	30	6	6	11	29	20	6	6	11	29	20

-5	5	1	1	5	-27	-5	9	1	1	30	-23	-1	-4	12	51	-40	-2	1	12	40	43	3	5	12	44	41
-1	5	1	1	5	-31	-2	9	1	1	84	-75	-2	-3	12	37	33	0	1	12	30	27	-7	6	12	29	-30
-2	5	1	1	5	-34	-1	9	1	1	30	-35	-1	-3	12	33	25	2	1	12	37	42	-1	6	12	55	-47
-11	7	1	1	7	-35	-6	10	1	1	79	-76	-2	-2	12	30	-30	3	1	12	30	23	2	6	12	55	-47
-2	7	1	1	7	-35	-5	10	1	1	36	-32	0	-2	12	36	-33	-6	2	12	29	-37	3	6	12	29	-12
-3	7	1	1	7	-37	-3	10	1	1	36	-37	3	-2	12	31	-47	-5	2	12	41	-51	-3	7	12	29	25
-3	7	1	1	7	-37	-7	11	1	1	54	-57	-4	-1	12	33	36	-6	3	12	39	46	-2	7	12	49	53
-3	7	1	1	7	-37	-7	11	1	1	56	-45	-2	-1	12	48	45	2	3	12	46	47	-2	7	12	30	27
-3	7	1	1	7	-37	-1	11	1	1	36	-40	-1	-1	12	52	56	3	3	12	56	53	-3	8	12	29	-33
-7	8	1	1	8	-51	-2	11	1	1	41	-44	-6	0	12	50	-45	-7	4	12	29	-31	0	8	12	27	-24
-5	8	1	1	8	-73	-5	12	1	1	41	-36	-5	0	12	48	-49	2	4	12	37	-35	-4	9	12	33	30
-1	8	1	1	8	-24	-3	12	1	1	56	41	-2	0	12	43	-42	-7	5	12	29	-29	-3	9	12	45	35
2	8	1	1	8	40	-2	12	1	1	50	50	3	0	12	54	-52	-6	5	12	44	39	-2	9	12	52	45
3	8	1	1	8	37	-6	13	1	1	59	-52	-6	1	12	29	29	-5	5	12	25	27	-6	10	12	33	-29
-11	9	1	1	9	-47	-6	13	1	1	44	-40	-3	1	12	34	41	2	5	12	27	32	-5	11	12	39	-40



# References

### References

- (1) W.P.Griffith *Coord.Chem.Rev.*, (1972) , 8 , pp 369-96
- (2) W.A.Nugent and B.L.Haymore *Coord.Chem.Rev.*, (1980) , 31 ,  
pp 123-75
- (3) M.A.A.F.de C.T.Carrondo , R.Shakir and A.C.Skapski *JCS Dalton Trans.*, (1978) , pp 844-8
- (4) M.J.Wright and W.P.Griffith *Transition Met.Chem.*, (1982),  
7 , pp 53
- (5) O.R.Chambers , M.E.Harman , D.S.Rycroft , D.W.A.Sharp and  
J.M.Winfield *J.Chem.Res.(M)*., (1977) , pp 1846-73
- (6) Yu.V.Kokunov , Yu.D.Chubar , V.A.Bochkareva and Yu.A.Buslaev  
*Koord.Khim.*, (1975) , 1(8) , pp 1100-5
- (7) B.Krebs and A.Muller *J.Inorg.Nucl.Chem.*, (1968) , 30 ,  
pp 463-6
- (8) L.A.Woodward , J.A.Creighton and K.A.Taylor *Trans.Faraday Soc.*, (1960) , 56 , pp 1267-72
- (9) K.Dehnicke *J.Inorg.Nucl.Chem.*, (1965) , 27 , pp 809-15
- (10) K.Dehnicke and J.Strahle *Z.Anorg.Allg.Chem.*, (1965) , 339  
pp 171
- (11) J.Strahle *Z.Anorg.Allg.Chem.*, (1970) , 375 , pp 238
- (12) K.Dehnicke and W.Kolitsch *Z.Naturforsch.*, (1977) , 32B ,  
pp 1485
- (13) W.P.Griffith and D.Pawson *JCS Dalton Trans.*, (1973) ,  
pp 1315-20
- (14) B.Knopp , K-P Lorcher and J.Strahle *Z.Naturforsch.*, (1977),  
32B , pp 1361

- (15) F.L.Phillips and A.C.Skapski *J.Cryst.Mol.Struct.*, (1975) ,  
5 , pp 83
- (16) F.L.Phillips and A.C.Skapski *Acta Crystallogr.*, (1975) ,  
B31 , pp 2667
- (17) W.Liese , K.Dehnicke , I.Walker and J.Strahle *Z.Naturforsch.*  
(1979) , 34B , pp 693
- (18) U.Weiherr , K.Dehnicke and D.Fenske *Z.Anorg.Allg.Chem.*,(1979)  
457 , pp 105
- (19) U.Weiherr , K.Dehnicke and D.Fenske *ibid.*, pp 115-22
- (20) U.Weiherr , K.Dehnicke and D.Fenske *Z.Anorg.Allg.Chem.*,(1979)  
456 , pp 71-80
- (21) M.G.B.Drew , G.W.A.Fowles , D.A.Rice and N.Rolfe *JCS Chem.*  
*Commun.*, (1971) , pp 231
- (22) W.Liebelt and K.Dehnicke *Z.Naturforsch.*, (1979) , 34B ,pp 7
- (23) F.Eisner and O.Ruff *Ber.Deuts.Chem.Gesellschaft*, (1905) ,  
38 , pp 742-7
- (24) H.C.Clark and H.J.Emeleus *J.Chem.Soc.*, (1957) , pp 4778
- (25) M.Harman , D.W.A.Sharp and J.M.Winfield *Inorg.Nucl.Chem.Lett*  
(1974) , 10 , pp 183
- (26) A.A.Opalovskii and G.E.Blokhina *Izv.Vyshh.Ucheb.Zaved.Khim.*  
*Khim.Technol.*, (1972) , 15(11) , pp 1617-9
- (27) C.Y.Chou , J.C.Huffman and E.A.Maatta *JCS Chem.Comm.*,  
(1984) , pp 1184-5
- (28) B.R.Ashcroft , D.C.Bradley , G.R.Clark , R.J.Errington ,  
A.J.Nielson and C.E.F.Rickard *JCS Chem.Comm.*, (1987) ,  
pp 170-1
- (29) D.Fenske , R.Kujanek and K.Dehnicke *Z.Anorg.Allg.Chem.*,  
(1983) , 507 , pp 51-8

- (30) J.Fawcett , R.D.Peacock and D.R.Russell *JCS Dalton Trans.*,  
(1980) , 1 , pp 2294-6
- (31) H.W.Roesky , U.Seseke , M.Noltemeyer , P.G.Jones and  
G.M.Sheldrick *JCS Dalton Trans.*, (1986) , pp 1309-10
- (32) B.Glavincevski and S.Brownstein *Inorg.Chem.*, (1881) ,  
20(10) , pp 3580-1
- (33) W.Kafitz , K.Dehnicke , E.Schweda and J.Strahle  
*Z.Naturforsch.*, (1984) , 39B , pp 1114-7
- (34) D.Baker , J.Fawcett and R.D.Peacock *Unpublished work*
- (35) K.Dehnicke and J.Strahle *Angew.Chem.Int.Ed.Engl.*, (1981),  
20 , pp 413
- (36) W.Dukat , J.H.Holloway and J.Rook *Unpublished work*
- (37) G.M.Sheldrick SHELX 76 program for crystal structure  
determination , University of Cambridge , 1976
- (38) R.Bougon , T.Bui Huy and P.Charpin *Inorg.Chem.*, (1975) ,  
14(8) , pp 1822-30
- (39) F.N.Tebbe and E.L.Muetterties *Inorg.Chem.*, (1968) , 7 ,  
pp 172
- (40) A.M.Noble and J.M.Winfield *JCS(A).*, (1971) , 8 , pp 948-53
- (41) E.A.Cohen , A.J.R.Brown and S.L.Manatt *J.Mag.Res.*, (1969) ,  
1 , pp 436-49
- (42) I.J.Lawrenson *J.Chem.Soc.*, (1965) , pp 1117
- (43) M.E.Redwood and C.J.Willis *Can.J.Chem.*, (1967) , 45 ,  
pp 389-95
- (44) Mei-Ku Lo , V.W.Weiss and W.H.Flygare *J.Chem.Phys.*, (1966),  
45(7) , pp 2439-49
- (45) H.M.Seip and R.Seip *Acta.Chem.Scand.*, (1966) , 20 , pp 2698
- (46) A.C.Legon *Trans.Faraday Soc.*, (1969) , 65 , pp 2595

- (47) M.H.Chisholm , D.M.Hoffman and J.C.Huffman *Inorg.Chem.*, (1983) , 22 , pp 2903
- (48) D.C.Bradley , M.B.Hursthouse , K.M.Abdul-Malik , A.J.Nielson and R.L.Short *JCS Dalton Trans.*, (1983) , pp 2651
- (49) H.W.Roesky , J.Sundermeyer , J.Schinkowiak , P.G.Jones , M.Noltemeyer , T.Schroeder and G.M.Sheldrick *Z.Naturforsch.*, (1985) , 40B , pp 736
- (50) J.Fawcett , R.D.Peacock and D.R.Russell *JCS Dalton Trans.*, (1987) , pp 567-71
- (51) R.C.Plumb and D.F.Hornig *J.Chem.Phys.*, (1955) , 23(5) , pp 947
- (52) A.Cabana and C.Sandorfy *Spectrochim.Acta.*, (1962) , 18 , pp 843
- (53) D.M.J.Chan , M.H.Chisholm , K.Foltig , J.C.Huffman and N.S.Marchant *Inorg.Chem.*, (1986) , 25 , pp 4170-4
- (54) W.Kolitsch and K.Dehnicke *Z.Naturforsch.*, (1970) , 25B , pp 1080
- (55) G.W.Fraser , C.J.W.Gibbs and R.D.Peacock *JCS(A).*, (1970) , pp 1708
- (56) A.M.Noble and J.M.Winfield *JCS(A).*, (1970) , pp 2574 ;  
L.B.Handy , K.G.Sharp and F.E.Brinckman *Inorg.Chem.*, (1972) , 11 , pp 523
- (57) A.Majid , D.W.A.Sharp , J.M.Winfield and I.Hanley *JCS Dalton Trans.*, (1973) , pp 1876
- (58) J.A.Kerr and D.M.Timlin *Int.J.Chem.Kinet.*, (1971) , 3 , pp 427
- (59) H.Burger *Spectrochim.Acta.A.*, (1968) , 24(12) , pp 2015-22
- (60) A.Majid , R.A.Mclean , D.W.A.Sharp and J.M.Winfield *Z.Anorg.Allg.Chem.*, (1971) , 385 , pp 85

- (61) J.H.Taylor , W.S.Benedict and J.Strong *J.Chem.Phys.*, (1952)  
20 , pp 1884
- (62) W.C.Tulloch , D.D.Coffman and E.L.Muetterties *JACS.*, (1964)  
86 , pp 357
- (63) P.Huppmann , G.Kloter , J.S.Thrasher , K.Seppelt and  
D.D.DesMarteau *Inorg.Chem.*, (1984) , 23 , pp 2217
- (64) H.Hartl , P.Huppmann , D.Lentz and K.Seppelt *Inorg.Chem.*,  
(1983) , 22 , pp 2183
- (65) J.S.Thrasher , J.L.Howell and A.F.Clifford *Inorg.Chem.*,  
(1982) , 21 , pp 1616-22
- (66) D.E.Milligan and M.E.Jacox *J.Chem.Phys.*, (1967) , 47 ,  
pp 5157
- (67) H.Dubost and A.Abouaf-Marquin *Chem.Phys.Lett.*, (1972) , 17  
pp 269
- (68) J.Overend and J.C.Evans *Trans.Faraday Soc.*, (1959) , 55 ,  
pp 1817
- (69) A.J.Edwards and B.R.Stevenson *J.Chem.Soc.(A).*, (1968) ,  
pp 2503
- (70) J.Reedijk , A.P.Zwr and W.L.Groeneveld *Rec.Trav.Chem.*,  
(1967) , 86 , pp 1127
- (71) J.Fawcett and R.D.Peacock *Unpublished work*
- (72) J.Fawcett and R.D.Peacock *Unpublished work*
- (73) M.F.A.Dove , E.M.Lloyd-Jones and J.C.P.Sanders paper  
presented at the International 'Centenary of the Discovery of  
*Fluorine*' Symposium , Paris , August 1986
- (74) R.W.Cockman and R.D.Peacock *J.Fluorine Chem.*, (1986), 30(4)  
pp 469-70
- (75) J.Chatt , R.Choukroun , J.R.Dilworth , J.Hyde , P.Vella and  
J.Zubieta *Transition Met.Chem.*, (1979) , 4 , pp 59-63

- (76) M.F.Lappert and G.Srivastava *Inorg.Nucl.Chem.Lett.*, (1965)  
1 , pp 53
- (77) A.F.Shihada *Z.Anorg.Allg.Chem.*, (1974) , 408 , pp 9-14
- (78) A.Slawisch *Naturwissenschaften*, (1969) , 56 , pp 369
- (79) A.A.Kutznetsova , Yu.G.Podzolko and Yu.A.Buslaev *Russ.J.*  
*Inorg.Chem.*, (1969) , 14 , pp 393
- (80) A.Slawisch *Z.Anorg.Allg.Chem.*, (1970) , 374 , pp 291-6
- (81) J.B.Raynor 'Group Theory Tables' , University of Leicester
- (82) J.Chatt and J.R.Dilworth *JCS Chem.Comm.*, (1974) , pp 517
- (83) R.D.Peacock *Proc.Chem.Soc.*, (1957) , pp 59
- (84) A.J.Edwards , R.D.Peacock and R.W.H.Small *J.Chem.Soc.*,  
(1962) , pp 4486
- (85) T.A.O'Donnell and D.F.Stewart *Inorg.Chem.*, (1966) , 5 ,  
pp 1434
- (86) R.T.Paine and L.B.Asprey *Inorg.Synth.*, (1979) , 19 ,  
pp 137-40
- (87) W.E.Falconer , G.R.Jones , W.A.Sunder , I.Haigh and  
R.D.Peacock *J.Inorg.Nucl.Chem.*, (1973) , 35 , pp 751-3
- (88) N.Freestone and J.H.Holloway *Unpublished work*
- (89) J.R.Dilworth , S.J.Harrison , R.A.Henderson and D.R.M.Walton  
*JCS Chem.Comm.*, (1984) , pp 176-7
- (90) K.Seppelt and W.Sundermeyer *Chem.Ber.*, (1969) , 102 ,  
pp 1247-52
- (91) R.T.Paine and L.B.Asprey *Inorg.Chem.*, (1974) , 13(6) ,  
pp 1529
- (92) R.T.Paine and L.B.Asprey *Inorg.Chem.*, (1975) , 14 , pp 1111
- (93) P.R.Hammond and R.R.Lake *JCS Chem.Comm.*, (1968) , 16 ,  
pp 987-8

## Abstract

"Transition metal fluoride derivatives with nitrogen-containing ligands"  
by G.A.Griffith.

The reaction between  $WF_6$  and  $C_6F_5NH_2$  is found to proceed via iminolysis.  $^{19}F$  nmr analysis of acetonitrile (MeCN) solutions show the product to be a mixture containing  $[C_6F_5NH_3]^+[WF_5(NC_6F_5)]^-$ ,  $[C_6F_5NH_3]^+[W_2F_9(NC_6F_5)_2]^-$ ,  $[C_6F_5NH_3]^+F^-$  and the unique mixed imido-, oxo-species  $[O=WF_4-F-WF_4(NC_6F_5)]^-$  - formed from traces of oxyfluoride impurities. The  $^{19}F$  nmr spectrum of a trifluoroacetic acid (TFA) solution showed the presence of the dimeric anion salt and fluorination products. An X-ray crystallographic study of a single crystal of  $[C_6F_5NH_3]^+[W_2F_9(NC_6F_5)_2]^-$ , grown from TFA, revealed the compound to adopt a triclinic (space group  $P\bar{1}$ ) structure, with two formula units in the unit cell, each with a slightly differing geometry about the bridging fluorine atom.

The reaction of  $Me_3SiNCO$  with  $MF_6$  ( $M = Mo, W$ ) was examined. The products are assigned as  $MF_5NCO$  from IR spectra recorded. The reaction between  $MoF_6$  and  $(Me_3Si)_2NH$  results in the formation of  $MoF_4NH$ . Addition of MeCN to  $MoF_4NH$  produces a 1:1 adduct,  $MoF_4NH.MeCN$ . Analysis of the IR spectra of the two compounds indicates that  $MoF_4NH$  adopts a cis-fluorine bridged chain structure, and  $MoF_4NH.MeCN$  adopts a pseudo-octahedral ( $C_4v$ ), monomeric structure in the solid state.  $WOF_4$  reacts with  $Me_3SiNCO$  to form  $WOF_3NCO$ , identified from its mass spectrum.

The hexafluorides  $MF_6$  ( $M = Mo, Re$ ), when allowed to react with tetrakis-trimethylsilylhydrazine (TTSH) undergo reduction to the pentafluoride in approximately 80% yield. Tungsten hexafluoride is believed to react with TTSH to form the diazene compound,  $WF_4N-NWF_4$ .