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Acid Hydrolysis of *trans*-Difluoro-, *trans*-Fluorochloro-, and *trans*-Fluorobromobis(trimethylenediamine)chromium(III) and *trans*-Difluoro- and *trans*-Fluorochlorobis(ethylenediamine)chromium(III) Cations[1]

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Received June 20, 1973

The products of the acid hydrolysis reactions of *trans*-$\mathrm{Cr(tmd)_2FX^+}$ ($\mathrm{X = F, Cl, Br}$) and *trans*-$\mathrm{Cr(en)_2FY^+}$ ($\mathrm{Y = F, Cl}$) are characterized by ion-exchange separations, analytical Cr:N ratios and halide release, and visible absorption spectra. The primary halide replacements in *trans*-$\mathrm{Cr(tmd)_2FX^+}$ give a single product, *trans*-$\mathrm{Cr(tmd)_2FOH_2{}^{2+}}$, and are free of side reactions. The rate of fluoride release is acid catalyzed and is first order in $[\mathrm{H^+}]$ up to 2.0 M $\mathrm{H^+}$. The value of the second-order rate constant ($50°$, $\mu = 2.0\ M$) is $2.6 \times 10^{-4}\ M^{-1}\ \mathrm{sec}^{-1}$; $\Delta H^* = 26$ kcal mol^{-1} and $\Delta S^* = +6$ cal deg^{-1} mol^{-1}. The rates of chloride and bromide replacement are first order in Cr(III) and are not acid catalyzed; rate constants at $50°$ (μ, M; ΔH^*, kcal mol^{-1}; ΔS^*, cal deg^{-1} mol^{-1}) are 1.3×10^{-3} sec^{-1} (2.0; 18; -14) and 1.1×10^{-2} sec^{-1} (1.0; 16; -17), respectively. At long times compared to the primary hydrolysis, reactions of *trans*-$\mathrm{Cr(tmd)_2FX^+}$ produce *cis*-$\mathrm{Cr(tmd)_2FOH_2{}^{2+}}$ and blue $\mathrm{Cr(tmd)(OH_2)_3F^{2+}}$, and estimates of rate constants for these processes are given. The hydrolysis of *trans*-$\mathrm{Cr(en)_2FY^+}$ is more complicated, and the nature of the products as well as their relative amounts depends upon the $[\mathrm{H^+}]$. It is found that Cr–N bond rupture competes favorably with halide replacement, and complexes containing the monodentate $\mathrm{enH^+}$ ligand are found among the reaction products. The rates of fluoride release from *trans*-$\mathrm{Cr(en)_2F_2{}^+}$ and two characterized intermediate hydrolysis products, *trans*-$\mathrm{Cr(en)(enH)(OH_2)F_2{}^{2+}}$ and *trans*-$\mathrm{Cr(en)(OH_2)_2F_2{}^+}$, are dependent upon $[\mathrm{H^+}]$, but a strict first-order dependence was not established. Chloride release from *trans*-$\mathrm{Cr(en)_2FCl^+}$ is not acid catalyzed. A comprehensive reaction scheme for the reactions of *trans*-$\mathrm{Cr(en)_2FY^+}$ in acid solution at $50°$ is presented, and rate constants for the formation of all detected intermediate reaction products are given. The relative reactivity of halide hydrolysis between corresponding tmd and en complexes is nearly the same, but the en complexes are considerably more susceptible to Cr–N bond rupture.

Introduction

Although the preparative chemistry of a number of bis(diamine) complexes of chromium(III) which contain the small, highly basic fluoro ligand is well characterized,[3] there remains a paucity of information on the kinetic and mechanistic behavior of these complexes in acid solution. Fehrmann and Garner[4] studied the rate of fluoride release from *cis*-$\mathrm{Cr(en)_2F_2{}^+}$ and found the reaction acid catalyzed. Acid catalysis of fluoride release is known to be a characteristic of related complexes of Co(III).[5] However, recently Pyke and Linck[6] studied the acid hydrolysis of the *trans*-$\mathrm{Cr(en)_2F_2{}^+}$ in perchloric acid solution up to 0.5 M in $\mathrm{H^+}$ but found no evidence for acid catalysis of fluoride release. These workers did observe Cr–N bond cleavage and presented evidence for a partly unwrapped, protonated $\mathrm{enH^+}$ ligand. They also postulated reclosure of this opened ring along with change of stereochemical configuration.

In an effort more fully to elucidate the acid hydrolysis of the fluoro ligand and acid hydrolysis of other halides in fluorohalobis(diamine)chromium(III) complexes and to establish a basis for discussion of mechanism, the reactions of the *trans*-$\mathrm{Cr(tmd)_2FX^+}$ ($\mathrm{X = F, Cl, Br}$) and *trans*-$\mathrm{Cr(en)_2FY^+}$ ($\mathrm{Y = F, Cl}$) with varying concentrations of $\mathrm{H^+}$ have been studied in detail. The complexes selected for this study are all characterized by a trans arrangement of the acido ligands, and both five- and six-membered chelate rings are represented. Thus in addition to investigating the relative rates of hydrolysis of a series of related halo complexes, it should also be possible to study the influence of chelate ring size on halide hydrolysis reactivity. A recent report[7] that chelate ring size has little effect on hydrolysis reactivity of chloride and bromide in *trans*-$\mathrm{Cr(AA)_2X_2{}^+}$ ($\mathrm{X = Cl}$ or Br; AA = en or tmd) has been confirmed for the halide hydrolysis of the fluorohalo complexes of the present investigation.

Experimental Section

Preparation of Compounds. For the most part published procedures were used to prepare the chromium complexes used in this study. The *trans*-$\mathrm{[Cr(en)_2F_2]ClO_4}$ and *trans*-$\mathrm{[Cr(tmd)_2F_2]ClO_4}$ salts were prepared from chloride salts[3a] by treatment of an aqueous solution of the complex with a concentrated aqueous solution of sodium perchlorate. The precipitated perchlorate salts were collected, washed three times with 5-ml portions of ice water and 30 ml of acetone, and air-dried. The final products were dried at 85° for 4 hr prior to analysis. The *trans*-$\mathrm{[Cr(en)_2FOH_2](ClO_4)_2}$ and *trans*-$\mathrm{[Cr(tmd)_2FOH_2](ClO_4)_2}$ salts were prepared by treatment of the difluoro complex with perchloric acid according to the literature method.[3a] Preparations for *trans*-$\mathrm{[Cr(tmd)_2FX]ClO_4}$ ($\mathrm{X = Cl, Br}$) and *trans*-$\mathrm{[Cr(en)_2FCl]ClO_4}$ were taken from the literature,[3b,c] as was that for *cis*-$\mathrm{[Cr(en)_2FCl]Cl}$[3a] and $\mathrm{[Cr(en)_3]Br_3 \cdot H_2O}$.[8] Elemental analyses of these compounds are collected in Table I, while visible absorption spectra are included in Table II (see below).

Ion Exchange. All columns were prepared in the following fashion unless otherwise noted. A 50-g sample of Baker ion-exchange resin (CGC-240, 100–200 mesh, strong acid, sulfonated polystyrene, 8% cross-linked, $\mathrm{Na^+}$ form) was washed four times with 100-ml portions of water. The resin was suspended in 200 ml of water, and to this well-stirred solution was added 3 ml of 50% w/v sodium hydroxide and 3 ml of 30% hydrogen peroxide. The suspension was heated at 75° for 1 hr, the liquid decanted, and the process repeated two more times. The cleaned resin was poured into an ion-exchange column (50 cm × 1 cm) and allowed to pack by gravity to a height of 15 cm. The resin was converted to the $\mathrm{H^+}$ form by passing 300 ml of 6 M sulfuric acid through the column. Excess acid was removed by elution of the column with water. The elution with water was continued until treatment of the eluate with 1 drop of 0.1 M $\mathrm{Ba^{2+}}$ indicated the absence of excess $\mathrm{SO_4{}^{2-}}$ ion. The column was placed in a

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(1) Abbreviations used: trimethylenediamine, tmd; ethylenediamine, en.

(2) Abstracted in part from the Ph.D. dissertation of J. M. DeJovine, Northern Illinois University, Aug 1973.

(3) (a) J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnuson, *Inorg. Chem.*, 7, 736 (1968); (b) J. W. Vaughn, *Inorg. Nucl. Chem. Lett.*, 4, 183 (1968); (c) J. W. Vaughn, J. M. DeJovine, and G. J. Seiler, *Inorg. Chem.*, 9, 684 (1970); (d) J. W. Vaughn and B. J. Krainc, *ibid.*, 4, 1077 (1965); and references cited in these papers.

(4) K. R. A. Fehrmann and C. S. Garner, *J. Amer. Chem. Soc.*, **83**, 1276 (1961).

(5) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Amer. Chem. Soc.*, 78, 4883 (1956).

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(7) M. C. Couldwell and D. A. House, *Inorg. Chem.*, **11**, 2025 (1972).

(8) H. L. Schalfer and A. Kling, *Z. Anorg. Allg. Chem.*, 302, 1 (1959).

Table I. Elemental Analyses of Chromium Compounds

	% Cr		% C		% H		% N	
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
trans-[Cr(en)$_2$F$_2$]ClO$_4$	16.8	16.5	15.5	15.4	5.2	5.1	18.1	18.5
trans-[Cr(tmd)$_2$F$_2$]ClO$_4$	15.4	15.3	21.3	21.2	5.9	6.0	16.6	16.6
trans-[Cr(en)$_2$FOH$_2$](ClO$_4$)$_2$			11.8	11.6	4.4	4.4	13.7	13.8
trans-[Cr(tmd)$_2$FOH$_2$](ClO$_2$)$_2$	11.9	12.0	16.5	16.3	5.0	4.8	12.8	12.8
trans-[Cr(en)$_2$FCl]ClO$_4$			14.7	15.0	4.9	5.0	16.8	16.8
trans-[Cr(tmd)$_2$FCl]ClO$_4$	14.7	14.6	20.4	20.4	5.7	6.1	15.8	15.3
trans-[Cr(tmd)$_2$FBr]ClO$_4$	13.1	13.0	18.1	18.4	5.0	5.3	14.1	14.0
cis-[Cr(en)$_2$FCl]Cl			18.3	18.2	6.1	6.1	21.4	21.6
[Cr(en)$_3$]Br$_3$·H$_2$O					5.3	5.9	17.1	17.0

Table II. Visible Absorption Maxima and Molar Absorptivities of Some Difluoro-, Fluoroacido-, Fluoroaquo-, and Aquochromium(III) Complexes Containing Ethylenediamine and Trimethylenediamine

Cation	Medium, T°C	$\lambda_{\max}$ (ϵ), nm (l. mol^{-1} cm^{-1})			
trans-Cr(en)$_2$F$_2^{+}$	H$_2$O, 25	532 (19.0)	468 (23.0)	405 (16.3)	350 (18.0)
trans-Cr(en)$_2$F$_2^{+}$ [a]	H$_2$O, 25	532 (19.0)	466 (24.3)	400 (16.0)	350 (18.0)
trans-Cr(en)$_2$OH$_2$F^{2+}	H$_2$O, 25	519 (22.5)	458 (24.0)	368 (29.6)	
trans-Cr(en)$_2$OH$_2$F^{2+} [a]	H$_2$O, 25	519 (24.2)	454 (25.6)	371 (31.2)	
trans-Cr(en)(enH)(OH$_2$)$_2$F^{3+}	1.5 M H$_2$SO$_4$, 4	515 (45.8)	380 (28.5)		
trans-Cr(en)(enH)(OH$_2$)$_2$F^{3+} [b]	2.0–2.5 M HCl	512 (47.3)	378 (29.4)		
trans-Cr(en)(enH)(OH$_2$)F$_2^{2+}$	0.75 M H$_2$SO$_4$, 4	518 (40.6)	410 sh (10.0)	366 (18.1)	
trans-Cr(en)(enH)(OH$_2$)F$_2^{2+}$ [b,c]	0.4–0.7 M HClO$_4$	519 (40.0)	410 sh (10.0)	365 (18.6)	
trans-Cr(en)(OH$_2$)$_2$F$_2^{+}$	0.15 M H$_2$SO$_4$, 4	545 (36.2)	410 sh (10.0)	382 (12.1)	
trans-Cr(en)(OH$_2$)$_2$F$_2^{+}$ [b]		543 (37.0)	410 sh (10.1)	371 (12.5)	
blue-Cr(en)(OH$_2$)$_3$F^{2+}	0.75 M H$_2$SO$_4$, 4	533 (39.7)	390 (20.3)		
cis-Cr(en)$_2$OH$_2$F^{2+}	1.50 M H$_2$SO$_4$, 4	507 (70.2)	376 (35.1)		
cis-Cr(en)$_2$OH$_2$F^{2+} [a]	0.10 M HClO$_4$, 25	506	378		
trans-Cr(en)$_2$FCl^{+}	H$_2$O, 25	553 (18.7)	459 (20.6)	381 (25.8)	
trans-Cr(en)$_2$FCl^{+} [d]	H$_2$O, 25	553 (19.8)	460 (21.5)	381 (27.4)	
trans-Cr(tmd)$_2$F$_2^{+}$	H$_2$O, 25	542 (16.5)	462 (20.9)	397 (16.8)	360 (16.4)
trans-Cr(tmd)$_2$F$_2^{+}$ [e]	H$_2$O, 25	542	464	394	360
trans-Cr(tmd)$_2$FCl^{+}	H$_2$O, 25	564 (19.6)	461 (20.0)	386 (31.8)	
trans-Cr(tmd)$_2$FCl^{+} [e]	H$_2$O, 25	564	460	386	
trans-Cr(tmd)$_2$FBr^{+}	H$_2$O, 25	578 (22.4)	465 (20.1)	390 (34.9)	
trans-Cr(tmd)$_2$FBr^{+} [e]	H$_2$O, 25	575	467	387	
trans-Cr(tmd)$_2$OH$_2$F^{2+}	H$_2$O, 25	533 (20.9)	460 (22.4)	375 (37.8)	
trans-Cr(tmd)$_2$OH$_2$F^{2+} [e]	H$_2$O, 25	534	460	375	
cis-Cr(tmd)$_2$OH$_2$F^{2+}	1.5 M H$_2$SO$_4$, 4	511 (27.0)	376 (30.8)		
blue-Cr(tmd)(OH$_2$)$_3$F^{2+}	0.15 M H$_2$SO$_4$, 4	535 (41.5)	390 (33.2)		
cis-Cr(tmd)$_2$(OH$_2$)$_2^{3+}$	3.0 M H$_2$SO$_4$	489 (30.1)	368 (36.2)		
cis-Cr(tmd)$_2$(OH$_2$)$_2^{3+}$ [f]	0.6–1.5 M HNO$_3$, 20–23°	488 (29.8)	370 (37.8)		

[a] Reference 3a. [b] Reference 6. [c] This ion was reported as *cis*-Cr(en)$_2$FOH$_2^{2+}$ in ref 6. [d] Reference 3c. [e] Reference 3b. [f] Reference 7.

refrigerated cabinet (Puffer-Hubbard Uni-therm) at near 4° where all exchanges took place.

To determine the elution characteristics of the ion-exchange columns employed, the following method was utilized. Three different complexes were selected to typify cations of 1+, 2+, and 3+ charge type. These were *trans*-[Cr(en)$_2$F$_2$]ClO$_4$, *trans*-[Cr(en)$_2$FOH$_2$](ClO$_4$)$_2$, and [Cr(en)$_3$]Br$_3$. Approximately 0.4 mmol of one of the solid salts was dissolved in 200 ml of ice water and the solution was charged onto the ion-exchange resin. The column was eluted successively with 200-ml volumes of 0.15, 0.30, 0.75, 1.0, 1.5, 2.0, 2.5, and 3.0 M sulfuric acid. The elution rate was 2.25 ml/min, and approximately 7-ml fractions were collected by a Gilson Model MF Mini-Escargot Automatic Fraction Collector. The collected fractions were combined in a 2:1 ratio and chromium was determined for each combined fraction. In all cases the chromium recovery was 95 ± 5%. Plots of percentage of total chromium *vs.* tube number were utilized to establish the elution characteristics of a particular cation.

Analytical Methods. Chromium was determined by first oxidizing the Cr(III) to CrO$_4^{2-}$ with hydrogen peroxide in sodium hydroxide solution. The solutions were heated at near 90° for 2 hr to complete the oxidation and to destroy the excess peroxide. The solutions were cooled and diluted to volume, and the absorbance was measured at 372 nm. The chromium concentration was calculated using 4820 M^{-1} cm^{-1} for the molar absorptivity of CrO$_4^{2-}$ at 372 nm. Nitrogen was determined in two ways. In those cases where solid samples of the complexes were available, nitrogen was determined by use of a Perkin-Elmer 240 Elemental Analyzer. To determine Cr:N ratios in the eluate from an ion-exchange column, use was made of a micro Kjeldahl method similar to that described by Dixon.[9] An aliquot of the eluate from the ion exchange column which was thought to contain 1–5 mg of nitrogen was placed in a 100-ml Kjeldahl flask. The solution was diluted with 25 ml of water; 1.5 g of a catalyst (15:1 K$_2$SO$_4$–HgO) was added along with 2 Hengar granules and 4 ml of concentrated sulfuric acid. The reaction mixture was digested on a gas-heated digestion rack for 30 min after the solution turned yellow. The yellow solution was made basic with concentrated sodium hydroxide and the ammonia distilled over into 10 ml of a saturated boric acid solution which contained 6 drops of a screened indicator. The distillate was titrated with 0.01 M hydrochloric acid to the pink end point. Blanks were carried out in all cases as parallel determinations. By determination of both Cr and N in aliquots of the same eluted fraction it was possible to determine Cr:N ratios. Uncomplexed fluoride was determined by means of an Orion Ionalyzer Fluoride Electrode, Model 94-09, coupled to a Radiometer Model 26 pH meter. The sample to be analyzed was dissolved in water and diluted to a known volume. A 5-ml aliquot which contained 10–100 ppm of fluoride was taken and diluted with 10 ml of water, and 50% w/v sodium hydroxide was added until the solution became basic. The basic solution was heated at 80° for 15 min to decompose the complex. The solution of the decomposed complex was acidified by the dropwise addition of 2 M perchloric acid and quantitatively transferred to a 100-ml volumetric flask which contained 50 ml of 1.0 M sodium acetate. The solution was diluted to volume and the electrode potential measured by use of the fluoride specific ion electrode *vs.* a saturated colomel electrode. The potential reading was converted to ppm of F$^-$ by use of a standard curve of ppm of F$^-$ *vs.* mV. The standard solutions were prepared from Orion fluoride standards in 0.5 M sodium acetate. Carbon was determined by use of a Perkin-Elmer 240 Elemental Analyzer.

Characterization of Solution Species and Intermediate Hydrolysis Products. The following ions were not isolated as solid compounds

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[9] J. P. Dixon, "Modern Methods in Organic Microanalysis," Van Nostrand, Princeton, N. J., 1968, p 66.

but were characterized in solution by elution characteristics, analytical Cr:N ratios, and visible absorption spectra.

***cis*-Cr(en)$_2$(OH$_2$)F^{2+}.** Aqueous solutions of this cation were obtained by two different synthetic routes. A solution of 0.13 g (0.5 mmol) of *cis*-[Cr(en)$_2$FCl]Cl in 10 ml of water was treated with 0.21 g (1.0 mmol) of silver perchlorate. The resulting solution was allowed to aquate in the dark at room temperature for 90 min, the silver chloride was removed by filtration, and the blue-red filtrate was charged onto a cation-exchange column. A blue-red fraction was eluted from the column by the first 50 ml of the 1.5 *M* sulfuric acid. Elution with 1.5 *M* sulfuric acid is indicative of a cation of charge 2+. A second route to aqueous solutions of this ion was based on the earlier work of Fehrmann and Garner.[4] A solution of *cis*-Cr(en)$_2$F$_2^+$ in 0.5 *M* perchloric acid was allowed to aquate in the dark for 2 hr at 50°. The solution was chromatographed as described for the first method of preparation. The results were the same as those found for reaction of the *cis*-chlorofluoro complex with silver ion.

***cis*-Cr(tmd)$_2$(OH$_2$)F^{2+}.** A solution of 0.175 g (0.5 mmol) of *trans*-[Cr(tmd)$_2$(OH$_2$)F](ClO$_4$)$_2$ in 50 ml of 1.0 *M* perchloric acid was allowed to aquate in the dark for 3 days at 50°. At the end of 3 days the solution was diluted with 300 ml of water and charged onto the cation-exchange column described previously. The column was eluted as previously described. The 1.5 *M* sulfuric acid eluted a rose-colored fraction. The eluate had a Cr:N ratio of 1:3.8 (see the analytical section for how this ratio was determined). Measurement of fluoride ion release during the synthesis indicated less than 10% loss of coordinated fluoride from the starting material.

Blue Cr(tmd)(OH$_2$)$_3$F^{2+} and *cis*-Cr(tmd)$_2$(OH$_2$)$_2$$^{3+}$. A solution of 0.175 g (0.5 mmol) of *trans*-[Cr(tmd)$_2$(OH$_2$)F](ClO$_4$)$_2$ in 50 ml of 1.0 *M* perchloric acid was allowed to aquate for 6 days at 50° in the dark. The solution was diluted with 300 ml of water and charged onto the previously described ion-exchange column. The column was eluted as described previously. The 0.75 *M* sulfuric acid eluted a blue-purple fraction from the column. The electronic spectrum consisted of two bands in the visible region and the solution was characterized by a Cr:N ratio of 1:1.89. This fraction represented about 64% of the available chromium.

No other fractions were eluted from the column until the acid concentration reached 2.5 *M*. The 2.5 *M* acid eluted an orange solution of *cis*-Cr(tmd)$_2$(OH$_2$)$_2$$^{3+}$ with a Cr:N ratio of 1:4.12 from the column.

***trans*-Cr(en)(enH)(OH$_2$)F$_2$$^{2+}$.** This ion was prepared and characterized in solution as described by Pyke and Linck.[6]

***trans*-Cr(en)(enH)(OH$_2$)$_2$F^{3+}.** This ion can be obtained in solution by two different routes. A solution of 0.1 g (0.38 mmol) of *trans*-[Cr(en)$_2$F$_2$] in 50 ml of 0.15 *M* perchloric acid was allowed to aquate in the dark for 6 hr at 50°. At the end of 6 hr the solution was diluted with 250 ml of ice water and the solution charged onto the ion-exchange column. The column was eluted as previously described. The 1.5 *M* sulfuric acid eluted *trans*-Cr(en)(enH)(OH$_2$)$_2$F^{3+} from the column. An alternate route to this ion starts with *trans*-[Cr(en)$_2$(OH$_2$)F]ClO$_4$. A solution of the perchlorate salt was allowed to aquate in 2.0 *M* perchloric acid for 2 hr at 50°. The solution was ion exchanged as described previously and *trans*-Cr(en)(enH)(OH$_2$)$_2$F^{3+} was obtained in a 90% yield. The Cr:N ratio of this solution was 1:3.7, and the aquation took place with less than 10% fluoride ion release from the starting material.

***trans*-Cr(en)(OH$_2$)$_2$F$_2$$^+$.** This ion was also obtained by a method similar to that of Pyke and Linck.[6] A 0.13-g (0.4-mmol) sample of *trans*-[Cr(en)$_2$F$_2$]ClO$_4$ was dissolved in 50 ml of 0.15 *M* perchloric acid. The solution was allowed to aquate in the dark for 6 hr at 50°. The reaction mixture was quenched with 250 ml of ice water and the diluted solution charged onto the ion exchange column. The column was eluted with 50 ml of 0.15 *M* sulfuric acid and the blue-purple eluate collected. The elution characteristics and the electronic spectrum of the ion agree well with the literature values.[6] This species *trans*-Cr(en)(OH$_2$)$_2$F$_2$$^+$ represented 50% of the total chromium available in the reaction mixture and negligible fluoride ion release took place during the acid hydrolysis.

Blue Cr(en)(OH$_2$)$_3$F^{2+}. The solution of *trans*-Cr(en)(OH$_2$)$_2$F$_2$$^+$ collected from the ion-exchange column was diluted to 100 ml with 0.15 *M* sulfuric acid and allowed to aquate in the dark at 50° for 3 hr. The solution was quenched and ion exchanged as described previously, the 0.75 *M* sulfuric acid fraction eluted blue Cr(en)(OH$_2$)$_3$F^{2+} from the column. This fraction had a Cr:N ratio of 1:2.05 and accounted for 80% of the available chromium. Fluoride ion loss from the starting material accounted for 58% of the available fluorine.

Kinetics. Rate data were collected by three methods depending upon the reaction to be studied: (1) ion-exchange techniques, (2) spectrophotometry, and (3) halide release measurements. In monitoring a reaction by ion exchange, aliquots were withdrawn from a reaction mixture at time intervals, quenched with ice water, and charged onto a refrigerated column. The reactant and product(s) were then separated and the relative amounts of each were determined. In this manner both loss of reactant and increase in product(s) could be determined simultaneously and independently. Spectrophotometric methods have been described previously.[10] Both scan and fixed-wavelength techniques were employed using a Cary 14 spectrophotometer. Isosbestic points determined experimentally were obtained by scanning a portion of the spectrum at time intervals. Halide release measurements were employed for fluoride and chloride. To determine uncomplexed fluoride, a reaction aliquot (5 ml containing 10–100 ppm of F$^-$) was pipetted into 25 ml of ice-cold 1.0 *M* sodium acetate in a 50-ml volumetric flask and diluted to volume with ice water. The electrode potential of the fluoride ion selective electrode was determined and the F$^-$ concentration was obtained from standard curves. For chloride release measurements an Orion chloride ion selective electrode (No. 94-174) and a Corning Model 112 digital pH meter were used in conjunction with a ceramic junction calomel electrode (Corning No. 476109). Working curves were established with standard potassium chloride solutions. In all cases measurement of the [Cl$^-$] was made at ice-bath temperature.

Rate constants for all reactions studied were evaluated by a computer fit to concentration or absorbance *vs.* time data by a procedure described previously.[10] Good first-order (pseudo-first-order) kinetics were obtained in all cases; the standard deviations in calculated values of k_{obsd} were 1–2% in almost all cases. Kinetic experiments could generally be reproduced to within ±5%, and the values of k_{obsd} reported in this paper in almost all cases represent averages of several independent experiments.

Results

Visible absorption spectra for the complexes prepared and the cations isolated in this study are given in Table II, along with some data reported in the literature. It should be noted that the stereochemical assignments for *trans*-Cr(en)(enH)(OH$_2$)$_2$F^{3+}, *trans*-Cr(en)(enH)(OH$_2$)F$_2$$^{2+}$, *trans*-Cr(en)(OH$_2$)$_2F_2$$^+$, and *cis*-Cr(tmd)$_2$(OH$_2$)F^{2+} should be considered tentative since their structures are unproven. However, we feel that these assignments represent the most plausible structures based on our observations.

Hydrolysis of *trans*-Cr(tmd)$_2$FX$^+$. Both spectrophotometric and ion-exchange chromatographic studies show that the primary acid hydrolysis reactions of *trans*-Cr(tmd)$_2$F$_2$$^+$ and *trans*-Cr(tmd)$_2$FX$^+$ (X = Cl, Br) produce a single product, *trans*-Cr(tmd)$_2$FOH$_2$$^{2+}$, eq 1 and 2. The reactions

$$\textit{trans}\text{-Cr(tmd)}_2\text{F}_2^+ + \text{H}_3\text{O}^+ \rightarrow \textit{trans}\text{-Cr(tmd)}_2\text{FOH}_2^{2+} + \text{HF} \qquad (1)$$

$$\textit{trans}\text{-Cr(tmd)}_2\text{FX}^+ + \text{H}_2\text{O} \rightarrow \textit{trans}\text{-Cr(tmd)}_2\text{FOH}_2^{2+} + \text{X}^- \quad (\text{X} = \text{Cl, Br}) \qquad (2)$$

are essentially complete and free of side reactions under the conditions of the study. The fluoroaquo product was identified by both spectral and chromatographic comparison with an authentic sample. Spectrophotometric study of reactions 2 both showed three isosbestic points (at 533, 432, and 387 nm for *trans*-Cr(tmd)$_2$FBr$^+$ and 552, 420, and 400 nm for *trans*-Cr(tmd)$_2$FCl$^+$) within experimental error of those expected from comparison of reactant and product spectra. Reaction 1 did not show isosbestic points, nor were they expected in the wavelength range investigated. However, fluoride ion release studies showed that 1 equiv of fluoride was evolved during the course of the reaction.

Rate data collected for reactions 1 and 2 are presented in Table III. The data for reaction 1 show a first-order dependence on H$^+$, and thus the reaction is second-order overall. Second-order rate constants determined from $k_{\text{obsd}}/[\text{H}^+]$ are included in Table III. The data for reactions 2 indicate they

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(10) W. R. Mason, *Inorg. Chem.*, **9**, 1528 (1970).

Table III. Rate Data for the Acid Hydrolysis of *trans*-$Cr(tmd)_2FX^+$

$[H^+]$, M	$10^4 \times k_{obsd}$ sec^{-1}	$10^4 \times k_2$, M^{-1} sec^{-1}	$[H^+]$, M	$10^4 \times k_{obsd}$, sec^{-1}	$10^4 \times k_2$, M^{-1} sec^{-1}
trans-$Cr(tmd)_2F_2^+ + H_3O^+ \rightarrow$ *trans*-$Cr(tmd)_2FOH_2^{2+} + HF$					
50°[a]			35°[a]		
0.51	1.40	2.7	1.02	0.39	0.38
1.02	2.65	2.6	2.00	0.80	0.40
1.53	3.78	2.5	65°[a]		
2.01	5.05	2.5			
1.53[b]	4.20	2.7	0.51	9.4	18.4
1.53[c]	3.92	2.6	1.02	17.9	17.5
0.51[d]	0.86	1.7			
2.04[e]	4.61	2.4			
0.49[e]	1.39	2.8			

$[H^+]$, M	$10^3 k_{obsd}$, sec^{-1}	$[H^+]$, M	$10^3 k_{obsd}$, sec^{-1}
trans-$Cr(tmd)_2FCl^+ + H_2O \rightarrow$ *trans*-$Cr(tmd)_2FOH_2^{2+} + Cl^-$			
50°[a]		40°[a]	
0	1.35	2.00	3.96
0.50	1.39	45°[a]	
1.00	1.28		
1.50	1.33	2.00	6.6
2.00	1.30		
0.50[d]	1.68	60°[a]	
0.50[f]	1.51	2.00	27.0
0.50[g]	1.43		
0[h]	1.14		
2.00[i]	1.27		
trans-$Cr(tmd)_2FBr^+ + H_2O \rightarrow$ *trans*-$Cr(tmd)_2OH_2F^{2+} + Br^-$			
25°[a,f]		30°[a,f]	
0	1.21	0.10	1.96
0.10	1.20	35°[a,f]	
0.50	1.18		
1.00	1.16	0.10	3.40
0[j]	1.34	40°[a,f]	
		0.10	4.8

[a] $[Cr(III)] = 0.017$–$0.040\ M$, $\mu = 2.0\ M$ ($NaClO_4$). [b] $[Cr(III)] = 0.059\ M$. [c] $[Cr(III)] = 0.044\ M$. [d] $\mu = 0.51\ M$ ($HClO_4$). [e] Rate of F^- release. [f] $\mu = 1.00\ M$ ($NaClO_4$). [g] $\mu = 1.50\ M$ ($NaClO_4$). [h] $\mu = 2.00\ M$ ($LiClO_4$). [i] $[Cr(III)] = 0.013$–$0.014\ M$. [j] $\mu = 0$.

Table IV. Activation Parameters and Rate Constants for Acid Hydrolysis of *trans*-$Cr(tmd)_2FX^+$

Complex	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}	$k(50°, \mu = 2.0\ M)$
trans-$Cr(tmd)_2F_2^+$	25.8 ± 0.3	$+6.2 \pm 0.5$	$2.6 \times 10^{-4}\ M^{-1}\ sec^{-1}$
trans-$Cr(tmd)_2FCl^+$	18.0 ± 0.3	-14.0 ± 2.0	$1.3 \times 10^{-3}\ sec^{-1}$
trans-$Cr(tmd)_2FBr^+$	16.4 ± 0.3	-17.3 ± 2.0	$1.1 \times 10^{-2}\ sec^{-1}$ [a]

[a] Calculated from ΔH^* and rate at lower temperature; $\mu = 1.0\ M$.

are first order and essentially independent of H^+. The rates were unaffected by changes in initial Cr(III) concentrations but do show some dependence on ionic strength and the nature of the reaction medium. Activation parameters calculated from the temperature dependence of the rates are given in Table IV along with rate constants at 50° and $\mu = 2.0\ M$.

Subsequent reactions of the *trans*-$Cr(tmd)_2FOH_2^{2+}$ hydrolysis product were also studied in 0.15 and in 2.0 M $HClO_4$ solutions. In 0.15 M $HClO_4$, two products were separated by ion exchange after solutions of the *trans*-$Cr(tmd)_2FOH_2^{2+}$ were thermostated at 50° for 7 days. The first product (29% of the total chromium) was eluted with 0.75 M H_2SO_4, while the second (69% of the total chromium) was eluted with 1.50 M H_2SO_4. The first product was found to have a Cr:N ratio of 1:1.89 and from comparative elution characteristics a charge of 2+. The visible spectrum of this product showed two bands (535 nm, ϵ 41.5; 390 nm, ϵ 33.2) and is quite similar to that found for blue $Cr(en)(OH_2)_3F^{2+}$. Therefore the logical assignment of the first product is blue $Cr(tmd)(OH_2)_3F^{2+}$. The second product was found to have a Cr:N ratio of 1:3.83 and is characterized by a slightly greater column retention than *trans*-$Cr(tmd)_2FOH_2^{2+}$ and therefore is assigned as *cis*-$Cr(tmd)_2OH_2F^{2+}$. The visible spectra (Table II) of this product, as well as its elution characteristics, are consistent with this assignment. Furthermore, there was no measurable loss of fluoride ion from *trans*-$Cr(tmd)_2FOH_2^{2+}$ in 0.15 M $HClO_4$.

In 2.0 M $HClO_4$ ion-exchange studies showed three species after solutions of *trans*-$Cr(tmd)_2FOH^{2+}$ were thermostated at 50° for 3 days. The first two products eluted at 0.75 M H_2SO_4 (6% of the total Cr) and at 1.50 M H_2SO_4 (72% of the total Cr) were identical with those found in the reactions in 0.15 M $HClO_4$. A third product was separated by elution with 2.5 M H_2SO_4 (22% of the total Cr). The relative amounts of these three products changed as a function of reaction time. Results of separations gave 9, 49, and 40%, respectively, after 7 days at 50° and 10, 47, and 44% after 10 days. The product eluted at 2.5 M H_2SO_4 is consistent with a complex with a 3+ charge, and it was found to have a Cr:N ratio of 1:4.05. The complex was identified as *cis*-$Cr(tmd)_2(OH_2)_2^{3+}$;[7] its electronic spectra are in excellent agreement with that reported previously. Furthermore, at 2.0 M $HClO_4$, fluoride ion is evolved during the course of the reactions, which is also consistent with the formation of a diaquo complex.

In order to estimate the rates of the reactions of *trans*-$Cr(tmd)_2FOH_2^{2+}$, the rate of loss of the complex was monitored spectrophotometrically at both 0.10 and 2.0 M $HClO_4$. Since the initial and the major product appears to be the *cis*-$Cr(tmd)_2FOH_2^{2+}$ in both cases, the rate k_1 of eq 3 was estimated as the initial rate of loss of the trans complex. At 50° the rate constants were found to be 5.1×10^{-6} sec^{-1} at 0.10 M $HClO_4$ ($\mu = 2.00\ M$) and 5.7×10^{-6} sec^{-1} at 2.0 M $HClO_4$ ($\mu = 2.0\ M$). The *cis*-$Cr(tmd)_2FOH_2^{2+}$ reacts subsequently to give (depending upon the acid strength) blue $Cr(tmd)(OH_2)_3F^{2+}$ and *cis*-$Cr(tmd)_2(OH_2)_2^{3+}$, eq 4. The rate of

$$\textit{trans}\text{-}Cr(tmd)_2FOH_2^{2+} \xrightarrow{k_1} \textit{cis}\text{-}Cr(tmd)_2FOH_2^{2+} \qquad (3)$$

$$\begin{tikzcd}
 & \textit{cis}\text{-}Cr(tmd)_2(OH_2)_2^{3+} + HF \\
\textit{cis}\text{-}Cr(tmd)_2FOH_2^{2+} \arrow[ur, "k_2{[H^+]}"] \arrow[dr, "k_3"'] & \\
 & \text{blue } Cr(tmd)(OH_2)_3F^{2+}
\end{tikzcd} \qquad (4)$$

loss of *cis*-$Cr(tmd)_2FOH_2^{2+}$ in 2.0 M $HClO_4$ was estimated from its apparent half-life at 50° determined by monitoring the ion-exchange fraction as a function of time; the rate constant was 1.3×10^{-6} sec and corresponds to $k_3 + k_2(2.0\ M\ H^+)$ in eq 4. Estimates for k_3 and k_2 at 50° and 2.0 M $HClO_4$ ($\mu = 2.0\ M$) were obtained from the ratio of the product complexes separated by ion exchange. The results were $k_3 = \sim 0.3 \times 10^{-6}$ sec^{-1} and $k_2(2.0\ M\ H^+) = \sim 1.0 \times 10^{-6}$ sec^{-1}. It should be emphasized at this point that the reactions of *trans*-$Cr(tmd)_2FOH_2^{2+}$ and subsequent reactions of *cis*-$Cr(tmd)_2FOH_2^{2+}$ are quite slow compared with the primary hydrolyses of the *trans*-$Cr(tmd)_2FX^+$ complexes. The rate constants therefore are less precise and should be taken only as estimates. Also it is not known for certain that k_2 corresponds to a second-order path, but the rate does depend on $[H^+]$.

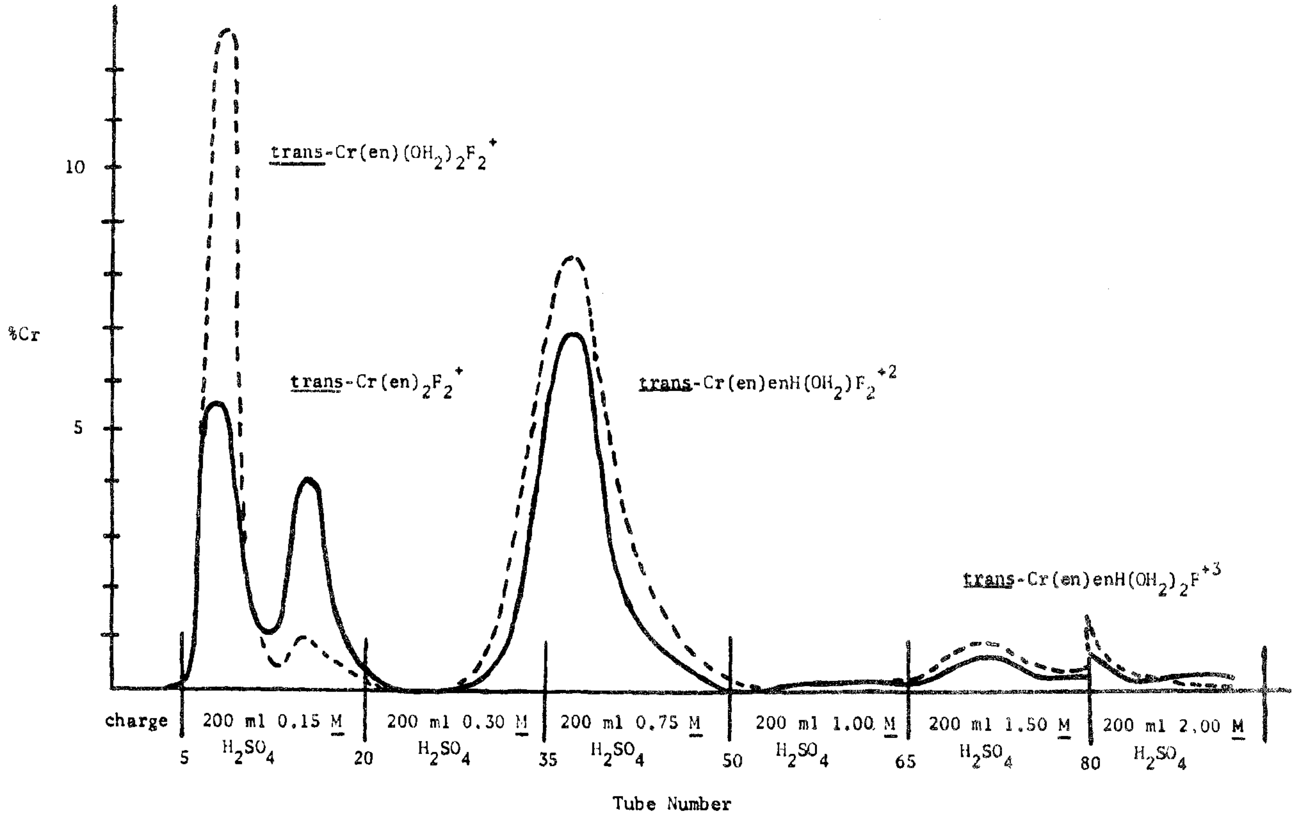

Figure 1. Ion exchange of reaction aliquot from hydrolysis of *trans*-$Cr(en)_2F_2^+$ in 0.15 *M* $HClO_4$ at 50°: ——, after 1 hr; - - - - - - -, after 3 hr.

Hydrolysis of *trans*-$Cr(en)_2F_2^+$ and Daughter Ions. In contrast to the tmd complexes, the primary hydrolysis of *trans*-$Cr(en)_2F_2^+$ was complicated by Cr-N bond rupture and secondary hydrolyses which occurred at comparable rates. In addition the H^+ concentration affected the product distribution.

In 4.0-6.0 *M* $HClO_4$ at 50° repetitive scan spectrophotometry showed that *trans*-$Cr(en)_2F_2^+$ is converted into *trans*-$Cr(en)_2OH_2F^{2+}$. The spectra after 60 min agreed well with that of an authentic sample of the fluoroaquo complex. The rate of this transformation showed a definite dependence on H^+ concentration. At lower acid concentrations, however, a mixture of products was observed, and the distribution was time dependent. The rates were also less sensitive to H^+ concentrations. Ion-exchange separations of reactions run at 50° in 0.15 *M* $HClO_4$ for 15 min to 3 hr showed three products in addition to the *trans*-$Cr(en)_2F_2^+$ starting material, as shown in Figure 1. These three products (complex charge indicated by their elution characteristics) were eluted with 0.15 *M* H_2SO_4 (charge 1+), 0.75 *M* H_2SO_4 (charge 2+), 1.00 *M* H_2SO_4 (charge 2+), and 1.5 *M* H_2SO_4 (charge 3+). The identification of these products is based not only on their elution characteristics but also on the experimentally determined Cr:N ratio of the eluted fraction, and their visible spectra. The monopositive cation eluted at 0.15 *M* H_2SO_4 had a Cr:N ratio of 1:2.05. Since there was very little loss of fluoride (<6%) even after 24 hr, this product is assigned as *trans*-$Cr(en)(OH)_2F_2^+$. The visible spectra of this product agreed favorably with the literature report for this complex.[6] The dipositive cation eluted with 0.75 *M* H_2SO_4 was characterized by a Cr:N ratio of 1:3.92 and a spectrum which agreed well with that reported for *trans*-$Cr(en)(enH)OH_2F_2^{2+}$,[6] a complex which contains a unidentate ethylenediamine ligand. The tripositive cation eluted with 1.5 *M* H_2SO_4 was found in very small amounts (<6% of the total Cr) and had a Cr:N ratio of 1:3.88. Its visible spectra showed two maxima (515 nm (ϵ 45.3) and 380 nm (ϵ 28.5)) which agreed favorably with a product formed from the *trans*-$Cr(en)(enH)OH_2F_2^{2+}$ reported by Pyke and Linck.[6] These workers however assigned the product as *cis*-$Cr(en)_2OH_2F^{2+}$ on the basis of the two-band spectrum and the finding that its column retention is greater than the *trans*-$Cr(en)_2OH_2F^{2+}$. An authentic sample of *cis*-$Cr(en)_2OH_2F^{2+}$, prepared in this study, exhibits visible spectra with maxima at 507 nm (ϵ 70.2) and 378 nm (ϵ 35.1). Thus the spectral agreement is outside of experimental error. Furthermore, there is a marked difference in reactivity between the authentic *cis*-$Cr(en)_2OH_2F^{2+}$ and the product eluted with 1.5 *M* H_2SO_4. The *cis*-$Cr(en)_2OH_2F^{2+}$ is fairly unreactive in 3 *M* $HClO_4$. After 2 hr at 50° ion-exchange separation revealed a single, unidentified product consistent with 3+ charge eluted with 2.5 *M* H_2SO_4 which accounted for 36% of the Cr. Under the same conditions the product from the primary hydrolysis reaction mixture was much more reactive giving a single product (~100% total Cr) which was eluted from an ion-exchange column with 0.75 *M* H_2SO_4 and was identified (see below) as blue $Cr(en)(OH_2)_3F^{2+}$. Thus the evidence points to the assignment of the minor hydrolysis product at 0.15 *M* $HClO_4$ as *trans*-$Cr(en)(enH)(OH_2)_2F^{3+}$.

The reaction of *trans*-$Cr(en)_2F_2^+$ in 2 *M* $HClO_4$ at 50° after 1 hr produced four products which could be separated by ion-exchange chromatography. In addition to the products identified from the reactions in 0.15 *M* $HClO_4$, a cation eluted with 1.0 *M* H_2SO_4 was found to account for 24% of the Cr; this cation was identical with authentic *trans*-$Cr(en)_2OH_2F^{2+}$. Fluoride release measurements indicated 0.75 mol of fluoride release per mole of Cr after 1 hr. In addition to *trans*-$Cr(en)_2OH_2F^{2+}$, the fraction identified as *trans*-$Cr(en)(enH)(OH_2)_2F^{3+}$ in the reactions at 0.15 *M* $HClO_4$ accounted for 40% of the Cr. The reaction of this cation described above produces a single product identified as blue $Cr(en)(OH_2)_3F^{2+}$. Since this is a dipositive cation it is expected to be eluted by 0.75–1.0 *M* H_2SO_4. Consequently it is likely that the fraction eluted with 0.75 *M* H_2SO_4 contains this cation. The total Cr eluted with 0.75 *M* H_2SO_4 was 23%. The per cent Cr as *trans*-$Cr(en)_2OH_2F^{2+}$ and *trans*-$Cr(en)(enH)(OH_2)_2F^{3+}$ is 54%, which is ~21% less than 75% of the products expected as being derived from the difluoro cation by fluoride ion loss. Therefore it is likely that the product eluted with 0.75 *M* H_2SO_4 is predominantly blue $Cr(en)(OH_2)_3F^{2+}$. The visible spectra of this fraction were consistent with this assignment. Table V summarizes the product distributions found from the ion-exchange studies of reaction mixtures at 0.15 and 2.0 *M* $HClO_4$ at 50°.

Table V. Product Distributions (%) from the Hydrolysis of *trans*-$Cr(en)_2F_2^+$ at 50° in 0.15 and 2.00 *M* $HClO_4$ Determined by Ion-Exchange Chromatography

Cation	Reaction time 15 min	1 hr	3hr	6 hr	24 hr
0.15 *M* $HClO_4$					
trans-$Cr(en)_2F_2^+$ (reactant)	48	13	3		
trans-$Cr(en)(OH_2)_2F_2^+$	4	21	33	36	11[a]
trans-$Cr(en)(enH)OH_2F_2^{2+}$	43	62	53	60	81[a]
trans-$Cr(en)(enH)(OH_2)_2F^{3+}$	1.5	5.0	5.7	3.3	3.0
2.00 *M* $HClO_4$					
trans-$Cr(en)_2F_2^+$ (reactant)		3.2			
trans-$Cr(en)_2(OH_2)_2F_2^+$		5.2			
Blue $Cr(en)(OH_2)_3F^{2+}$ *trans*-$Cr(en)(enH)OH_2F_2^{2+}$		23.1			
trans-$Cr(en)(enH)(OH_2)_2F^{3+}$		40			
trans-$Cr(en)_2OH_2F^{2+}$		24			

[a] Since the only manner in which *trans*-$Cr(en)(OH_2)_2F_2^+$ can disappear by aquation is with the formation of blue $Cr(en)(OH_2)_3F^{2+}$, it is probable that the fraction containing dipositive ions contains *both trans*-$Cr(en)(enH)(OH_2)F_2^{2+}$ and blue $Cr(en)(OH_2)_3F^{2+}$ after 24 hr of reaction time. See arguments in the text for the dipositive ion fraction from the 2 *M* $HClO_4$ reaction.

Since mixtures of products resulted from the hydrolysis of *trans*-$Cr(en)_2F_2^+$ at $[H^+]$ between 0.15 and 4.0 *M*, a variety of methods were used to obtain kinetic data. The individual reactions studied and rate constants obtained along with the kinetic method used are given in Table VI. In the case of the initial hydrolysis of *trans*-$Cr(en)_2F_2^+$ and the subsequent hydrolysis of *trans*-$Cr(en)(enH)(OH_2)F_2^{2+}$ parallel reactions were observed, and rate constants were estimated by taking both paths into account. The hydrolyses of *trans*-$Cr(en)_2(OH_2)F^{2+}$ and of *trans*-$Cr(en)(OH_2)_2F_2^+$ were studied using pure samples of the cationic complexes. The reaction of *trans*-$Cr(en)_2(OH_2)F^{2+}$ involved two steps (paths (3) → (4) and (4) → (5) in Table VI) with the final product being blue $Cr(en)(OH_2)_3F^{2+}$. The rate of the first step was found by studying the loss of reactant monitored spectrophotometrically while that of the second was determined by monitoring the ion-exchange per cent Cr due to reactant and product as a function of time. The hydrolysis of *trans*-$Cr(en)(OH_2)_2F_2^+$ was monitored spectrophotometrically; isosbestic points were observed at 352 and 550 nm which are consistent with those expected from a comparison of reactant and product spectra. It is to be noted that the rates of paths in which a loss of F^- is involved depend on H^+. It is not certain, however, that the rates are first order in $[H^+]$. The constants given in Table VI are observed pseudo-first-order constants for the reaction conditions indicated.

Hydrolysis of *trans*-$Cr(en)_2FCl^+$. The reaction products resulting from the hydrolysis of *trans*-$Cr(en)_2FCl^+$ in 0.15 *M* $HClO_4$ at 50° were separated by ion exchange after reaction times of 15 min, 30 min, and 3 hr. After 15 or 30 min, five products were separated. One unidentified product was eluted just prior to the *trans*-$Cr(en)_2FCl^+$ reactant with 0.15 *M* H_2SO_4 and amounted to 1% or less of the total Cr and is probably an impurity in the reactant. Two products were eluted with 0.75 *M* H_2SO_4. In order to separate these products, twice the normal volume of 0.75 *M* H_2SO_4 was used to elute. The product eluted first was identified as blue $Cr(en)(OH_2)_3F^{2+}$. The second cation contained chloride and was characterized by a visible spectrum with two maxima at 515 nm (ϵ 32.3) and 395 nm (ϵ 21.0) and is assigned as *trans*-$Cr(en)(enH)(OH_2)FCl^+$. The fourth and fifth products were eluted with 1.0 and 1.5 *M* H_2SO_4, respectively, and were identical in characteristics to *trans*-$Cr(en)_2OH_2F^{2+}$ and *trans*-$Cr(en)(enH)(OH_2)_2F^{3+}$ identified among the hydrolysis products of the *trans*-$Cr(en)_2F_2^+$. The product distributions for the hydrolysis of *trans*-$Cr(en)_2FCl^+$ are given in Table VII.

Rate data for the hydrolysis of *trans*-$Cr(en)_2FCl^+$ at 50° in 0.15 *M* $HClO_4$ are included in Table VI. The rate of loss of *trans*-$Cr(en)_2FCl^+$ was determined by monitoring the decrease in the ion-exchange fraction corresponding to the reactant. This loss corresponds to contributions from both paths (7) → (3) and (7) → (8) of Table VI. In order to estimate the rate of (7) → (3) an upper and lower limit were established for the Cr–N bond rupture process, path (7) → (8) as follows. The lower limit was taken from the time dependence of the *trans*-$Cr(en)(enH)(OH_2)FCl^{2+}$ fraction in the ion exchange, assuming the rate of loss of this fraction *via* path (8) → (4) was negligible. A value of $\sim 1 \times 10^{-4}$ sec^{-1} was determined. A reasonable upper limit might be approximated by the rate of Cr–N bond rupture for *trans*-$Cr(en)_2F_2^+$ (path (1) → (2) in Table VI); this value in 0.15 *M* $HClO_4$ is $\sim 2 \times 10^{-4}$ sec^{-1}. Thus the maximum value for path (7) → (3) is $\sim 7 \times 10^{-4}$ sec^{-1}. The rate of chloride loss from *trans*-$Cr(en)(enH)(OH_2)FCl^{2+}$ (path (8) → (4) in Table VI) can be estimated by measuring the total rate of chloride ion release from *trans*-$Cr(en)_2FCl^+$, which corresponds to contributions from both paths (7) → (3) and (8) → (4) in Table VI. Using the approximated rate for path (7) → (3), the result is $\sim 2 \times 10^{-4}$ sec^{-1} for path (8) → (4). It must be emphasized that the rate constants for paths (7) → (3), (7) → (8), and (8) → (4) are not precise, and they should not be considered more than rough estimates.

Discussion

The rate of fluoride release from *trans*-$Cr(tmd)_2F_2^+$ is characterized by a first-order dependence on $[H^+]$. At H^+ concentrations less than 0.10 *M*, the rates are very slow at 50°. Also the rate of fluoride release from *trans*-$Cr(en)_2F_2^+$, *trans*-$Cr(en)(enH)(OH_2)F_2^{2+}$, and *trans*-$Cr(en)(OH_2)_2F_2^+$ is dependent on $[H^+]$, although it is not certain that a first-order dependence is obeyed since the reactions were complicated by concurrent and/or consecutive processes of comparable rates. The rate of fluoride release from *trans*-$Cr(en)_2F_2^+$ at $[H^+] < 0.5$ *M* is slow compared to the disappearance of the reactant. Consequently at low acid concentrations (<0.50 *M*) our results are in substantial agreement with those of Pyke and Linck.[6] However at $[H^+] > 4.0$ *M* the loss of fluoride by an acid-dependent path predominates. Thus the rate law for the loss of the *trans*-$Cr(en)_2F_2^+$ cation should contain at least two terms, one independent of $[H^+]$ (path (1) → (2)), and one dependent on $[H^+]$ (path (1) → (3)).

Acid catalysis of fluoride release has been observed for *cis*-$Cr(en)_2F_2^+$,[4] *cis*- and *trans*-$Co(en)_2F_2^+$,[5] and $Co(NH_3)_5F^{2+}$ [11] and has been explained in terms of a reactive protonated com-

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(11) S. C. Chan, *J. Chem. Soc.*, 2375 (1964).

Table VI. Rate Data for the Acid Hydrolysis of *trans*-$Cr(en)_2F_2^+$, *trans*-$Cr(en)_2FCl^+$, and Daughter Ions at 50°

$$\begin{tikzcd}
(1)\ trans\text{-}Cr(en)_2F_2^+ \arrow[r] \arrow[d, "H^+"] & (2)\ trans\text{-}Cr(en)(enH)(OH_2)F_2^{2+} \arrow[r] \arrow[d, "H^+"] & (6)\ trans\text{-}Cr(en)(OH_2)_2F_2^+ \arrow[d, "H^+"] \\
(3)\ trans\text{-}Cr(en)_2OH_2F^{2+} \arrow[r] & (4)\ trans\text{-}Cr(en)(enH)(OH_2)_2F^{3+} \arrow[r] & (5)\ \text{blue } Cr(en)(OH_2)_3F^{2+} \\
(7)\ trans\text{-}Cr(en)_2FCl^+ \arrow[r] \arrow[u] & (8)\ trans\text{-}Cr(en)(enH)(OH_2)FCl^{2+} \arrow[u] &
\end{tikzcd}$$

Path	$[H^+]$,[a] M	10^2[Cr(III)], M	μ, M	10^4k,[b] sec^{-1}	Method
(1) → (2)	0.15	3.3-3.6	2.0	2.0	Estimated from spectrophtrophotometric decrease in (1) less F^- release from (1)
	0.50	3.8-4.1	2.0	1.7	
	2.00	3.8-4.5	2.0	0.4	
(1) → (3)	0.15	3.4-4.2	0.15	0.7	F^- release from (1)
	0.50	3.2-4.1	0.50	0.9	
	2.00	3.8	2.0	3.2	
	4.00	3.9-5.1	4.0	8.9	
	6.00	3.1-28.4	6.0	22.4	Spectrophotometric decrease in (1)
(3) → (4)	0.15	2.5-2.7	2.0	3.9	Spectrophotometric decrease in (3)
	0.50	4.0-4.1	2.0	3.9	
	1.00	2.5-2.6	2.0	4.1	
	2.00	0.34-3.9	2.0	3.9	
	4.00	3.3-3.5	4.0	2.3	
	6.00	3.5-5.8	6.0	0.72	
(4) → (5)	2.00	2.6	2.0	0.93	Ion-exchange decrease in (4)
	2.0	2.6	2.0	1.03	Ion-exchange increase in (5)
(6) → (5)	0.15	0.5	0.7	1.28	Spectrophotometric decrease in (6)
	0.30	0.5	0.3	1.43	
	1.54	0.5	1.54	3.2	
	3.54	0.5	3.54	8.8	
	0[c]	0.5	0	22.2	
	0.15	0.5	0.15	1.24	F^- release from (6)
(2) → (4)	1.50[d]	0.11	2.25	0.13	Ion-exchange increase in (4)
(2) → (6)	1.50[d]	0.11	2.25	0.47	Ion-exchange increase in (6)
(2) → (6) + (2) → (4)	1.50[d]	0.11	2.25	0.74	Ion-exchange decrease in (2)
(7) → (3) + (7) → (8)	0.15	0.5	0.15	8.4	Ion-exchange decrease in (7)
(7) → (3) + (8) → (4)	0.15	0.7	0.15	9.0	Cl^- release from (7)
(7) → (3)	0.15	0.5	0.15	<7	Estd; see text
(7) → (8)	0.15	0.5	0.15	>1; <2	
(8) → (4)	0.15	0.5	0.15	<2	

[a] $HClO_4$. [b] First-order constants observed; in most cases averages of two or more independent experiments with error less than ±10%. [c] H_2O, pH 6.4. [d] H_2SO_4.

Table VII. Product Distributions (%) from the Hydrolysis of *trans*-$Cr(en)_2FCl^+$ at 50° in 0.15 M $HClO_4$ Determined by Ion-Exchange Chromatography

Cation	Reaction time		
	15 min	30 min	3 hr
trans-$Cr(en)_2FCl^+$ (reactant)	24	6.5	
impurity eluted with 0.15 M H_2SO_4	0.3	0.7	<1.0
trans-$Cr(en)(OH_2)_3F^{2+}$	~7	9	54
trans-$Cr(en)(enH)(OH_2)FCl^{2+}$	~7	12	
trans-$Cr(en)_2OH_2F^{2+}$	39	30	4
trans-$Cr(en)(enH)(OH_2)_2F^{3+}$	29	42	31

plex. The same explanation may be applied in the present case and is illustrated for *trans*-$Cr(tmd)_2F_2^+$ in eq 5 and 6.

$$H^+ + trans\text{-}Cr(tmd)_2F_2^+ \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} trans\text{-}Cr(tmd)_2FFH^{2+} \qquad (5)$$

$$trans\text{-}Cr(tmd)_2FFH^{2+} + H_2O \underset{\text{slow}}{\overset{k}{\longrightarrow}} trans\text{-}Cr(tmd)_2FOH_2^{2+} + HF \qquad (6)$$

Since the rate of fluoride release from *trans*-$Cr(tmd)_2F_2^+$ in the absence of appreciable concentrations of H^+ is very low and a linear dependence on H^+ is observed up to 2.0M H^+, the rapidly established equilibrium of eq 5 must lie predominantly to the left, and direct, uncatalyzed fluoride replacement does not contribute to the reaction to any significant extent. The second-order constant k_2 is then given by kK. The value of K is not known but must be <0.05 M^{-1} in order to account for the observed linear dependence on H^+. Such a low value for K is not unreasonable; some recent investigations of fluoride protonation in $Cr(H_2O)_5F^{2+}$ show that the H^+ association constant is ~10^{-3} M^{-1} at 30°.[12]

Table VIII. Comparative Rates of Fluoride Release in Acid Solution

Reactant	10^4k, M^{-1} sec^{-1} (μ, M; T, °C)	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
trans-$Co(en)_2F_2^+$ [c]	2.0 (. . .; 25)[a]	28	
cis-$Co(en)_2F_2^+$ [c]	~30 (0.1; 25)[b]		
$Co(NH_3)_5F^{2+}$ [d]	1.1 (0.1; 25)	29	+22
cis-$Cr(en)_2F_2^+$ [e]	~10 (0.1; 50)[b]	22	
trans-$Cr(tmd)_2F_2^+$	2.6 (2.0; 50)	26	+6
trans-$Cr(en)_2F_2^+$	~3.5 (6.0; 50)[b]		
trans-$Cr(en)(enH)(OH_2)F_2^{2+}$	~0.1 (2.3; 50)[b]		
trans-$Cr(en)(OH_2)_2F_2^+$	~2.1 (1.5; 50)[b]		

[a] Estimated by plotting k_{obsd} *vs.* $[H^+]$; data from ref 5. [b] Estimated from $k_{obsd}/[H^+]$; first-order dependence not established, consequently value may not be reliable. [c] Reference 5. [d] Reference 11. [e] Reference 4.

Some comparative rate data for fluoride release are given in Table VIII. The somewhat greater reactivity of the Co(III) complexes appears to be due to a larger favorable activation entropy, since activation enthalpies are more favorable for the Cr(III) complexes. It is important to point out, however, that under the conditions used to obtain rate data on these systems, there will be contributions to both ΔH^* and ΔS^* due to the rapid preequilibrium step. A stronger association of the proton (and hence a greater desolvation of

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[12] J. W. Vaughn and E. L. King, unpublished research, 1972.

H^+) with Co–F relative to Cr–F would account for both the higher ΔH^* and more positive ΔS^*, but a detailed interpretation in view of the limited data would be speculative.

The higher reactivity of Cr–FH^{n+1} compared to Cr–F^{n+} can be rationalized on the basis of the dissociative character of water replacement reactions for haloamine complexes of Cr(III). The neutral HF molecule is expected to be a better leaving group than anionic F^- if dissociative activation is important. Comparison of the rate of fluoride ion replacement with rates for bromide and chloride replacement in the series of *trans*-Cr(tmd)$_2$FX$^+$ (X = F, Cl, Br) complexes shows the rate ordering Br > Cl > F. Chloride is also replaced in the *trans*-Cr(en)$_2$FCl$^+$ cation more rapidly than F^- in *trans*-Cr(en)$_2$F$_2^+$. A similar order of reactivity has been found for the primary halide replacements in the related *trans*-Cr(tmd)$_2$Cl$_2^+$ ($k = 7.9 \times 10^{-5}$ sec^{-1} at 35°)[7] and *trans*-Cr(tmd)$_2$Br$_2^+$ ($k = 1.15 \times 10^{-3}$ sec^{-1} at 35°)[7] and also for *trans*-Cr(en)$_2$Cl$_2^+$ ($k = 2.3 \times 10^{-5}$ sec^{-1} at 25°)[13] and *trans*-Cr(en)$_2$Br$_2^+$ ($k = 3.3 \times 10^{-4}$ sec^{-1} at 25°).[14] The relative order Br > Cl > F parallels the Cr–X bond strength and is thus also consistent with dissociative activation.

The halide replacements reported here and those cited above are for the most part stereoretentive giving trans products from trans reactants. This behavior contrasts the behavior of a variety of trans Co(III) substrates of a similar type. For example, the acid hydrolysis of *trans*-Co(en)$_2$X$_2^+$ (X = Cl, Br) gives a mixture of *cis*- and *trans*-haloaquo products.[15] The greater tendency for *trans*-dihalochromium(III) complexes to give *trans*-haloaquo products on acid hydrolysis has been noted by others[16] and may be indicative of a five-coordinate square-pyramidal transition state. It may be pointed out that the π-bonding repulsion arguments[17] usually advanced to explain rearrangement to a trigonal-bipyramidal transition state for trans Co(III) complexes are less attractive for Cr(III) since the electron repulsions are expected to be lower.[18]

From a comparison of the relative rates reported here of corresponding tmd and en complexes toward the acid hydrolysis of a halide ligand, one must conclude that the halide replacement reactivity is not very dependent upon the ring size. Recent studies[7] of the related *trans*-Cr(tmd)$_2$X$_2^+$ and *trans*-Cr(en)$_2$X$_2^+$ (X = Cl, Br) also show the same result. This similarity of reactivity for these Cr(III) complexes contrasts the behavior of related tmd and en complexes of Co(III) where large differences in reactivity have been observed. For example, the relative rates of X replacement by water at 25° in *trans*-Co(tmd)$_2$X$_2^+$ and *trans*-Co(en)$_2$X$_2^+$ were found to be 1700:1 for X = Cl[15,19,20] and 680:1 for X = Br.[15,19] It has been suggested by Couldwell and House[7] that the greater relative reactivity between tmd and en complexes in the case of Co(III) is due to greater conformational flexibility of the chelate rings and enhanced stability of a twist-boat conformer for the tmd ligand in which there are severe steric interactions with the leaving halide. The lack of a strong dependence of hydrolysis rates on the ring size for Cr(III) was suggested due to the greater stability of the chair conformer for both tmd and en ligands. The chair conformation is not expected to produce such severe steric interactions with the leaving halide. The results suggest that there is little difference in ring strain in the activation step for the en and tmd complexes for Cr(III). This contrasts the popular view that five-membered chelate rings are less reactive than six-membered rings,[17] but the arguments were developed as a result of studies of Co(III) complexes.

In contrast to the similarity of reactivity toward halide hydrolysis, the tmd and en complexes studied here show markedly different reactivity toward Cr–N bond rupture and the eventual replacement of the chelate ligand. The tmd complexes undergo simple halide hydrolyses with no side reactions during the primary replacement step. Only at long times do processes involving Cr–N bond rupture appear. For the en complexes, the Cr–N bond rupture competes favorably with the rate of the hydrolysis of Cr–X (X = Cl, F). A greater reactivity of the Cr–N bond in related *trans*-Cr(en)$_2$X$_2^+$ compared to *trans*-Cr(tmd)$_2$X$_2^+$ (X = Cl, Br) has also been noted recently.[7] Thus a greater reactivity for the Cr–N bond in the five-membered en complexes than in six-membered tmd complexes appears to be characteristic for a number of haloamine complexes of Cr(III), just the opposite of the reactivity order expected on the basis of ring-strain arguments. The greater reactivity of the en complexes may reflect a more efficiently solvated transition state leading to a monodentate diamine complex. The additional methylene unit in the tmd ligand would lengthen the chain which would extend outward into the solvation shell on dissociation of the first Cr–N bond. Such an extended chain, especially if protonated at the free N end, would certainly disrupt the solvation shell more than the shorter, more compact monodentate enH$^+$. It is interesting to note that no evidence for a partly unwrapped, monodentate tmd or tmdH$^+$ complex was found. Where a tmd ligand was lost in the secondary hydrolysis of *trans*-Cr(tmd)$_2$FX$^+$, it was lost completely to give the *blue*-Cr(tmd)(OH$_2$)$_3$F$^+$. This observation suggests that the order of lability of the two successive Cr–N bond ruptures accompanying the loss of a diamine ligand is Cr–N$_1$ < Cr–N$_2$ for tmd, but Cr–N$_1$ > Cr–N$_2$ for en.

Registry No. *trans*-Cr(en)$_2$F$_2^+$, 24407-74-7; *trans*-Cr(en)$_2$FCl$^+$, 42476-29-9; *trans*-Cr(tmd)$_2$F$_2^+$, 42476-30-2; *trans*-Cr(tmd)$_2$FCl$^+$, 42476-31-3; *trans*-Cr(tmd)$_2$FBr$^+$, 42476-32-4; *trans*-Cr(en)$_2$OH$_2$F^{2+}, 28101-89-5; *trans*-Cr(en)(enH)(OH$_2$)$_2$F^{3+}, 42476-34-6; *trans*-Cr(en)(enH)(OH$_2$)F$_2^{2+}$, 34398-37-3; *trans*-Cr(en)(OH$_2$)$_2$F$_2^+$, 34398-38-4; Cr(en)(OH$_2$)$_3$F^{2+}, 42476-37-9; *cis*-Cr(en)$_2$OH$_2$F^{2+}, 34431-44-2; *trans*-Cr(tmd)$_2$OH$_2$F^{2+}, 42476-39-1; *cis*-Cr(tmd)$_2$OH$_2$F^{2+}, 42476-40-4; Cr(tmd)(OH$_2$)$_3$F^{2+}, 42476-41-5; *cis*-Cr(tmd)$_2$(OH$_2$)$_2^{3+}$, 38985-25-0; *trans*-Cr(en)(enH)(OH$_2$)FCl^{2+}, 42476-43-7.

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