

Fig. 2.—Infrared spectra of Be(II) chelates with various β -diketones.

drawn with respect to the Be-O bands from the present calculations.

Fig. 1 indicates, however, that the strong bands at 1040, 824 and 500 cm.^{-1} are characteristic of the Be-O compounds. As is shown in Fig. 2, bis-(benzoylacetato)-Be(II) and basic beryllium acetate also show three analogous strong bands at similar frequencies. This fact may suggest that

they are characteristic of the chelate ring involving the Be-O bond.¹² Table I indicates that the band at 1040 cm.^{-1} corresponds to ν_4 , involving the coupling of ring deformation and Be-O stretching.

West and Riley⁴ previously suggested that the strong band at 824 cm.^{-1} in bis-(acetylacetonato)-Be(II) may be a Be-O stretching mode. Since this band may correspond to a ν_{12} vibration in the present calculation, it may be a coupled vibration between the Be-O stretching and C-CH₃ bending modes. The band at 500 cm.^{-1} may be a purer Be-O stretching vibration, although a calculation of the L-matrix is necessary to determine the character of these bands.

Acknowledgment.—The authors are indebted to the Massachusetts Institute of Technology Computation Center for the use of its I.B.M. 704 computer for their calculations.

(12) The structure of basic beryllium acetate is different from the other two compounds, although it has a chelate ring containing the Be-O bond; see Bragg and Morgan, *Proc. Roy. Soc. (London)*, **104**, 437 (1923).

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Kinetics of Hydrolysis of *cis*-Difluoro-bis-(ethylenediamine)-chromium(III) Cation¹

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The rates of release of fluoride by acid and base hydrolysis of *cis*-[Cr(en)₂F₂]⁺ were determined over a range of pH 1-8. At 25° the pseudo first-order aquation rate constant for loss of the first fluoride in 0.1 *f* HClO₄ is 5.3×10^{-6} sec.⁻¹, much less than the corresponding rate constants of *cis*-[Co(en)₂F₂]⁺ and *cis*-[Cr(en)₂Cl₂]⁺ in 0.1 *f* HNO₃. The Arrhenius activation energy is 23 ± 1 kcal./mole. The aquation of *cis*-[Cr(en)₂F₂]⁺ is acid catalyzed like the cobalt analog but, unlike the dichloro cobalt and chromium analogs, presumably because the difluoro complexes aquate by a mechanism involving an intermediate reactive protonated complex. Cation-exchange and spectral evidence indicate that the aquation product is largely, if not entirely, *cis*-[Cr(en)₂(H₂O)F]⁺². Fluoride is taken up by one or more reaction products in later stages of the hydrolysis. The aquation appears not to be accelerated by visible light.

As part of a program of comparing the kinetics of substitution reactions of cobalt(III) and chromium(III) complexes an investigation was undertaken of the rates of loss of fluoride in acid and base hydrolysis of *cis*-[Cr(en)₂F₂]⁺. Evidence on the *cis-trans* configuration of the fluoroaquo aquation product was obtained from ion-exchange and spectral experiments.

Experimental

Preparation of Compounds.—The synthesis and characterization of *cis*-difluoro-bis-(ethylenediamine)-chromium(III) iodide has been described elsewhere.²

Anal. Calcd. for [Cr(en)₂F₂]I: Cr, 15.43; F, 11.27; I, 37.65; C, 14.25; H, 4.78. Found: Cr, 15.18; F, 11.46; I, 37.38; C, 14.34; H, 4.54.

All other chemicals were reagent-grade, except sodium azide, which was practical grade.

Rate Procedure.—Known weights of the complex were dissolved in 65- to 100-ml. portions of buffer solution in a thermostatically controlled bath, and aliquots removed at known times for fluoride analysis, and in some cases for spectral observation or ion-exchange experiments. The pH of the reaction mixture was assumed to be that of the buffer solution itself,³ which was measured at 25-30° with a Beckman Model G pH meter.

(1) This investigation was supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-34, Project 12.

(2) K. R. A. Fehrmann and C. S. Garner, *This Journal*, **82**, 6294 (1960).

Cation-exchange Resin Experiments.—Information on the nature of the hydrolysis products was obtained by absorbing several reaction mixtures (*ca.* 25% reaction) on Dowex 50W-X8 cation-resin columns (100- to 200-mesh, in H⁺ form) and subjecting them to fractional elution after washing iodide ion from each column with water. The reaction mixtures and resin columns were cooled to 0° to reduce hydrolysis during processing. Complexes adsorbed from 0.1 *f* HClO₄ reaction mixtures were successively subjected to elution with 100 ml. of 0.6 *f* HClO₄ and 80 ml. of 3 *f* HClO₄ or with 100 ml. of 1.2 *f* HCl. Investigations carried out in this Laboratory⁴ on *cis*- and *trans*-[Cr(en)₂Cl₂]⁺, and their aquation products, have shown that *cis*-[Cr(en)₂Cl₂]⁺, and hence *cis*-[Cr(en)₂F₂]⁺, is essentially completely eluted by the 0.6 *f* HClO₄ without loss of the haloaquo products and that *trans*- and *cis*-[Cr(en)₂(H₂O)Cl]⁺², and hence any of the *trans*- and *cis*-[Cr(en)₂(H₂O)F]⁺² remaining, are eluted by the 1.2 *f* HCl and 3 *f* HClO₄, respectively, in agreement with the general rule that the *cis* isomer, because of its greater dipole moment, is more difficult to elute. F/Cr atom ratios in the fractions eluted with HClO₄ were determined, fluorine as described earlier² for the analysis of *cis*-[Cr(en)₂F₂]I and chromium by decomposition and oxidation of the complex to Cr(VI) by boiling with alkaline peroxide solution, followed by spectrophotometric determination of the chromium concentration.

(3) The assumption was found valid at pH 2 in a check experiment. Borate and phthalate buffers were prepared according to Clark and Lubs (N. A. Lange, ed., "Handbook of Chemistry," 9th Ed., Handbook Publishers, Inc., Ohio, 1956, pp. 951-952); other buffers made had about the same buffer capacity.

(4) D. J. MacDonald and C. S. Garner, unpublished research.

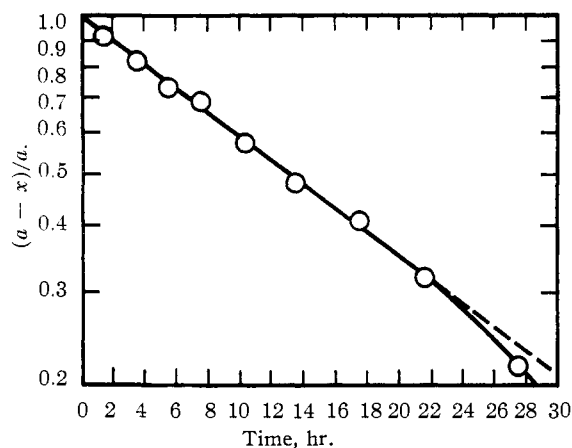


Fig. 1.—Rate of hydrolysis of *cis*-[Cr(en)₂F₂]⁺ in HNO₃, pH 1.02, at 24.96°.

An attempt was made to examine similarly the hydrolysis products of a pH 8 reaction run using 0.6 *f* NaClO₄ and 3 *f* NaClO₄, each in pH 8 buffer. The adsorbed color band was completely eluted by the 0.6 *f* NaClO₄ without evidence of any separation, probably because *cis*-[Cr(en)₂(OH)F]⁺ was formed in large proportion and would presumably be eluted with unreacted *cis*-[Cr(en)₂F₂]⁺.

Fluoride Determination in Hydrolysis Runs.—Run aliquots were allowed to flow through a 8-mm. × 150-mm. column of a mixed anion-cation exchange resin (Dowex 2-X8, 50- to 100-mesh, Cl⁻ form, mixed with Dowex 50W-X8, same mesh, Na⁺ form) which adsorbed the complexes and the iodide, both of which interfere with the fluoride determination. Uncomplexed fluoride was completely washed from the column with 3 3-ml. portions of 0.1 *f* NaCl. Negligible hydrolysis occurred during the 3-min. separation procedure. The effluent was titrated for fluoride by the method of Rowley and Churchill⁵ modified as follows. Sodium alizarin sulfonate indicator⁵ was added, then NaOH or HCl to a fading pink color. Chloroacetate buffer⁵ (0.5 ml.) was added to the solution and to each of a number of 20-ml. 0.1 *f* NaCl titration blanks. If the column effluent was colored, an attempt was made to match the color by adding crystal violet, methylene blue and/or methyl orange to the blanks. The sample then was titrated with 0.025 *N* Th(NO₃)₄ to the first detectable color change to red as compared with a blank. The same volume of Th(NO₃)₄ was added to each of several blanks to which known amounts of NaF were previously added and the colors of the sample and the NaF controls compared until two such controls sufficiently closely bracketed the sample to allow interpolation. The titration flasks, shielded from direct illumination, should stand on a white surface and be viewed against a white background. The entire method was checked by running several samples of the difluoro complex to which known amounts of NaF were added.

Effect of Light on Hydrolysis Rate.—To see if light accelerated the aquation reaction, a fresh pH 2 reaction mixture was divided and one half run in a black-painted reaction flask normally used and the other half run simultaneously in the same bath in an uncoated flask exposed during the daytime to diffuse sunlight and laboratory fluorescent light and during nights to light from a 150-watt incandescent bulb 20 cm. from the pair of flasks. Aliquots were taken from both flasks at the same intervals and analyzed for fluoride.

Spectra in Hydrolysis Runs.—To make an additional check on whether *trans*-[Cr(en)₂(H₂O)F]⁺² was formed in the aquation reaction and to see if a spectrophotometric method could replace the tedious titration of fluoride released in the hydrolysis, we examined the absorption spectra of pH 1 (perchlorate buffer), pH 3 (chloroacetate buffer) and pH 8 (borate buffer) 40° hydrolysis reaction mixtures in matched quartz cells over the range 350–600 mμ, using a Cary Model 11 recording spectrophotometer. Since the spectral changes during the "first-order" part of the reaction were small, a

(5) R. J. Rowley and H. V. Churchill, *Ind. Eng. Chem., Anal. Ed.*, **9**, 551 (1937).

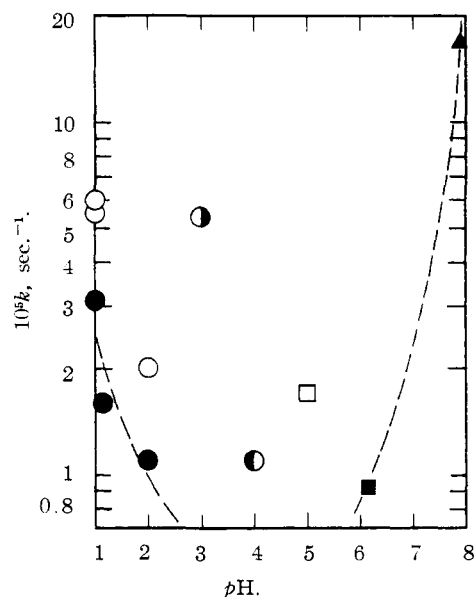


Fig. 2.—pH dependence in hydrolysis of *cis*-[Cr(en)₂F₂]⁺ at 40.50°: ●, HClO₄; ■, H₂O; ▲, H₃BO₃-NaH₂BO₃ (non-complexing buffers); ○, HNO₃; ○, chloroacetic acid-Na chloroacetate; ○, KH phthalate-KNa phthalate; □, HN₃-NaN₃ (complexing buffers).

spectrophotometric method of following the hydrolysis rate was not practical.

Results and Discussion

Based on loss of one fluoride per molecule, the apparent fraction of complex hydrolyzed, $(a - x)/a$, where a and x are respectively the initial formal concentration of complex and the formal concentration of uncomplexed fluoride at time t , was plotted *vs.* t on semilogarithm graph paper for each run and the best fitting curve drawn visually. The initial slope of each curve (determined when necessary with a tangent meter) was used to calculate the pseudo first-order rate constant k from the equation $k = \{d \ln[(a - x)/a]/dt\}_0$. The results are summarized in Table I (errors are estimated probable errors; μ = ionic strength).

The rate plot shown in Fig. 1 is typical of the early stages of all hydrolysis runs except those in chloroacetate and azide buffers. The positive deviation from linearity presumably arises from loss of the second fluoride, but it is impossible to calculate a reliable rate constant for the secondary hydrolysis.

Fig. 2 shows the pH dependence of the hydrolysis rate. If the data obtained in nitrate, chloroacetate, phthalate and azide buffers are excluded (see below), the remaining data define the dashed curve, which corresponds to the same general pH dependence found by Basolo, Matoush and Pearson⁶ in the hydrolysis of *trans*-[Co(en)₂F₂]⁺. Thus, the aquation of *cis*-[Cr(en)₂F₂]⁺ is acid catalyzed and presumably for the same reason as postulated for the *trans* cobalt analog, namely, a rapid acid-base pre-equilibrium, followed by slow aquation of the protonated complex (which is

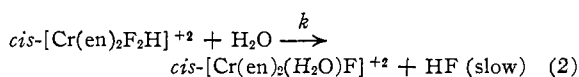
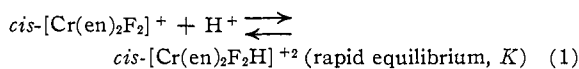
(6) F. Basolo, W. R. Matoush and R. G. Pearson, *THIS JOURNAL*, **78**, 4883 (1956).

TABLE I
 APPARENT SPECIFIC RATES OF HYDROLYSIS OF *cis*-[Cr(en)₂F₂]⁺ IN THE DARK

Buffer solution	pH	Temp., °C.	a, mf.	μ	% hydr. ^a	10 ⁵ k, sec. ⁻¹
HClO ₄	1.04	10.13	2.99	0.10	35	0.078 ± 0.008
HClO ₄	1.04	24.96	2.99	.10	23	0.53 ± .05
HClO ₄	1.04	34.93	2.91	.10	45	2.1 ± .2
HClO ₄	1.04	40.50	2.95	.10	..	3.1 ± .8
HClO ₄	1.16	40.50	6.41	.075	..	1.6 ± .1
HClO ₄ ^b	2.00	39.94	2.97	.013	40	1.1 ± .3
HClO ₄ ^b	2.00	39.94	2.97	.013	40	1.1 ± .1 ^c
HNO ₃ -NaNO ₃	1.02	24.96	2.94	.15	60	1.4 ± .1
HNO ₃ -NaNO ₃	1.02	40.50	2.86	.15	..	5.5 ± 1.4
HNO ₃ -NaNO ₃	1.04	40.50	3.09	.15	37	6.0 ± 0.6
HNO ₃ -NaNO ₃	1.02	49.78	2.86	.15	..	7.9 ± 2.0
HNO ₃ -NaNO ₃ ^b	2.02	40.50	2.74	.063	15	2.0 ± 0.2
ClCH ₂ CO ₂ H-ClCH ₂ CO ₂ Na	3.00	40.50	3.08	.061	..	5.4 ± 1.4
KHC ₈ H ₄ O ₄ -KNaC ₈ H ₄ O ₄	3.97	40.50	3.03	.055	18	1.1 ± 0.1
HN ₃ -NaN ₃	5.00	40.50	3.05	.10	..	1.7 ± .4
Water	6.13	40.50	3.02	.003	27	0.92 ± .07
H ₃ BO ₃ -NaH ₂ BO ₃	7.91	40.50	3.04	.011	40	17 ± 1.5

^a % apparent hydrolysis at point where nonlinearity of rate plot becomes noticeable. ^b Poor buffer capacity. ^c Reaction mixture exposed to light (see Experimental).

assumed much more reactive than the nonprotonated complex)



corresponding to the rate law $R = k'K(H^+)/([Cr(en)_2F_2]^+) = k([Cr(en)_2F_2]^+)$ at constant pH. As pointed out earlier⁶ acid-catalyzed aquation of haloamminecobalt(III) cations is limited to the fluoro compounds, presumably because of the greater base strength and hydrogen bonding tendency of fluoride ion compared to chloride or bromide ions. This explanation is supported by the acid-catalyzed aquation found for *cis*-[Cr(en)₂F₂]⁺ and the absence of acid catalysis for *cis*- and *trans*-[Cr(en)₂Cl₂]⁺. The increase in apparent rate of hydrolysis at high pH is assumed due to base hydrolysis, but the data do not permit estimating the base hydrolysis constant for *cis*-[Cr(en)₂F₂]⁺.

The abnormally high apparent rates of hydrolysis found with certain buffer solutions may arise partly from replacement of ligand fluoride by buffer anion. Chloroacetate ion presumably complexes like acetate ion, known⁷ to form stable complexes with chromium(III); one of the higher hydrolysis rates observed is in chloroacetate buffer. Chromium(III) complexes are also known with azide and nitrate; in these buffers high rates are obtained. Phthalate ion, which gives a high hydrolysis rate, probably replaces one fluoride in *cis*-[Cr(en)₂F₂]⁺ to form an uncharged complex, since this would account for the reaction mixtures in phthalate buffer giving highly colored effluents at early reaction times when passed through mixed anion-cation exchange resins (see Experimental, section on fluoride determination). On the other hand, perchlorate ion, for which lower hydrolysis rates were found at pH 1-2, normally is non-

(7) "Abegg's Handbuch der Anorganischen Chemie," Vol. IV, F. Auerbach, ed., Verlag von S. Hirzel, Leipzig, Germany, Teil 1. 2. Hälfte, 1921, pp. 179-180.

complexing. The buffer effect on the rates may arise from some cause other than complexing for some of the buffers.

Table II compares the aquation rates of chromium(III) and cobalt(III) dihalo-bis-(ethylenediamine) complexes at pH 1 and 25°. Because of the acid catalysis the specific rates given for the

 TABLE II
 SPECIFIC RATES AND ACTIVATION ENERGIES OF AQUATION OF Cr(III) AND Co(III) COMPLEXES OF TYPE [M(en)₂X₂]⁺ IN HNO₃ AT pH 1 AND 25°

X	Iso-mer	10 ⁵ k, sec. ⁻¹		E _a , kcal./mole	
		Cr	Co	Cr	Co
F	<i>cis</i>	0.53 ± 0.05 ^a	ca. 5 ^b	23 ± 1 ^a
F	<i>trans</i>	0.92 ^b	29 ^b
Cl	<i>cis</i>	33.0 ^c	25 ^d	21.1 ^c	22.3 ^e
Cl	<i>trans</i>	2.25 ± 0.03 ^f	3.2 ^g	23.23 ± 0.17 ^f	24.2 ^e - 28 ^g
Br	<i>trans</i>	14 ^b	26 ^b

^a This investigation, HClO₄ solution; values in HNO₃ (10⁵k = 1.4 ± 0.1, E_a = 14 ± 2) abnormal. ^b See ref. 6. ^c See ref. 9. ^d R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955). ^e J. P. Mathieu, *Bull. soc. chim. France*, **3**, 2152 (1936). ^f See ref. 4. ^g R. G. Pearson, C. R. Boston and F. Basolo, *THIS JOURNAL*, **75**, 3089 (1953).

difluoro complexes should not be directly compared with specific rates for the other complexes; the difluoro rate constants for the hypothetical uncatalyzed aquation are probably at least one order of magnitude smaller. As pointed out earlier,⁶ the rates for the *cis*-[Co(en)₂X₂]⁺ complexes correlate at least qualitatively with the crystal-field strengths of the ligand X⁻ ions; data are still insufficient for similarly comparing rates of the corresponding *trans* complexes or of either the *cis* or *trans* chromium complexes. From crystal-field theory one would expect for complexes of the type considered here a greater rate (and a smaller activation energy) for the d³ chromium complexes than for the d⁶ cobalt analogs. Comparisons of the limited data available have generally supported this.⁸ Thus the acid-catalyzed aquation of *cis*-

(8) See, e.g., F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chap. 3.

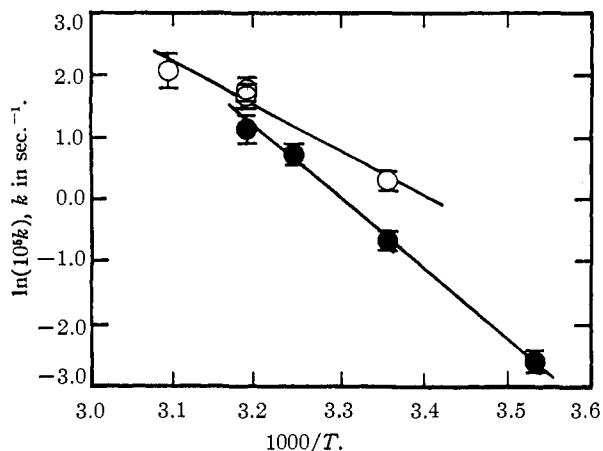


Fig. 3.—Temperature dependence of rate of aquation of $cis-[Cr(en)_2F_2]^+$: ●, $HClO_4$, pH 1.04; ○, HNO_3 , pH 1.02.

$[Cr(en)_2F_2]^+$ seems abnormally slow compared with that of the cobalt analog although the rate constant for aquation of the latter complex was stated to be "only semi-quantitative" and may have been affected by nitrate ion effects of the kind encountered with the chromium complex. Moreover, the rate constants being compared are composite constants which include the equilibrium constants K of reaction 1 and the corresponding cobalt reaction, which may differ somewhat. Clearly further kinetic investigations of non-cobalt complexes are desirable, as well as further studies in perchlorate media.

The apparent activation energy for the acid-catalyzed aquation of $cis-[Cr(en)_2F_2]^+$ in $HClO_4$ of pH 1.04 was calculated from an Arrhenius plot (Fig. 3) over the range 10–40°. The value is comparable with those for aquation of similar chromium(III) complexes. The approximate value of 14 ± 2 kcal./mole found from Fig. 3 in HNO_3 of pH 1.02 is abnormally low and presumably reflects the unknown reaction associated with the high rates found in nitrate buffer.

From the cation-exchange experiments on reaction mixtures 0.1 f in $HClO_4$, one may conclude that the aquation of $cis-[Cr(en)_2F_2]^+$ produces $cis-[Cr(en)_2(H_2O)F]^{+2}$ predominantly, if not entirely. The fraction eluted from the cation-exchange resin (after elution of unreacted $cis-[Cr(en)_2F_2]^+$) which should have contained any $trans-[Cr(en)_2(H_2O)F]^{+2}$ formed was essentially colorless, and the fraction in which any $cis-[Cr(en)_2(H_2O)F]^{+2}$ present should have been found was an intense bluish purple color and had a F/Cr atom ratio of 1.03, in good agreement with that expected for the fluoroaquo complex. The fact that the visible absorption spectra of the reaction mixtures changed relatively little during the "first-order" part of the aquation supports the conclusion

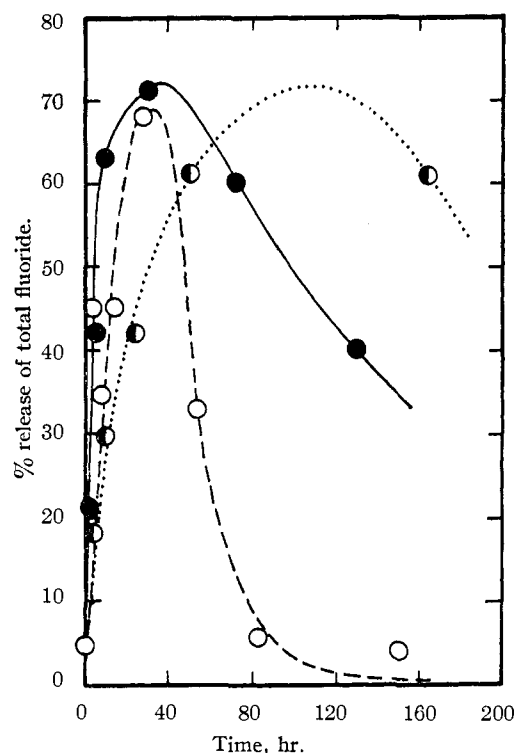


Fig. 4.—Per cent. release of total fluoride from $cis-[Cr(en)_2F_2]^+$ at 40.50°: ●, HNO_3 , pH 1.04; ○, chloroacetic acid-Na chloroacetate, pH 3.00; ◐, $HOAc-NaOAc$, pH 5.00.

that little or no $trans-[Cr(en)_2(H_2O)F]^{+2}$ was produced, since the *trans* isomer would be expected to have a substantially different spectrum.

At later stages of the hydrolysis of $cis-[Cr(en)_2F_2]^+$ there is an uptake of ionic fluoride from the solution as shown in Fig. 4. The uptake appears to become important at about the same stage of reaction (ca. 50–60% net loss of total ligand fluoride from the original complex) at which broadened absorption peaks and a high absorption minimum appear in the visible absorption spectrum of reaction mixtures. Since these spectral features are characteristic of polymers, the fluoride uptake may be associated with a polymerization reaction. Chromium(III) has a strong tendency to form polynuclear complexes with acetate, and presumably chloroacetate, as both ligands and bridges,⁷ and it is suggestive of the possible role of polymerization in fluoride uptake that such uptake is more pronounced with the reaction mixture in chloroacetate buffer (see Fig. 4).

The rate of aquation of $cis-[Cr(en)_2F_2]^+$ is unaffected by visible light (see Experimental and Table I), like the *cis*-dichloro analog,⁹ but in contrast to the *trans*-dichloro analog.⁴

(9) J. Selbin and J. C. Bailar, Jr., *THIS JOURNAL*, **79**, 4285 (1957).