Spectroscopic Studies of Inorganic Fluoro-complexes. Part IV.[1] Fluorine-19 Nuclear Magnetic Resonance Studies of Platinum(IV) Fluoro-complexes

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A number of chlorofluoro-, fluorohydroxo-, and chlorofluorohydroxo-platinate(IV) species have been characterized in solution by ^{19}F n.m.r. spectroscopy. The ^{19}F chemical shifts, δ, are given to a good approximation by $\delta = pC + qT$, where C and T are constants characteristic of Cl^- or OH^- and p and q are the number of substituents *cis* and *trans* to the fluorine atom, respectively. The fluorohydroxoplatinate complexes are protonated in acid solution, and pK values of the aqua-species have been determined from the ^{19}F chemical shifts as a function of pH. The observed reactions can be rationalized in terms of a *trans* effect of ligands, in the order $Cl^- > OH^- \gg F^-$. Solvent shifts of ^{195}Pt–^{19}F coupling constants are reported.

THE present work is concerned with the characterization, from the ^{19}F n.m.r. spectra in aqueous solution, of a number of anionic platinum(IV) species. Parts II [2] and III [1] of this series described ^{19}F n.m.r. spectra of fluoro-complexes of silicon(IV), germanium(IV), tin(IV), and titanium(IV). These complexes were rapidly formed and coexisted in a labile equilibrium. In contrast, the Pt^{IV} fluoro-complexes are comparatively slow to react, as is typical of Pt^{IV} complexes, and are thermodynamically completely unstable to hydrolysis in aqueous solution. The species obtained are thus determined by kinetic, rather than thermodynamic, considerations.

The $[PtF_6]^{2-}$ ion is well characterized,[3] and the ^{19}F n.m.r. spectrum of $K_2[PtF_6]$ in liquid hydrogen fluoride has been reported by Matwiyoff *et al.*[4] The complex $K_2[PtCl_3F_3]$ was prepared by Brown *et al.*[5] and those of the type $M_2[Pt(OH)_4F_2]$, $M[Pt(OH_2)(OMe)_3F_2]$, and $M_2[Pt(OMe)F_5]$ have been described by Kolditz and Gisbier.[6]

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[1] Part III, P. A. W. Dean and D. F. Evans, *J. Chem. Soc.* (*A*), 1970, 2569.

[2] P. A. W. Dean and D. F. Evans, *J. Chem. Soc.* (*A*), 1968, 1154.

[3] F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science, 1973.

[4] N. A. Matwiyoff, L. B. Asprey, W. E. Wageman, M. J. Reisfeld, and E. Fukushima, *Inorg. Chem.*, 1969, **8**, 750.

[5] D. H. Brown, K. R. Dixon, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1966, 1244.

[6] L. Kolditz and J. Gisbier, *Z. anorg. Chem.*, 1969, **366**, 265.

RESULTS AND DISCUSSION

Identification of the Complexes.—The following criteria were used. (*a*) The order of appearance of the n.m.r. lines, where applicable, and the fine structure, if any, observed. (*b*) Anions containing an OH group behaved as weak bases, and in acid solution appreciable changes in the ^{19}F chemical shifts were observed. (*c*) It was previously found[2] for Sn^{IV} fluoro-complexes of the type $[SnF_{6-n}X_n]^{2-}$ that the ^{19}F chemical shifts, δ (relative to the $[SnF_6]^{2-}$ ion), are given, to a good approximation, by the empirical expression (1), where C and T are

$$\delta = pC + qT \qquad (1)$$

constants characteristic of the ligand X and p and q are the number of substituents *cis* and *trans* to the fluorine atom, respectively. For complexes with more than one substituent X equation (2) is applicable. Very recently

$$\delta = \sum_{X} p_X C_X + \sum_{X} q_X T_X \qquad (2)$$

it has been shown by Dean and Ferguson[7] that equation (1) provides a reasonable representation of the ^{19}F chemical shifts of fluorothiocyanato- and cyanatofluorotitanates.

For Pt^{IV} fluoro-complexes which could be unambiguously characterized by the first two criteria it was found that equations (1) and (2) also applied quite accurately. In addition to characterizing the species found, equations (1) and (2) are also useful in making probable assignments in complexes containing equal numbers of fluoro-ligands in two different environments.

Nomenclature used for the Complexes.—The spatial positions of the ligands are designated following the sequence given in ref. 8, and the locants are given in the formulae in italics as right superscripts after the symbol for the ligand. The fluoro-ligands are not labelled, since their positions are clear from the numbering of the other ligands. This nomenclature differs from that used in Parts II[2] and III[1] in that letters rather than numbers are used as locant designators.

The $[PtF_6]^{2-}$ *Ion and Its Reactions.*—The ^{19}F n.m.r. spectrum of $Na_2[PtF_6]$ or $[Et_4N]_2[PtF_6]$ in aqueous solution [Figure 1(*a*)] consisted of a single line (δ 286 p.p.m. relative to CF_3CO_2H as external reference) and two satellites due to spin–spin splitting by the ^{195}Pt isotope (34% abundant, spin $\frac{1}{2}$), $J(^{195}Pt-^{19}F)$ 2 003 Hz. This spectrum is very similar to that reported for $K_2[PtF_6]$ in liquid HF by Matwiyoff *et al.*[4] who also discuss possible reasons for the fact that the ^{19}F resonance lies at such a high applied field.

Attempts to prepare mixed fluoro-complexes directly from the $[PtF_6]^{2-}$ ion were unsuccessful. Although $[PtF_6]^{2-}$ reacted with Cl^- or I^- ion in acidic solutions with the liberation of F^-, no mixed fluoro-complexes could be detected in the ^{19}F n.m.r. spectrum. This is in agreement with the work of Sharpe,[9] who showed from *X*-ray powder photographs of the precipitated potassium salts that only $K_2[PtCl_6]$ or $K_2[PtBr_6]$ were produced with limited amounts of hydrochloric or hydrobromic acids, indicating that the rate-determining step is the first.

The $[PtF_6]^{2-}$ ion is comparatively resistant to hydrolysis in neutral, acidic, or alkaline solutions. However, overnight exposure of an aqueous solution of $[Et_4N]_2[PtF_6]$, in the presence of $[Et_4N][OH]$, to radiation of wavelength <313 nm caused appreciable decomposition with the liberation of F^- (detected by its n.m.r. spectrum). Nevertheless, no mixed fluorohydroxo-complexes could be observed in the ^{19}F n.m.r. spectrum of the resulting solution, and the main product is presumably the $[Pt(OH)_6]^{2-}$ ion. A similar unirradiated solution showed no detectable hydrolysis.

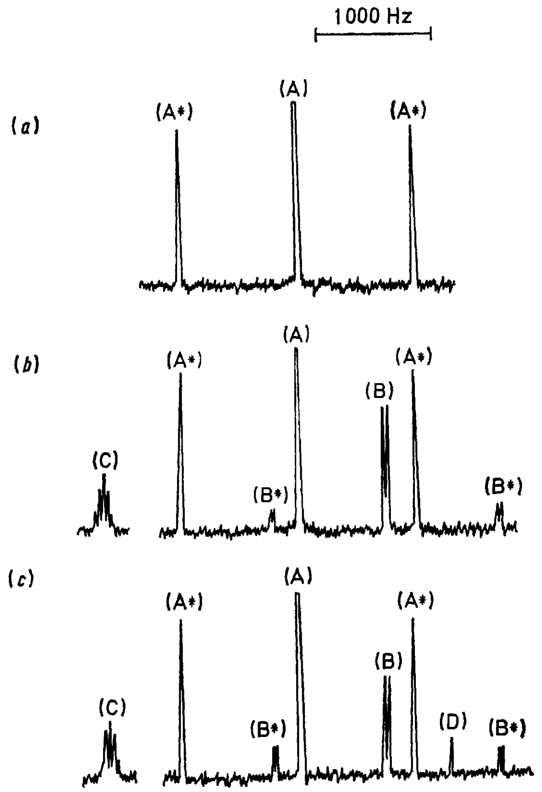

FIGURE 1 ^{19}F N.m.r. spectra of aqueous solutions of (*a*) $M_2[PtF_6]$, (*b*) the product of the reaction of BrF_3 with imperfectly dried $Na_2[PtCl_6]$, and (*c*), as (*b*) plus NaOH after *ca.* 24 h. * = Satellite; (A) = $[PtF_6]^{2-}$; (B) = $[Pt(OH)F_5]^{2-}$, F^{b-e}; (C) = $[Pt(OH)F_5]^{2-}$, F^{f}; and (D) = $[Pt(OH)_2{}^{af}F_4]^{2-}$, F^{b-e}

Reaction of BrF_3 *with Hydrated* $Na_2[PtCl_6]$.—The reaction of BrF_3 with anhydrous $Na_2[PtCl_6]$ under vigorous conditions yielded pure $Na_2[PtF_6]$.[10] When imperfectly dried $Na_2[PtCl_6]$ was used a pale yellow solid was obtained, whose i.r. spectrum showed a strong O–H stretch at 3 500 cm^{-1}. The ^{19}F n.m.r. spectrum of an aqueous solution is shown in Figure 1(*b*). In addition

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[7] P. A. W. Dean and B. J. Ferguson, *Canad. J. Chem.*, 1974, **52**, 667.

[8] 'Nomenclature of Inorganic Chemistry,' 2nd edn., I.U.P.A.C., Butterworths, London, 1970, p. 57.

[9] A. G. Sharpe, *J. Chem. Soc.*, 1950, 3444.

[10] B. Cox, *J. Chem. Soc.*, 1954, 3251.

to the strong $[PtF_6]^{2-}$ resonance an AX_4 pattern (with ^{195}Pt satellites) was observed. Below pH 4, the chemical shifts of both the doublet and quintuplet were pH dependent (see below and Figure 4). Accordingly the species responsible can be assigned as $[Pt(OH)F_5]^{2-}$, which in acid solutions is protonated to the $[Pt(OH_2)F_5]^-$ ion.

Addition of sodium hydroxide to the solution containing $[Pt(OH)F_5]^{2-}$ caused no immediate reaction. After 24 h, however, the intensity of the $[Pt(OH)F_5]^{2-}$ resonances had decreased, and a new singlet (D) (with ^{195}Pt satellites) was observed [Figure 1(*c*)]. The intensity of the F^- resonance also increased. The ^{19}F chemical shift of the new species was pH dependent, and it can be seen from Figure 4 that a diacidic base is present. Accordingly, the new species can be assigned as $[Pt(OH)_2{}^{af}F_4]^{2-}$, which in acid solution is protonated, first to $[Pt(OH)^a(OH_2)^fF_4]^-$ and then to $[Pt(OH_2)_2{}^{af}F_4]$. The product of reaction of BrF_3 with $Na_2[Pt(OH)_2{}^{af}Cl_4]$ under mild conditions when dissolved in water gave an ^{19}F n.m.r. spectrum similar to Figure 1(*c*), although the relative proportion of the $[Pt(OH)_2{}^{af}F_4]^{2-}$ ion was greater.

The reaction of BrF_3 with pure $Na_2[PtCl_6]\cdot 6OH_2$ under mild conditions in the presence of bromine as a moderator gave a pale yellow solid that had retained a small amount of chlorine. The ^{19}F n.m.r. spectrum of an aqueous solution showed resonances due to $[PtF_6]^{2-}$ (identified by adding $[Et_4N]_2[PtF_6]$ to the solution), $[Pt(OH)F_5]^{2-}$, and a second AX_4-type resonance [Figure 2(*a*)]. The chemical shifts of the AX_4 resonances (E) and (F) were independent of pH, and the species responsible can be assigned as $[PtClF_5]^{2-}$.

Addition of NaOH to solutions containing $[PtClF_5]^{2-}$ caused rapid decomposition of this ion, and a new single resonance (G) (with ^{195}Pt satellites) was observed [Figure 2(*b*) and (*c*)]. The intensity of this resonance when all the $[PtClF_5]^{2-}$ had decomposed was approximately equal to that of the doublet of $[PtClF_5]^{2-}$ in the original solution, showing that all four equatorial fluorines (F^{b-e}) remained bonded to the platinum. The chemical shift δ of the singlet was pH dependent, and a plot of δ against pH indicated a monoacidic base as present (see discussion below). The data are thus consistent with the species being $[PtCl^a(OH)^fF_4]^-$. The same solution after standing for 1 h gave the ^{19}F n.m.r. spectrum shown in Figure 2(*c*). The $[PtClF_5]^{2-}$ had completely disappeared and, in addition to $[PtCl^a(OH)^fF_6]^{2-}$, a new species was present which gave rise to the two triplets (H) and (I). The chemical shifts δ of both triplets were pH dependent. A detailed analysis of the plot of δ against pH for the low-field triplet indicated that a diacidic base was present (see below), and the new species can be assigned as $[Pt(OH)_2{}^{ab}F_4]^{2-}$. (The high-field triplet was obscured by other resonances at several pH values.)

$[PtCl_3{}^{abc}F_3]^{2-}$ *and* $[PtCl_2{}^{ab}F_4]^{2-}$ *and Their Reactions.*—The reaction of BrF_3 with $K_2[PtCl_6]$ under mild conditions in the presence of 1,1,2-trichloro-1,2,2-trifluoroethane as a moderator gave $K_2[PtCl_3F_3]$.[5] The ^{19}F n.m.r. spectrum of an aqueous solution of the complex consisted of a single line with ^{195}Pt satellites, and accordingly the anion has the symmetrical structure $[PtCl_3{}^{abc}F_3]^{2-}$. It was reported by Brown *et al.*[5] that in aqueous solution slow decomposition occurred to give a precipitate containing $K_2[PtCl_6]$, $K_2[PtF_6]$, and hydroxo-species. The complexes $K_2[PtCl_6]$ and $K_2[PtF_6]$ were identified by *X*-ray powder photography. However, while decomposition of $K_2[PtCl_3F_3]$ in aqueous solution was observed in the present work, no ^{19}F resonance due to $[PtF_6]^{2-}$ could be detected. Although $K_2[PtF_6]$ is only sparingly soluble in water, its solubility is sufficient to give a ^{19}F n.m.r. line of moderate intensity.

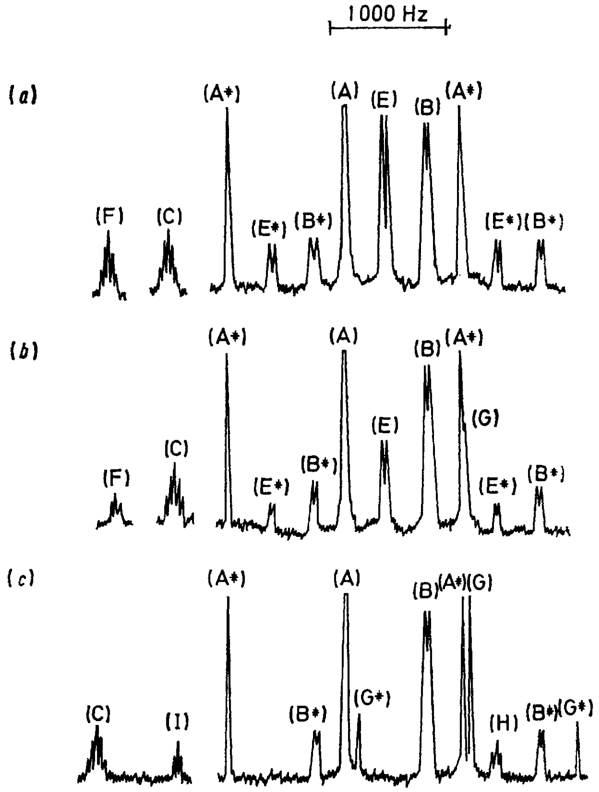

FIGURE 2 ^{19}F N.m.r. spectra of aqueous solutions of (*a*) the product of the reaction of BrF_3 with $Na_2[PtCl_6]\cdot 6OH_2$ under mild conditions, (*b*) as (*a*) plus NaOH after *ca.* 15 min, and (*c*) as (*b*) after *ca.* 1 h. * = Satellite; (E) = $[PtCl^aF_5]^{2-}$, F^{b-d}; (F) = $[PtCl^aF_5]^{2-}$, F^f; (G) = $[PtCl^a(OH)^fF_4]^{2-}$, F^{b-e}; (H) = $[Pt(OH)_2{}^{ab}F_4]^{2-}$, F^{ce}; and (I) = $[Pt(OH)_2{}^{ab}F_4]^{2-}$, F^{df}

The reaction of BrF_3 with $K_2[PtCl_4]$ under similar conditions is also reported[4] to give $K_2[PtCl_3F_3]$. A number of samples were prepared in this way, and the ^{19}F n.m.r. spectra of aqueous solutions showed the presence, not only of $[PtCl_3F_3]^{2-}$ but also another species which gave rise to two triplets. The chemical shift of these two triplets did not change on acidification, and the species responsible can be assigned as $[PtCl_2{}^{ab}F_4]^{2-}$. The observed chemical shifts were consistent with this interpretation. Normally, the proportions of $K_2[PtCl_2F_4]$

were comparatively small (*ca.* 20% of the $K_2[PtCl_3F_3]$). However, in one sample the ^{19}F n.m.r. spectrum [Figure 3(*a*)] showed the presence of much more $[PtCl_2F_4]^{2-}$, and also some $[PtClF_5]^{2-}$, possibly as the result of a more vigorous reaction during the preparation of this sample.

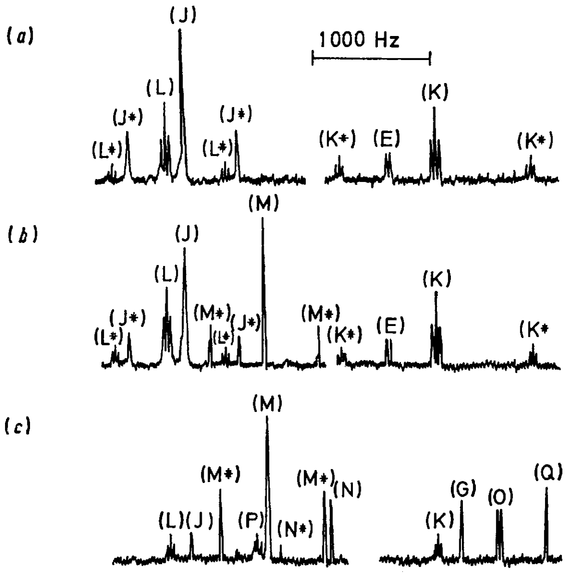

FIGURE 3 ^{19}F N.m.r. spectra of aqueous solutions of (*a*) the product of the reaction of BrF_3 with $K_2[PtCl_4]$, (*b*) as (*a*) plus NaOH after *ca.* 5 min, (*c*) as (*b*) after *ca.* 15 min. * = Satellite; (J) = $[PtCl_3{}^{abc}F_3]^{2-}$, F^{d-f}; (K) = $[PtCl_2{}^{ab}F_4]^{2-}$, F^{ce}; (L) = $[PtCl_2{}^{ab}F_4]^{2-}$, F^{df}; (M) = $[PtCl_2{}^{abc}(OH)^dF_2]^{2-}$, F^{ef}; (N) = $[PtCl_3{}^{abc}(OH)_2{}^{de}F]^{2-}$, F^f; (O) = $[PtCl_2{}^{ab}(OH)^dF_3]^{2-}$, F^{ce}; (P) = $[PtCl_2{}^{ab}(OH)^dF_3]^{2-}$, F^f; and (Q) = $[PtCl_2{}^{ab}(OH)_2{}^{df}F_2]^{2-}$, F^{ce}

Both $[PtCl_3F_3]^{2-}$ and $[PtCl_2F_4]^{2-}$ underwent rapid decomposition in NaOH solution [Figure 3(*b*) and (*c*)]. For $[PtCl_3{}^{abc}F_3]^{2-}$ the first product (shown by experiments with pure $K_2[PtCl_3F_3]$) gave a single ^{19}F resonance (M) with ^{195}Pt satellites. After a few more minutes, another single resonance (N) (also with ^{195}Pt satellites) appeared. The intensity of the free-fluoride resonance steadily increased with time. The species (M) and (N) can be assigned as $[PtCl_2{}^{abc}(OH)^dF_2]^{2-}$ and $[PtCl_3{}^{abc}(OH)_2{}^{de}F]^{2-}$, respectively, and the observed ^{19}F chemical shifts are in good agreement with those calculated from equation (2). Finally, after standing for *ca.* 1 h at 35 °C the ^{19}F n.m.r. spectrum showed only a single intense resonance due to free fluoride ion.

For $[PtCl_2{}^{ab}F_4]^{2-}$ in the presence of NaOH, the first product gave an AX_2 pattern with ^{195}Pt satellites, corresponding to either $[PtCl_2{}^{ab}(OH)^cF_3]^{2-}$ or $[PtCl_2{}^{ab}(OH)^dF_3]^{2-}$. The chemical shifts of the doublet (P) and triplet (O) indicate that the latter is correct. On further reaction, a single resonance (Q) with ^{195}Pt satellites appeared. The species responsible is clearly $[PtCl_2{}^{ab}(OH)_2{}^{df}F_2]^{2-}$, both from the method of formation and also the observed ^{19}F chemical shift. Finally, the lines due to $[PtCl_2{}^{ab}F_4]^{2-}$ and $[PtCl_2{}^{ab}(OH)^dF_3]^{2-}$ soon disappeared, but that due to $[PtCl_2{}^{ab}(OH)_2{}^{df}F_2]^{2-}$ was still present, although decreased in intensity, after 24 h. Addition of perchloric acid to solutions containing any of the above chlorofluorohydroxo-complexes caused very rapid decomposition.

Table 1 gives details of the ^{19}F n.m.r. spectra of all the complexes identified, together with ^{19}F chemical shifts calculated from equations (1) and (2). The values of *C* and *T* used were, respectively, (Cl) 3·6 and −101·4, (OH) 7·0 and −65·2, and (H_2O) 2·5 and −33·5. It can be seen that the calculated and observed ^{19}F chemical shifts agree quite closely.

TABLE 1

^{19}F N.m.r. spectra of the fluoroplatinate complexes

Complex	Assignment	Chemical shift/p.p.m.		$J(^{195}Pt-^{19}F)$ Hz	$J(^{19}F-^{19}F)$/ Hz
		obs.*	calc.		
$[Pt(OH)F_5]^{2-}$	F^{b-e}	8·0	7·0	1 936	34
	F^f	−65·5	−65·2	1 049	
$[Pt(OH_2)F_5]^-$	F^{b-e}	2·2	2·5	1 945	35
	F^f	−35·0	−33·5		
$[Pt(OH)_2{}^{ab}F_4]^{2-}$	F^{ce}	12·8	14·0	1 905	30
	F^{df}	−57·9	−58·2	1 081	
$[Pt(OH)^a(OH_2)^bF_4]^-$	F^{ce}	8·4	9·5		
	F^{df}	−43·2	−44·6		
$[Pt(OH_2)^{ab}F_4]$	F^{ce}	5·3	5·0		
	F^{df}	−29·4	−31·0		
$[Pt(OH)_2{}^{af}F_4]^{2-}$	F^{b-e}	14·5	14·0	1 926	
$[Pt(OH)^a(OH_2)^fF_4]^-$	F^{b-e}	8·5	9·5		
$[Pt(OH_2)_2{}^{af}F_4]$	F^{b-e}	4·7	5·0		
$[PtClF_5]^{2-}$	F^{b-e}	3·7	3·6	1 931	39
	F^f	−99·9	−101·4		
$[PtCl_2{}^{ab}F_4]^{2-}$	F^{ce}	8·3	7·2	1 882	40
	F^{df}	−98·0	−98·8	1 115	
$[PtCl_3{}^{abc}F_3]^{2-}$	F^{d-f}	−96·2	−95·2	1 077	
$[PtCl^a(OH)^fF_4]^{2-}$	F^{b-e}	11·1	10·6	1 882	
$[PtCl^a(OH_2)^fF_4]^{2-}$	F^{b-e}	6·4	6·1		
$[PtCl_2{}^{ab}(OH)^dF_3]^{2-}$	F^{ce}	15·5	14·2		
	F^f	−89·3	−91·8		
$[PtCl_2{}^{ab}(OH)_2{}^{df}F_2]^{2-}$	F^{ce}	20·4	21·2	1 788	
$[PtCl_3{}^{abc}(OH)^dF_2]^{2-}$	F^{ef}	−87·8	−88·2	1 091	
$[PtCl_3{}^{abc}(OH)_2{}^{de}F]^{2-}$	F^f	−81·4	−81·2	1 050	

* Relative to the $[PtF_6]^{2-}$ ion as internal reference. Positive values are to higher applied fields.

Calculation of Dissociation Constants of Aqua-complexes.—As mentioned above the aqua-complexes are acidic, and from the ^{19}F chemical shifts as a function of pH it is possible to derive their dissociation constants. For a monobasic acid, $A \rightleftharpoons B + H^+$, since proton exchange is rapid on an n.m.r. time scale, we obtain equation (3) where K is the dissociation constant, δ the

$$\delta = \frac{[H^+]\delta_A + K\delta_B}{[H^+] + K} \qquad (3)$$

observed chemical shift, and δ_A and δ_B the chemical shifts of pure A and B, respectively; δ_B is equal to the observed chemical shift at pH $\geqslant 4$, and an approximate value for δ_A can be found from the limiting value of δ at very high acidities. Since this value of δ_A may be affected by solvent effects, a least-squares computer program fitted the values of δ to equation (3), with both K and δ_A being varied. The values of δ_A calculated in this way were close to those found directly.

For a dibasic acid where $A \rightleftharpoons BH + H^+$ (K_1) and $BH \rightleftharpoons B + H^+$ (K_2), equation (4) is applicable. The

$$\delta = \frac{\delta_A[H^+]^2 + K_1\delta_{BH}[H^+] + K_1K_2\delta_B}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (4)$$

shift δ_B and an approximate value for δ_A could be found as above, and δ_{BH} will be approximately equal to $(\delta_A + \delta_B)/2$. A least-squares computer program was then used to fit the values of δ to equation (4) varying δ_A, δ_{BH}, K_1, and K_2. The refined values of δ_A and δ_{BH} were again close to the initial approximations.

The pK values obtained are given in Table 2, together with literature results for related complexes, and Figure 4 shows the observed and calculated plots of δ against [H$^+$]. The pK values are of limited accuracy only, largely because it was not practicable to keep the ionic strength of the solutions constant. However, the method used is applicable to species which are present only as minor constituents of a mixture, and which are undergoing slow decomposition.

TABLE 2

pK Values of platinum aquafluoro- and related complexes

Complex	pK_1	pK_2
$[Pt(OH_2)F_5]^-$	1·0	
$[PtCl(OH_2)_6F_4]^-$	2·1	
$[Pt(OH_2)_2{}^{ab}F_4]$	*ca.* 0·5	2·0
$[Pt(OH_2)_2{}^{af}F_4]$	*ca.* 0·6	4·5
$[Pt(OH_2)Cl_3]^-$	3·8 [a]	
$[Pt(OH_2)_2{}^{af}Cl_4]$	1·9 [b]	5·5
$[Pt(NH_3)_4Cl_2{}^{ab}]^{2+}$	9·7 [c]	
$[Pt(NH_3)_4Cl_2{}^{af}]^{2+}$	11·3 [c]	

[a] C. M. Davidson and R. F. Jameson, *Trans. Faraday Soc.*, 1965, **61**, 2462. [b] L. E. Cox and D. G. Peters, *Inorg. Chem.*, 1970, **9**, 1927. [c] R. C. Johnson, F. Basolo, and R. G. Pearson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 59.

Solvent Shifts of ^{195}*Pt–*^{19}*F Coupling Constants*.—The ^{195}Pt–^{19}F coupling constants in $[PtF_6]^{2-}$, $[PtCl_2{}^{ab}F_4]^{2-}$, and $[PtCl_3{}^{abc}F_3]^{2-}$ were appreciably dependent on the solvent (Table 3). For $[PtF_6]^{2-}$, the variation with solvent is similar to that found for the ^{119}Sn–^{19}F coupling constants in $[SnF_6]^{2-}$,[11] but in the opposite direction. Following Bell and Danyluk [12] it was suggested [11] that the ^{119}Sn–^{19}F coupling constant in $[SnF_6]^{2-}$ has an absolute negative sign, and this was confirmed by McFarlane and Wood [13] using the unambiguous technique of heteronuclear double irradiation on $[(PhMe_2CCH_2)_3SnF]$. The present results would therefore indicate that the ^{195}Pt–^{19}F coupling constant in $[PtF_6]^{2-}$ has an absolute positive sign.

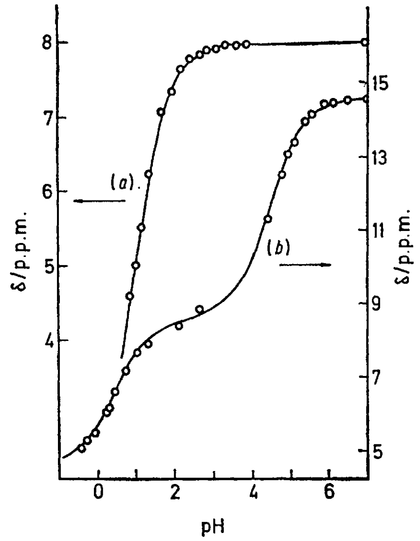

FIGURE 4 Plot of δ (p.p.m. relative to internal $[PtF_6]^{2-}$) against pH for (*a*) F^{b-e} of $[Pt(OH)F_5]^{2-}$ and (*b*) F^{b-e} of $[Pt(OH)_2{}^{af}F_4]^{2-}$

TABLE 3

Platinum–fluorine coupling constants (Hz) of platinum fluoro-complexes in various solvents

			$[PtCl_2{}^{ab}F_4]^{2-}$	
Solvent	$[PtF_6]^{2-}$	$[PtCl_3{}^{abc}F_3]^{2-}$	F^{ce}	F^{df}
HF (anhydrous)	2 080 *			
98% H_2SO_4	2 065			
HCO_2H	2 007			
H_2O	2 003	1 077	1 882	1 115
MeOH	1 999	1 080		
EtOH	1 999	1 081		
Pr^{n}OH	1 993			
$HCONMe_2$	1 981	1 152		
$HCONH_2$	1 981			
Me_2SO	1 976	1 223	1 858	1 236

* Ref. 3.

For $[PtCl_2{}^{ab}F_4]^{2-}$ it can be seen that the two ^{195}Pt–^{19}F coupling constants behave differently when the solvent is changed from water to Me_2SO; $J(^{195}Pt–^{29}F_{ce})$ decreases (as in $[PtF_6]^{2-}$) but $J(^{195}Pt–^{19}F_{df})$ (involving fluorines *trans* to chlorine) increases very markedly, in a similar manner to $J(^{195}Pt–^{19}F)$ in $[PtCl_3{}^{abc}F_3]^{2-}$. Possible explanations are as follows. (*a*) The two ^{195}Pt–^{19}F

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[11] P. A. W. Dean and D. F. Evans, *J. Chem. Soc.* (*A*), 1967, 69.

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coupling constants in $[PtCl^{ab}F_4]^{2-}$ have opposite signs. It has been shown by McFarlane *et al.*,[14] using homonuclear double irradiation, that in $[WOF_5]^-$ the signs of the two $^{183}W-^{19}F$ coupling constants are opposite. However, in this complex the reduced coupling constants are both very much less than in the platinum fluoro-complexes. Attempts to obtain the relative sign of the $^{195}Pt-^{19}F$ coupling constants in $[PtCl_2{}^{ab}F_4]^{2-}$ by double irradiation were unsuccessful, partly due to the instability of the solutions and the difficulty in obtaining samples rich in $[PtCl_2{}^{ab}F_4]^{2-}$. (*b*) In terms of reaction-field theory, solute-dipole orientation effects of the type discussed by Smith and Ihrig.[15] (*c*) Preferential solvation of the chlorine atoms affecting the *trans* Pt–F bonds.

General Discussion.—Substitution reactions of Pt^{IV} complexes are frequently catalysed by Pt^{II} complexes, and the usually accepted mechanism in these cases involves $Pt^{II}-Pt^{IV}$ bridged complexes.[3,16] Very marked *trans* effects in the order $I > Br > SCN > Cl$ are observed. It is not clear whether a similar mechanism is involved in the fluoro-complexes studied in this paper. Apart from complexes of the type $[PtF(PR_3)_3][BF_4]$ (R = Et or Ph),[17] no Pt^{II} fluoro-complexes are known, and addition of $[PtCl_4]^{2-}$ had no effect on the rate of reaction of Cl^- or I^- with $[PtF_6]^{2-}$ in acid solution. However, regardless of the exact mechanism involved, the hydroxo-substitution reactions of the fluoro-complexes can be rationalized by postulating a strong *trans* effect in the order $Cl > OH \gg F$. Thus for $[Pt(OH)F_5]^{2-}$ and $[PtClF_5]^{2-}$ the fluorine *trans* to the substituent is replaced, with $[PtClF_5]^{2-}$ reacting much more rapidly. In $[PtCl_2{}^{ab}F_4]^{2-}$, it is the two fluorines *trans* to the chlorines which undergo rapid substitution. Similarly the ions $[PtF_6]^{2-}$, $[Pt(OH)_2{}^{af}F_4]^{2-}$, and $[PtCl_2{}^{ab}(OH)_2{}^{df}F_2]^{2-}$ in which all the fluorines are *trans* to each other are considerably more stable to hydrolysis than related ions in which a fluorine is *trans* to chlorine or hydroxide. In a different context, the *trans*-effect order given above can explain the reactions of anhydrous $K_2[PtCl_6]$ with BrF_3. Under mild conditions, only $K_2[PtCl_3{}^{abc}F_3]$ is formed, while under vigorous conditions pure $K_2[PtF_6]$ is obtained. In $[PtCl_6]^{2-}$ three chlorines are *trans* to other chlorines, and hence are easily replaced. The only surprising feature is the formation of $[Pt(OH)_2{}^{ab}F_4]^{2-}$ by hydrolysis of $[PtCl^a(OH)^fF_4]^{2-}$.

There is also some evidence for the presence of a *trans* influence in these complexes. For d^6 and d^8 complexes, the *trans* influence is thought to arise largely from σ-bond rehybridization effects, which result in a bond *trans* to a ligand of high *trans* influence being weakened, with (probably) a corresponding reduction in its *s* character.[18] The higher *trans* influence of OH^- as compared with F^- provides a possible explanation of the fact that the p*K* of $[Pt(OH)^a(OH_2)^fF_4]^-$ is 2·5 units higher than that of $[Pt(OH)^a(OH_2)^bF_4]$. A weaker $Pt-OH_2$ bond in the former complex would presumably result in a weaker acid.

It can be seen from Table 1 that a chlorine or hydroxide *trans* to a fluorine produces a much larger change in both the ^{19}F chemical shift and $J(^{195}Pt-^{19}F)$ than does a *cis* ligand. In view of the difficulties involved in the theoretical interpretation of ^{19}F spin–spin coupling constants[19] and chemical shifts, any rationalization in terms of a *trans* influence can only be tentative. However, the values of $J(^{195}Pt-^{19}F)$ in Table 1 are at least consistent with a chlorine or hydroxide reducing both the bond strength and the *s* character of a *trans* Pt–F bond.

EXPERIMENTAL

Materials.—The complexes $Na_2[PtF_6]$ and $K_2[PtF_6]$ were prepared from the corresponding hexachloroplatinates and bromine trifluoride in the presence of bromine under vigorous conditions.[9,20] The complexes $[Et_4N]_2[PtF_6]$ and $[Pr^n{}_2H_2N]_2[PtF_6]$ were obtained by neutralization of $H_2[PtF_6]$(aq), which was formed when an aqueous solution of $Na_2[PtF_6]$ was passed down a cation-exchange resin in the acid form. They were purified by recrystallization from methanol and analysed correctly. The complex $K_2[PtCl_3F_3]$ was prepared by the method of Dixon *et al.*;[20] $Na_2[Pt(OH)_2{}^{af}Cl_4]$ was obtained from $K_2[Pt(OH)_2{}^{af}Cl_4]$[21] using a cation-exchange resin in the sodium form. Non-aqueous solutions of the $[Et_4N]^+$ and $[Pr^n{}_2H_2N]^+$ salts of $[PtCl_2{}^{ab}F_4]^{2-}$ and $[PtCl_3{}^{abc}F_3]^{2-}$ were made by shaking $Na_2[PtF_6]$ in the solvent with an excess of the corresponding potassium chlorofluoroplatinate, and removing the precipitated $K_2[PtF_6]$.

^{19}F *N.m.r. Measurements.*—Spectra were obtained at 35 °C on a Perkin-Elmer R14 spectrometer operating at 94·09 MHz. Acidic solutions containing F^- were studied in standard 5 mm n.m.r. tubes with a length of tightly fitting poly(tetrafluoroethylene) (ptfe) tubing inserted and sealed at the bottom with paraffin wax. Subsequently, Wilmad ptfe-coated tubes were used. The ions $[PtF_6]^{2-}$ or $CF_3SO_3{}^-$ were used as internal references, and trifluoroacetic acid as external reference. The salts $Na(O_3SCF_3)$ and $[Et_4N](O_3SCF_3)$ are readily soluble in water, and the ^{19}F resonance of dilute solutions is at 0·15 p.p.m. relative to external trifluoroacetic acid.

Measurement of $[H^+]$.—For pH values $\geqslant 1$, a Vibron 39A pH meter with Jena glass electrode was used. It has been shown that glass electrodes can be used reliably in acidic solutions containing fluoride ions.[22,23] Below pH 1, the readings were unsteady and for the dihydroxo-anions approximate values of $[H^+]$ were obtained from the chemical shift of F^{b-e} in $[Pt(OH)F_5]^{2-}$ or $[PtCl^a(OH)^fF_4]^{2-}$. The solutions were acidified with 9M-$HClO_4$.

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