The Aquation of *trans*-Bis(ethylenediamine)difluorochromium(III) and Related Ions in Aqueous Solutions of Strong Acids

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The hydrolysis of a series of fluoro-complexes in aqueous solutions of strong acids has been studied over a wide range of acid concentrations. The kinetic results have been analysed by the treatments of Hammett and Zucker, Bunnett, and Bunnett and Olsen. Analysis of the results indicates that hydroxonium ion acts as a proton-transfer agent in the rate-determining step. The mechanism involves attack by hydroxonium ion adjacent to the leaving protonated fluoro-ligand and should lead to retention of configuration. The hydrolysis of *trans*-$[Cr(en)_2F_2]^+$ (en = ethylenediamine) ion in perchloric acid is catalysed by added sodium fluoride, maximum catalysis being effected by only a five-fold excess of fluoride ion over complex-ion concentration. Addition of other salts has no effect on the rate constants, demonstrating that general acid–base catalysis is not involved.

THERE are several reports in the literature [1] concerning the rates of hydrolysis of partially and fully protonated forms of transition-metal complexes. If plots of rate constant against acid concentration are examined, the results may be divided into two classes, *viz.* (*i*) the maximum rate constant reaches a limiting value which is maintained as the acid concentration is increased further and (*ii*) the maximum rate constant is not a limiting value but decreases as the acid concentration is increased further. Examples which we may cite are, for case (*i*) *cis*-$[Co(en)_2(N_3)_2]^+$,[2] $[Co(NH_3)_5(N_3)]^{2+}$,[3] and $[Co(tren)(CO_3)]^+$,[4] and for case (*ii*) $[Co(NH_3)_5(PO_4)]$ [5] and *trans*-$[Co(cyclam)(NO_2)_2]^+$ (en = ethylenediamine, tren = 2,2′,2″-triaminotriethylamine, cyclam = 1,4,8,11-tetra-azacyclotetradecane).[6] There are at least two possible explanations for these observations. In most cases in which a limiting maximum rate constant is observed, the mechanism postulated involves the loss of a neutral molecule, *e.g.* HN_3 from $[Co(NH_3)_5(N_3)]^{2+}$ or CO_2 from $[Co(NH_3)_4(CO_3)]^+$. Conversely, in many cases in which the maximum rate constant is not limiting, the species leaving the transition state is an ion, *e.g.* NO^+ from a nitro-complex, or HPO_4^{2-} from a phosphato-complex. Such an explanation arises if the transition-state theory is applied and it is assumed that the transition state is more like the products than the reactants, *i.e.* for case (*i*) (above) equation (1) would hold and for case (*ii*)

$$k = k_0 a_{\mathrm{EH_2O^{3+}}} a_{\mathrm{HN_3}} / a_{\mathrm{EN_3H^{3+}}} \tag{1}$$

$$k = k_0 a_{\mathrm{EH_2O^{3+}}} a_{\mathrm{NO^+}} / a_{\mathrm{ENO_2H^{3+}}} \tag{2}$$

equation (2), where *e.g.* $E = Co(NH_3)_5$ and a = activity. The activities of ions of the same charge vary in a similar way with concentration and the activity of an uncharged species should change little with concentration.[7] Thus in case (*i*) little change in the activity ratio [equation (1)] with concentration would be expected. However, in case (*ii*) [equation (2)] the activity ratio will vary as that of a singly charged species varies with acid concentration.

A second explanation is that the limiting maximum rate constant is observed when a unimolecular mechanism is operative. As water is not involved in the transition state a change in the activity of water should not affect the observed rate constant. This explanation also requires that a bimolecular mechanism should lead to a non-limiting maximum rate constant. As the activity of water decreases the observed rate constant should decrease. The observations concerning the hydrolysis of acetate complexes are of interest in this context. Dasgupta and Tobe [8] observed a limiting maximum rate constant for the hydrolysis of *cis*- and *trans*-$[Co(en)_2(O_2CMe)_2]^+$ ions. In that investigation the solvents used were of constant ionic strength and hence of approximately constant water activity. However, Deutsch and Taube [9] observed a non-limiting maximum rate constant for the hydrolysis of $[Cr(OH_2)_5(O_2CMe)]^{2+}$ ion. They used solutions without added salts, *i.e.* the ionic strength was not kept constant, hence as the acid concentration increased the activity of water decreased. The possible explanation that the cobalt complex loses acetic acid whilst the chromium complex loses acetylium ion cannot be ruled out without a knowledge of the position of bond fission. Such a possibility may be investigated by studying the hydrolysis of isotopically labelled acetato-complexes. However, such experiments may be inconclusive if a ligand exchanges with the solvent. A study of the hydrolysis of acetato-complexes of cobalt [10] in dilute acidic solutions using oxygen-18 enriched water as solvent proved inconclusive. Although the aquo-product contained oxygen-18 the experiments did not conclusively prove the position of bond fission because the aquo-product exchanges with the solvent under the relevant experimental conditions.

The explanation that a limiting maximum rate constant is observed for unimolecular breakdown of the protonated substrate is suspect. Jolly and co-workers [11] have shown that the ion $[Co(NH_3)_5(NO_2)]^{2+}$ hydrolyses *via* an intramolecular (unimolecular) reaction of the conjugate acid although no maximum rate constant was observed. However, the rate constants for the hydrolyses of $[Co(cyclam)(NO_2)_2]^+$ and $[Co(teta)(NO_2)_2]^+$ (teta = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) show non-limiting maximum rate constants at high acidity.[6] Thus the activity of water in the solution is not the only factor which governs the observed kinetics.

Some of the difficulties in interpretation, discussed above, arise from a difficulty in establishing the exact nature of the entity which leaves the protonated substrate. It was considered to be of interest, therefore, to select for study a ligand which could not split into fragments or moieties as does, say, the nitro-ligand when $[Co(NH_3)_5(NO_2)]^{2+}$ ion is hydrolysed in concentrated sulphuric acid. The obvious choice for such a role is the fluoro-ligand which is (*a*) basic and takes part in acid-catalysed reactions and (*b*) being monoatomic cannot split into fragments. Thus we decided to study the hydrolysis behaviour of partially and fully protonated fluoro-complexes.

RESULTS

When complex ions of the type $[CrA_4F_2]^+$ (where A = NH_3, $\frac{1}{2}$ en, $\frac{1}{2}$ pd *etc.*) (pd = 1,3-diaminopropane) are dissolved in concentrated solutions of strong acids the spectra of the solutions are markedly different from those observed when water is the solvent. The spectrum of a solution of, say, *trans*-$[Cr(en)_2F_2]^+$ ion, in concentrated sulphuric acid reverts to that expected for an aqueous solution if it is diluted, care being taken to keep the solution cool to avoid aquation which would be appreciable at higher temperatures. Ionisation ratios I ($I = [BH^+]/[B]$ where $[BH^+]$ and [B] are the concentrations of protonated and unprotonated complex respectively) may be measured; the results are summarised in Table 1. The ionisation ratios were calculated using spectra which had to be measured as quickly as possible to minimise possible errors arising from the subsequent replacement of a fluoro-ligand. The values given are, therefore, not as precise as usual literature data.

TABLE 1

Ionisation ratio experiments

(*a*) *trans*-$[Cr(NH_3)_4F_2]^+$ ion; H_2SO_4; 25.0 °C

$[H_2SO_4]$/ mol dm^{-3}	$-H_0$	ϵ_{377}	log I_{377}	ϵ_{400}	log I_{400}
15.06	7.94	34.2	1.02	27.0	1.00
14.50	7.62	33.1	0.80	26.3	0.81
14.00	7.30	31.3	0.54	25.4	0.62
13.66	7.11	29.4	0.34	23.5	0.34
13.41	6.96	27.4	0.15	21.8	0.12
13.26	6.88	26.6	0.09	21.1	0.04
12.82	6.62	24.7	−0.06	20.2	−0.06
12.42	6.38	23.1	−0.20	18.9	−0.24
11.74	5.98	23.9	−0.14	18.1	−0.30
10.97	5.49	20.6	−0.44	17.2	−0.42
9.14	4.46	18.2	−0.75	15.4	−0.74

At $\lambda = 377$ nm, $\epsilon_B = 15.0$, $\epsilon_{BH^+} = 36.0$ dm^3 mol^{-1} cm^{-1}
At $\lambda = 400$ nm, $\epsilon_B = 13.0$, $\epsilon_{BH^+} = 28.4$ dm^3 mol^{-1} cm^{-1}

(*b*) *trans*-$[Cr(en)_2F_2]^+$ ion; H_2SO_4; 25.0 °C

$[H_2SO_4]$/ mol dm^{-3}	$-H_0$	ϵ_{375}	log I
14.40	7.55	33.4	0.80
14.00	7.31	32.3	0.65
13.52	7.03	29.3	0.35
13.07	6.76	28.9	0.31
12.26	6.23	28.0	0.24
11.49	5.81	26.8	0.15
10.86	5.42	23.7	−0.08
8.99	4.38	20.6	−0.32

At $\lambda = 375$ nm, $\epsilon_B = 13.0$, $\epsilon_{BH} = 36.6$ dm^3 mol^{-1} cm^{-1}

(*c*) *cis*-$[Cr(bipy)_2F_2]^+$ ion; $HClO_4$; 25.0 °C

$[HClO_4]$/ mol dm^{-3}	$-H_0$	ϵ_{444}	log I
11.06	7.17	78.9	0.48
10.56	6.68	75.5	0.24
10.09	6.25	74.1	0.16
9.58	5.68	73.8	0.14
9.15	5.28	72.1	0.05
8.11	4.35	70.3	−0.06
6.88	3.49	68.1	−0.18

At $\lambda = 444.4$ nm, $\epsilon_B = 56.0$, $\epsilon_{BH^+} = 86.6$ dm^3 mol^{-1} cm^{-1}

TABLE 2

Pseudo-first-order rate constants for the replacement of a fluoro-ligand

(*a*) From *trans*-$[Cr(en)_2F_2]^+$ ion at 10.0 °C in aqueous acid

$[HClO_4]$/ mol dm^{-3}	10^5k/ s^{-1}	$[H_2SO_4]$/ mol dm^{-3}	10^5k/ s^{-1}	$[HNO_3]$/ mol dm^{-3}	10^5k/ s^{-1}
6.11	0.64	4.06	1.0	3.12	0.50
7.00	1.3	6.10	1.8	4.15	0.80
7.54	1.6	7.35	1.9	4.44 [a]	0.90
8.23	2.1	8.09	2.0	5.00	1.1
9.25	3.3	9.13	3.2	5.85	1.4
9.69	4.1	9.71	3.5	5.96 [a]	1.4
10.63	5.5	10.19	5.0	7.02	2.0
10.66	6.4	11.16	5.3	7.97 [a]	3.2
11.07	12	12.14	7.4	8.07	3.2
11.93	18	13.14	13	10.04 [a]	3.4
8.23 [b]	18.5	14.10	17	10.15	3.6
8.23 [c]	64			11.08	3.8
				12.14	4.8
				13.14	5.1
				14.61	5.5

(*b*) From *cis*-$[Cr(bipy)_2F_2]^+$ ion in aqueous perchloric acid at 25.0 °C

$[HClO_4]$/mol dm^{-3}	6.88	8.12	9.15	9.58	10.08	10.56
10^5k/s^{-1}	0.40	0.80	1.8	5.7	6.4	20
$[HClO_4]$/mol dm^{-3}	11.06	11.37	11.86	12.18		
10^5k/s^{-1}	33	51	96	120		

[a] Indicates run followed by titrimetric estimation of fluoride ion; other runs studied spectrophotometrically. [b] Run at 20.0 °C. [c] Run at 30.0 °C. $E = 24.0$ kcal mol^{-1} (1 cal = 4.184 J) and $\log A = 15.4$ where $\log k = \log A - [(E/R)(1/T)]$.

When a solution of a *trans*-$[Cr(en)_2F_2]^+$ salt in an aqueous solution of a strong acid is allowed to stand one of the fluoro-groups is replaced slowly according to the overall equation (3).

$$trans\text{-}[Cr(en)_2F_2]^+ + H_3O^+ \longrightarrow [Cr(en)_2F{\cdot}H_2O]^{2+} + HF \quad (3)$$

Replacement of the second fluoro-group appears to be very slow indeed. The corresponding aquofluoro-complex may be isolated in good yield in a very pure state at the end of such a reaction. The results are summarised in Table 2.

In a separate study it was shown that aquobis(ethylenediamine)fluorochromium(III) ion was not anated by an excess of fluoride ion in 6.0—8.0 mol dm^{-3} perchloric acid. It should be mentioned that the aquofluoro-complex is anated if it is dissolved in 46% hydrofluoric acid.[12] However, the excess of fluoride used in this study was not of this order of magnitude. Thus we conclude that there was no contribution from the reverse reaction during the aquation of the difluoro-species. A careful examination of the pseudo-first-order plots for the aquation of *trans*-$[Cr(en)_2F_2]^+$ ion reveals that at later reaction times the reaction is proceeding slightly faster than in the earlier stages. This suggested that one of the products was acting as a catalyst. Runs performed using solutions containing sodium fluoride, added before the start of the experiment, confirm this observation. When sodium fluoride is added to the run solutions, the observed first-order rate constant increases. However, a ten-fold excess of fluoride ion, over complex-ion concentration, effects no more catalysis than a five-fold excess. The possibility of general acid–base catalysis had to be considered. Thus, some sodium salts which, on the basis of the Bronsted theory of general acid–base catalysis, were expected to behave as equal or better catalysts than fluoride ion, were chosen and added to run solutions. The results are summarised in Table 3. Added acetate, phosphate, and bisulphate ions effect no catalysis. Thus, the observed catalysis is specific to fluoride ion (or another fluoro-species, *e.g.* HF). Furthermore, when excess of fluoride ion is present the first-order plots give very good straight lines, there is no evidence of the slight increase in rate at later times as mentioned above.

TABLE 3

First-order rate constants for the replacement of a fluoro-group from *trans*-$[Cr(en)_2F_2]^+$ ion in 9.58 mol dm^{-3} perchloric acid at 25.0 °C in the presence of added salts; 10^2[complex] = 1.00 mol dm^{-3}

Added salt, X	10^4k/s^{-1}	[NaX]/[complex]
	3.1	0.00
F	3.7	1.08
F	4.1	2.98
F	5.1	4.78
F	5.1	9.54
HSO_4	3.3	1.04
HSO_4	3.1	5.04
CH_3COO	3.1	10.5
PO_4	3.1	5.25

We endeavoured to prepare a series of tetrakis(alkylamine)difluorochromium(III) salts. However, in our hands the literature method [13] yielded none of the desired products. Linck and co-workers [14] have also reported a similar inability to repeat the required preparations. However, we were able to prepare the ammonia analogues and separate the two isomers. In this study we have prepared salts of the following aquofluoro-species: $[Cr(pd)_2(OH_2)F]^{2+}$, $[Cr(bipy)_2(OH_2)F]^{2+}$, and $[Cr(phen)_2(OH_2)F]^{2+}$ (bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline), by treating the corresponding difluoro-species with concentrated perchloric acid.

Vaughn *et al.*[12] prepared $[Cr(en)_2F{\cdot}H_2O]^{2+}$ salts by adding concentrated aqueous perchloric acid to *trans*-$[Cr(en)_2F_2]^+$ salts. They concluded that the aquofluoro-product had the *trans* configuration, *i.e.* the reaction proceeds with retention of geometrical configuration. The difluoro-complex ions, $[Cr(phen)_2F_2]^+$ and $[Cr(bipy)_2F_2]^+$ have the *cis* configuration. It is probable that the aquofluoro-analogues will also have the *cis* structure. Discussions in the literature [15] concerning interligand interferences between 6 and 6′ protons of bipy ligands and of 2 and 9 protons of phen ligands suggest that the *cis* configuration is always preferred for complex ions of the type $[M(phen)_2X_2]^+$ and $[M(bipy)_2X_2]^+$ (where M = a transition metal). Thus we may conclude that all these preparative reactions proceed with retention of geometrical configuration, *i.e.* for ligands like en or pd *trans* reagent yields *trans* product whilst for complexes of the phen or bipy type a *cis* compound yields a *cis* product.

DISCUSSION

The Zucker–Hammett [16] analysis was applied to the kinetic results. Plots of log (rate constant) against acidity function are linear but have slopes much less than unity; see Table 4. This is not entirely unprecedented as Bunnett [17] has pointed out that similar results are obtained for the acid-catalysed hydrolysis of several esters, *e.g.* ethyl acetate or isopropyl acetate. Plots of log *k* against log [acid] have very high slopes. The Bunnett treatment [17] shows that plots of ($\log k + H_0$) against $\log a_w$ (a_w = activity of water) are curved, hence the slope, ω, cannot be evaluated. However, plots of ($\log k - \log$ [acid]) against $\log a_w$ are linear and the slopes, ω*, are given in Table 4. The ω* values suggest that water participates in the rate-determining step as a proton-transfer agent. Bunnett and Olsen [18] used a parameter ϕ as an indication of the mechanism of acid-catalysed hydrolyses. The parameter ϕ is the slope of a plot of ($\log k + H_0$) against ($H_0 + \log$ [acid]). The values of ϕ for the hydrolyses of the fluoro-complexes of chromium(III) indicate that water is involved in the rate-determining step as a proton-transfer agent.

TABLE 4

Parameters † calculated by various treatments of the kinetic results

Complex	Acid	$\frac{\log k}{-H_0}$	$\frac{\log k}{\log \text{acid}}$	$\frac{\log k}{\log I}$	ω*	ϕ
trans-$[Cr(en)_2F_2]^+$	$HClO_4$	0.22	4.0		−0.50	0.80
trans-$[Cr(en)_2F_2]^+$	H_2SO_4	0.22	curve	0.82	−0.40	0.82
cis-$[Cr(bipy)_2F_2]^+$	$HClO_4$	0.53	12.0		−1.04	0.50
$[Co(NH_3)_5F]^{2+}$	$HClO_4$	0.72	curve		−3.2	0.36

† ω Plots are all curved.

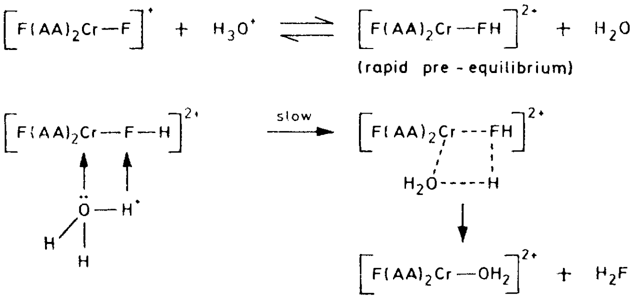
Another treatment, *i.e.* equation (4) as proposed by Yates and McClelland,[19] was applied to our results.

$$\log k + mH_0 = r \log a_w + \text{constant} \qquad (4)$$

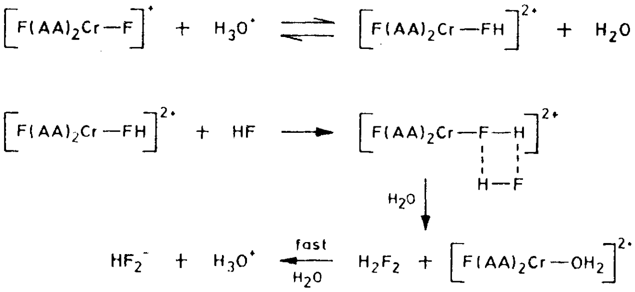
In equation (4) *m* is the slope of a plot of log ($[BH^+]/[B]$) against H_0 for the substrate concerned or a series of structurally similar compounds; *r* is the number of water molecules involved in the transition state. Application of this treatment to our systems gives values of $r = 0.8$ for *cis*-$[Cr(bipy)_2F_2]^+$ in perchloric acid (7—12 mol dm^{-3}) and for *trans*-$[Cr(en)_2F_2]^+$ in sulphuric acid (up to *ca.* 10 mol dm^{-3}). However, in the latter case the value of *r* decreases as the acid concentration is further increased. Thus it is possible that the reaction becomes unimolecular at very high acid concentrations.

The mechanism of the acid-catalysed hydrolysis of these complexes may be summarised as shown (Scheme 1, AA = a symmetrical bidentate ligand). A rapid pre-equilibrium involving the protonation of a fluoro-ligand is followed by the slow attack of a H_3O^+ ion, acting as a proton-transfer agent. The H_3O^+ ion attacks at a position adjacent to the protonated leaving fluoro-ligand and the reaction should therefore lead to retention of geometric configuration. The final step is the rapid loss of the fluoro-ligand probably as H_2F^- which would quickly be converted to the more commonly encountered HF_2^- ion. The attack by H_3O^+ ion adjacent to the leaving fluoro-ligand would lead to the retention of configuration reported by other workers performing preparative studies. Vaughn *et al.*[12] prepared $[Cr(en)_2F{\cdot}H_2O][ClO_4]_2{\cdot}H_2O$ from *trans*-$[Cr(en)_2F_2]Cl$ and concluded that it had the *trans* configuration. The hydrolysis of *cis*-$[Cr(bipy)_2F_2]^+$ ion would be expected to yield the *cis* aquofluoro-analogue since diacidobis(bipyridyl)metal complexes are all thought to have the *cis* configuration, thus minimising strain in the structure.[15] Two hydrogen atoms in the 6-positions, one from each ligand, would sterically hinder each other in such a way as to prevent formation of the *trans* complex.

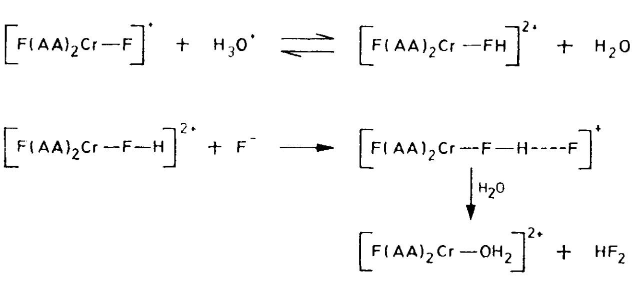
The catalysis by added sodium fluoride may be due to fluoride ion and/or hydrogen fluoride reacting *via* mechanisms summarised in Schemes 2 and 3 respectively.



SCHEME 1



SCHEME 2



SCHEME 3

The very low slopes, n in equation (5), of plots log([BH$^+$]/[B]) against Hammett acidity function, listed in Table 5, call for comment. Previous workers[20] have noted that if a solute possesses a group which is highly solvated by hydrogen bonding then the ratio log (Y_{BH^+}/Y_B), where Y denotes activity coefficient, will vary markedly with concentration. The fluoro-ligand being very electronegative will be highly solvated in this way.

A very low slope may also be observed if protonation is accompanied by another reaction, as, for example, with the $[Fe(phen)_2(CN)_2]^+$ ion.[21] Another point of interest is that it is not easy to decide the pK values of the protonated fluoro-complexes. If equation (5) is applied, the pK_{BH^+} values so evaluated differ by two or three units, *i.e.* the K_{BH^+} values differ by two or three orders of magnitude, from those estimated using equation (6). Equation (5) is a modification of Hammett's

$$H_0 = pK_{BH^+} + -n\log([BH^+]/[B]) \qquad (5)$$

$$\log([BH^+]/[B]) + H_0 = \phi(H_0 + \log H^+) + pK_{BH^+} \qquad (6)$$

classical equation and takes account of the fact that for certain bases, *e.g.* a series of substituted pyridine 1-oxides,[19] the slopes of log ([BH$^+$]/[B]) against H_0 are not unity and may differ from compound to compound. Equation (6) is due to Bunnett and Olsen [22] and has been tested for organic amides,[23] tertiary amines,[24] indoles,[25] and triarylcarbinols.[26] The deduced pK_{BH^+} value was often in good agreement with, but sometimes *ca.* 2 pK units different from, the figures obtained by the more conventional stepwise comparison method. The values quoted in Table 5 show that a similar discrepancy between pK_{BH^+} values, evaluated by the two methods, occurs in this investigation.

TABLE 5

Parameters evaluated from equations (5) and (6)

Complex ion	Acid	n	pK_{BH^+} [a]	pK_{BH^+} [b]
trans-$[Cr(en)_2F_2]^+$	H_2SO_4	0.31	−5.64	−2.3
trans-$[Cr(NH_3)_4F_2]^+$	H_2SO_4	0.48	−6.40	−3.5
cis-$[Cr(bipy)_2F_2]^+$	$HClO_4$	0.16	−4.80	

[a] Evaluated using equation (5). [b] Evaluated using equation (6).

EXPERIMENTAL

Preparations.—*trans*-Difluorotetrakis(pyridine)-chromium(III) nitrate,[13] *trans*-bis(ethylenediamine)difluoro-chromium(III) perchlorate,[12] *trans*-bis(1,3-diaminopropane)-difluorochromium(III) perchlorate, aquobis(ethylenediamine)fluorochromium(III) perchlorate [12] monohydrate, *cis*-difluorobis(1,10-phenanthroline)chromium(III) perchlorate monohydrate,[13] and *cis*-bis(2,2′-bipyridyl)difluorochromium(III) perchlorate [13] were all prepared by literature methods. Criteria used for purity were analyses (see Table 6) and visible absorption spectra.

Aquobis(1,3-*diaminopropane*)*fluorochromium*(III) *perchlorate*. A solution of *trans*-$[Cr(pd)_2F_2][ClO_4]$ (2 g) was dissolved in perchloric acid (72%, 10 cm^3) and the solution was filtered and allowed to stand for 1 h, at room temperature. The solution was then diluted by the dropwise addition of water (3 cm^3) and cooled to 0 °C in an ice-bath. Bright red crystals were filtered off, washed with alcohol and diethyl ether, and dried. Yield 1.4 g (Found: C, 16.8; H, 5.2; F, 4.4; N, 13.3. $C_{12}H_{26}Cl_2CrFN_4O_9$ requires C, 16.5; H, 5.05; F, 4.5; N, 12.8%).

Aquobis(2,2′-*bipyridyl*)*fluorochromium*(III) *perchlorate*—

Table 6

Analytical data

Compound	Analysis (%)							
	Calc.				Found			
	C	H	N	F	C	H	N	F
trans-$[Cr(en)_2F_2][ClO_4]$	15.5	5.2	18.1	12.3	15.8	5.2	18.3	12.3
trans-$[Cr(pd)_2F_2][ClO_4]$	21.4	6.0		11.3	21.4	6.0		11.7
$[Cr(en)_2F(OH_2)][ClO_4]_2 \cdot H_2O$	11.8	5.2	18.1	4.7	11.7	5.2	18.3	4.7
cis-$[Cr(bipy)_2F_2][ClO_4]$	47.8	3.2		7.5	47.4	3.8		7.1
cis-$[Cr(phen)_2F_2][ClO_4] \cdot H_2O$	50.7	3.2		6.6	50.5	3.9		6.2

water(2/5), $[Cr(bipy)_2F(OH_2)][ClO_4]_2 \cdot 2.5H_2O$. The complex *cis*-$[Cr(bipy)_2F_2][ClO_4]$ (1 g) was dissolved in perchloric acid (72%, 5 cm^3) and the filtered solution was allowed to stand for 1 h, at room temperature. The solution was diluted dropwise with water (2 cm^3) and cooled to 0 °C in an ice-bath. Bright orange-red crystals were filtered off, washed with alcohol and diethyl ether, and dried (Found: C, 37.2; H, 3.60; F, 3.05; N, 8.45. $C_{20}H_{23}Cl_2CrFN_4O_{11.5}$ requires C, 37.2; H, 3.60; F, 2.95; N, 8.70%).

Attempts were made to prepare an aquofluorobis(1,10-phenanthroline)chromium(III) complex. Although a solid was isolated analysis was not possible as the compound was explosive under certain conditions.

Visible and Ultraviolet Absorption Spectra.—The spectra were measured using a Unicam SP 500 series 2 spectrophotometer with silica cells.

Ionisation Ratio Measurements.—Solutions of acid were prepared by accurate dilution, by weight, of a stock sample. The acid solutions, in Polythene vessels, were placed in the thermostat bath to attain the required temperature. The weighed samples of complex were then added and dissolved as quickly as possible. The optical density of the solutions, at given wavelengths, was measured using a Unicam SP 500 spectrophotometer with silica cells. The optical density measurements were always performed as soon as possible after solution of the complex to avoid errors due to the aquation process.

Kinetic Measurements.—All runs were performed using polyethylene vessels and apparatus. Acid solutions were prepared by diluting, by weight, stock solutions of standard acid. The vessels containing run acids were placed in a thermostat to attain the required temperature. The weighed complex was added on a Polythene boat and the mixture was shaken to effect rapid solution. Aliquot samples were removed at timed intervals [*] and run into Polythene tubes placed in an acetone–solid carbon dioxide bath. The samples were carefully diluted whilst still in the cold bath. Later the samples were allowed to warm up to melting point and the solutions were analysed by one of the following methods.

(*i*) *Spectrophotometric method.* The solutions were diluted to a standard volume and the optical density, at appropriate wavelengths, was measured using a Unicam SP 500 spectrophotometer with silica cells.

(*ii*) *Estimation of fluoride ion.* Sodium acetate solution was added until the pH of the solution was in the range 3.8—5.0. The solution was diluted to a given volume with ethanol and the fluoride ions were titrated potentiometrically using a lanthanum crystal specific-ion electrode and a calomel electrode. In a preliminary study it had been shown that (*a*) sulphate ions interfered with the estimation of fluoride ion, (*b*) addition of ethanol enhances the sensitivity of the specific-ion electrode used, and (*c*) fluoro-complexes do not interfere with the estimation of uncomplexed fluoride ion.

The two analytical methods gave concordant results. (The titrimetric method could not be used for sulphuric acid solutions for reasons given above.)

Runs with added salts. Accurately weighed samples of the salts were added to the run acids and the vessels were shaken to effect solution. The vessels were placed in the thermostat bath and runs performed as described above.

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[*] For kinetic runs at 10.0 °C the aliquots were removed with a jacketted pipette to prevent the samples warming to room temperature.

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