

"Begin at the beginning and go on to the end,
then stop."

The King of Hearts.

SPECTROSCOPIC STUDIES OF
METAL COMPLEXES

A thesis submitted for
THE DEGREE OF DOCTOR OF PHILOSOPHY
OF THE UNIVERSITY OF LONDON

by

GEORGE KEVIN TURNER, B.Sc., (London), A.R.C.S.

Department of Chemistry
Imperial College of Science and Technology
London June 1974

ABSTRACT

PART I

Several anions of the type $[\text{PtF}_{6-n}\text{X}_n]^{m-}$ have been characterised in solution by ^{19}F n.m.r. spectroscopy ($\text{X} = \text{OH}^-$, Cl^- , H_2O). Anions containing two different groups X have also been studied. ^{19}F chemical shifts, ^{195}Pt - ^{19}F and ^{19}F - ^{19}F coupling constants are reported. The ^{19}F chemical shift δ (relative to the $[\text{PtF}_6]^{2-}$ ion) of a particular fluorine atom in these complexes is given, to a good approximation, by

$$\delta = pC + qT,$$

where C and T are constants characteristic of the ligand X, and p and q are the number of substituents cis and trans to the fluorine atom respectively.

The dissociation constants of a number of the acids where $\text{X} = \text{H}_2\text{O}$ and n is 1 or 2 have been determined from a study of the ^{19}F chemical shifts as a function of pH.

Evidence is given for the presence in these complexes of both a strong trans effect and a strong trans influence in the order $\text{Cl} > \text{OH} > \text{F}$.

PART II

Raman spectroscopy has been used to investigate solutions of metal salts in anhydrous liquid ammonia. Information concerning metal-nitrogen and metal-anion vibrations is presented.

The species present in solution were tentatively identified from the number, frequency and polarisation of the peaks observed.

TO
MY PARENTS
AND
TRICIA

ACKNOWLEDGEMENTS

I wish to express my gratitude to my Supervisor Dr. D.F. Evans for his guidance and encouragement throughout the course of this work.

I also thank my friends and colleagues for their companionship and useful discussions. Thanks are also due to my wife, Tricia, for the typing.

CONTENTS

PART I

	<u>Page</u>
<u>^{19}F NMR STUDIES OF PLATINUM (IV) FLUORIDES</u>	1
<u>INTRODUCTION</u>	2
<u>CHAPTER ONE</u> ^{19}F NMR OF $[\text{PtF}_6]^{2-}$	10
<u>CHAPTER TWO</u> ^{19}F NMR OF PLATINUM (IV) FLUORIDES INCORPORATING OTHER LIGANDS	19
Individual Complexes	23
<u>DISCUSSION</u>	
<u>Cis</u> and <u>Trans</u> Effects	48
<u>Cis</u> and <u>Trans</u> Influence	52
Platinum-Fluorine Spin-Spin Coupling Constants	54
^{19}F Chemical Shifts of Platinum (IV) Fluoro Complexes	61
<u>EXPERIMENTAL</u>	67
<u>APPENDICES</u>	77
<u>REFERENCES</u>	86

PART II

<u>RAMAN SPECTROSCOPIC STUDIES OF LIQUID AMMONIA</u>	
<u>SOLUTIONS OF METAL SALTS</u>	92
<u>INTRODUCTION</u>	93
<u>RESULTS AND DISCUSSION</u>	96
A. SILVER SALTS	96
B. MERCURIC SALTS	100
C. CADMIUM SALTS	104
<u>CONCLUSIONS</u>	106
<u>EXPERIMENTAL</u>	107
<u>REFERENCES</u>	109

PART I

^{19}F N.M.R. STUDIES OF
PLATINUM (IV) FLUORIDES

INTRODUCTION

¹⁹F N.M.R. SPECTROSCOPY

The theory and practice of high resolution n.m.r. spectroscopy are dealt with in the literature ¹⁻³ and so will not be considered in detail here.

Natural fluorine exists as one isotope only, having atomic weight 19, spin 1/2 and magnetic moment $\mu = 2.6288$ nuclear magnetons ⁴. Conditions for the observation of ¹⁹F resonances are almost as easily satisfied as those for proton resonances.

The chemical shifts observed in ¹⁹F n.m.r. spectra are large and spectra are usually first order and therefore easily interpreted. Because of this, the technique can readily be used to identify either species containing several differently shielded fluorine nuclei, or species in solutions containing a mixture of solutes and it is therefore unnecessary to isolate pure compounds.

Saika and Slichter⁵ divided the contributions to magnetic shielding of fluorine nuclei into three terms. First, the diamagnetic correction for the atom in question, which differs in different fluorine compounds by an amount that is only about one per cent of the observed range of chemical shifts. Second, the paramagnetic term which represents the contribution from the magnetic fields set up by the orbital motion of the valence electrons under the

influence of a static magnetic field. Third, contributions from other atoms. The paramagnetic term is usually the dominant one in all but the completely ionic fluoride ions. The magnitude of this effect depends on the amount of ionic character in a bond. This has been shown to be consistent with observations of chemical shifts found in an extensive series of binary fluorides, where the shielding generally decreases with increase in the electronegativity of the attached atom³. Exceptions may occur when a molecule has a low lying electronic energy level of suitable symmetry^{6,7}.

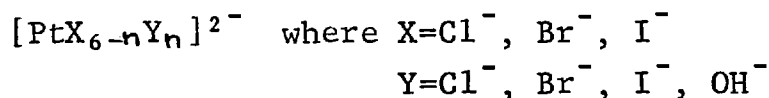
Both internal and external reference procedures have been used for ^{19}F chemical shift measurements. The most frequently used external reference compound is trifluoroacetic acid (TFA). Trichlorofluomethane is often used as an internal reference compound since it is miscible with most common solvents, but, unfortunately, it cannot be used for aqueous solutions. Also, the ^{19}F chemical shift of CFCl_3 , measured from an external reference, is highly solvent dependent⁸. Evans⁹ first noted the large solvent variation of ^{19}F chemical shifts and suggested that the changes were due to intermolecular van der Waals forces.

The solvent dependence of spin-spin coupling constants is well established^{10,11} although the nature of the interactions giving rise to the effect is still not clear. For systems where specific interactions, such as hydrogen bonding or self-association, do not occur, the influence of

intermolecular, electrostatic interactions between solute and solvent molecules on coupling constants has been given qualitative interpretations¹²⁻¹⁴. Bell and Danyluk¹⁴ suggested that the signs of coupling constants might be determined from their solvent dependencies, but this method should, however, be used with caution¹¹.

PLATINUM IV CHEMISTRY

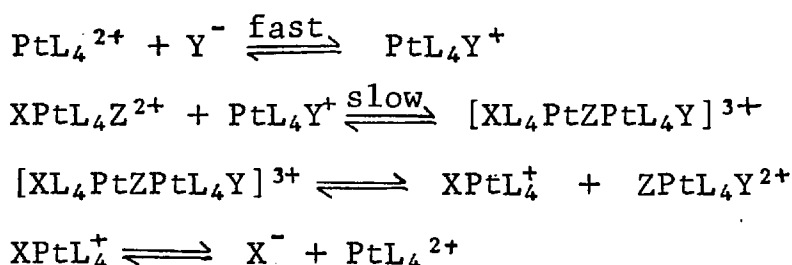
Platinum forms many compounds and complexes in which it is formally tetravalent. The vast majority of these have an octahedral arrangement of groups around the platinum and all are diamagnetic because of the large ligand field splitting which makes the d^6 metal low spin. Simple and mixed halogen complexes of platinum of the type:



are known (e.g. 15-17). Aqueous solutions of $[\text{PtX}_6]^{2-}$ and $[\text{PtY}_6]^{2-}$, ($\text{X}=\text{Cl}^-, \text{Br}^-, \text{I}^-$; $\text{Y}=\text{Cl}^-, \text{Br}^-, \text{I}^-$) and solutions of $[\text{PtX}_6]^{2-}$ with OH^- , rapidly establish an equilibrium to give intermediate mixed species. In solution platinum (IV) has a much greater preference for the heavier than the lighter halides, showing strong class b character.

Depending on the conditions, the reaction of halide or pseudo-halide ions with hexahalogenoplatinum (IV)

complexes can give substitution or reduction ¹⁸. Substitution reactions of platinum (IV) complexes are often catalysed by platinum (II) complexes ¹⁹ and in the absence of catalyst are either very slow or do not occur at all ²⁰. The mechanism of substitution reactions is thought to involve the formation of a platinum (II) - platinum (IV) bridged complex ^{21, 22} and is shown below.



where PtL_4^{2+} is the platinum (II) catalyst

$\text{XPtL}_4\text{Z}^{2+}$ is the platinum (IV) complex

X^- is the leaving ligand

Y^- is the entering ligand

Z^- is the bridging ligand, trans to X^-

The rate of substitution of a ligand in a metal complex depends on the other ligands attached to the metal, especially in the trans position. The trans effect of a ligand is the effect of a coordinated group on the rate of substitution reactions of the group opposite ²³. A ligand which exerts a large trans effect will labilise the ligand in the position trans to itself. There has been much work on the measurement and theory of trans effects, but these mainly involve platinum (II) (23 and references therein) or cobalt (III) complexes ²⁴. Data concerning the substitution reactions of platinum (IV) are scarce and many

of the old results are unreliable since traces of platinum (II) were not rigorously excluded. Cis effects are generally less important than trans effects and their origin is less clearly understood.

The trans influence of a ligand in a metal complex is defined^{25,26} as the extent to which the ligand weakens the bond trans to itself in the equilibrium state of the complex. A ligand, L, of high trans influence, induces metal rehybridisation in order to form a strong covalent bond with the metal M. This concentrates the metal orbital in the M - L bond at the expense of the metal - ligand bond trans to it. The trans influence has been the subject of a recent review²⁷.

PLATINUM FLUORIDES

Platinum forms either simple or complex fluorides in the II, IV, V and VI oxidation states²⁸⁻³³. Complex fluorides of platinum (II) have only recently been isolated and characterised^{33,34}. Tetrafluoroplatinum (IV) was first prepared by Moissan in 1900³⁵ by the action of fluorine on platinum. Sharpe³¹ prepared impure PtF₄ by the thermal decomposition of the bromine trifluoride - platinum tetrafluoride adduct (2BrF₃PtF₄) under vacuum at 180°C. Final traces of bromine cannot be removed below 300°C and above this temperature decomposition occurs, giving platinum

and fluorine. The bromine can be removed, however, by the action of fluorine at 200°C, to give pale brown, diamagnetic PtF_4 , which is vigorously hydrolysed by water³⁶.

Potassium hexafluoroplatinate (IV) was first prepared in 1924 by the action of $3\text{KF}\cdot\text{HF}\cdot\text{PbF}_4$ on platinum³⁷, but the separation of the products was not simple. A more convenient synthesis is the fluorination of potassium hexachloroplatinate (IV) with bromine trifluoride, which acts as both solvent and fluorinating agent³¹. Aqueous solutions of the free acid, H_2PtF_6 , have been prepared by cation exchange and from these solutions many other salts have been obtained³⁸⁻⁴¹.

The only mixed fluoro-halo platinates reported are $\text{M}_2\text{PtCl}_3\text{F}_3$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) prepared by the reaction of bromine trifluoride with M_2PtCl_6 or M_2PtCl_4 at 20°C.^{28,42} The distribution of the chlorine and fluorine atoms in the octahedron about the platinum atoms could not be determined from the infrared spectra, electronic spectra of solid and solution and X-ray powder data available. Aqueous solutions of $\text{M}_2\text{PtCl}_3\text{F}_3$ are stable for short periods, but on standing, or if heated, hexachloro- and hexafluoroplatinates (identified by their X-ray powder photographs) and complex species containing the hydroxyl group (identified by infrared spectroscopy) are reported to separate out²⁸.

Several fluorohydroxy and fluoromethoxy platinum (IV) complexes of the type $M_2[Pt(OH)_4F_2]$ ($M = H, Na, K$), $K[Pt(H_2O)(OMe)_3F_2]$, and $M_2[Pt(OMe)F_5]$ ($M = Na, K$), have been reported by Kolditz⁴³. Evidence for the molecular formulae of the complexes relied heavily on analytical data, with X-ray powder photography and thin layer chromatography lending support. Only chromatographic evidence of the existence of the $[Pt(OH)F_5]^{2-}$ and $[Pt(OH)_2F_4]^{2-}$ anions in solution was given. The structures of the complexes were not elucidated.

There is much current interest in the study of platinum fluoro complexes^{33,44-49}. However, there is little direct spectroscopic information concerning the species present in solution, in particular, few ^{19}F n.m.r. spectra have been observed. Dixon³³ reported the ^{19}F n.m.r. spectra of complexes of the type $[Pt(II)F(PR_3)_3]BF_4$, ($R = Ph, Et$) and confirmed the presence of square planar cations with platinum-fluorine bonds.

Matwiyoff et al⁴⁵ recorded the ^{19}F n.m.r. spectrum of potassium hexafluoroplatinate (IV) in anhydrous HF. They observed two satellite lines (relative intensity 16.8%) symmetrically disposed about the central high field resonance (relative intensity 66.3%, chemical shift 287 p.p.m. with respect to TFA external reference). The satellites arise from the coupling of ^{19}F with the ^{195}Pt isotope, which has spin 1/2 and natural abundance 33.7%. The coupling constant, $J_{^{195}Pt-^{19}F}$, was 2080 Hz.

A weak 1:4:1 triplet (chemical shift = 320 p.p.m. with respect to external CFCl_3 , or 243 p.p.m. with respect to external TFA, $J = 2090\text{Hz.}$) observed in the spectra of $[\text{ClF}_6]^+ [\text{PtF}_6]^-$ and $[\text{ClF}_2\text{O}]^+ [\text{PtF}_6]^-$ in anhydrous hydrogen fluoride was tentatively assigned to the $[\text{PtF}_6]^{2-}$ anion⁵⁰.

CHAPTER ONE ^{19}F N.M.R. OF $[\text{PtF}_6]^{2-}$

Matwiyoff et al ⁴⁵ reported the ^{19}F n.m.r. spectrum of K_2PtF_6 in anhydrous hydrogen fluoride. Spectra similar to those obtained by Matwiyoff were observed in this work for aqueous solutions of K_2PtF_6 or Na_2PtF_6 and for all solutions of the tetraethylammonium or di-n-propylammonium salts (Figure 5a). Sharp resonances and the presence of spin-spin coupling between ^{19}F and the ^{195}Pt isotope indicate that fluorine exchange is slow on an n.m.r. time scale. The coupling of ^{19}F with ^{195}Pt showed a large solvent dependence. Values of $J_{^{195}\text{Pt}-^{19}\text{F}}$ in various solvents are given in Table I.

Bell and Danyluk ^{14, 51} observed that for cis and trans 1,2-dichlorofluoroethylene $J_{^{13}\text{C}-\text{H}}$ increased and $J_{^{13}\text{C}-^{19}\text{F}}$ decreased in solvents of higher dielectric constant. Also $\delta_{\text{H}} \propto J_{^{13}\text{C}-\text{H}}$, $\delta_{\text{H}} \propto J_{\text{H}-^{19}\text{F}}$ and $\delta_{\text{F}} \propto J_{^{13}\text{C}-^{19}\text{F}}$, which indicate that the solvent influences both the shielding and the coupling constants by a similar mechanism. The reaction field of the solvent is probably the dominant factor involved. It was predicted, using the molecular orbital theory of Pople and Santry ⁵² for directly bonded coupling constants, that an increase in the magnitude of the reaction field would make the reduced coupling constants $K_{^{13}\text{C}-\text{H}}$ and $K_{^{13}\text{C}-^{19}\text{F}}$ more positive.

$$K_{A-B} = \frac{2\pi}{h \gamma_A \gamma_B} J_{A-B} \text{ cm}^{-3}$$

where γ_A and γ_B are the nuclear magnetogyric ratios of A and B respectively,

and J_{A-B} is the observed coupling, in Hz.

The values of γ_H , $\gamma_{^{13}\text{C}}$, $\gamma_{^{19}\text{F}}$ and $\gamma_{^{195}\text{Pt}}$ are all positive and therefore K_{A-B} and J_{A-B} values should be of the same sign. Since $K_{^{13}\text{C-H}}$ is positive it should increase in more polar solvents, whereas $K_{^{13}\text{C-}^{19}\text{F}}$ is negative and should therefore decrease, as observed. The solvent dependence of $J_{^{195}\text{Pt-}^{19}\text{F}}$ can be interpreted in terms of solvation of the $[\text{PtF}_6]^{2-}$ anion, which presumably falls in the order:



In water the observed coupling constant is greatest suggesting from arguments presented above that the reduced coupling constant has an absolute positive sign.

This result is in disagreement with the theoretical conclusions of Pople and Santry⁵², who from molecular orbital calculations suggested that for bonds to fluorine the coupling constants are usually negative.

Dean and Evans⁵³ found that the value of $J_{^{119}\text{Sn-}^{19}\text{F}}$, for the $[\text{SnF}_6]^{2-}$ ion, increased with decreasing solvation and that the reduced coupling constant is therefore negative.

This conclusion was confirmed by McFarlane and Wood ⁵⁴, who carried out heteronuclear double irradiation n.m.r. experiments on solutions of $(\text{PhMe}_2\text{CCH}_2)_3\text{SnF}$.

A plot of $J_{119\text{Sn}-19\text{F}}$ of $[\text{SnF}_6]^{2-}$ in various solvents, against $J_{195\text{Pt}-19\text{F}}$ of $[\text{PtF}_6]^{2-}$ in the same solvent, shows an approximate straight line of negative gradient. (Figure I). This indicates that the solvent-solute interactions are similar for the two ions, but, as suggested above, the reduced coupling constants are of opposite signs.

The variation of $J_{195\text{Pt}-19\text{F}}$ in DMSO — water solvent mixtures containing a constant mole fraction of $(\text{Et}_4\text{N})_2\text{PtF}_6$, shows a preferential effect by water. (Figure 2). This is to be expected since DMSO strongly solvates cations, but not anions, whereas water solvates both. In solvent mixtures containing only a small molar percentage of water there is competition between the solute ions and the DMSO for the water, DMSO forming strong hydrogen bonds with the water molecules.

$J_{195\text{Pt}-19\text{F}}$ showed no concentration dependence for solutions of $(\text{Et}_4\text{N})_2\text{PtF}_6$ or $[(\text{Pr}^n)_2\text{NH}_2]_2\text{PtF}_6$ in DMSO or water.

The ^{19}F n.m.r. resonance of the $[\text{PtF}_6]^{2-}$ ion occurs at a higher magnetic field than that reported for any diamagnetic complex in solution ¹ (in water, $\delta = 286$ p.p.m.,

TABLE I

SOLVENT DEPENDENCE OF $J_{195\text{Pt}-19\text{F}}$ AND $J_{119\text{Sn}-19\text{F}}$ OF $[\text{MF}_6]^{2-}$

SOLVENT	$J_{195\text{Pt}-19\text{F}}$ (Hz.)	$J_{119\text{Sn}-19\text{F}}^*$ (Hz.)
H ₂ O	2003	1557
MeOH	1999	1577
EtOH	1999	1584
Pr ⁿ OH	1993	1590
DMF	1981	-
H.CO.NH ₂	1981	1589
DMSO	1976	1603
H.COOH	2007	1570
40% HF (aq.)	2007	-
98% H ₂ SO ₄	2065	-

* Data from reference 53.

Figure 1.

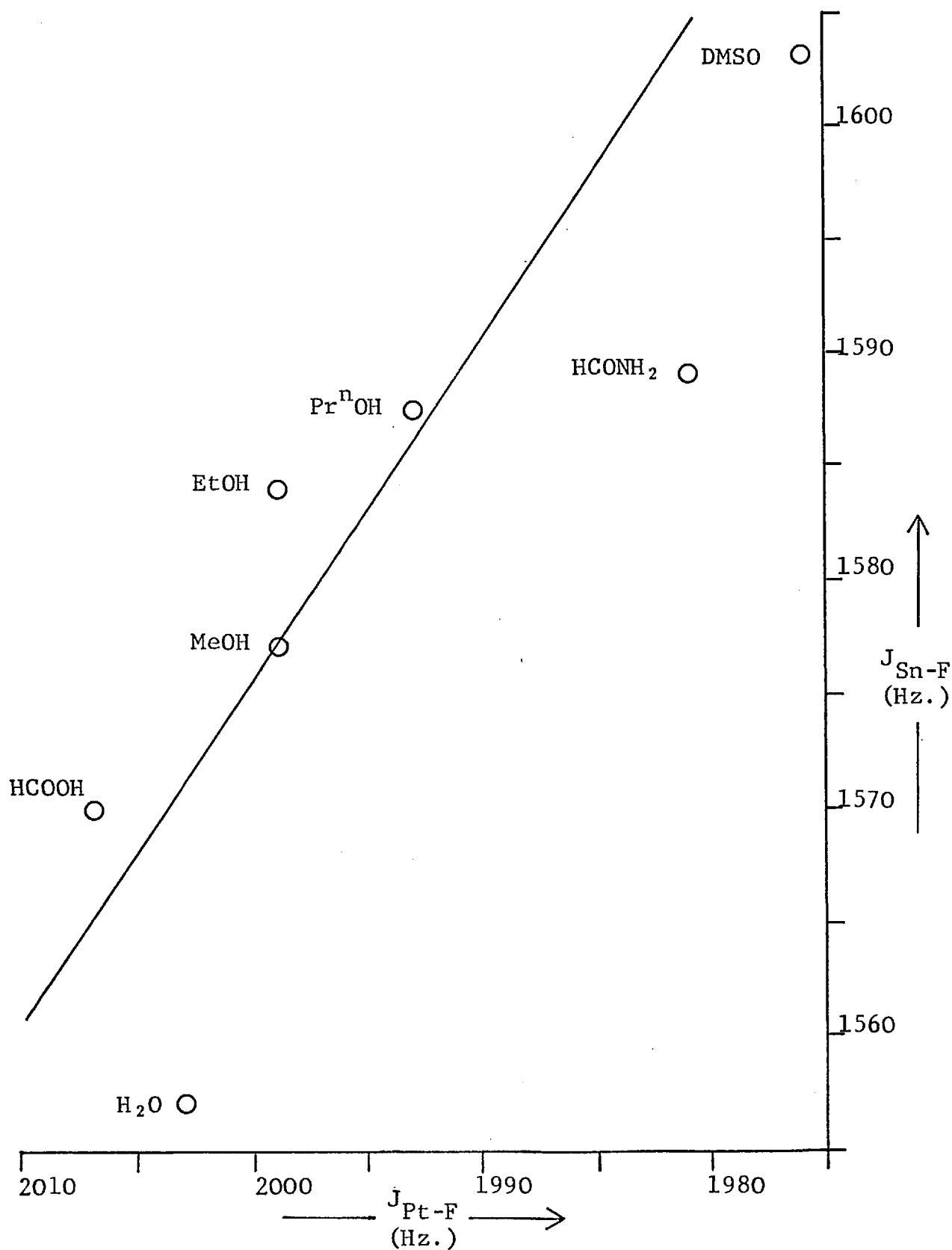
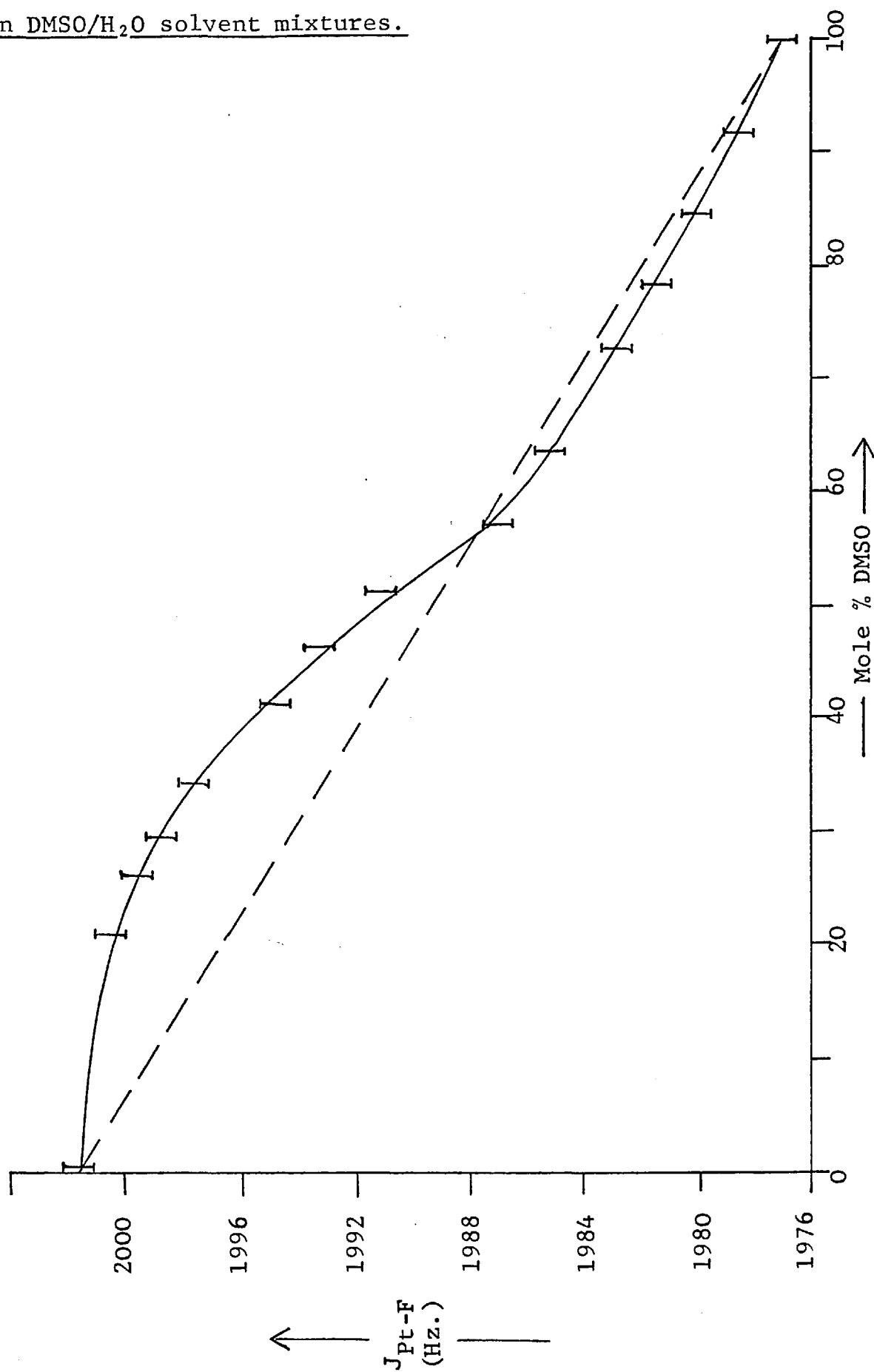
Plot of $J_{195\text{Pt}-19\text{F}}$ of $[\text{PtF}_6]^{2-}$ against $J_{119\text{Sn}-19\text{F}}$ of $[\text{SnF}_6]^{2-}$ in various solvents.

Figure 2. The variation of $J_{195\text{Pt}-19\text{F}}$ of $[\text{PtF}_6]^{2-}$
in DMSO/H₂O solvent mixtures.

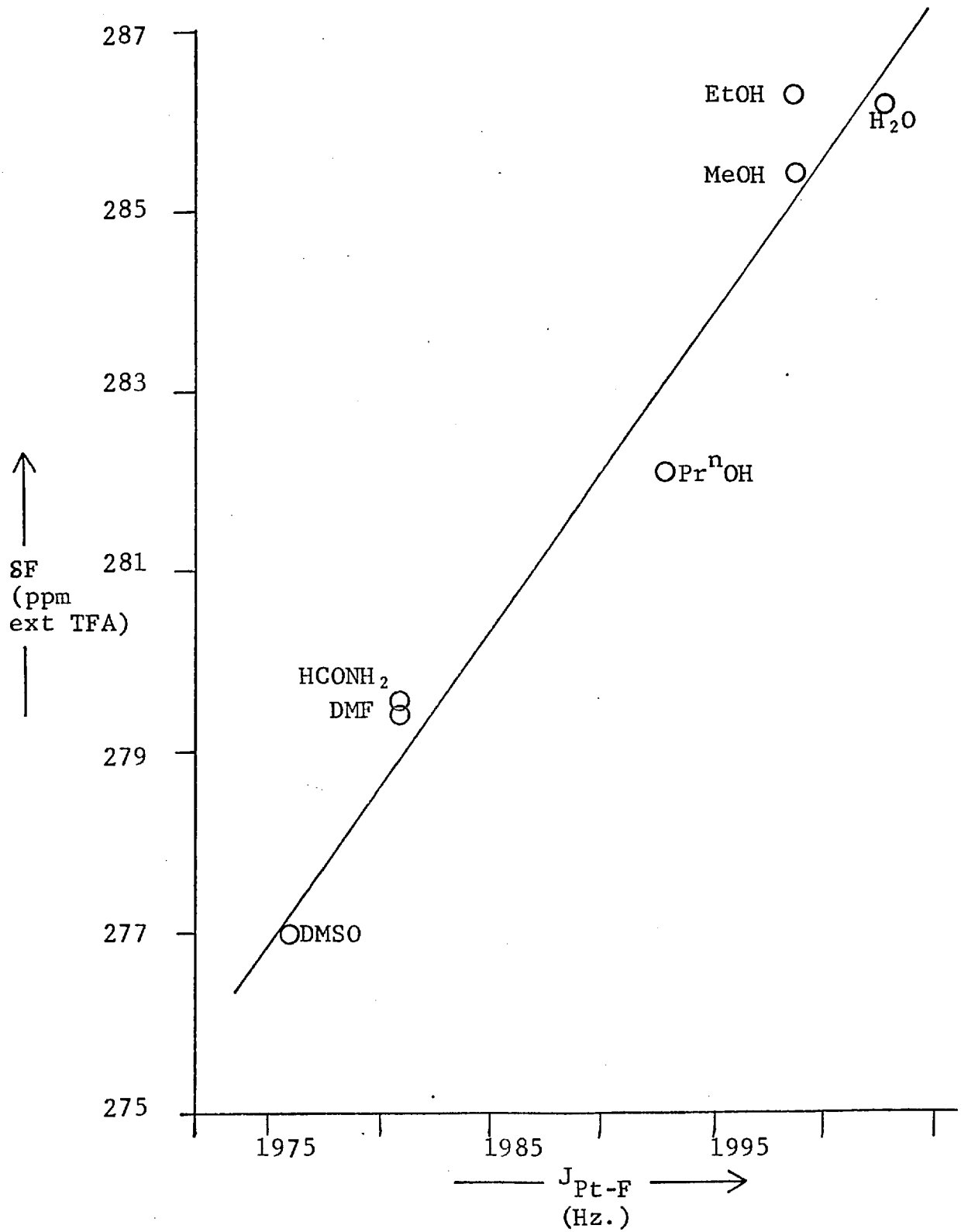


relative to external TFA). This shift is not due to solvent effects since powder samples of the complexes show high field shifts of the same magnitude as shown here ^{45,55-57}.

The high field shift cannot be rationalised using the unmodified theory of Saika and Slichter which would predict a shift to comparatively low field because of the high electronegativity of platinum (IV). The shift may be due to the mixing-in of an excited state of platinum (IV) under the influence of the magnetic field, by means of d-d transitions or of $F \rightarrow Pt$ charge transfer ⁴⁵. The anomalous high field ¹⁹F resonance of ClF was found to be due to mixing in of the $Cl \rightarrow F$ charge transfer state with the ground state in the magnetic field ⁶. Other investigations have shown the importance of the effect of the energy separation between the ground and excited states on the paramagnetic contribution to nuclear shielding ⁵⁸⁻⁶¹. The paramagnetic term will be greatest when several low-lying excited states exist with symmetry permitting them to be mixed with the ground state ⁵⁸.

Bell and Danyluck ^{14,51} concluded that the dominant factor affecting J and δ values is the reaction field of the solvent, which depends on the solvent dielectric. A plot of $J_{195Pt-19F}$ against δF (Figure 3) shows an approximately linear relationship for all solvents except 40% hydrofluoric acid, formic acid and concentrated (98%)

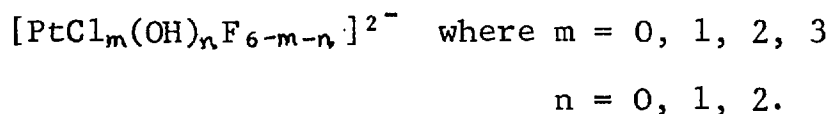
Figure 3. Plot of δF against $J_{195\text{Pt}-19\text{F}}$ of $[\text{PtF}_6]^{2-}$ in various solvents.



sulphuric acid in which the $[\text{HPtF}_6]^-$ ion may be formed. The values of J and S do not vary in a regular manner with the solvent dielectric. This is not surprising since both DMSO and water have high dielectric constants, but DMSO will not solvate the $[\text{PtF}_6]^{2-}$ anion strongly.

CHAPTER TWO ^{19}F N.M.R. OF PLATINUM (IV) FLUORO COMPLEXES INCORPORATING
OTHER LIGANDS

Using ^{19}F n.m.r. spectroscopy it has been possible to show the existence in aqueous solution of a variety of mixed platinum (IV) - fluoro complexes of the type;

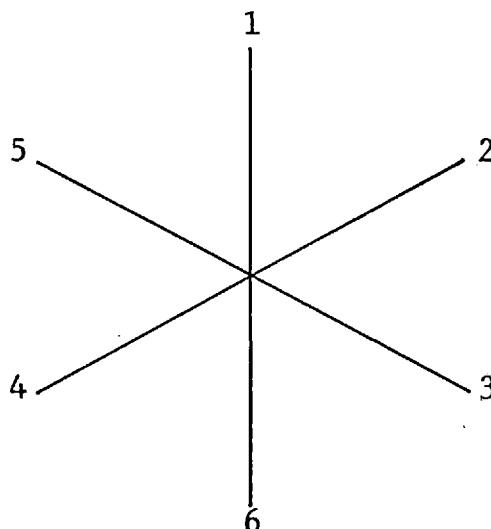


The addition of perchloric acid to solutions of the hydroxyl complexes causes protonation to give the corresponding aquo complexes. A large number of ^{19}F chemical shifts and ^{195}Pt - ^{19}F and ^{19}F - ^{19}F spin-spin coupling constants were measured and are presented in Table 5, Page 58. Some empirical interpretation of the data has been possible. Acid dissociation constants for some of the complex aquo species have been calculated.

Initial attempts to prepare mixed complexes from salts of the $[\text{PtF}_6]^{2-}$ ion proved fruitless, probably because of the kinetic stability but thermodynamic instability of this ion in solution. Other preparative routes were therefore investigated.

NOMENCLATURE USED FOR COMPLEXES

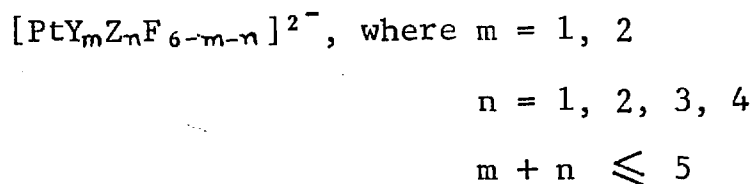
The ligands are numbered in the sequence previously adopted for octahedral complexes.⁶² (Figure 4) and the numbers are presented as right superscripts after the symbol for the ligand. The fluorines are not numbered since their positions are clear from the numbering of the other ligands.

Figure 4IDENTIFICATION OF THE COMPLEXESGENERAL

The species present in solution were normally identified by the fine structure, if any, observed for the ^{19}F resonances. The fine structure expected for ions of the type $[\text{PtY}_n\text{F}_{6-n}]^{2-}$, $n = 1 \rightarrow 5$, are presented below:

<u>ION</u>	<u>FINE STRUCTURE</u>
$[\text{PtYF}_5]^{2-}$	AX_4
$[\text{PtY}_{\frac{1}{2}}, {}^2\text{F}_4]^{2-}$ (<u>cis</u>)	A_2X_2
$[\text{PtY}_{\frac{1}{2}}, {}^6\text{F}_4]^{2-}$ (<u>trans</u>)	single line
$[\text{PtY}_{\frac{1}{3}}, {}^3\text{F}_3]^{2-}$	single line
$[\text{PtY}_{\frac{1}{3}}, {}^2, {}^6\text{F}_3]^{2-}$	AX_2
$[\text{PtY}_{\frac{1}{4}}, {}^4\text{F}_2]^{2-}$	single line
$[\text{PtY}_{\frac{2}{4}}, {}^5\text{F}_2]^{2-}$	single line
$[\text{PtY}_{\frac{5}{5}}\text{F}]^{2-}$	single line

Several mixed fluoro complexes incorporating two other types of ligand were also identified. There is a possibility of forming several different complexes of the type



but only five of these structures were encountered and all gave first order spectra.

Identification of ions giving rise to a single n.m.r. line was sometimes difficult. However, it was possible to make assignments in such circumstances using

the empirical correlation between chemical shift and the number of cis and trans substituents, first used for octahedral fluoro complexes by Dean and Evans⁵³. For a complex of the type $[\text{PtY}_n\text{F}_{6-n}]^{2-}$, the ^{19}F chemical shift of a particular fluorine, relative to $[\text{PtF}_6]^{2-}$, is given by:

$$\delta\text{F} = p\text{C} + q\text{T},$$

where p is the number of substituents in a position cis

to F, and may take any value from 0 to 4,

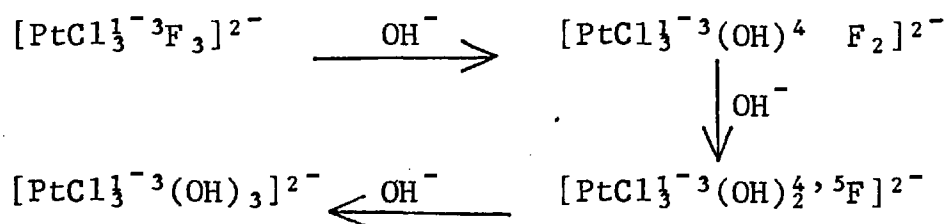
q is the number of substituents trans to F, and is either 0 or 1,

C and T are empirical constants characteristic of the substituent Y.

The relationship can easily be adapted for complexes having more than one type of substituent. Although the chemical shifts and values of C and T of substituents are very different for the platinum (IV) complexes studied here and the tin (IV) complexes studied by Dean and Evans, the relationship was found to be most useful.

The order of appearance of n.m.r. lines also helped in their assignments to different ions. For example, the reaction of the $[\text{PtCl}_3^{-3}\text{F}_3]^{2-}$ ion (which itself gives a single line) with hydroxide ions gives two complexes, each of which gives a single line. From the order of appearance of these lines and from the disappearance of that due to the $[\text{PtCl}_3^{-3}\text{F}_3]^{2-}$ ion, the reaction taking place is probably

the stepwise replacement of the fluorines by hydroxide ions:



Complexes having equal numbers of fluorines in two different environments were easily recognised by their n.m.r. spectra. However, direct assignment of the lines was impossible. For example, the $[\text{PtX}_2^{2-}\text{F}_4]^{2-}$ ion gives two triplets of equal intensity, but a direct assignment of either to the fluorines trans to X cannot be made. Using the empirical relationship mentioned above, probable assignments were made.

Complexes containing the hydroxyl group were identified by the large change in chemical shift observed on the addition of perchloric acid to the solution. This change is caused by protonation of the hydroxyl group, giving the corresponding aquo complex.

INDIVIDUAL COMPLEXES

All chemical shifts were measured relative to internal $[\text{PtF}_6]^{2-}$ unless otherwise stated and are reported in Table 5, Page 58. Representative spectra are reproduced in figures 5, 6 and 7.

FIGURES 5, 6 and 7 show ^{19}F n.m.r. spectra of aqueous solutions of the following platinum (IV) fluoro complexes:

Fig. 5 a M_2PtF_6 , (M = H, Na, K, Et_4N , $(\text{Pr}^n)_2\text{NH}_2$)
b Products of the reaction of bromine trifluoride with imperfectly dried sodium hexachloroplatinate.
c as 5b, plus sodium hydroxide ($\text{pH} > 10$) after ca. 24 hours.

Fig. 6 a Products of reaction of bromine trifluoride with sodium hexachloroplatinate (IV) hexahydrate, under mild conditions.
b as 6a, plus sodium hydroxide ($\text{pH} > 10$) after ca. 15 minutes.
c as 6b, after ca. 1 hour.

Fig. 7 a Products of the reaction of bromine trifluoride with potassium tetrachloroplatinate (II), under mild conditions.
b as 7a, plus sodium hydroxide ($\text{pH} > 10$) after ca. 5 minutes.
c as 7b, after ca. 10 minutes.
d as 7b, after ca. 15 minutes.

KEY TO SPECTRA, FIGURES 5, 6 and 7

	POSITION	SPECIES
A	F ¹⁻⁶	[PtF ₆] ²⁻
B	F ²⁻⁵	[Pt(OH) ¹ F ₅] ²⁻
C	F ⁶	
D	F ²⁻⁵	[Pt(OH) ^{1/2} , ⁶ F ₄] ²⁻
E	F ²⁻⁵	[PtCl ¹ F ₅] ²⁻
F	F ⁶	
G	F ²⁻⁵	[PtCl ¹ (OH) ⁶ F ₄] ²⁻
H	F ^{3,5}	[Pt(OH) ^{1/2} , ² F ₄] ²⁻
I	F ^{4,6}	
J	F ⁴⁻⁶	[PtCl ^{1/3} , ³ F ₃] ²⁻
K	F ^{3,5}	[PtCl ^{1/2} , ² F ₄] ²⁻
L	F ^{4,6}	
M	F ^{5,6}	[PtCl ^{1/3} , ³ (OH) ⁴ F ₂] ²⁻
N	F ⁶	[PtCl ^{1/3} , ³ (OH) ^{4/2} , ⁵ F] ²⁻
O	F ^{3,5}	[PtCl ^{1/2} , ² (OH) ⁴ F ₃] ²⁻
P	F ⁶	
Q	F ^{3,5}	[PtCl ^{1/2} , ² (OH) ^{4/2} , ⁶ F ₂] ²⁻

° represents satellites due to coupling between ¹⁹F and the ¹⁹⁵Pt isotope.

Figure 5

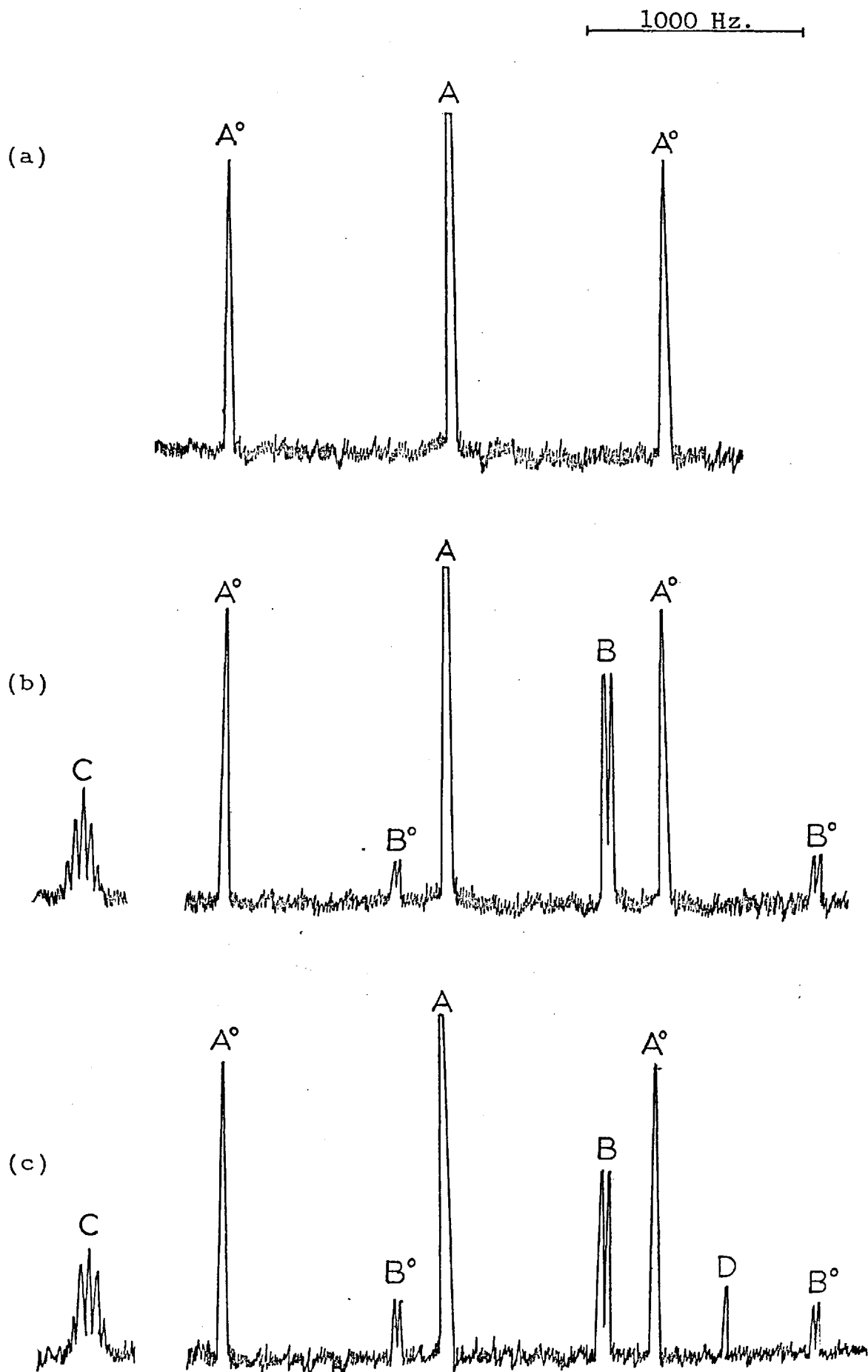


Figure 6

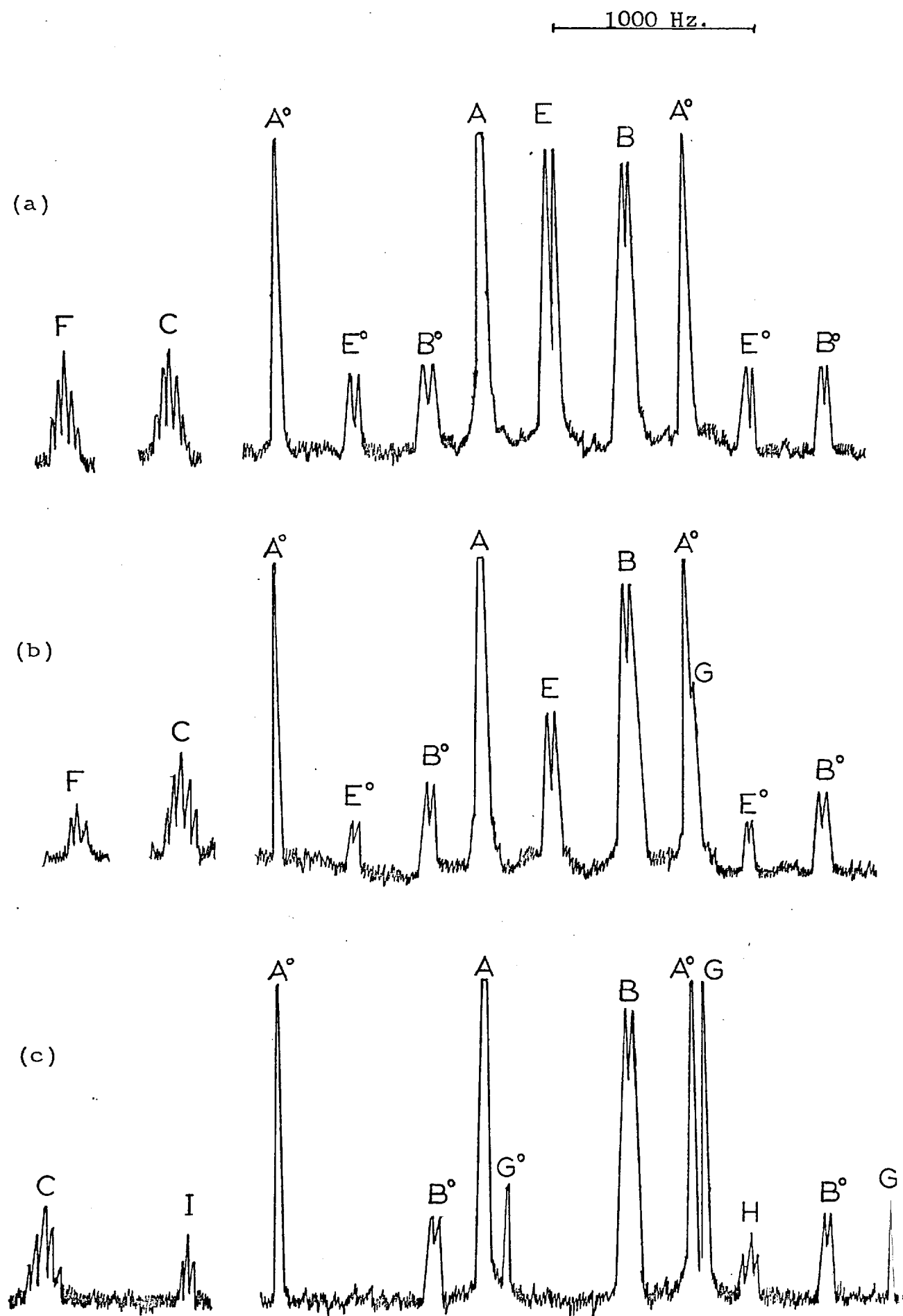
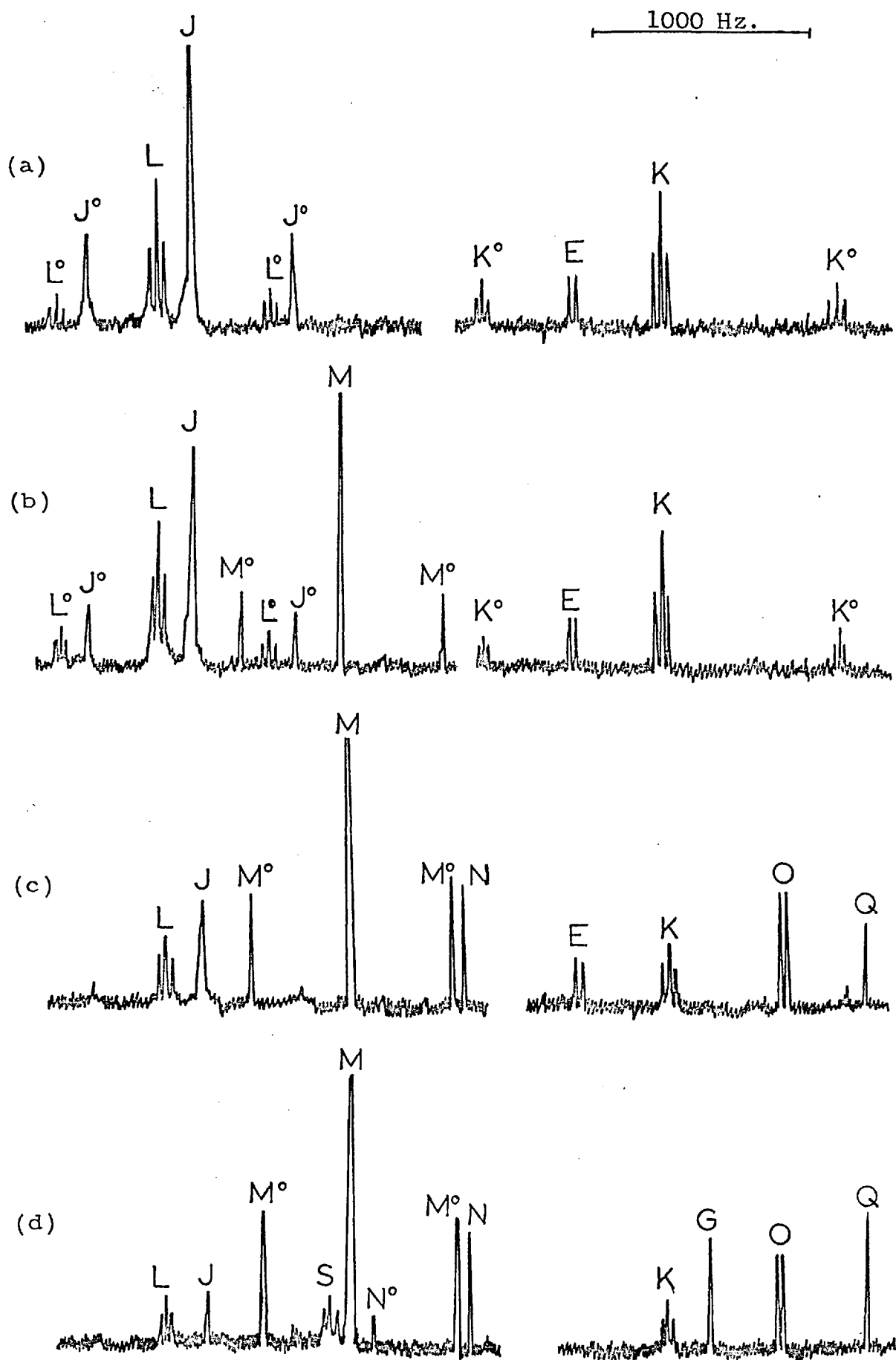
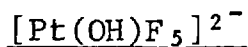


Figure 7



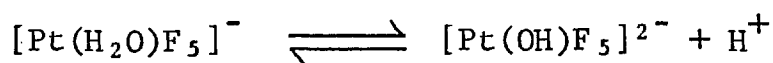


The reaction of bromine trifluoride with imperfectly dried sodium hexachloroplatinate (IV) gave a pale yellow solid, the infrared of which showed a strong absorption at 3500cm^{-1} , probably due to the presence of an hydroxyl group.

The ^{19}F n.m.r. spectrum of an aqueous solution of the product consisted of an intense signal due to the $[\text{PtF}_6]^{2-}$ ion and an AX_4 pattern showing ^{195}Pt - ^{19}F spin-spin coupling. The doublet of the AX_4 pattern was shifted to higher applied field than the central resonance of $[\text{PtF}_6]^{2-}$ and the quintuplet was to very much lower field. (Figure 5b).

The chemical shift of the doublet (F^{2-5} of $[\text{PtY}^1\text{F}_5]^{n-}$) varied with pH, increasing to a maximum value of 8.0 p.p.m. at $\text{pH} \geq 4.0$. The quintuplet was moved to higher field on decreasing the pH. On protonation the change in chemical shift of the quintuplet paralleled that of the doublet.

The data are consistent with the species being $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ which on protonation gives $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$. Since only one set of sharp resonances was observed for solutions of intermediate acidity, the reaction:



must be in rapid equilibrium, as expected for a proton transfer reaction.

A plot of δF^{2-5} of $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ against pH is given in figure 8.

$$\text{Using the equation: } K = \frac{[\text{H}^+](\text{SOB} - \text{SA})}{(\text{SB} - \text{SOB})} \quad * \quad \text{.....(I)}$$

where K = dissociation constant of the acid $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$

$[\text{H}^+]$ = Hydrogen ion concentration

SOB = observed chemical shift of F^{2-5}

SA = chemical shift of $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^- (\text{F}^{2-5})$

SB = chemical shift of $[\text{Pt}(\text{OH})\text{F}_5]^{2-} (\text{F}^{2-5})$,

the pK of $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$ was found to be 1.0.

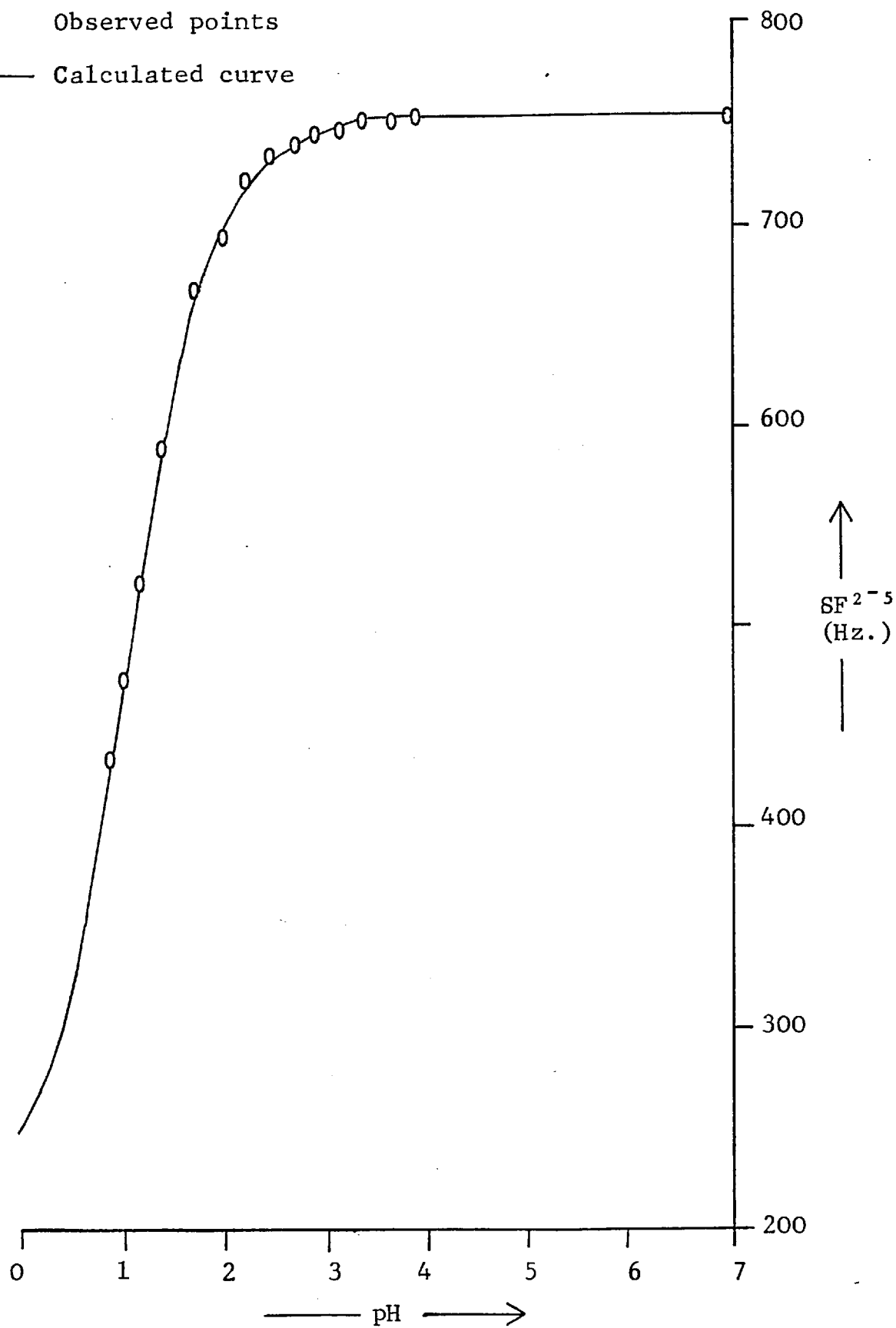
The value of SA was found as the limit of SOB when a large excess of perchloric acid was added to the solution. Since this addition greatly changes the ionic strength of the solution and therefore the properties of the solvent, the value of SA observed ($\text{SA}(\text{OB})$) may be somewhat unreliable. Several values of SA , varying around $\text{SA}(\text{OB})$, and several values of K were used in a computer program to find the values that gave the best fit between calculated and observed chemical shifts. (See appendix III).

* see Appendix I for derivation.

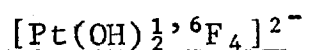
Figure 8.

pH dependence of SF^{2-5} of $[Pt(OH)F_5]^{2-}$

○ Observed points
— Calculated curve



Using $\delta A = 188$ Hz. and $K = 0.101$, the root mean square deviation for fifteen points was only 1.11 Hz., showing very good agreement between calculated and observed shifts. The value of δOB in strong (approximately 5 molar) perchloric acid solution was 207 Hz., which is in reasonable agreement with the value of $\delta A = 188$ Hz. used to give the best fit.



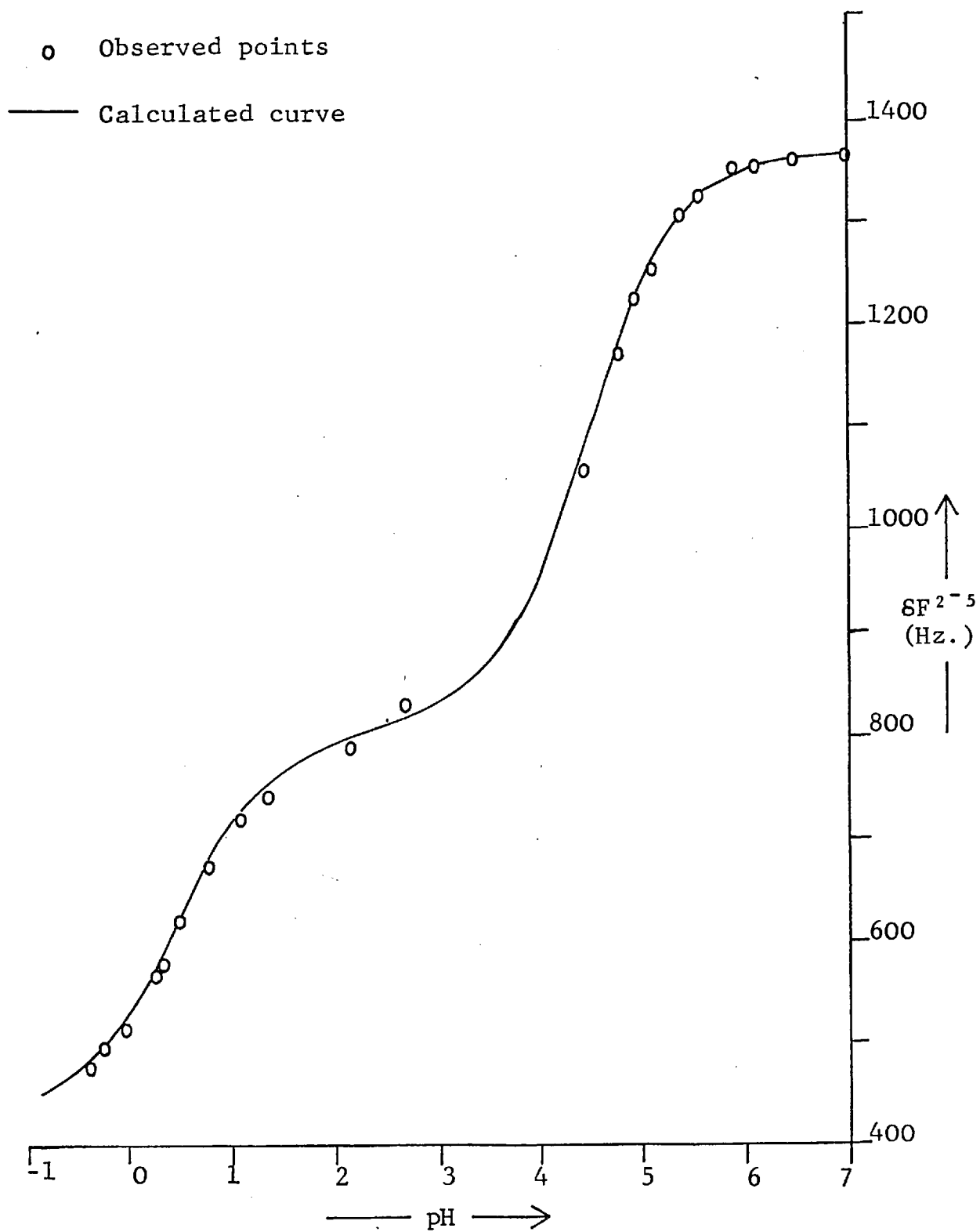
Addition of sodium hydroxide to solutions containing the $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ ion caused no immediate change in the ^{19}F n.m.r. spectra. After 24 hours, however, the intensity of the AX_4 pattern due to $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ had decreased and a new singlet, showing ^{195}Pt - ^{19}F spin-spin coupling, was observed at $\delta = 14.5$ p.p.m. (Figure 5c). The intensity of the resonance due to free fluoride had increased slightly.

The chemical shift of the singlet decreased on making the solution acidic. A plot of observed chemical shift against pH shows that the acid formed is dibasic (Figure 9).

The species giving rise to the singlet resonance must have all fluorines equivalent and contain two hydroxyl groups. Since it is formed by the reaction of hydroxide ions

Figure 9.

pH dependence of δF^{2-5} of $[\text{Pt}(\text{OH})_2^{1,6}\text{F}_4]^{2-}$



with $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ the species is presumably $[\text{Pt}(\text{OH})\frac{1}{2}'\text{F}_4]^{2-}$, which on protonation gives first $[\text{Pt}(\text{OH})^1(\text{H}_2\text{O})^6\text{F}_4]^-$ and then $\text{Pt}(\text{H}_2\text{O})\frac{1}{2}'\text{F}_4$.

Using the equation:

$$\delta\text{OB} = \frac{\delta\text{A}[\text{H}^+]^2 + \delta\text{BH}K_1[\text{H}^+] + \delta\text{BK}_1K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} \quad \text{....(II)}$$

where K_1 and K_2 are the first and second acid dissociation constants of $\text{Pt}(\text{H}_2\text{O})\frac{1}{2}'\text{F}_4$ respectively.

$[\text{H}^+]$ = hydrogen ion concentration

δOB = observed chemical shift of F^{2-5}

δA = chemical shift of $\text{Pt}(\text{H}_2\text{O})\frac{1}{2}'\text{F}_4$

δBH = chemical shift of $[\text{Pt}(\text{OH})^1(\text{H}_2\text{O})^6\text{F}_4]^-$

δB = chemical shift of $[\text{Pt}(\text{OH})\frac{1}{2}'\text{F}_4]^{2-}$,

values of δA , δBH , K_1 and K_2 that gave the best fit between observed and calculated points were found using a computer program. (Appendix IV).

Values of δA were taken around the value of δOB in strong perchloric acid solution. The value used to give the best fit ($\delta\text{A} = 440$ Hz.) was in good agreement with the observed shift of 426 Hz. Values of δBH were taken around $\frac{\delta\text{A} + \delta\text{B}}{2}$, the value predicted by the additivity

2

relationship of substituent effects on chemical shifts. The value used to give the best fit was $\delta\text{BH} = 800$ Hz., whereas

* see Appendix II for derivation.

$$\frac{\delta A + \delta B}{2} = 902 \text{ Hz.}, \text{ showing only reasonable agreement.}$$

Using $\delta A = 440 \text{ Hz.}$, $\delta B_H = 800 \text{ Hz.}$,
 $K_1 = 0.24$ ($pK_1 = 0.6$) and $K_2 = 3.05 \times 10^{-5}$ ($pK_2 = 4.5$)
the root mean square deviation for twenty points was found
to be 8.9 Hz.

No chemical shifts were measured between pH 2.8
and pH 4.5, since the weak peak due to $[\text{Pt}(\text{OH})\frac{1}{2}, \text{}^6\text{F}_4]^{2-}$
was obscured by the upfield sideband of the $[\text{PtF}_6]^{2-}$
resonance.

In strongly acidic solutions ($\text{pH} < 1.0$) the
hydrogen ion concentration was calculated from the shift of
the doublet resonance (F^{2-5}) of $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$, which is
present in the solution, using the equation:

$$[\text{H}^+] = \frac{K' (\delta B' - \delta \text{OB}')}{(\delta \text{OB}' - \delta A')} \dots\dots\dots (\text{III})$$

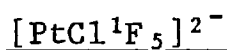
(derived from equation (I)).

where $K' =$ dissociation constant of $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^- = 0.101$
 $\delta B' =$ chemical shift (F^{2-5}) of $[\text{Pt}(\text{OH})\text{F}_5]^{2-} = 800 \text{ Hz.}$
 $\delta A' =$ chemical shift (F^{2-5}) of $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^- = 207 \text{ Hz.}$
 $\delta \text{OB}' =$ observed chemical shift.

The observed value of $\delta \text{F}^{2-5} = 207 \text{ Hz.}$ was used
for $\delta A'$ instead of the value of $\delta A' = 188 \text{ Hz.}$ used to give the
best fit between observed and calculated points. This was

because any change in the solvent properties should affect $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ and $[\text{Pt}(\text{OH})\frac{1}{2}, ^6\text{F}_4]^{2-}$ similarly.

Spectra similar to 5c were obtained for solutions of the product of reaction of bromine trifluoride with the sodium salt of trans-dihydroxytetrachloroplatinate(IV) but the intensity of the peaks due to the $[\text{Pt}(\text{OH})\frac{1}{2}, ^6\text{F}_4]^{2-}$ ion were relatively more intense.

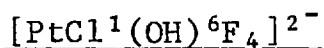


The reaction of bromine trifluoride with sodium hexachloroplatinate (IV) hexahydrate under mild conditions gave a pale yellow solid that had retained a small amount of chlorine. The infrared of the solid showed the presence of hydroxyl groups ($\nu = 3500 \text{ cm}^{-1}$). The ^{19}F n.m.r. spectrum of an aqueous solution of the product showed resonances due to $[\text{PtF}_6]^{2-}$, (identified by an increase in intensity on adding $(\text{Et}_4\text{N})_2\text{PtF}_6$ to the solution), $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$, (identified by its chemical shift, value of $J_{195\text{Pt}-19\text{F}}$ and change in chemical shift on acidifying the solution) and a second AX_4 type spectrum. (See Figure 6a). The chemical shifts of the AX_4 resonances were independent of pH.

The quintuplet of the AX_4 pattern occurred to low field of the $[\text{PtF}_6]^{2-}$ resonance, in the same region as

the ^{19}F resonance of the $[\text{PtCl}_3^1\text{F}_3]^{2-}$ ion in which all fluorines are trans to chlorines. (See Page 42).

These data suggest that the species present in solution is the $[\text{PtCl}^1\text{F}_5]^{2-}$ ion in which F^6 is trans to the chlorine. The additivity relationship of substituent effects on chemical shifts confirms this assignment.



Addition of sodium hydroxide to solutions containing the $[\text{PtClF}_5]^{2-}$ ion caused the intensity of the ^{19}F n.m.r. lines due to this ion to decrease rapidly and a new singlet resonance, showing ^{195}Pt - ^{19}F spin-spin coupling, was observed at $\delta = 11.1$ p.p.m. (Figures 6b and 6c).

The intensity of the singlet resonance was approximately equal to that of the doublet of $[\text{PtClF}_5]^{2-}$ in the original solution, showing that all four equatorial fluorines (F^{2-5}) remain bonded to the platinum.

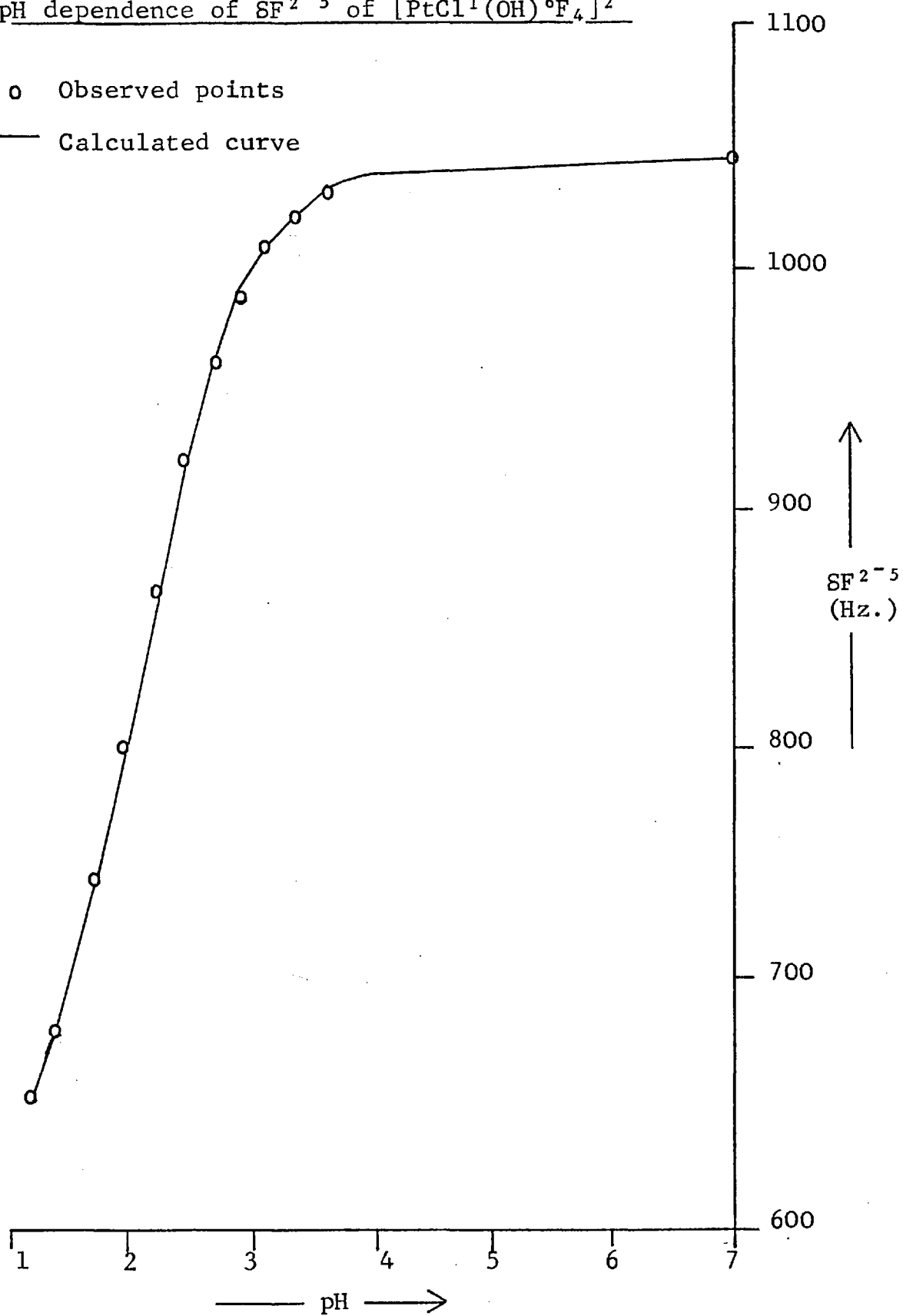
The chemical shift of the singlet was pH dependent. A plot of chemical shift against pH indicates that the acid formed is monobasic. (Figure 10).

The data are consistent with the species being $[\text{PtCl}^1(\text{OH})^6\text{F}_4]^{2-}$, which, on protonation gives $[\text{PtCl}^1(\text{H}_2\text{O})^6\text{F}_4]^-$.

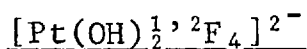
Figure 10.

pH dependence of δF^{2-5} of $[\text{PtCl}^1(\text{OH})^6\text{F}_4]^{2-}$

o Observed points
— Calculated curve



Using an expression similar to equation I, the dissociation constant of $[\text{PtCl}^1(\text{H}_2\text{O})^6\text{F}_4]^-$ was found to be 0.009 ($\text{pK} = 2.0$). A computer program, similar to that used for $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$, was used to find the values of chemical shift and dissociation constant of the acid that gave the best fit between observed and calculated points. (Appendix I). Using δF^{2-5} of $[\text{PtCl}^1(\text{H}_2\text{O})^6\text{F}_4]^- = 604$ Hz. and $K = 0.0090$, the root mean square deviation for fifteen points was 2.4 Hz., showing very good agreement between calculated and observed shifts.



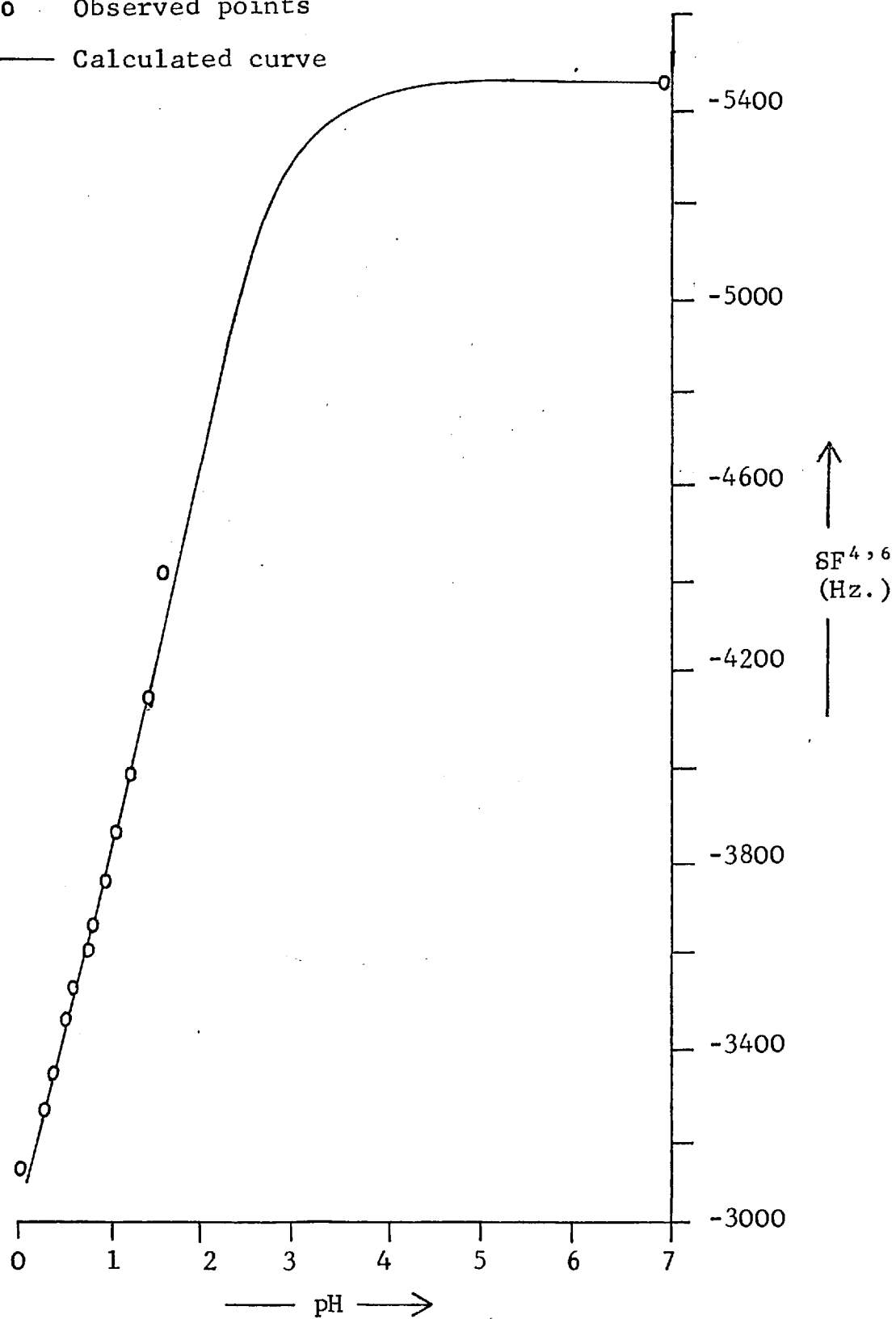
The ^{19}F n.m.r. spectra of solutions containing the $[\text{PtCl}^1(\text{OH})^6\text{F}_4]^{2-}$ ion also showed two weak triplets of equal intensity, one to high field of the $[\text{PtF}_6]^{2-}$ resonance and the other to low field. (Figure 6c). (A_2X_2 spectra indicate $[\text{PtY}_{\frac{1}{2}}^1, {}^2\text{F}_4]^{n-}$). The chemical shifts of both triplets were pH dependent, moving closer to the $[\text{PtF}_6]^{2-}$ resonance on increasing the acidity of the solutions.

A plot of chemical shift of the low field triplet against pH is given in Figure 11. The chemical shift of the up field triplet could not be measured at several pH values since the triplet was obscured by either the sideband of $[\text{PtF}_6]^{2-}$ or by the $[\text{PtCl}^1(\text{OH})^6\text{F}_4]^{2-}$ resonance. Using the additivity relationship for substituent effects on chemical

Figure 11.

pH dependence of $\delta F^{4,6}$ of $[\text{Pt}(\text{OH})_2^{2-}\text{F}_4]^{2-}$

o Observed points
— Calculated curve



shifts, the shifts of the low field and high field triplets in alkaline and strongly acidic solutions correspond to the predicted values for $\delta F^{4,6}$ and $\delta F^{3,5}$ of $[\text{Pt}(\text{OH})\frac{1}{2}'^2\text{F}_4]^{2-}$ and $\text{Pt}(\text{H}_2\text{O})\frac{1}{2}'^2\text{F}_4$ respectively. It is not obvious from Figure 11 that the species giving rise to the two triplets is behaving as a dibasic acid. A computer program was used to find the best fit between calculated and observed points, assuming the acid to be either dibasic or monobasic.

(Appendices III and IV). From the results obtained, the acid is most probably dibasic, i.e. $\text{Pt}(\text{H}_2\text{O})\frac{1}{2}'^2\text{F}_4$:

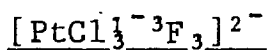
Dibasic: Minimum root mean square deviation = 26.7 Hz.

Monobasic: Minimum root mean square deviation = 65.2 Hz.

(both for thirteen points).

The observed shift of the low field triplet in five molar perchloric acid solution was -2720 Hz., which is in good agreement with the value of $\delta A = -2761$ Hz. used in the computer program to give the best fit. The difference is probably due to solvent effects or to the formation of the $[\text{HPtF}_6]^-$ ion.

In strongly acidic solutions ($\text{pH} < 1.0$) the hydrogen ion concentration was calculated from the change of chemical shift on protonation of the doublet, F^{2-5} of $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$, which is present in the solution. (using equation III).



Aqueous solutions of potassium trichlorotrifluoroplatinate (IV) gave ^{19}F n.m.r. spectra that showed a central high field resonance ($\delta = 190.0$ p.p.m. relative to external TFA, $\delta = -96.2$ p.p.m. relative to internal $[\text{PtF}_6]^{2-}$), showing ^{195}Pt - ^{19}F spin-spin coupling ($J_{^{195}\text{Pt}-^{19}\text{F}} = 1077$ Hz.).

Since only a singlet resonance was observed the anion must have the all cis structure in solution, i.e. it must be $[\text{PtCl}_3^- \text{F}_3]^{2-}$. ($[\text{PtCl}_3^{1,2,6}\text{F}_3]^{2-}$ would give an AX_2 type ^{19}F n.m.r. spectrum). Since platinum (IV) complexes have rigid octahedral geometry the all cis structure is probably present in the solid state.

The solution was allowed to stand for 24 hours, during which time a yellow precipitate was formed. The ^{19}F n.m.r. spectrum of the remaining solution showed that the concentration of the $[\text{PtCl}_3^- \text{F}_3]^{2-}$ ion had decreased and a new peak due to free fluoride ions had appeared. The region in which the resonance due to the $[\text{PtF}_6]^{2-}$ ion normally appears was searched thoroughly, but no lines were observed, indicating that $[\text{PtF}_6]^{2-}$ had not been formed. Brown, Dixon and Sharp²⁸ reported that solutions of trichlorotrifluoroplatinates decompose to give precipitates of hexachloroplatinates, hexafluoroplatinates and complex species containing hydroxyl species (the former were

identified by X-ray powder photography and the latter by infrared spectroscopy). Although potassium hexafluoroplatinate is only slightly soluble, the ^{19}F n.m.r. spectra due to saturated solutions of this complex show fairly intense resonances and so if any $[\text{PtF}_6]^{2-}$ had been formed from the decomposition of $[\text{PtCl}_3^{-3}\text{F}_3]^{2-}$, it would presumably have been detected.

$J_{^{195}\text{Pt}-^{19}\text{F}}$ of the $[\text{PtCl}_3^{-3}\text{F}_3]^{2-}$ ion was appreciably solvent dependent:

TABLE 2

SOLVENT	$J_{^{195}\text{Pt}-^{19}\text{F}}$ (Hz.).
H ₂ O	1077
MeOH	1080
EtOH	1081
Pr ⁿ OH	1081 (±10)
DMF	1152
DMSO	1223

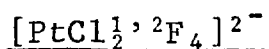


The addition of sodium hydroxide to an aqueous solution of potassium trichlorotrifluoroplatinate(IV) caused the intensity of the ^{19}F n.m.r. line due to it to decrease and a new singlet, showing $^{195}\text{Pt}-^{19}\text{F}$ spin-spin

coupling, appeared 8.3 p.p.m. up field of it. (Figure 7b). After several more minutes the intensity of the $[\text{PtCl}_3^{-3}\text{F}_3]^{2-}$ resonance had decreased further, the singlet 8.3 p.p.m. up field of it had increased in intensity and a new singlet line showing $^{19}\text{Pt}-^{19}\text{F}$ spin-spin coupling was observed 14.0 p.p.m. up field of the $[\text{PtCl}_3^{-3}\text{F}_3]^{2-}$ resonance. The resonance due to free fluoride ions steadily increased in intensity. On standing for approximately one hour at 35°C the ^{19}F n.m.r. spectrum showed only a single, intense resonance due to free fluoride ions.

From the additivity relationship of substituent effects on chemical shifts, the order of appearance of the two new lines in the spectrum and their lack of fine structure, the species present in solution are probably the $[\text{PtCl}_3^{-3}(\text{OH})\text{F}_2]^{2-}$ and $[\text{PtCl}_3^{-3}(\text{OH})_2\text{F}]^{2-}$ ions ($\delta = 8.3$ and 14.0 p.p.m. respectively, relative to internal $[\text{PtCl}_3^{-3}\text{F}_3]^{2-}$).

Addition of perchloric acid to solutions containing the $[\text{PtCl}_3^{-3}(\text{OH})\text{F}_2]^{2-}$ and $[\text{PtCl}_3^{-3}(\text{OH})_2\text{F}]^{2-}$ ions caused decomposition of these species before any appreciable change in chemical shift, due to protonation, had been observed.



The reaction of bromine trifluoride with potassium tetrachloroplatinite (II), under mild conditions, gave a bright yellow solid which had retained an appreciable amount of chlorine. The ^{19}F n.m.r. spectra of solutions of the product showed lines due to the $[\text{PtCl}_{\frac{1}{3}}^{-3}\text{F}_3]^{2-}$ ion, the reported product ²⁸, (identified by the increase in intensity of the line on adding $\text{K}_2\text{PtCl}_3\text{F}_3$ to the solution), $[\text{PtClF}_5]^{2-}$ (identified from its chemical shift and the chemical shift of the product of reaction with hydroxide ions) and an A_2X_2 pattern, showing ^{195}Pt - ^{19}F spin-spin coupling, due to $[\text{PtY}_{\frac{1}{2}}^{\frac{1}{2}}, ^2\text{F}_4]^{2-}$. (Figure 7a). The chemical shifts of the two triplets did not alter on acidifying the solution and so the species giving rise to these lines does not contain any hydroxyl groups.

From the additivity relationship of substituent effects on chemical shifts, the observed fine structure of the resonances and since both the $[\text{PtClF}_5]^{2-}$ and $[\text{PtCl}_{\frac{1}{3}}^{-3}\text{F}_3]^{2-}$ ions occur in the same reaction product, the species giving rise to the triplets was identified as the $[\text{PtCl}_{\frac{1}{2}}^{\frac{1}{2}}, ^2\text{F}_4]^{2-}$ ion.

Both $J_{^{195}\text{Pt}-^{19}\text{F}3,5}$ and $J_{^{195}\text{Pt}-^{19}\text{F}4,6}$ of the $[\text{PtCl}_{\frac{1}{2}}^{\frac{1}{2}}, ^2\text{F}_4]^{2-}$ ion were solvent dependent. Values are given in Table 3.

TABLE 3

SOLVENT DEPENDENCE OF $J_{\text{Pt-F}}$ OF $[\text{PtCl}_2^{1/2}, ^2\text{F}_4]^{2-}$

	IN WATER	IN DMSO
$J_{19^5\text{Pt}-19\text{F}^{3,5}}$ (Hz.)	1882	1858
$J_{19^5\text{Pt}-19\text{F}^{4,6}}$ (Hz.)	1115	1236

$[\text{PtCl}_2^{1/2}, ^2(\text{OH})^4\text{F}_3]^{2-}$ and $[\text{PtCl}_2^{1/2}, ^2(\text{OH})_2^4, ^6\text{F}_2]^{2-}$

Addition of sodium hydroxide to a solution containing the $[\text{PtCl}_2^{1/2}, ^2\text{F}_4]^{2-}$ ion causes the intensities of the ^{19}F n.m.r. lines due to it to decrease and a new AX_2 pattern showing $^{195}\text{Pt}-^{19}\text{F}$ spin-spin coupling was observed. ($\delta\text{X} = 15.5$ p.p.m., $\delta\text{A} = -89.3$ p.p.m.). (Figure 7c). On standing the intensities of the AX_2 resonances decreased and a new singlet, also showing $^{195}\text{Pt}-^{19}\text{F}$ spin-spin coupling, was observed at $\delta = 20.4$ p.p.m. (Figure 7d).

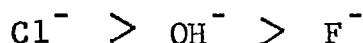
From the additivity relationship of substituent effects on chemical shifts, the order of appearance and fine structure of the ^{19}F n.m.r. lines, the AX_2 and singlet lines were identified as arising from the $[\text{PtCl}_2^{1/2}, ^2(\text{OH})^4\text{F}_3]^{2-}$ and $[\text{PtCl}_2^{1/2}, ^2(\text{OH})_2^4, ^6\text{F}_2]^{2-}$ ions respectively.

The lines due to $[\text{PtCl}_{\frac{1}{2}}{}^2\text{F}_4]^{2-}$ and $[\text{PtCl}_{\frac{1}{2}}{}^2(\text{OH})^4\text{F}_3]^{2-}$ soon disappeared, but that due to $[\text{PtCl}_{\frac{1}{2}}{}^2(\text{OH})^4{}^6\text{F}_2]^{2-}$ remained, although it had decreased in intensity, after 24 hours.

Addition of perchloric acid to solutions containing the above chloro-hydroxy-fluoro-platinum complexes caused immediate decomposition before any appreciable change in chemical shift due to protonation was observed.

DISCUSSIONCIS AND TRANS EFFECTS IN Pt (IV) FLUORO COMPLEXES

The formation of the substituted fluoro complexes of platinum (IV) can be explained by considering the trans effects of the ligands. Substitution reactions of octahedral platinum (IV) complexes usually proceed by a platinum (II) catalysed path and the chief requirement of this mechanism is that the trans ligand is labile and therefore easily dissociated from the metal ¹⁹. Gray and Langford ⁶³ suggested that the trans effect of a ligand depends on metal-ligand σ overlap integral, which increases with decreasing electronegativity. Mason and Towl ⁶⁴ found that, for platinum (IV) complexes, the σ -donor ability of a ligand (which depends on its electronegativity) is the most important factor affecting the lability of the trans ligand. From these results a tentative order of ligands of decreasing trans effect in platinum (IV) complexes is:



There is considerable evidence that chlorine has a stronger trans labilising ability than the hydroxyl group ²³, but there are no data available for fluorine.

The rates of reactions of $[\text{PtClF}_5]^{2-}$, $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ and $[\text{PtF}_6]^{2-}$ with hydroxide ions support the above ordering of ligands. The fluorine trans to chlorine in $[\text{PtClF}_5]^{2-}$ is

rapidly replaced by a hydroxyl group, but the four fluorines trans to each other are not substituted. After only 20 minutes the $[\text{PtClF}_5]^{2-}$ has reacted to give approximately 100% $[\text{PtCl}^1(\text{OH})^6\text{F}_4]^{2-}$. $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ reacts slowly under similar conditions and after one day only 5-10% had reacted to give $[\text{Pt}(\text{OH})\frac{1}{2},^6\text{F}_4]^{2-}$. $[\text{PtF}_6]^{2-}$, in which all fluorines are trans to fluorine, reacts extremely slowly (less than 5% reaction after 3 months at ca 20°C) and no intermediate substitution products were observed.

Substitution reactions of the $[\text{PtF}_6]^{2-}$ ion are acid catalysed³¹. The reaction of $(\text{Et}_4\text{N})_2\text{PtF}_6$ (0.14M) with an excess of Cl^- or I^- was followed using ^{19}F n.m.r. spectroscopy. Neutral solutions reacted extremely slowly. Acidic solutions gave ca. 80% reaction after one day, but no mixed halo-fluoroplatinates were detected. Potassium tetrachloroplatinite (II) (ca. 10^{-3}M) had no effect on the rates of reaction and so the mechanism of substitution of $[\text{PtF}_6]^{2-}$ probably does not involve a platinum (II) bridged intermediate.

A cis labilising effect is also operating in the platinum (IV) complexes. If we consider the three complexes $[\text{PtCl}\frac{1}{3},^3\text{F}_3]^{2-}$, $[\text{PtCl}\frac{1}{2},^2\text{F}_4]^{2-}$ and $[\text{PtClF}_5]^{2-}$, we see that the rate of replacement of a fluorine by hydroxide is increased by increasing the number of cis substituents:

RATE OF REPLACEMENT OF FLUORINE	$[\text{PtCl}_3^- \text{F}_3]^{2-} > [\text{PtCl}_2^- \text{F}_4]^{2-} > [\text{PtClF}_5]^{2-}$		
NUMBER OF Cl^- <u>CIS</u> TO F^-	2	1	0
NUMBER OF F^- <u>TRANS</u> TO Cl^-	3	2	1

If the cis effect of chlorine is the same as that of fluorine, then one would expect the rates of reaction of the above complexes to be in the same ratio as the number of fluorines trans to chlorine, i.e. 3:2:1. However, $[\text{PtCl}_3^- \text{F}_3]^{2-}$ has almost completely reacted before much $[\text{PtClF}_5]^{2-}$ has reacted. (See Figure 7).

Also, $[\text{PtCl}_2^- \text{F}_2]^{2-}$, in which the two fluorines are trans to each other and therefore have four substituted cis groups, is much less stable than $[\text{PtF}_6]^{2-}$.

The cis effect is, however, much less important than the trans effect in platinum (IV) complexes.

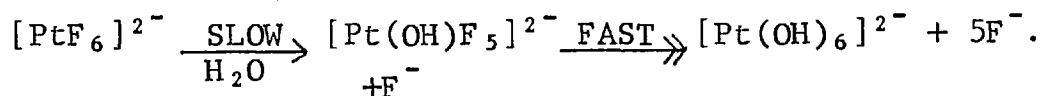
Aqueous solutions of the alkali metal hexahaloplatinates, M_2PtX_6 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), are slowly hydrolysed to give acidic solutions¹⁷. The hydrolyses are catalysed by light⁶⁵. Balzani et al⁶⁶ found that $[\text{PtBr}_6]^{2-}$ when irradiated at wavelengths corresponding to any of its

electron transfer or d-d bands gave the same quantum yield of the aquated product $[\text{PtBr}_5(\text{H}_2\text{O})]^-$. They proposed the mechanism:



involving heterolytic fission of a Pt—Br bond. Since employing different wavelengths of irradiation causes the same photoreaction and gives the same quantum yield of product, it suggests that radiationless transitions occur resulting in the lowest energy excited state and the complex reacts whilst in this state.

Alkaline solutions of $[\text{PtF}_6]^{2-}$ were decomposed when irradiated by light of wavelength less than 3130\AA . In a typical experiment, a solution of $(\text{Et}_4\text{N})_2\text{PtF}_6$ was irradiated for 19 hours. Approximately 30% decomposition had taken place in this solution, but no reaction in the reference solution was observed. No intermediate hydroxy-fluoro-platinum (IV) complexes were detected, probably because the rate of replacement of the first fluorine is extremely slow compared with the rates of the subsequent replacements:



$[\text{PtF}_6]^{2-}$ absorbs only weakly at 3180\AA ($\epsilon = 37$) but $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ and the more highly substituted complexes absorb more strongly. This, together with the greater trans effect of the hydroxyl group will contribute to the higher rate of reaction of the substituted fluoro complexes.

CIS AND TRANS INFLUENCE

The Pt-X bond length in the system L-Pt-X varies with change of L. An unusually long Pt-X bond length indicates that L has a high trans influence. Unlike platinum (II) complexes the Pt(IV)-X bond length, as determined by X-ray studies, does not differ noticeably with changes in L ⁶⁷.

Information concerning trans influences in platinum (IV) complexes has been obtained from metal-ligand stretching vibrations. In particular, ν (Pt-Me) for the methylplatinum compounds $[\text{Pt}(\text{Me})_3\text{X}_3]^{n-}$ and $[\text{Pt}(\text{Me})_3\text{X}]_4$ have been measured and the relative trans influences of X in both types of compound are found to be comparable, even though X is monodentate and triply-bridging respectively ²⁷. However, it was impossible to calculate force constants for the compounds and it has been assumed that a lower stretching frequency corresponds to a weaker bond. Interpretation of data is complicated by the possibility of vibrational coupling and changes in vibrational frequency due to changes in mass, solid state and counter-ion effects. These complications have usually been ignored.

Acid dissociation constants are a good guide to bond strengths. The substituted platinum (IV) amines show marked changes in pK values with variations in the type and

the positions of the substituents ^{68,69}. It is assumed that the stronger the acid, the greater the protonic nature of the N-hydrogens and the stronger the Pt-N bond. The acid strengths of $[\text{Pt}(\text{NH}_3)_5\text{X}]^{3+}$ decrease in the order $\text{Cl}^- > \text{Br}^- > \text{OH}^-$ ⁷⁰ and it follows that the strength of the Pt-N bond trans to X decreases in the same order.

The pK values of several platinum (IV) complexes are presented in Table 4.

TABLE 4

ION	pK ₁	pK ₂	REFERENCE
$[\text{Pt}(\text{NH}_3)_5\text{Cl}]^{3+}$	8.1		69
$[\text{Pt}(\text{NH}_3)_5\text{Br}]^{3+}$	8.3		68
$[\text{Pt}(\text{NH}_3)_5(\text{OH})]^{3+}$	9.5		68
$[\text{Pt}(\text{NH}_3)_4\text{Cl}_{\frac{1}{2},2}]^{2+}$	9.7		69
$[\text{Pt}(\text{NH}_3)_4\text{Cl}_{\frac{1}{2},6}]^{2+}$	11.3		69
$\text{PtCl}_4(\text{H}_2\text{O})_{\frac{1}{2},6}$	1.9	5.5	16
$[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$	1.0		
$[\text{PtCl}^1(\text{H}_2\text{O})^6\text{F}_4]^-$	2.1		
$\text{Pt}(\text{H}_2\text{O})_{\frac{1}{2},2}\text{F}_4$	0.5	2.0	
$\text{Pt}(\text{H}_2\text{O})_{\frac{1}{2},6}\text{F}_4$	0.6	4.5	

Grinberg and Gil'dengershel ⁷¹ suggested that, for cis and trans $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$, the greater acidity of the cis isomer may be caused by the fact that the cis complex

is polar, the negative charge being near the chloro groups and the positive charge near the amines making the N-hydrogens more protonic. The polarity of the fluoro-complexes can have little effect on their pK values since the pK₁ values of cis and trans Pt(H₂O)₂F₄ are approximately equal. The large difference in the pK₂ values of these two complexes is therefore probably caused by the Pt-O bond being stronger in the cis than in the trans isomer, as a result of the fluorine exerting a lower trans influence than the hydroxyl group. From the data presented in Table 4 ligands may be placed in the following order of decreasing trans influence: OH⁻ > Cl⁻ > H₂O, F⁻

Cis substituents also affect the pK values of platinum fluoro complexes and ligands may be placed in the following order of decreasing cis influence:



The effect is probably due to a general inductive effect.

PLATINUM-FLUORINE SPIN-SPIN COUPLING CONSTANTS

The coupling between two directly bonded nuclei is dominated by the Fermi contact term⁵². This assumes that the interaction of the nuclear spin with electronic orbital motion contributes a negligible amount to the coupling, and that the Fermi contact interaction at the nucleus, between nuclear spin and s-electrons, makes the

dominant contribution. Shoolery ⁷² noted that $J_{13\text{C-H}}$ depends linearly on the percentage s -character of the carbon orbital used in the C-H bond.

Malinowski ⁷³ first noted that substituent effects on $J_{13\text{C-H}}$ were directly additive. $J_{13\text{C-H}}$ of a compound of the type H-CXYZ was found to be dependent on X, Y and Z, according to the equation:

$$J_{13\text{C-H}} = \xi_X + \xi_Y + \xi_Z,$$

where ξ_X , ξ_Y and ξ_Z are contributions which are associated with X, Y and Z respectively. ξ values are dependent on the atom of the substituent directly bonded to the carbon, and decrease in the order: Halogen > O > N > C. In later work it was found that there were consistent deviations from direct additivity of substituent effects on $J_{13\text{C-H}}$, particularly for the more electronegative substituents, and interaction terms had to be introduced ⁷⁴. More recently Malinowski and co-workers ^{75,76} found that directly bonded coupling constants which do not obey the direct additivity rule could be correlated by pairwise interactions. The following equation was used successfully for couplings between $^{13}\text{C-H}$, $^{13}\text{C-F}$, $^{29}\text{Si-H}$ and $^{117}/^{119}\text{Si-H}$;

$$J(\text{XYZ}) = \eta_{xy} + \eta_{yz} + \eta_{zx}$$

where $J(\text{XYZ})$ is the coupling of the directly bonded nuclei for a series of compounds containing substituents X, Y and Z

and η_{xy} is an empirical parameter associated with X and Y but independent of Z.

Gutowski and Juan ⁷⁷ suggested that $J_{13\text{C-H}}$ in H-CXYZ depends predominantly on the Fermi contact interaction, and that the additivity observed by Malinowski ⁷³ results from changes in the hybridisation of the carbon $2s$ -orbital. The origin of the interaction terms is uncertain.

Vladimiroff and Malinowski ⁷⁸ gave a theoretical interpretation of additivity of substituent effects on coupling constants. Using McWeeny group functions for the Fermi contact term in spin coupling, the effect of substituents are directly additive. If the group wave functions perturb each other then second order terms cannot be neglected.

Dean ⁷⁹ reported that, for octahedral tin-fluoro complexes, $J_{\text{Sn-F}}$ did not vary in a simple manner. It was found that the coupling constants fall into two sets depending on whether there is a fluorine or a substituent trans to the fluorines and that $J_{\text{Sn-F}}$ depends on both the number and spacial arrangement of the cis substituents.

The value of $J_{\text{Pt-F}}$ of the compounds containing the Pt(IV)-F bond will depend largely on the s-character of the bonding hybrid orbital used by platinum in that bond. Weakening a Pt-F bond will reduce the s-character of that bond and any decrease in covalency will reduce the coupling. Values of $J_{\text{Pt-F}}$ for a number of platinum (IV) complexes are

presented in Table 5. The values can be divided into two sets:

1788 \rightarrow 2003 Hz., for the F-Pt-F system,

1049 \rightarrow 1115 Hz., for the X-Pt-F system.

The data suggest that the Pt-F bond trans to X is more ionic than trans to fluorine, indicating as expected, that X has a greater trans influence than fluorine.

Unfortunately it was not possible to measure $J_{\text{Pt-F}}$ of $[\text{PtCl}_1\text{F}_5]^{2-}$ and $[\text{Pt}(\text{H}_2\text{O})_1\text{F}_5]^-$ and so direct comparison of trans influences of the ligands could not be made.

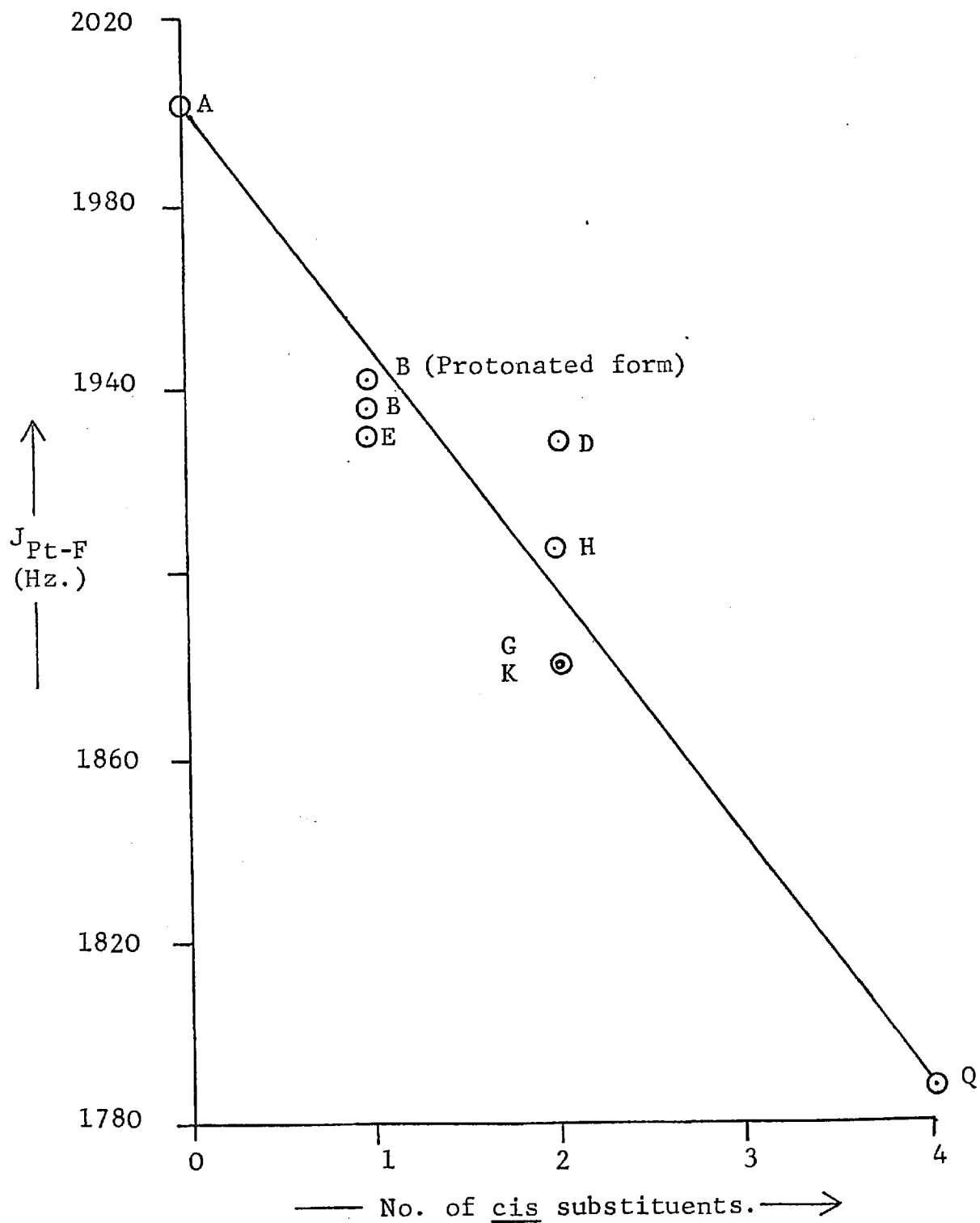
$J_{\text{Pt-F}}$ of the F-Pt-F system is dependent on the cis substituents. $J_{\text{Pt-F}}^{2-5}$ of $[\text{PtXF}_5]^{n-}$ decreases in the order : $\text{F}^- > \text{H}_2\text{O} > \text{OH}^- > \text{Cl}^-$. This can be explained in terms of the electronegativity of the ligands which decreases in the above order. Increasing the electronegativity of X will decrease the ionic character of the Pt-F bonds. The value of $J_{\text{Pt-F}}$ (in F-Pt-F) decreases additively with the number of cis substituents. (See Figure 12). Increasing the number of less electronegative substituents decreases the positive charge on the platinum, therefore less electron density is removed from the fluorines and the Pt-F bonds become more ionic. A less regular behaviour is observed for fluorines trans to X, where an increase in the number of cis hydroxyl groups causes an increase in $J_{\text{Pt-F}}$, but an increase in the number of cis chloro groups causes $J_{\text{Pt-F}}$ to decrease.

$J_{\text{Pt-F}}$ of the $[\text{PtCl}_3\text{F}_3]^{2-}$ ion was found to be

TABLE 5

COMPLEX	FLUORINE POSITIONS	SOB p.p.m.	SCAL p.p.m.	$J_{\text{Pt-F}}$ Hz.	$J_{\text{F-F}}$ Hz.
$[\text{PtF}_6]^{2-}$	1 - 6	0	0	2003	-
$[\text{PtCl}^1\text{F}_5]^{2-}$	2 - 5	3.7	3.6	1931	40
	6	-99.9	-101.4		38
$[\text{Pt}(\text{OH})^1\text{F}_5]^{2-}$	2 - 5	8.0	7.0	1936	34
	6	-65.5	-65.2	1049	34
$[\text{Pt}(\text{H}_2\text{O})^1\text{F}_5]^-$	2 - 5	2.2	2.5	1945	35
	6	-35.0	-33.5		35
$[\text{PtCl}^1(\text{OH})^6\text{F}_4]^{2-}$	2 - 5	11.1	10.6	1882	-
$[\text{PtCl}^1(\text{H}_2\text{O})^6\text{F}_4]^-$	2 - 5	6.4	6.1		-
$[\text{Pt}(\text{OH})_2^2\text{F}_4]^{2-}$	3, 5	12.8	14.0	1905	30
	4, 6	-57.9	-58.2	1081	30
$[\text{Pt}(\text{OH})^1(\text{H}_2\text{O})^2\text{F}_4]^-$	3, 5	8.4	9.5		
	4, 6	-43.2	-44.6		
$\text{Pt}(\text{H}_2\text{O})_2^2\text{F}_4$	3, 5	5.3	5.0		
	4, 6	-29.4	-31.0		
$[\text{PtCl}_2^2\text{F}_4]^{2-}$	3, 5	8.3	7.2	1882	41
	4, 6	-98.0	-98.8	1115	39
$[\text{PtCl}_2^2(\text{OH})^4\text{F}_3]^{2-}$	3, 5	15.5	14.2		
	6	-89.3	-91.8		
$[\text{PtCl}_2^2(\text{OH})_2^4\text{F}_2]^{2-}$	3, 5	20.4	21.2	1788	-
$[\text{PtCl}_3^-3\text{F}_3]^{2-}$	4 - 6	-96.2	-95.2	1077	-
$[\text{PtCl}_3^-3(\text{OH})^4\text{F}_2]^{2-}$	5, 6	-87.8	-88.2	1091	-
$[\text{PtCl}_3^-3(\text{OH})_2^4\text{F}]^{2-}$	6	-81.4	-81.2	1050	
$[\text{Pt}(\text{OH})_2^2\text{F}_4]^{2-}$	2 - 5	14.5	14.0	1926	-
$[\text{Pt}(\text{OH})^1(\text{H}_2\text{O})^6\text{F}_4]^-$	2 - 5	8.5	9.5		
$\text{Pt}(\text{H}_2\text{O})_2^2\text{F}_4$	2 - 5	4.7	5.0		

Figure 12. Plot of $J_{\text{Pt-F}}$ against the number of cis substituents. (For assignments see Page 25).



solvent dependent and increased on decreasing the solvating power of the solvent. A plot of $J_{\text{Pt-F}}$ of the $[\text{PtCl}_3^- \text{F}_3]^{2-}$ ion against $J_{\text{Pt-F}}$ of the $[\text{PtF}_6]^{2-}$ ion shows an approximate straight line of negative gradient, indicating that $J_{\text{Pt-F}}$ of the $[\text{PtCl}_3^- \text{F}_3]^{2-}$ ion probably has an absolute negative sign.

In the $[\text{PtCl}_2 \text{F}_4]^{2-}$ ion we have the interesting situation where there are two chemically different types of fluorine nuclei. The two platinum-fluorine spin-spin coupling constants, $J_{\text{Pt-F}^{3,5}}$ and $J_{\text{Pt-F}^{4,6}}$, were both solvent dependent, but changed in opposite senses, suggesting that the reduced coupling constants are of opposite signs. $J_{\text{Pt-F}^{3,5}}$ (fluorine trans to fluorine) decreased on decreasing the solvating power of the solvent, as did $J_{\text{Pt-F}}$ of the $[\text{PtF}_6]^{2-}$ ion which has, as suggested above (Page 11), an absolute positive sign. $J_{\text{Pt-F}^{4,6}}$ (fluorines trans to chlorines) increased on decreasing the solvating power of the solvent as did $J_{\text{Pt-F}}$ of the $[\text{PtCl}_3^- \text{F}_3]^{2-}$ ion, which, as suggested above, may have an absolute negative sign. The data suggest that, for $[\text{PtCl}_2 \text{F}_4]^{2-}$, $J_{\text{Pt-F}^{3,5}}$ is positive and $J_{\text{Pt-F}^{4,6}}$ is negative. (See Table 6, Page 61).

It is possible that the two coupling constants have the same sign and that the above phenomenon may be due to changes in specific solvent-solute interactions. In particular, hydrogen bonding will be affected by the presence

in the ions of the chlorine atoms. The two fluorines trans to a chlorine will be more ionic than the two fluorines trans to each other. Hydrogen bonding between the solvent and the fluorines trans to chlorines will therefore be stronger.

TABLE 6

ION	COUPLING	SOLVENT		PROBABLE SIGN OF J_{Pt-F}
		H ₂ O	DMSO	
$[PtF_6]^{2-}$	$J_{Pt-F^{1-6}}$	2003	1976	+
$[PtCl_3^- ^3F_3]^{2-}$	$J_{Pt-F^{4-6}}$	1077	1223	-
$[PtCl_2 ^2F_4]^{2-}$	$J_{Pt-F^{3,5}}$	1882	1858	+
	$J_{Pt-F^{4,6}}$	1115	1236	-

Heteronuclear spin decoupling experiments should tell us if the two coupling constants are of the same or opposite signs. However, initial experiments proved fruitless, due to the instability of the solutions, lack of suitable internal reference and instrumental inadequacies.

¹⁹F CHEMICAL SHIFTS OF PLATINUM (IV) FLUORO COMPLEXES

Jolly, Harris and Briggs⁸⁰ studied the ¹H n.m.r. spectra of cobalt (III) ammine complexes in concentrated sulphuric acid solution. Two separate resonances of relative intensities 4:1 were observed for solutions containing complexes of the type $[Co(NH_3)_5X]^{2+}$, due to the NH₃ groups

cis and trans to the substituent X respectively. The values of the chemical shifts of these pentammine complexes, relative to internal $[\text{Co}(\text{NH}_3)_6]^{3+}$, were used to help with the assignment of resonances in the n.m.r. spectra of complexes of the type $[\text{Co}(\text{NH}_3)_4\text{X}^1\text{Y}^2]^+$ and of solutions containing mixtures of species. An additive relationship between the number and positions of substituents and the chemical shift of the ammine protons was found from the limited number of complexes studied.

Other workers have reported an additivity relationship between substituents and the chemical shifts of the following nuclei in various compounds: ^1H , ^{11}B , ^{13}C , ^{19}F , ^{27}Al and ^{31}P .^{78,81-86}

Often the substituent effects on chemical shifts of nuclei do not obey a simple additivity relationship. Each substituent does not contribute a fixed increment to the nuclear shielding, but its contribution is dependent upon the other substituents present. Pairwise interactions can account for these inconsistencies. For substituents far removed from the nucleus under investigation the direct additivity relationship is often followed. For example, the substituent effects on proton shifts for compounds of the type H-CXYZ are pairwise additive, whereas for the methyl protons in the substituted ethanes $\text{H}_3\text{C-CXYZ}$ they are directly additive⁷⁸.

Vladimiroff and Malinowski ⁷⁸ in their theoretical interpretation of additivity of substituent effects on chemical shifts of different nuclei used McWeeny group wavefunctions and therefore eliminated the average energy approximation. They found that theoretical expressions of chemical shifts could be divided into first and second order terms. There is a directly additive contribution from each substituent group for both of these terms and pairwise contributions arise because each group suffers a correction in its group wavefunction due to the presence of each neighbouring group. The pairwise terms are smaller than the directly additive terms because the corrections to group wavefunctions are only small, but they should not be neglected since the first and second order terms are often of opposite signs and therefore partially cancel each other.

Dean and Evans ⁵³ have shown that for octahedral, substituted fluoro-stannates of the type $[\text{SnX}_n\text{F}_{6-n}]^{m-}$ the ^{19}F chemical shift of a particular fluorine depends on the number and positions of the substituents X, according to the expression:

$$\delta\text{F} = p\text{C} + q\text{T} \quad (\text{See Page 22}).$$

The general expression for calculating the ^{19}F chemical shifts of complexes having more than one type of substituent is:

$$\delta\text{F} = \sum_{\text{X}} p_{\text{X}}\text{C}_{\text{X}} + \sum_{\text{X}} q_{\text{X}}\text{T}_{\text{X}} \quad \dots\dots\dots(\text{IV})$$

where p_x, q_x, C_x and T_x are the values of p, q, C and T for the ligand X . It was found that by introducing empirical interaction terms for ligands cis to each other in the plane containing the Sn-F bond, a better fit between observed and calculated shifts could be obtained. The interaction terms appeared to be small compared with values of C and T and since their inclusion complicates the relationship, making it less useful, they were not generally taken into account. Values of C are usually negative and range from -44.4 to +0.6 p.p.m., but values of T cover a smaller range and vary from -11.4 to +14.0 p.p.m. for the ligands studied. Using the theory of Saika and Slichter⁵, replacement of a fluorine in $[\text{SnF}_6]^{2-}$ by a less electronegative ligand should produce a shift to higher applied field and hence other factors must be operating. Dean and Evans⁵³ suggested that cis parameters were largely due to intramolecular van der Waals interactions.

Equation IV was used in this work for platinum (IV) fluoro complexes and values of C and T of the ligands Cl^- , OH^- and H_2O were calculated. Approximate values of C and T were found from the ^{19}F chemical shifts of F^{2-5} and F^6 of $[\text{PtXF}_5]^{n-}$, ($X = \text{Cl}^-$, OH^- and H_2O). Refinements to these values were made by incorporating chemical shift data of complexes containing more than one substituted ligand.

Calculated values of δF , using equation IV and

the values of C and T from Table 7, are presented in Table 5, Page 58. The root mean square deviation between calculated and observed chemical shifts of eighteen complexes (involving 26 chemical shift values) was only ca. 1 p.p.m.

TABLE 7

LIGAND	C(p.p.m.)	T(p.p.m.)
Cl ⁻	3.6	-101.4
OH ⁻	7.0	-65.2
H ₂ O	2.5	-33.5

The theoretical expression derived by Saika and Slichter⁵ was found to be useless for predicting ¹⁹F chemical shifts of platinum (IV) fluoro complexes. Since F is always bonded to platinum (IV) the expression would predict that the chemical shifts of the substituted complexes should be the same, but in fact they cover a range of ca. 120 p.p.m.

In the platinum (IV) fluoro complexes replacement of a fluorine from [PtF₆]²⁻ by a less electronegative ligand X, should increase the ionic character of the Pt-F bonds. The trans influence of X is probably greater than its cis influence and so the Pt-F bond trans to X will therefore be longer and more ionic than the Pt-F bonds cis to X. An increase in the ionic character of a fluorine should produce

a shift to higher applied field ⁵. Therefore the ¹⁹F resonance of F⁶ of [PtXF₅]ⁿ⁻ should be shifted to much higher field than that of [PtF₆]²⁻ and the F²⁻⁵ resonance should also be to higher field. It is observed that F⁶ is at much lower field and F²⁻⁵ to slightly higher field. Increasing the number of substituents cis to a particular fluorine causes the chemical shift of that fluorine to move to higher applied field. The disagreement between observed chemical shifts and those predicted from the theory of Saika and Slichter demonstrates the importance of considering the energies of all the charge-transfer excited states which can be mixed-in under the influence of the applied magnetic field.

The order of magnitude and opposite signs of the chemical shifts of fluorines cis and trans to a substituent are probably due to different contributions from the terms in the expression for chemical shifts. Van der Waals interactions are likely to be small (probably second order) for fluorines trans to a substituent and electronic factors presumably play the dominant role in determining the chemical shift. For fluorines cis to a substituent intramolecular van der Waals interactions may be important, as suggested for fluoro-stannates ⁷⁹, although electronic factors are probably larger.

EXPERIMENTAL

MATERIALS

Materials were obtained commercially where possible.

Sodium hexachloroplatinate (IV) hexahydrate and potassium tetrachloroplatinite (II) were from Johnson, Matthey and Co. Ltd. Platinum was recovered and recycled using standard literature methods ^{87,88}.

Bromine trifluoride was obtained from B.D.H., and was used without purification.

Fluorine gas was obtained from Fluorochem Ltd.

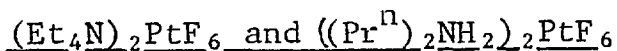
SOLVENTS

Freshly opened bottles were used where possible and anhydrous solvents were stored over Linde 3A Molecular Sieves.

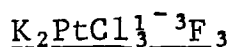
PREPARATIONS

Na₂PtF₆ and K₂PtF₆

The method used was essentially that of Dixon, Sharp and Sharpe ⁴². The anhydrous metal hexachloroplatinate (IV) was reacted under vigorous conditions with bromine trifluoride and the product purified by dissolving in water and precipitating with acetone. The infrared ^{42,49}, Raman ⁴⁹ and electronic spectra ⁴⁷ were in good agreement with published results.



An aqueous solution of sodium hexafluoroplatinate (IV) was passed down a column containing Amberlite IR-120(H) cation exchange resin and the hexafluoroplatinic acid was then reacted with a slight excess of either tetraethylammonium hydroxide (25% aqueous solution) or di-n-propylamine. Water was removed under vacuum at 25-30°C on a rotary evaporator and the solid obtained was washed several times with acetone, to remove excess Et_4NOH or $(\text{Pr}^n)_2\text{NH}$. The product was recrystallised from dry methanol. Analyses were good.



The method used was that of Dixon, Sharp and Sharpe⁴². Potassium hexachloroplatinate (IV) was reacted under mild conditions with bromine trifluoride, using 1,1,2-trichlorotrifluoroethane as moderator. The product was purified by dissolving in water and precipitating with acetone. The infrared^{28,42} and electronic²⁸ spectra were in good agreement with published results. The Raman spectrum of the solid showed peaks at: 372 ± 5 (m,broad), 273(m) and 217(m) cm^{-1} . Aqueous solutions gave weak Raman spectra that initially showed only one peak at $375(\text{w})\text{cm}^{-1}$, but after several minutes a yellow precipitate had been formed and intense peaks due to the hexachloroplatinate (IV) ion⁴⁹ were observed at 345(vs), 320(s), 160(s) cm^{-1} .

$K_2PtCl_{1/2}'^2F_4$

The preparation was as for $K_2PtCl_{1/3}^{-3}F_3$, except potassium tetrachloroplatinite (II) was the starting material. The product was a mixture of $K_2PtCl_{1/3}^{-3}F_3$, $K_2PtCl_{1/2}'^2F_4$ and K_2PtClF_5 , (identified by the ^{19}F n.m.r. spectra of aqueous solutions of the product). Pure $K_2PtCl_{1/2}'^2F_4$ was not isolated.

 $K_2PtCl_4(OH)_{1/2}'^6$ and $Na_2PtCl_4(OH)_{1/2}'^6$

$K_2PtCl_4(OH)_{1/2}'^6$ was prepared by the method of Cox and Peters¹⁶, from the reaction of hydrogen peroxide with potassium tetrachloroplatinite (II). The sodium salt was prepared from the potassium salt by cation exchange, using a column containing Zeo-Karb 225 resin (Na^+ form). Infrared and electronic spectra of both salts were in good agreement with the published results for the potassium salt¹⁶.

 $Na_2Pt(OH)_{1/2}'^6F_4$ and $K_2Pt(OH)_{1/2}'^6F_4$

Reaction of sodium or potassium trans-dihydroxy-tetrachloroplatinate (IV) with bromine trifluoride under mild conditions gave a product that contained mainly $[PtF_6]^{2-}$, but also large amounts of $[Pt(OH)F_5]^{2-}$ and $[Pt(OH)_{1/2}'^6F_4]^{2-}$. The infrared of the product showed bands at 3500 and 1630 cm^{-1} due to the hydroxyl groups.

Na₂PtClF₅

Reaction of bromine trifluoride with sodium hexachloroplatinate (IV) hexahydrate, using bromine as a moderator, gave a product that retained some chlorine. (The product, after digesting with sodium hydroxide, filtering and making the filtrate acidic with nitric acid, gave a precipitate of silver chloride with silver nitrate solution). The product also contained $[\text{PtF}_6]^{2-}$ and $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$.

PLATINUM TETRAFLUORIDE

PtF₄ was prepared by Sharp's method³¹. In a typical preparation 2g of platinum tetrabromide were reacted with about 4cm³ of bromine trifluoride. The resulting red solution was transferred to a vacuum line and the excess bromine trifluoride was removed, initially at room temperature for 3h and then at 180°C for a further 2h. The last traces of bromine were removed by reacting the red-brown product with fluorine for 6h at 200°C. A pale brown solid (PtF₄) was obtained. Attempts to repeat the preparations of complexes by Kolditz⁴³ were, on the whole, unsuccessful and no ¹⁹F n.m.r. data were obtained.

Et₄NX and (Prⁿ)₂NH₂X, (X = F, Cl, Br, I)

An aqueous solution of HX was reacted with a slight excess of tetraethylammonium hydroxide or di-n-propylamine. Water was removed on a rotary evaporator. The resulting solid was washed free from base with acetone

and was then recrystallised several times from dry methanol. Analyses were good.

Et₄NSO₃CF₃

A slight excess of tetraethylammonium hydroxide was added to freshly distilled trifluoromethylsulphonic acid. Water was removed on a rotary evaporator, the solid washed with acetone and recrystallised from methanol.

(Found: C, 38.88; H, 7.07; N, 5.04. C₉H₂₀F₃NO₃S requires: C, 38.70; H, 7.22; N, 5.02%). The ¹⁹F n.m.r. spectrum of an aqueous solution of the salt showed a single sharp resonance. (δ = 0.15 p.p.m. relative to external TFA).

VIBRATION SPECTRA

INFRARED spectra were measured down to 250 cm⁻¹ on a Perkin Elmer Model 457 instrument, using nujol mulls between sodium chloride (4,000 → 600 cm⁻¹) or polythene (600 → 250 cm⁻¹) plates. Spectra were calibrated using a polystyrene film.

RAMAN spectra were measured on a CARY 81 spectrophotometer with a CRL 52 Kr Laser, using excitation at 5682 Å.

U.V.-VISIBLE SPECTRA were recorded on either a Perkin Elmer Model 402 or CARY Model 14 spectrophotometer.

MEASUREMENT OF ^{19}F n.m.r. SPECTRA

Spectra were measured at $35 \pm 1^\circ\text{C}$ using a Perkin Elmer R14 permanent magnet spectrometer, operating at 94.09 M.Hz.

Standard Perkin Elmer or Wilmad precision glass n.m.r. tubes (5mm outside diameter) were used for neutral or alkaline solutions. Acidic solutions were run in either non-spinning tubes made from polythene tubing of outside diameter ca. 5mm, heat sealed at one end, or in standard glass tubes with a length of tight fitting PTFE tubing inserted and sealed at the base with paraffin wax. The latter type of tubes had the advantage that they would spin and therefore greater resolution was obtainable.

External TFA, internal $\text{Et}_4\text{NSO}_3\text{CF}_3$ or internal M_2PtF_6 ($\text{M} = \text{Na}$, Et_4N or $(\text{Pr}^{\text{n}})_2\text{NH}_2$) were used as reference compounds for ^{19}F chemical shift measurements. Although trichlorofluoromethane is commonly used as an internal reference compound in non-aqueous solutions, no one compound is generally used for aqueous solutions. (TFA is often used as an external reference). Salts of trifluoromethylsulphonic acid should fill this gap and the tetraethylammonium salt should prove to be particularly useful since it is extremely soluble in water (and many polar solvents), has a fairly high molecular weight (279) and therefore can easily be used for quantitative measurements.

Areas of peaks were measured under conditions of no saturation, either from integration or by weighing the paper enclosed by each peak. Normally several photocopies of the spectra were made and the peaks cut out and weighed. The standard deviation in weights, and therefore areas, obtained by this method was small (ca. 5%) for all except the least intense peaks.

PREPARATION OF SOLUTIONS

Neutral or alkaline solutions were made up and stored in glassware and acidic solutions in polythene. Any insoluble material was removed by centrifuging.

Non-aqueous solutions of the Et_4N^+ and $(\text{Pr}^n)_2\text{NH}_2^+$ salts of $[\text{PtCl}_2, ^2\text{F}_4]^{2-}$ and $[\text{PrCl}_3, ^3\text{F}_3]^{2-}$ were made by shaking a solution of either $(\text{Et}_4\text{N})_2\text{PtF}_6$ or $((\text{Pr}^n)_2\text{NH}_2)_2\text{PtF}_6$ in the non-aqueous solvent with an excess of the corresponding potassium chloro-fluoro-platinate. The insoluble potassium hexafluoroplatinate (IV) formed was removed by centrifuging. Pure samples of the alkylammonium salts could not be isolated.

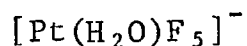
pH MEASUREMENTS

The pH values of solutions were measured using a Vibron 39A pH meter with Jena glass electrode. The electrode was not allowed to remain in contact with acidic solutions containing fluoride ions for more than a few

seconds. In strongly acidic solutions ($\text{pH} < 1$) the pH readings were unsteady and the pH was therefore calculated from the change of chemical shift on protonation of F^{2-5} of $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ or $[\text{PtCl}^1(\text{OH})^6\text{F}_4]^{2-}$, using equation V in Appendix I. It has been reported that glass electrodes can be used reliably and without damage in acidic solutions containing fluoride ions ^{89,90}.

MEASUREMENT OF pKa

1.



An aqueous solution of the sodium salt of the acid was brought to $\text{pH } 10 \pm 1$ using dilute sodium hydroxide solution. The chemical shift, δF^{2-5} , of $[\text{Pt}(\text{OH})\text{F}_5]^{2-}$ was measured relative to internal $[\text{PtF}_6]^{2-}$. The pH was adjusted to approximately 7 by adding dilute perchloric acid. δF^{2-5} was again measured. 2 μL aliquots of concentrated perchloric acid (9.34 M) were added to the solution and the pH and δF^{2-5} were measured after each addition. When $\text{pH} \approx 1$, 5 μL aliquots of perchloric acid were added, and only the chemical shift was measured. The limit of δF^{2-5} in strongly acidic solution (δF^{2-5} of $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$) was found by extrapolating the plot of chemical shift against volume of acid added. From the data obtained the dissociation constant of $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$ was calculated (See Appendix I).

2.

OTHER ACIDS

The method used was as outlined above for $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$. In strongly acidic solutions ($\text{pH} < 1$) the hydrogen ion concentration was calculated from the change in SF^{2-5} of $[\text{Pt}(\text{OH})\text{F}_5]^-$ on protonation, using equation V, Appendix I. For dibasic acids, the mathematical treatment of data is outlined in Appendix II.

IRRADIATION EXPERIMENTS

Neutral and alkaline solutions of $(\text{Et}_4\text{N})_2\text{PtF}_6$ contained in a 1 mm quartz U.V. cell were irradiated with light from a Phillips mercury lamp TYP 93110E E27. Reference samples of the solutions were stored in the dark. The U.V. and ^{19}F n.m.r. spectra of the solutions and reference solutions were checked before and after irradiation. The following filters were used: ⁹¹

1.

An aqueous solution containing 100g/L of both $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in a 250 cm³ quartz flask (diameter ca. 5 cm) was used to isolate U.V. light of wavelength less than 3500 Å. The flask also acted as a lens for focussing light on the sample.

2.

An aqueous solution of potassium hydrogen phthallate (5g/L) contained in 1 cm quartz U.V. cell was used to

absorb light of wavelength less than 3130 \AA . A 250 cm^3 quartz flask filled with water was placed between the lamp and the filters to focus the light and absorb heat.

APPENDIX I

Calculation of the dissociation constants of the monobasic acids $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$ and $[\text{PtCl}^1(\text{H}_2\text{O})^6\text{F}_4]^-$.

If A is the protonated form, and B^- the unprotonated form of the acid, then



and the dissociation constant, $K = \frac{[\text{B}^-][\text{H}^+]}{[\text{A}]}$ (I)

Since A and B^- are in rapid equilibrium, the observed ^{19}F chemical shift will depend on both the mole fractions of the two species and their respective chemical shifts, according to the equation:

$$\text{SOB} = \frac{[\text{A}]}{[\text{A}] + [\text{B}^-]} \text{SA} + \frac{[\text{B}^-]}{[\text{A}] + [\text{B}^-]} \text{SB} \dots \text{(II)}$$

where SOB is the observed chemical shift,

SA and SB are the chemical shifts of A and B respectively.

From equation (I), $[\text{A}] = \frac{[\text{B}^-][\text{H}^+]}{K}$ (III)

Substitute (III) into (II),

$$\frac{[\text{B}^-][\text{H}^+]}{K} \text{SOB} + [\text{B}^-] \text{SOB} = \frac{[\text{B}^-][\text{H}^+]}{K} \text{SA} + [\text{B}^-] \text{SB}$$

$$\text{SOB} \frac{[\text{B}^-]}{K} ([\text{H}^+] + K) = \frac{[\text{B}^-]}{K} ([\text{H}^+] \text{SA} + K \text{SB})$$

$$\text{SOB} = \frac{[\text{H}^+] \text{SA} + \text{K SB}}{[\text{H}^+] + \text{K}} \dots\dots\dots (\text{IV})$$

$$\text{SOB} [\text{H}^+] + \text{K SOB} = [\text{H}^+] \text{SA} + \text{K SB}$$

$$\text{K} = \frac{[\text{H}^+] (\text{SOB} - \text{SA})}{(\text{SB} - \text{SOB})} \dots\dots\dots (\text{V})$$

An approximate value of K was found from the point of half neutralisation of the acid, i.e. when $[\text{A}] = [\text{B}^-]$. Equation (II) then becomes: $\text{SOB} = 1/2 (\text{SA} + \text{SB})$ and equation (I) gives $\text{K} = [\text{H}^+]$ or $\text{pK} = \text{pH}$. The pH at which $\text{SOB} = 1/2(\text{SA} + \text{SB})$ therefore gives a value of pK, and therefore K.

The value of SA was found as the limit of SOB when a large excess of HClO_4 had been added to the solution. Since this addition greatly changes the ionic strength, and therefore the properties of the solvent, the value of SA may be somewhat unreliable. The value of K obtained above is therefore also unreliable.

Several values of SA and of K varying around the approximate values obtained above were used together with values of $[\text{H}^+]$ (from pH) to calculate values of chemical shift, using the equation:

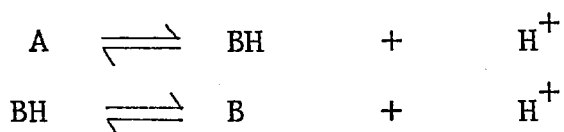
$$\text{SCALC} = \frac{[\text{H}^+] \text{SA} + \text{K SB}}{[\text{H}^+] + \text{K}} \dots\dots\dots (\text{VI})$$

Using a computer program (Appendix III), the values of SCALC were found and compared with the

corresponding values of δ_{OB} . From a least squares calculation the values of δ_A and K giving the best fit between calculated and observed chemical shifts were obtained.

APPENDIX IICalculation of the dissociation constants of the dibasic acids $\text{Pt}(\text{H}_2\text{O})\frac{1}{2}'^2\text{F}_4$ and $\text{Pt}(\text{H}_2\text{O})\frac{1}{2}'^6\text{F}_4$.

If A is the doubly protonated, BH the singly protonated and B the completely deprotonated forms of the acids, then:



and the dissociation constants:

$$K_1 = \frac{[\text{BH}][\text{H}^+]}{[\text{A}]} \dots\dots\dots \text{(I)}$$

$$K_2 = \frac{[\text{B}][\text{H}^+]}{[\text{BH}]} \dots\dots\dots \text{(II)}$$

The observed chemical shift depends on the mole fractions of the species present, and their respective chemical shifts, according to the equation:

$$\text{SOB} = \frac{[\text{A}] \text{SA}}{[\text{A}] + [\text{BH}] + [\text{B}]} + \frac{[\text{BH}] \text{SBH}}{[\text{A}] + [\text{BH}] + [\text{B}]} + \frac{[\text{B}] \text{SB}}{[\text{A}] + [\text{BH}] + [\text{B}]} \dots \text{(III)}$$

where SA, SBH and SB are the chemical shifts of A, BH and B respectively.

$$\text{From equation (I), } [\text{BH}] = \frac{[\text{A}]K_1}{[\text{H}^+]}$$

$$\text{From equation (II), } [\text{B}] = \frac{[\text{BH}] K_2}{[\text{H}^+]} = \frac{[\text{A}] K_1 K_2}{[\text{H}^+]^2}$$

Substituting these values into equation (III) gives:

$$\text{SOB} = \frac{[A]}{[A] + [\text{BH}] + [B]} \left\{ \text{SA} + \frac{K_1 \text{SBH}}{[\text{H}^+]} + \frac{K_1 K_2 \text{SB}}{[\text{H}^+]^2} \right\}$$

$$\text{SOB} = \frac{[A]}{[A] + \frac{[A] K_1}{[\text{H}^+]} + \frac{[A] K_1 K_2}{[\text{H}^+]^2}} \left\{ \frac{\text{SA} [\text{H}^+]^2 + K_1 \text{SBH} [\text{H}^+] + K_1 K_2 \text{SB}}{[\text{H}^+]^2} \right\}$$

$$\text{SOB} = \frac{\text{SA} [\text{H}^+]^2 + K_1 \text{SBH} [\text{H}^+] + K_1 K_2 \text{SB}}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2} \dots\dots\dots (\text{IV})$$

Approximate values of K_1 and K_2 were calculated as shown below:

Using the additivity relationship of substituent effects on chemical shifts, $\text{SBH} = 1/2 (\text{SA} + \text{SB})$ from (I), when $[A] = [\text{BH}]$, $K_1 = [\text{H}^+]$ and $\text{p}K_1 = \text{pH}$.

From equation (III),

$$\text{SOB} = \frac{1}{2[A] + [B]} \left\{ [A] \text{SA} + [A] \frac{(\text{SA} + \text{SB})}{2} + [B] \text{SB} \right\}$$

But, assuming $K_1 \ll K_2$, then $[B] \simeq 0$.

$$\text{SOB} = \frac{1}{2[A]} \left\{ [A] \text{SA} + [A] \frac{(\text{SA} + \text{SB})}{2} \right\}$$

$$\text{SOB} = \frac{3\text{SA} + \text{SB}}{4}$$

when $\text{SOB} = \frac{3\text{SA} + \text{SB}}{4}$, then $\text{pH} = \text{p}K_1$.

Similarly for K_2

When $[\text{BH}] = [B]$, $K_2 = [\text{H}^+]$ and $\text{SOB} = \frac{3\text{SB} + \text{SA}}{4}$

The value of SA was found as the limit of SOB when

a large excess of HClO_4 had been added to the solution. Since this value is only approximate, then the values of K_1 and K_2 obtained above will be approximate. Also, the additivity relationship of substituent effects on chemical shifts is not exact and so the value of δ_{BH} used is unreliable.

Several values of δ_{A} , δ_{BH} , K_1 and K_2 , varying around the approximate values obtained above, were used together with values of $[\text{H}^+]$ to calculate values of chemical shift using the accurate equation:

$$\text{SCALC} = \frac{\delta_{\text{A}}[\text{H}^+]^2 + K_1 \delta_{\text{BH}} [\text{H}^+] + K_1 K_2 \delta_{\text{B}}}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2} \dots (\text{V})$$

Using a computer program (Appendix IV) the values of SCALC were found and compared with the corresponding values of δ_{OB} . From a least squares calculation the values of δ_{A} , δ_{BH} , K_1 and K_2 giving the best fit between calculated and observed chemical shifts were obtained.

APPENDIX III

Computer program for finding best fit between observed and calculated shifts for the monobasic acid $[\text{Pt}(\text{H}_2\text{O})\text{F}_5]^-$.

```

COMMON H(15), DOB (15)
DO 6 J = 1,15
  6 READ (5,1000) H(J), DOB(J)
1000 FORMAT.....
DO 30 L = 1, 20
DO 30 M = 1, 20
  BL = L
  BM = M
  DB = 753.0
  DA = 179.0 + 1.0*BM
  DISSK = 0.090 + 0.001*BL
  SUMSQ = 0.0
DO 40 N = 1,15
  DCAL = (H(N)*DA + DISSK*DB)/(DISSK + H(N))
  DEVSQ = (DCAL - DOB(N))**2
  40 SUMSQ = SUMSQ + DEVSQ
  RMSD = SQRT (SUMSQ/15.0)
  30 WRITE (6,1001) DA, DB, DISSK, RMSD
1001 FORMAT.....
STOP

```

where

H	=	$[\text{H}^+]$ (Hydrogen ion concentration)
DA	=	δA
DB	=	δB
DISSK	=	K (dissociation constant)
DCAL	=	δCAL
RMSD	=	Root Mean Square Deviation

APPENDIX IV

Computer program for finding the best fit between observed and calculated shifts for the dibasic acid $\text{Pt}(\text{H}_2\text{O})_{\frac{1}{2}}\cdot 6\text{F}_4$.

```

COMMON H(20), DOB (20)
DO 6 J = 1,20
  6 READ (5,1000) H (J), DOB(J)
1000 FORMAT.....
DO 30 K = 1,4
DO 30 L = 1,5
DO 30 M = 1,4
DO 30 MM = 1,8
BK = K
BL = L
BM = M
BMM = MM
DB = 1346.0
DISK 1 = 0.23 + 0.01*BK
DISK 2 = 0.00003 + 0.0000005*BL
DA = 420.0 + 5.0*BM
DBH = 740.0 + 10.0*BMM
SUMSQ = 0.0
DO 40 N = 1,20
DCAL = (DA*H(N)**2+DBH*DISK1*H(N)+DISK1*DISK2*
DB)/(H(N)**2+DISK1*H(N)+DISK1*DISK2)
DEVSQ = (DCAL - DOB(N))**2
40 SUMSQ = SUMSQ + DEVSQ
RMSD = SQRT (SUMSQ/20.0)
30 WRITE (6,1001) DA, DISK1, DISK2, DBH, RMSD
1001 FORMAT.....
STOP

```

Computer program for calculating SCAL of $\text{Pt}(\text{H}_2\text{O})_2^{1,6}\text{F}_4$
(a dibasic acid)

```
COMMON H(20), DOB(20)
DO 6 J = 1,20
6 READ (5,1000) H (J), DOB(J)
1000 FORMAT.....
DB = 1364.0
DBH = 800.0
DA = 440.0
DISK1 = 0.24
DISK2 = 0.0000305
DO 40 N = 1,20
DCAL = (DA*H(N)**2+DBH*DISK1*H(N)+DISK1*DISK2*
DB)/(H(N)**2+DISK1*H(N)+DISK1*DISK2)
DIFF = DCAL - DOB(N)
WRITE (6,1002) DCAL, DOB(N), DIFF, H(N)
1002 FORMAT.....
40 CONTINUE
STOP
```

REFERENCES

1. J.W. Emsley and L. Phillips, "Progress in NMR Spectroscopy" Volume 7, Ed. J.W. Emsley, J. Feeney and L.H. Sutcliffe, Pergamon Press, 1971.
2. J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High Resolution NMR Spectroscopy" Volumes 1 and 2, Pergamon Press, 1965.
3. H.S. Gutowski and C.J. Hoffman, J. Chem. Phys., 1951, 19, 1259.
4. "Tables of Isotopes" Sixth Edition, John Wiley.
5. A. Saika and C.P. Slichter, J. Chem. Phys., 1954, 22, 26.
6. C.D. Cornwell, J. Chem. Phys., 1966, 44, 874.
7. J.R. Holmes, B.B. Stewart and J.S. MacKenzie, J. Chem. Phys., 1962, 37, 2728.
8. J.W. Emsley and L. Phillips, Mol. Phys., 1966, 11, 437.
9. D.F. Evans, Proc. Chem. Soc., 1958, 115.
10. P. Lazlo, "Progress in NMR Spectroscopy" Volume 3, P.231 Ed. J.W. Emsley, J. Feeney and L.H. Sutcliffe, Pergamon Press, 1967.
11. M. Barfield and N.D. Johnston Jr., Chem. Rev., 1973, 73, 53.
12. W.T. Raynes and T.A. Sutherley, Mol. Phys., 1969, 17, 547.
ibid. 1970, 18, 129.
13. R.H. Cox and S.L. Smith, J. Magn. Resonance, 1970, 1, 432.
14. C.L. Bell and S.S. Danyluk, J. Mol. Spectroscopy, 1970, 35, 376.

15. A.J. Pož, J.Chem. Soc., 1960, 3431.
16. L.E. Cox and D.G. Peters, Inorg. Chem., 1970, 9, 1927.
17. C.M. Davidson and R.F. Jameson, Trans. Faraday Soc., 1965, 61, 2462.
18. B. Corain and A.J. Pož, J. Chem. Soc.(A), 1967, 1633.
19. W.R. Mason, Coordination Chem. Rev., 1971, 7, 241.
20. F.R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science, 1973.
21. F. Basolo, A.F. Messing, P.H. Wilks, R.G. Wilkins and R.G. Pearson, J. Inorg. Nuclear Chem., 1958, 8, 203.
22. B.I. Peshchevitskii and G.D. Mal'chikov, Chem. Abs., 1968, 68, 110926.
23. F. Basolo and R.G. Pearson, Prog. Inorg. Chem., 1962, 4, 381.
24. J.M. Pratt and R.G. Thorp, Adv. Inorg. Chem. Radiochem., 1969, 12, 375.
25. A. Pidcock, R.E. Richards and L.M. Venanzi, J. Chem. Soc.(A), 1966, 1707.
26. L.M. Venanzi, Chem. Brit., 1968, 162.
27. T.G. Appleton, H.C. Clark and L.E. Manzer, Coordination Chem. Rev., 1973, 10, 335.
28. D.H. Brown, K.R. Dixon and D.W.A. Sharp, J. Chem. Soc.(A), 1966, 1244.
29. A.G. Sharpe, Adv. Fluorine Chem., 1960, 1, 29.
30. N. Bartlett, "Preparative Inorganic Reactions" Volume 2, Ch. 8, Ed. W.L. Jolly, Interscience, 1965.
31. A.G. Sharpe, J. Chem. Soc., 1953, 197.
ibid. 1950, 3444.

32. N. Bartlett and D.H. Lohmann, J. Chem. Soc., 1962, 5253.
33. K.R. Dixon and J.J. McFarland, Chem. Comm., 1972, 1274.
34. J. McAvoy, K.C. Moss and D.W.A. Sharp, J. Chem. Soc., 1965, 1376.
35. H. Moissan, "Le Fluor et ses Composés" Steinheil, Paris, 1900.
36. N. Bartlett and D.H. Lohmann, J. Chem. Soc., 1964, 619.
37. H.I. Schlesinger and M.W. Tapley, J. Amer. Chem. Soc., 1924, 46, 276.
38. T.P. Perros and C.R. Naeser, J. Amer. Chem. Soc., 1953, 75, 2516.
39. R.S. Clark Jnr. and T.P. Perros, J. Amer. Chem. Soc., 1953, 75, 5734.
40. T.E. Wheeler, T.P. Perros and C.R. Naeser, J. Amer. Chem. Soc., 1955, 77, 3488.
41. M.K. Norr, T.P. Perros and C.R. Naeser, J. Amer. Chem. Soc., 1958, 80, 5035.
42. K.R. Dixon, D.W.A. Sharp and A.G. Sharpe, Inorg. Synth., 1970, 12, 232.
43. L. Kolditz and J. Gisbier, Z. Anorg. Allgem. Chem., 1969, 366, 265.
44. R.D.W. Kemmitt and D.W.A. Sharp, J. Chem. Soc., 1963, 2567.
45. N.A. Matwiyoff, L.B. Asprey, W.E. Wageman, M.J. Reisfield and E. Fukushima, Inorg. Chem., 1969, 8, 750.
46. R.D.W. Kemmitt, R.D. Peacock and J. Stocks, Chem. Comm., 1969, 554.
47. L.B. Asprey and N.A. Matwiyoff, J. Inorg. Nuclear Chem., 1970, 32, 1048.

48. R.D.W. Kemmitt, R.D. Peacock and J. Stocks,
J. Chem. Soc. (A), 1971, 846.
49. L.A. Woodward and M.J. Ware, Spectrochim. Acta.,
1963, 19, 775.
50. K.O. Christie, J.F. Hon and D. Pilipovich, Inorg. Chem.,
1973, 12, 84.
51. C.L. Bell and S.S. Danyluk, J. Amer. Chem. Soc.,
1966, 88, 2344.
52. J.A. Pople and D.P. Santry, Mol. Phys., 1964, 8, 1.
53. P.A.W. Dean and D.F. Evans, J. Chem. Soc. (A), 1968, 1154.
54. W. McFarlane and R.J. Wood, Chem. Comm., 1969, 262.
55. M.L. Afanas'ev and K.A. Grigorova, Spectroscopy Lett.,
1969, 2, 107.
56. S.V. Zemskov, K.A. Grigorova, I.M. Cheremisina and
E.V. Sobolov, Chem. Abs., 1970, 73, 41323.
57. K.A. Grigorova, A.A. Opalovsky and S.U. Zemskov,
Sixth Int. Symposium Fluorine Chem., Chem. Soc., 1970, C35.
58. E. Pitcher, A.D. Buckingham and F.G.A. Stone,
J. Chem. Phys., 1962, 36, 124.
59. S.S. Dharmatti and C.R. Kaneker, J. Chem. Phys.,
1959, 31, 1436.
60. R. Freeman, G.R. Murray and R.E. Richards,
Proc. Roy. Soc., 1957, A, 242, 455.
61. J.S. Griffiths and L.E. Orgel, Trans. Faraday Soc.,
1957, 53, 601.
62. W.C. Fernelius, Adv. Chem. Series, No. 8, Amer. Chem. Soc.,
1951.

63. H.B. Gray and C. Langford, "Ligand Substitution Processes" Benjamin, New York, 1966.
64. R. Mason and A.D.C. Towl, J. Chem. Soc. (A), 1970, 1601.
65. E.H. Archibald and W.A. Gale, J. Chem. Soc., 1922, 121, 2849.
66. V. Balzani, F. Manfin and L. Moggi, Inorg. Chem., 1967, 6, 354.
67. "Tables of Interatomic Distances and Configurations of Molecules and Ions", Chem. Soc., Special Publ. No.11, 1958.
68. "Stability Constants of Metal-Ion Complexes", Chem. Soc., Special Publ. No. 17, London, 1964.
69. R.C. Johnson, F. Basolo and R.G. Pearson, J. Inorg. Nuclear Chem., 1962, 24, 59.
70. A.A. Grinberg and K.I. Gil'dengershel, Chem. Abs., 43, 1673E.
71. A.A. Grinberg, L.V. Urublevskaya, K.I. Gil'dengershel and A.I. Stetsenko, Russ. J. Inorg. Chem., 1959, 4, 462.
72. J.N. Shoolery, J. Chem. Phys., 1959, 31, 1427.
73. E.R. Malinowski, J. Amer. Chem. Soc., 1961, 83, 4479.
74. A.W. Douglas, J. Chem. Phys., 1964, 40, 2413.
75. E.R. Malinowski, T. Vladimiroff and R.F. Tavares, J. Chem. Phys., 1966, 70, 2046.
76. E.R. Malinowski and T. Vladimiroff, J. Amer. Chem. Soc., 1964, 86, 3515.
77. H.S. Gutowski and C. Juan, Disc. Faraday Soc., 1962, 34, 52.
78. T. Vladimiroff and E.R. Malinowski, J. Chem. Phys., 1967, 46, 1830.
79. P.A.W. Dean, Ph.D. Thesis, London University, 1967.

80. W.L. Jolly, A.D. Harris and T.S. Briggs, Inorg. Chem., 1965, 4, 1064.
81. E.R. Malinowski, J. Phys. Chem., 1972, 76, 1593.
82. E.R. Malinowski, J. Amer. Chem. Soc., 1969, 91, 4701.
83. G.B. Savitsky and K. Namikawa, J. Phys. Chem., 1964, 68, 1956.
84. S.O. Grim, W. McFarlane, E.F. Davidoff and T.J. Marks, J. Phys. Chem., 1966, 70, 581.
85. S.O. Grim and W. McFarlane, Nature, 1965, 208, 995.
86. T.S. Smith and E.A. Smith, J. Phys. Chem., 1959, 63, 1701.
87. G.B. Kauffman and L.A. Teter, Inorg. Synth., 1963, 7, 232.
88. G.B. Kauffman and D.O. Cowan, Inorg. Synth., 1963, 7, 240.
89. A.K. Covington and J.M. Thain, J. Chem. Ed., 1972, 49, 555.
90. N.E. Vanderborgh, Talanta, 1968, 15, 1009.
91. J.G. Calvert and J.N. Pitts, "Photochemistry" Ch. 7, John Wiley and Sons, 1966.

PART II

RAMAN SPECTROSCOPIC STUDIES OF
LIQUID AMMONIA SOLUTIONS
OF METAL SALTS

INTRODUCTION

The vibration spectra of many metal ammine complexes are now well understood, although general agreement about assignments has only been reached recently ¹. The internal stretching and deformation modes of the complexed ammonia molecules have caused no difficulty in assignment, but the location of the metal-nitrogen stretching vibration, which is often weak and therefore easily missed, has been more of a problem. Because of the relatively heavy mass of the metal and the low bond order of the coordinate bond, the M-N stretching vibration occurs in the lower frequency region. ν (M-N) for most amines lies between 400 and 500 cm^{-1} , whilst δ (N-M-N) is between 240 and 330 cm^{-1} . The important exceptions to this correlation are the hexa-ammines of divalent metals, for which ν (M-N) is near 300 cm^{-1} and δ (N-M-N) near 200 cm^{-1} ¹.

The M-N stretching frequency in metal amines is of particular interest since it provides direct information about the coordinate bond. Powell and Sheppard ² reported a linear relationship between the Raman active M-N stretching, or NH_3 rocking frequency, and the stability constant in a series of ammine complexes of various metals.

The vibration spectra of many metal ammine complexes have been determined in the solid state, but

relatively few studies have been carried out on complexes in solution. Several metals form ammine complexes that are unstable even in the solid state and therefore they have not been well characterised by infrared and Raman spectroscopy. There have been few vibration spectra studies on linear diammines, linear complexes of the type X-M-NH₃ and substituted tetrahedral ammine complexes.

The coordination of species present in solution may be determined from the frequency and number of Raman active metal-ligand vibrations. Linear diammines give rise to three normal modes of vibration, of which ν_1 , the symmetric stretching vibration, is Raman active. Tetrahedral tetra-ammines give rise to four normal modes of vibration, all of which are Raman active. Octahedral hexa-ammines give rise to six normal modes of vibration, of which only three are Raman active.

Anhydrous liquid ammonia was chosen as solvent for this study for several reasons:

1. It favours the formation of metal-ammine complexes because of the high concentration of ammonia (ca. 35M at 20°C³).
2. It has a sufficiently high dielectric constant to make it a fairly good ionising solvent, ($\epsilon = 22$ at -34°C⁴).
3. Its Raman spectrum is transparent in the metal-ligand vibration frequency region⁵.

The choice of metal salts was limited by solubility considerations. The salts of Ag^+ , Hg^{2+} and Cd^{2+} were chosen because they were soluble and were expected to give linear, tetrahedral and octahedral complexes respectively.

RESULTS AND DISCUSSIONA. SILVER SALTS

The Raman active Ag-L and important ligand and anion vibration frequencies ($\Delta\nu$ in cm^{-1}) for solutions of silver salts in liquid ammonia are presented below:

ANION	ClO_4^-	I^-	CN^-	SCN^-	NO_3^-
Ag-L VIBRATIONS	380 w	376 w	239 s dP	-	-
LIGAND OR ANION VIBRATIONS	460 s	-	2124 s P 2141 s P	740 w	710 w 1046 w
APPROXIMATE MOLARITY OF SOLUTION	1.0	0.6	0.4	0.6	1.0

Solid $[\text{Ag}(\text{NH}_3)_2]\text{ClO}_4$ showed a weak Raman peak at $\Delta\nu = 380 \text{ cm}^{-1}$ and a medium intensity, broad infrared band at $442 \pm 2 \text{ cm}^{-1}$.

Literature values of Ag-N vibration frequencies (in cm^{-1}) in complexes of the type $[\text{Ag}(\text{NH}_3)_2]\text{X}$ are presented below:

ANION	NO ₃ ⁻			ClO ₄ ⁻		SO ₄ ²⁻
PHASE	MULL	MULL	AQUEOUS SOLUTION	MULL	AQUEOUS SOLUTION	MULL
ν_1 ($\nu(\text{Ag-N}_2)$ sym R)	386		369		372 (P?)	400
ν_2 ($\nu(\text{Ag-N}_2)$ asym IR)	471	430 vb		430 vb		476
ν_3 ($\delta(\text{N-Ag-N})$ sym IR)	176 208					211 221
REFERENCE	6	7				6

All three normal vibration modes of the $[\text{H}_3\text{N-Ag-NH}_3]^+$ species have been located in the solid state. The Raman active symmetric stretch, ν_1 , occurs between 369 and 400 cm^{-1} and varies considerably with the anion. In liquid ammonia solution AgClO_4 and AgI give rise to weak peaks at 380 and 376 cm^{-1} respectively and these can be attributed to ν_1 of the linear $[\text{H}_3\text{N-Ag-NH}_3]^+$ ion. The value of 442 cm^{-1} for ν_3 of solid $[\text{Ag}(\text{NH}_3)_2]\text{ClO}_4$ is in reasonable agreement with the published value ⁷.

AgCN

No values for the frequency of the symmetric Ag-CN stretch of silver cyanide have been reported. Aqueous solutions containing the $[\text{Ag}(\text{CN})_2]^-$ ion give a Raman peak ($\delta(\text{Ag-CN})$) at 239 ⁸ or 250 cm^{-1} ⁹. The symmetric NC-Ag-CN stretch of this species is very weak and broad, but a value of 360 cm^{-1} was calculated from infrared active combinations¹⁰.

The observed low frequency peak in the Raman spectrum of AgCN in liquid ammonia, at $\Delta\nu = 239 \text{ cm}^{-1}$, can therefore be assigned to an Ag-CN bend.

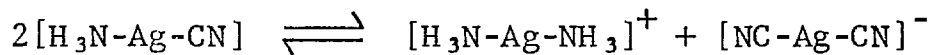
Compounds of the type X-Ag-CN can only give rise to one Raman active C-N stretching vibration and so the two polarised peaks observed in the spectrum of AgCN in liquid ammonia are probably due to two separate species. The observed C-N frequencies for silver cyanide complexes and for the free cyanide ion are given below:¹¹

SPECIES	PHASE	(cm^{-1})
AgCN	SOLID	2164
$[\text{Ag}(\text{CN})_2]^-$	AQUEOUS SOLUTION	2135
$[\text{Ag}(\text{CN})_3]^{2-}$	" "	2105
$[\text{Ag}(\text{CN})_4]^{3-}$	" "	2092
$(\text{CN})^-$	" "	2080

$\nu(\text{C-N})$ of metal cyano complexes depends on :

1. The electronegativity of the metal,
2. The oxidation number of the metal,
3. The coordination number of the metal.

For the silver cyano complexes only the coordination number changes and as it increases the C-N stretching frequency decreases. In liquid ammonia solution the peak at 2141 cm^{-1} is therefore due to a more strongly coordinated CN group than the peak at 2124 cm^{-1} and is probably due to the $\text{H}_3\text{N-Ag-CN}$ species. The low frequency peak is probably due to the $[\text{NC-Ag-CN}]^-$ anion, formed from the following equilibrium:



No peaks due to Ag-NH₃ vibrations were observed.

B. MERCURIC SALTS

Raman active Hg-L and important ligand and anion vibration frequencies ($\Delta\nu$ in cm^{-1}) for solutions of mercuric salts in liquid ammonia are presented below:

ANION	NO_3^-	SCN^-	I^-	CN^-
Hg-L VIBRATIONS	301 w 411 ms P	290 w 409 m P	131 vs P 353 s P	257 w dP 335±5 sh P? 368 m P
LIGAND OR ANION VIBRATIONS	710 w 1045 vs	740 m		2165 s P
APPROXIMATE MOLARITY OF SOLUTIONS	0.5	0.5	0.7	0.7

Barrow et al ¹² observed a band at 408 cm^{-1} in the infrared spectrum of solid $[\text{Hg}(\text{NH}_3)_4](\text{ClO}_4)_2$, which they ascribed to ν_3 of the tetra-ammine (the asymmetric Hg-N stretch). The Raman active vibration at $410 \pm 1 \text{ cm}^{-1}$ (P) observed in liquid ammonia solutions of $\text{Hg}(\text{NO}_3)_2$ and $\text{Hg}(\text{SCN})_2$ is probably due to ν_1 , the symmetric Hg-N stretch of the $[\text{Hg}(\text{NH}_3)_4]^{2+}$ ion. ν_1 and ν_3 of tetrahedral molecules often occur at similar frequencies ¹³. The weaker peaks observed at 301 ($\text{Hg}(\text{NO}_3)_2$) and 290 cm^{-1} ($\text{Hg}(\text{SCN})_2$) are probably due to a deformation mode, ν_2 or ν_4 , of the tetra-ammine.

HgI₂

The Raman active, polarised, symmetric Hg-I stretching vibrations of the HgI₂, [HgI₃]⁻ and [HgI₄]²⁻ species in tri-n-butyl phosphate solution have the frequencies 148, 125 and 117 cm⁻¹ respectively^{14,15,16}. The intense, polarised peak at $\Delta\nu = 131$ cm⁻¹ in the spectrum of HgI₂ in liquid ammonia can therefore be attributed to the symmetric Hg-I stretching mode.

The symmetric (Hg-N) stretching modes of the linear complexes [Hg(NH₃)₂]X₂, (X = Cl, Br) have the frequencies 413 and 380 cm⁻¹ respectively⁷ and for [Hg(NH₃)₄]²⁺ it occurs around 410 cm⁻¹ in the solid and solution¹². The peak observed at 353 cm⁻¹ (P) in the spectrum of HgI₂ in liquid ammonia can therefore be attributed to a symmetric Hg-N stretching vibration. The species in solution therefore contains at least one Hg-I and one Hg-NH₃ bond. From the stability constant data for HgI₂ and mercuric ammine complexes in aqueous solution (Table 1) it can be concluded that a molecule of ammonia will not displace an iodide that is coordinated to a mercuric ion. Although there is a difference in solvents the relative sizes of the stability constants are unlikely to change drastically. The species in solution is probably therefore HgI₂(NH₃)₂.

TABLE 1

SPECIES	Log ₁₀ (FORMATION CONSTANT) ^{*†}
HgI ₂	23
[Hg(NH ₃) ₂] ²⁺	17
[Hg(NH ₃) ₃] ²⁺	18
[Hg(NH ₃) ₄] ²⁺	19

* in aqueous solution, data from reference 17.

Hg(CN)₂

Since the formation constant of Hg(CN)₂ is 10³⁴ (aqueous solution, 25°C¹⁷) it is very unlikely that an ammonia molecule will replace a cyanide ion. The observed vibration frequencies can be explained by assuming the species in solution is Hg(CN)₂(NH₃)₂. This complex should give rise to two Hg-C, two Hg-N, two C-N stretching vibrations, one C-Hg-C and one N-Hg-N deformation modes. Since Raman peaks due to Hg-NH₃ vibrations are generally less intense than those due to Hg-CN vibrations, and since the asymmetric stretching vibrations are also generally weak, the observed spectrum can be assigned as follows:

Δν (cm ⁻¹)	ASSIGNMENT
257 w dP	δ(C-Hg-C)
335±5 sh (P?)	ν _s (Hg-N)
368 s P	ν _s (Hg-CN)
2165 s P	ν _s (C-N)

The C-N and symmetric Hg-CN stretching frequencies (cm^{-1}) of mercuric cyanide complexes in aqueous solution are presented below^{18,19}:

SPECIES	$\nu_s(\text{Hg-CN})$	$\nu_s(\text{C-N})$
$\text{Hg}(\text{CN})_2$	413 m P	2190 m P
$[\text{Hg}(\text{CN})_3]^-$	358 m P	2160 s P
$[\text{Hg}(\text{CN})_4]^{2-}$	344 w P	2146 s P

The decrease in both $\nu_s(\text{Hg-CN})$ and $\nu_s(\text{C-N})$ as the coordination number of the mercuric ion increases is attributed to the fact that π bonding between mercury and carbon is unimportant and as the number of σ bonds increases so the Hg-CN bond strength decreases. π bonding between mercury and nitrogen is also unimportant. The value of $\nu_s(\text{Hg-CN})$ of $\text{Hg}(\text{CN})_2(\text{NH}_3)_2$ in liquid ammonia falls between the values for $\text{Hg}(\text{CN})_2$ and $[\text{Hg}(\text{CN})_3]^-$. This indicates that the Hg-CN bond in the ammine complex is weaker than in $\text{Hg}(\text{CN})_2$, but stronger than in $[\text{Hg}(\text{CN})_3]^-$ and also that the Hg-NH₃ bond is much weaker than the Hg-CN bond. This is expected from stability constant data.

C. CADMIUM SALTS

The Raman spectrum of $\text{Cd}(\text{SCN})_2$ in liquid ammonia showed peaks at 336 (ms P) and 738 cm^{-1} ($\nu(\text{SCN})$). The Raman and infrared of $[\text{Cd}(\text{NH}_3)_6](\text{ClO}_4)_2$ were recorded in the solid state and frequencies and assignments of vibrations are presented below:

$\Delta\nu(\text{cm}^{-1})$	R/IR	ASSIGNMENT
263 w	(R)	ν_2 s(N-Cd-N)
328 s P	(R)	ν_1 ν_s (Cd-N)
276 ± 2	(IR)	ν_4 ν_a (Cd-N)
462 s P	(R)	} ClO_4^- VIBRATIONS
630 m dP	(R)	

Schultz²⁰ recorded the Raman spectrum of the $[\text{Cd}(\text{NH}_3)_6]^{2+}$ ion in aqueous solution and reported ν_s (Cd-N) at 340 cm^{-1} . The peaks at 336 and 328 cm^{-1} in the spectra of $\text{Cd}(\text{SCN})_2$ in liquid ammonia and solid $[\text{Cd}(\text{NH}_3)_6](\text{ClO}_4)_2$ respectively can therefore be assigned to this vibrational mode. The peak at 263 cm^{-1} in the spectrum of the perchlorate is assigned to the symmetric N-Cd-N deformation.

The infrared spectrum of the perchlorate complex showed only one band in the low frequency region, at 276 cm^{-1} . This is ν_4 , the asymmetric Cd-N stretching vibration of the

$[\text{Cd}(\text{NH}_3)_6]^{2+}$ ion. The value of 276 cm^{-1} is in good agreement with values of 298, 291 and 271 cm^{-1} for the complexes $[\text{Cd}(\text{NH}_3)_6]\text{X}_2$, where X = Cl, Br and I respectively²¹.

The Raman spectrum of solid $[\text{Cd}(\text{NH}_3)_6](\text{ClO}_4)_2$ reported here initially showed only one intense peak in the M-L region, at 328 cm^{-1} . After approximately 20 minutes in the laser beam the sample gave an extra peak at 390 cm^{-1} (P), due to ν_1 (symmetric Cd-N stretch) of $[\text{Cd}(\text{NH}_3)_4](\text{ClO}_4)_2$, formed by the decomposition of the hexa-ammine. Barrow et al¹² reported the infrared of the tetra-ammine and found a strong band at 381 cm^{-1} , the asymmetric Cd-N stretch (ν_3). ν_1 and ν_3 of tetrahedral species are often close together¹³.

CONCLUSIONS

With the limited amount of data obtained it has not been possible to identify unambiguously both the geometry and stoichiometry of the species present in the solution.

In general only peaks which are inherently intense (i.e. symmetric vibrational modes) were observed. This was mainly due to two factors:

1. Although the solutions were often saturated, most were still fairly dilute.
2. The use of large diameter tubes for solutions, instead of conventional capillary-sized tubes, cut down the signal intensity by a factor of approximately one half, as shown by the intensities of signals due to CCl_4 in the different sized tubes.

EXPERIMENTAL

MATERIALS

All chemicals were of A.R. or G.P.R. quality, or were prepared by standard literature procedures^{22,23}.

Simple salts were dried under vacuum at 50-60°C for at least 24h prior to use.

The ammonia (redistilled, anhydrous, I.C.I.) was thoroughly dried before use by condensing onto sodium in the presence of a crystal of ferric chloride. The sodamide formed acted as dehydrating agent.

Raman tubes for liquid ammonia solutions were made from Pyrex glass tubing (o.d. 4.5-5.0 mm, i.d. 2.2-2.5 mm, length at least 10 cm). One end of the tubing was sealed to give a flat surface. Solutions were prepared by placing a known weight of anhydrous metal salt in the Raman tube, attaching to the vacuum line and evacuating. 6-8 cm of liquid ammonia were then condensed into the tube, the tube isolated from the vacuum line and the contents frozen in liquid nitrogen. It was then sealed 3-4 cm above the level of solid ammonia, placed in a metal tube and heated to 40-50°C (15-20 atm. pressure), approximately 20°C above the temperature at which the tubes had to be handled.

Tubes which contained any undissolved material

were centrifuged and the solid collected at the non-flat end.

RAMAN SPECTRA were measured on a CARY 81 spectrophotometer, with a CRL 52 Kr laser, using excitation at 6471 or 5638 Å.

Spectra of CCl_4 in a conventional size capillary tube and in a tube of the same size as those used for liquid ammonia solutions were recorded using the same instrument settings.

REFERENCES

1. D.M. Adams, "Metal-Ligand and Related Vibrations". Arnold, London. 1967 ch. 6.
2. D.B. Powell and N. Sheppard, J. Chem. Soc., 1956, 3108.
3. "Monograph: Anhydrous Ammonia" I.C.I.
4. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry" Interscience, 2nd Edn. 1966.
5. R. Cavagnat, J.J. Martin and G. Turrell, Appl. Spectrosc., 1969 23 172.
6. A.L. Geddes and G.L. Bottger, Inorg. Chem., 1969, 8, 802.
7. M.G. Miles, J.H. Patterson, C.W. Hobbs, M.J. Hopper, J. Overend and R.S. Tobias, Inorg. Chem., 1968, 7, 1721.
8. H. Browne and G. Engelbrecht, Z. Physik. Chem., 1931, B11, 409.
9. L.H. Jones, Spectrochim. Acta., 1963, 19, 1675.
10. L.H. Jones, J. Chem. Phys., 1957, 26, 1578.
11. L.H. Jones and R.A. Penneman, J. Chem. Phys., 1954, 22, 965.
12. G.M. Barrow, R.H. Krüger and F. Basolo, J. Inorg. Nuclear Chem., 1956, 2, 340.
13. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds" Wiley, New York, 1963, P.104.
14. E.L. Short, D.N. Waters and D.F.C. Morris, J. Inorg. Nuclear Chem., 1964, 26, 902.
15. H. Browne and G. Engelbrecht, Z. Physik. Chem., 1932, B19, 303.
16. J.A. Rolfe, D.E. Sheppard and L.A. Woodward, Trans. Faraday Soc., 1954, 50, 1275.

17. "Stability Constants", Chem. Soc., Special Publ. No. 17, London, 1964.
18. W.P. Griffith, J. Chem. Soc., 1964, 4070.
19. L.A. Woodward and H.F. Owen, J. Chem. Soc., 1959, 1055.
20. H. Shultz, J. Chem. Phys., 1942, 10, 194.
21. L. Sacconi, A. Sabatini and P. Gans, Inorg. Chem., 1964, 3, 1772.
22. J.N. Friend, "A Text Book of Inorganic Chemistry-Metal Ammines" 1928.
23. G. Brauer, "Handbook of Preparative Chemistry" Academic Press, 1962.

"If anyone can explain it, I'll give him sixpence."

Alice.