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Contribution from the Departments of Chemistry, Colgate University, Hamilton, New York 13346,
and University of New Haven, West Haven, Connecticut 06516

Photo- and Thermochemistry of *cis*-$[Cr(en)_2F_2]^+$ and *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ in Acidic Aqueous Solution

Bruce Herbert, David Reinhard, Michael J. Saliby, and Peter S. Sheridan*

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The *cis*-$[Cr(en)_2F_2]^+$ ion is shown to undergo three consecutive aquations in acidic aqueous solution, leading to *cis*-$[Cr(en)_2F(H_2O)]^{2+}$, $[Cr(en)(en{-}H)F(H_2O)_2]^{3+}$, and $[Cr(en)F(H_2O)_3]^{2+}$, respectively. Kinetic studies of the first reaction confirm earlier findings of an acid-catalyzed and an acid-independent path ($k_{obsd} = k_0 + k_1[H^+]$, with $k_0 = 6.3 \times 10^{-4}$ s^{-1} and $k_1 = 4.8 \times 10^{-3}$ M^{-1} s^{-1} at 70 °C; for k_{obsd}, $\Delta H^* = 90.8 \pm 1.0$ kJ mol^{-1} and $\Delta S^* = -40.7 \pm 2.4$ J mol^{-1} K^{-1}). Ring opening upon aquation of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ is not acid catalyzed ($k = 1.88 \times 10^{-4}$ s^{-1} at 70 °C, $\Delta H^* = 83.4 \pm 1.9$ kJ mol^{-1}, and $\Delta S^* = 74.0 \pm 3.8$ J mol^{-1} K^{-1}). Ligand field irradiation of *cis*-$[Cr(en)_2F_2]^+$ in acidic solution causes efficient ($\phi = 0.35 \pm 0.04$) amine labilization; the resulting $[Cr(en)(en{-}H)F_2(H_2O)]^{2+}$ loses monodentate ethylenediamine when heated in solution. The *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ ion is also photosensitive, generating $[Cr(en)(en{-}H)F(H_2O)_2]^{3+}$ and $[Cr(en{-}H)_2F_2(H_2O)_2]^{2+}$ in successive photoinduced aquations. The photochemical results are discussed in terms of available photolability models.

Introduction

The photochemical study of six-coordinate Cr(III) complexes is now entering its fourth decade.[1-3] It has been 20 years since Adamson[4] first proposed the empirical rules that catalyzed a burst of activity testing which of the ligands will be lost upon ligand field excitation of the complex.[5-21] Several more theoretically based models quickly followed,[22-25] and it has now been a decade since Vanquickenborne[26,27] presented a photolability model, based on the angular overlap approximation to MO theory, which has become the current standard. The more important tests of these photolysis models have involved photochemical studies of Cr(III)–fluoro–amine species,[11,28-32] as the unique properties of the F^- ligand set them apart from the other Cr(III)–halo–amine complexes.[33,34]

In the decade since this work, high-pressure mechanistic studies[35] and pulsed laser studies[36] have explored the photophysics of the photochemical process, and work has proceeded on chemical studies of other bis(amine) systems,[37-39] but there has been a paucity of work on complexes with the *cis*-$[CrN_4X_2]^+$ chromophore. The thermal reactivity of most *cis*-dihalotetrakis(amine)chromium(III) complexes in aqueous solutions hinders their photochemical study, but the unusually robust Cr–F moiety suggests that studies of *cis*-$[CrN_4F_2]^+$ ions could be important tests of the photolability models. The $[Cr(tren)F_2]^+$ ion (where tren is β,β',β''-triaminotriethylamine, a tripodal, tetradentate amine that forces a cis configuration on the two fluorides) efficiently releases fluoride upon photolysis,[40] a result not anticipated by photolability models. The possible constraints of the tren ligand call into question whether the models could be expected to apply to such a complex, however, and studies on less sterically constrained systems are needed.

In a kinetic study of the aquation of *cis*-$[Cr(en)_2F_2]^+$, Garner[41] includes a footnote describing an experiment that compared the rates of aquation of $HClO_4$ solutions of *cis*-$[Cr(en)_2F_2]^+$ in a "black-painted reaction flask and...in an uncoated flask exposed during the daylight to diffuse sunlight and laboratory fluorescent light and during nights to light from a 150-W incandescent bulb 20 cm from the pair of flasks". No difference in the rates of fluoride release was observed, leading to the conclusion that "The rate of aquation of *cis*-$[Cr(en)_2F_2]^+$ is unaffected by visible light...." Given the more recent evidence of Cr(III)–amine photosensitivity and the importance of Cr(III)–F complexes in the testing of photochemical models, we have pursued a more thorough study of the thermal and photochemical behavior of *cis*-$[Cr(en)_2F_2]^+$ and its reaction products.

Experimental Section

Materials. *cis*-$[Cr(en)_2F_2]^+$ was prepared as the iodide salt by the method of Vaughn;[42] purity was ensured by comparison of electronic spectra [observed maxima at 516 nm (ε73) and 378 nm (ε37); literature[42] values at 516 nm (ε75.5) and 378 nm (ε39.5)] and by chromium and fluorine analyses. Other reagents were of reagent grade and used without

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* To whom correspondence should be addressed at Colgate University.

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further purification. Column chromatography media was Sephadex SP C-25 (40–120 mesh) cation-exchange resin; eluants were aqueous solutions of $NaBF_4$, Na_2SO_4, $NaNO_3$, $HClO_4$, or NaOH.

Analyses. Chromium was determined spectrophotometrically as chromate ion at 372 nm after oxidation of Cr(III) with alkaline peroxide.[43] A Cr(VI) standard curve was prepared with solutions of $[KCr(SO_4)_2]\cdot 12H_2O$ that had undergone identical alkaline oxidations.

Fluoride ion was determined with a fluoride ion electrode (Corning) in combination with a double-junction reference electrode (Corning 476067) and an Orion 601A digital pH meter. Fluoride standard series were prepared with NaF dissolved in 0.10 M HOAc/0.10 M NaOAc buffer solutions. Fluoride was also measured by titration with Th^{4+}.[44]

Electronic spectra were recorded on a Beckman Acta MIV spectrophotometer.

Reaction Conditions. Kinetic studies were done in dilute $HClO_4$; ionic strength was controlled with $NaClO_4$. Reactions were monitored spectrophotometrically. For the photochemical studies, irradiation was done with a 200-W Hg short-arc lamp in an Oriel housing. For preparative purposes, a Corning glass filter that absorbed light below about 400 nm was used; quantum yield studies were done with an interference filter (Oriel) that passed light at 502 nm (fwhh of ca. 20 nm). Quantum yields were based on spectral changes during the first 5–10% of reaction, and incident intensity was determined by using Reinecke actinometry.[45] Photolyses were performed at room temperature, and identical samples held in the dark showed no detectable spectral changes during the photolysis periods.

Results

Thermal Reactions and Aquation Products. Reaction of *cis*-$[Cr(en)_2F_2]^+$ in 0.40 M $HClO_4$ at 40 °C causes a slight blue shift of the maximum, with isosbestics at 506, 395, and 363 nm. Isosbestics are maintained for about 2 h, after which time they are lost and the low energy absorption band undergoes a red shift (vide infra). When a solution of *cis*-$[Cr(en)_2F_2]^+$ is allowed to react just until loss of isosbestics (5 h at 25 °C in 0.1 M $HClO_4$), ion-exchange chromatography reveals the presence of four species in solution:

(a) The first band (eluted with 0.15 M Na_2SO_4 solution) is the red-violet *cis*-$[Cr(en)_2F_2]^+$ starting material (I; λ_{max} at 516 and 378 nm).

(b) The second band displays λ_{max} at 505 nm (ϵ 72.5) and 373 nm (ϵ 32.0), consistent with the published spectrum of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ (II).[42]

(c, d) Under the described conditions, the third and fourth bands are too dilute to be carefully characterized, but more extensive reaction of *cis*-$[Cr(en)_2F_2]^+$ (1 h at 65 °C) yields more of these products. The more rapidly eluted material (III; removed with an eluant of 0.3 M $HClO_4$) has λ_{max} values at 518 and 376 nm, while the less rapidly moving cation (IV) has λ_{max} values of 530 nm (ϵ 42.1) and 387 nm (ϵ 24.4).

These results show that, in acidic aqueous solution, *cis*-$[Cr(en)_2F_2]^+$ undergoes three successive aquations; the first releases fluoride ion, leading to the *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ ion (reaction 1), and is followed by aquation of the monofluoro ion to give $[Cr(en)(en\text{-}H)F(H_2O)_2]^{3+}$ with a protonated, monodentate ethylenediamine ligand (reaction 2). Hydrolysis of the pendant ethylenediamine (reaction 3) leads to the eventual aquation product, IV, $[Cr(en)F(H_2O)_3]^{2+}$. (Kinetic studies of the first two reactions are presented below.)

$$\textit{cis}\text{-}[Cr(en)_2F_2]^+ + H_2O \rightarrow \textit{cis}\text{-}[Cr(en)_2F(H_2O)]^{2+} + F^- \quad (1)$$

$$\textit{cis}\text{-}[Cr(en)_2F(H_2O)]^{2+} + H_3O^+ \rightarrow [Cr(en)(en\text{-}H)F(H_2O)_2]^{3+} \quad (2)$$

$$[Cr(en)(en\text{-}H)F(H_2O)_2]^{3+} + H_2O \rightarrow [Cr(en)F(H_2O)_3]^{2+} + en\text{-}H^+ \quad (3)$$

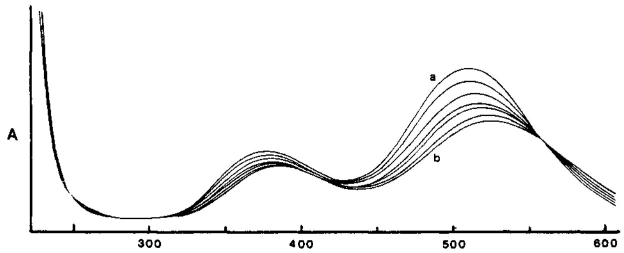

Figure 1. Spectral changes upon heating a chromatographically separated sample of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ in 0.40 M $HClO_4$ solution.

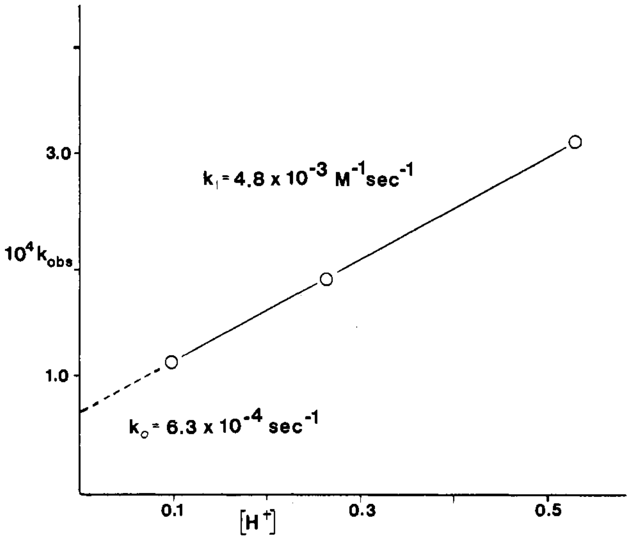

Figure 2. Graph of k_{obsd} vs $[H^+]$ (70 °C) for the aquation of *cis*-$[Cr(en)_2F_2]^+$. The *y* intercept corresponds to the rate constant for the acid-independent path; the slope is proportional to k_1, the rate constant for the acid-dependent path.

Plots of ϵ vs λ for both the difluoro and the chromatographically isolated *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ ion allow prediction of the wavelengths expected for the isosbestic points for reaction 1. Comparison of these values with the observed values

predicted	505, 398, 360 nm
observed	506, 395, 362 nm

further supports the supposition that *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ is the only product formed upon aquation of *cis*-$[Cr(en)_2F_2]^+$.

Supporting evidence for reaction 2 comes from a comparison of the aquation of a chromatographically separated sample of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ with the aquation of a separate sample of *cis*-$[Cr(en)_2F(H_2O)]I_2\cdot H_2O$.[46] The spectral changes accompanying aquation of these separate samples are indistinguishable and show an isosbestic at 553 nm; a second isosbestic is observed initially at about 408 nm but is lost near the end of the reaction. These spectral changes are shown in Figure 1 and represent the changes caused by the complete loss of a bidentate ethylenediamine (reactions 2 and 3).

After completion of the reaction between II and IV, product solutions were loaded onto a cation-exchange column and the resin was washed with water. Analysis of the washings for F^- ion (with Th^{4+}) showed that <1% of the coordinated F^- ion was released during the two-step aquation, consistent with retention of the Cr–F moiety in the product ion.

Heating III in acidic aqueous solution (65 °C) causes a clean red shift in the 518-nm peak with isosbestics near 576 and 420 nm (Figure 1); the spectrum eventually becomes indistinguishable from that of IV (λ_{max} at 530 and 384 nm). No increase in free fluoride ion could be detected (F^- electrode) as the reaction proceeded from III to IV, and thermal degradation of IV indicates that it has a F/Cr ratio of 1.02 (±0.1; two determinations).

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(46) Sample kindly provided by Prof. J. W. Vaughn.

Table I. Rate Data for the Aquation of *cis*-$[Cr(en)_2F_2]^+$

temp, °C	$[H^+]$, M	μ,[a] M	10^4k_{obsd}, s^{-1}
25.0	0.097	0.098	0.0570 ± 0.0010
42.0	0.097	0.098	0.504 ± 0.005
55.0	0.097	0.098	1.86 ± 0.06
70.0	0.097	0.098	8.19 ± 0.26
70.0	0.097	0.500	11.4 ± 0.6
70.0	0.265	0.500	18.1 ± 0.7
70.0	0.500	0.500	30.5 ± 0.5

[a] Ionic strength adjusted with $NaClO_4$.

Table II. Rate Data for the Aquation of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$

temp, °C	$[H^+]$, M	μ,[a] M	10^4k_{obsd}, s^{-1}
40.0	0.100	0.101	0.108 ± 0.003
55.0	0.100	0.101	0.512 ± 0.025
65.0	0.100	0.101	1.30 ± 0.08
70.0	0.100	0.101	1.88 ± 0.10
70.0	0.100	0.101	1.90[b] ± 0.10
70.0	0.100	0.200	2.59 ± 0.02
70.0	0.100	0.500	2.72 ± 0.09
70.0	0.200	0.500	2.71 ± 0.24
70.0	0.500	0.500	2.80 ± 0.05

[a] Ionic strength adjusted with $NaClO_4$. [b] Determined at 365 nm.

Kinetic Studies. Aquation of *cis*-$[Cr(en)_2F_2]^+$. Reaction 1 was monitored at 553 nm, the isosbestic point observed for reactions 2 and 3. As shown in Table I and Figure 2, the data are consistent with the two-term rate expression

$$\text{rate} = [Cr](k_0 + k_1[H^+]) = [Cr]k_{obsd}$$

where $k_{obsd} = (k_0 + k_1[H^+])$ and $[Cr] = [cis\text{-}Cr(en)_2F_2^+]$. At 70 °C, $k_0 = 6.3 \times 10^{-4}$ s^{-1} and $k_1 = 4.8 \times 10^{-3}$ M^{-1} s^{-1}. Activation parameters for k_{obsd} are $\Delta H^* = 90.8 \pm 1.0$ kJ mol^{-1} and $\Delta S^* = -40.7 \pm 2.4$ J mol^{-1} K^{-1} (at 70 °C).

Aquation of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$. Samples of *cis*-$[Cr(en)_2F(H_2O)]I_2{\cdot}H_2O$, separated from I^- by anion-exchange chromatography, were aquated in $HClO_4$ solutions, and the progress of the reaction was monitored at 496 nm. The data (Table II) do not suggest significant acid catalysis and show that the rate constant increases as ionic strength increases. Activation parameters are $\Delta H^* = 83.4 \pm 1.9$ kJ mol^{-1} and $\Delta S^* = 74.0 \pm 3.8$ J mol^{-1} K^{-1}).

Photochemical Behavior of *cis*-$[Cr(en)_2F_2]^+$. Excitation of the low-energy ligand field band of acidic aqueous solutions of *cis*-$[Cr(en)_2F_2]^+$ causes a red shift in that band (isosbestics at 569, 413, and 251 nm) and a decrease in the intensity of the absorbance (Figure 3). Continued photolysis eventually leads to loss of isosbestics, but when a solution of *cis*-$[Cr(en)_2F_2]^+$ (0.001 M) is photolyzed 75% of the way to loss of isosbestics, only 2.9% (±0.1%; two determinations) of the coordinated F^- ion is released to the solution.

Cation-exchange chromatographic separation of a photolyzed solution (pH 3–5) of *cis*-$[Cr(en)_2F_2]^+$ yields two bands:

(a) The first band, eluted with 0.05 M $NaBF_4$ or 0.05 M $NaNO_3$, had a spectrum indistinguishable from that of the *cis*-$[Cr(en)_2F_2]^+$ starting materal; thermal decomposition of the eluted material leads to a solution with a F/Cr ratio of 2.0 (±0.01; three determinations).

(b) A red-violet second band moved down the column at a rate consistent with a 2+-charged species. It had absorbance maxima at 527 nm (ϵ 66.8) and 383 nm (ϵ 34.2) and displayed a F/Cr ratio of 2.0 (±0.1; three determinations).

The spectral changes (red shift with decreased intensity), the elution behavior, and the Cr/F analysis all suggest that the primary photochemical reaction is the aquation of one end of a coordinated ethylenediamine, leading to $[Cr(en)(en\text{-}H)F_2(H_2O)]^{2+}$ (V) (reaction 4).

$$cis\text{-}[Cr(en)_2F_2]^+ + H_3O^+ \xrightarrow{h\nu} \underset{\text{V}}{cis\text{-}[Cr(en)(en\text{-}H)F_2(H_2O)]^{2+}} \quad (4)$$

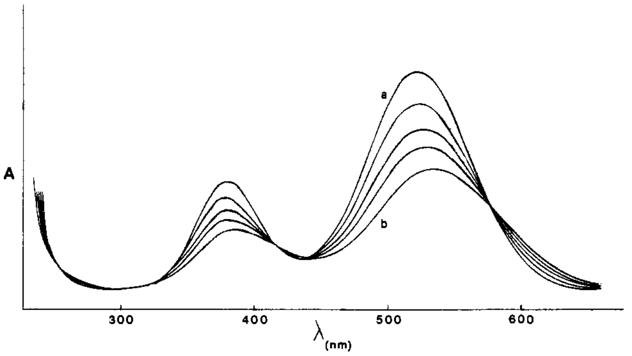

Figure 3. Spectral changes induced upon ligand field photolysis of *cis*-$[Cr(en)_2F_2]^+$ (I) in acidic aqueous solution (20 °C). With a colored-glass filter (λ_{max} > 400 nm), the spectra were obtained after 0, 20, 50, 80, 120, and 150 s of total elapsed photolysis time.

The quantum yield for formation of V, is 0.35 ± 0.04 (three determinations), which is a typical value for photoinduced ligand loss from a Cr(III)–amine complex.

Further support for the photogeneration of a complex with a protonated, monodentate ethylenediamine ligand came from an experiment in which an acidic solution of *cis*-$[Cr(en)_2F_2]^+$ was photolyzed to approximately 20% of the way to loss of isosbestics. When enough NaOH solution was added to this solution to bring the pH to 11, the photoproduct could be chromatographically separated from the starting material by elution with very dilute (0.001 M; pH 11) NaOH solution. At this pH the photoproduct did not adhere to the cation-exchange column, passing through at a rate characteristic of an uncharged species; this is consistent with the formation of $[Cr(en)(\text{mono-en})F_2(OH)]$, the conjugate base of V. Reacidification (dilute $HClO_4$) of this neutral species regenerated an electronic spectrum indistinguishable from that of the initial photoproduct.

Chemical Behavior of $[Cr(en)(en\text{-}H)F_2(H_2O)]^{2+}$. Preliminary studies of the thermal and photochemical behavior of V indicates that this ion undergoes further amine loss. When V is heated (55 °C) in acidic solution, the spectra of chromatographically separated samples of $[Cr(en)(en\text{-}H)F_2(H_2O)]^{2+}$ undergo a red shift, but with little loss in intensity, ending at a spectrum with λ_{max} values of 543 and 390 nm. Ligand field photolysis of V also causes a spectral red shift but is accompanied by a more dramatic decrease in the intensity of the absorbance bands. The resulting solutions were too dilute for careful chromatographic separation and characterization of the products, but both the thermal and photochemical products behave as cations on the cation-exchange column, with the photochemically generated ion having less mobility (suggesting a higher charge) than the thermally produced ion.

On the basis of these preliminary results, we assert that the thermal reaction causes complete loss of the monodentate ethylenediamine ligand, while photolysis of V leads to hydrolysis, and subsequent protonation, of the other ethylenediamine chain (reactions 5 and 6).

$$\underset{\text{V}}{[Cr(en)(en\text{-}H)F_2(H_2O)]^{2+}} + H_2O \xrightarrow{\Delta} \underset{\text{VI}}{[Cr(en)F_2(H_2O)_2]^+} + en\text{-}H^+ \quad (5)$$

$$[Cr(en)(en\text{-}H)F_2(H_2O)]^{2+} + H_3O^+ \xrightarrow{h\nu} \underset{\text{VII}}{[Cr(en\text{-}H)_2F_2(H_2O)_2]^{3+}} \quad (6)$$

Photolysis of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$. Ligand field irradiation of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ (II) causes a red shift and an intensity decrease in the lowest energy ligand field band. An isosbestic point occurs at 552 nm; photolysis to greater than 50% of the way to the loss of the isobestic causes the release of less than 2.9% of the coordinated fluoride ion.

Chromatographic separation of the photolyzed solution yields three distinct bands: the starting material and two photoproducts.

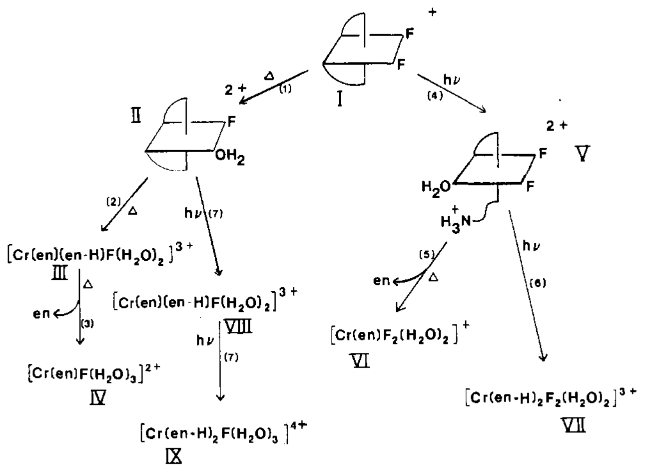

Figure 4. Thermal and photochemical reactions of *cis*-$[Cr(en)_2F_2]^+$ in acidic aqueous solution. Species identified in the text are labeled with Roman numerals; numbered reactions corresond to reactions numbered in text. While the primary photoproduct, V, has cis fluorides, the site of the labilized amine is unknown.

The dication starting material (II) comes off the column first, followed by the two photoproducts. The major photoproduct (VIII) elutes next (with 0.3 M $HClO_4$ as the eluant) as a red band with absorption maxima at 520 and 382 nm. A small amount of a violet material (IX) is also observed, and even with 2.0 M $HClO_4$ as the eluant, it elutes very slowly; it has absorption maxima at 546 and 382 nm.

On the basis of spectral changes, the lack of F^- release during photolysis, and the elution behavior, the major photoproduct (VIII) is identified as $[Cr(en)(en\text{-}H)F(H_2O)_2]^{3+}$. The slowly eluting violet material (IX) is tentatively identified as the secondary photoproduct, $[Cr(en\text{-}H)_2F(H_2O)_3]^{4+}$ (reaction 7). A species

$$\underset{\text{II}}{cis\text{-}[Cr(en)_2F(H_2O)]^{2+}} + H_2O \xrightarrow{h\nu} \underset{\text{VIII}}{[Cr(en)(en\text{-}H)F(H_2O)_2]^{2+}} \xrightarrow{h\nu} \underset{\text{IX}}{[Cr(en\text{-}H)_2F(H_2O)_3]^{4+}} \quad (7)$$

of the same composition as VIII (identified as III) is obtained upon heating II (vida supra); their electronic spectra are very similar, and they may well be the same species. Both III and VIII are chromatographically separated intermediates, and they could not be obtained in sufficient concentrations to compare their chemistries.

Discussion

A variety of thermal and photochemical reactions have been presented here; Figure 4 gives an overview of the observed reactions, and Table III summarizes the electronic spectra of the observed ions. Spectra of some known trans ions are included for comparison with the cis system.

Thermal Reactions. Results presented are consistent with the initial study of Garner,[41] as the primary thermal reaction of *cis*-$[Cr(en)_2F_2]^+$ in acidic aqueous solution is shown to be the stereoretentive release of F^- ion (reaction 1). This contrasts with isomeric *trans*-$[Cr(en)_2F_2]^+$, which undergoes amine aquation under these conditions. On the basis of spectral changes and the chromatographic behavior and Cr/F analyses of the product ions, two subsequent amine aquations of the resulting *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ ion (reactions 2 and 3) are reported.

Table III. Electronic Spectral Maxima of Chromium(III)–Fluoro–Ethylenediamine Complexes

no.	complex	λ, nm (ε, M^{-1} cm^{-1})	ref
I	*cis*-$[Cr(en)_2F_2]^+$	516 (73), 378 (37)	*a*
		516 (75.5), 378 (39.5)	47
	trans-$[Cr(en)_2F_2]^+$	465 (21.0), 397 (13.2), 351 (14.4)	48
II	*cis*-$[Cr(en)_2F(H_2O)]^{2+}$	505 (72.5), 373 (32.0)	*a*
		503 (74.2), 373 (32.4)	42
	trans-$[Cr(en)_2F(H_2O)]^{2+}$	519 (23.1), 457 (23.9), 369 (29.9)	31
III	$[Cr(en)(en\text{-}H)F(H_2O)_2]^{3+}$	518 (49), 376 (27)	*a*
	trans-$[Cr(en)(en\text{-}H)F(H_2O)_2]^{3+}$	519 (40), 410 sh (11.0), 366 (18.6)	50
IV	$[Cr(en)F(H_2O)_3]^{2+}$	530 (42), 387 (24)	*a*
		529 (38.3), 382.5 (22.0)	50
V	$[Cr(en)(en\text{-}H)F_2(H_2O)]^{2+}$	527 (66.8), 383 (34.2)	*a*
VI	$[Cr(en)F_2(H_2O)_2]^+$	543 (54), 390 (28)	*a*
		542 (37), 410 (10.1), 37.1 (12.5)	49
VII	$[Cr(en\text{-}H)_2F_2(H_2O)_2]^{3+}$	538 (47), 390 (28)	*a*
VIII	$[Cr(en)(en\text{-}H)F(H_2O)_2]^{3+}$	520 (48), 382 (25)	*a*
IX	$[Cr(en\text{-}H)_2F(H_2O)_3]^{3+}$	546, 389	*a*

[a] This work.

While a monodentate ethylenediamine complex, III, is an obvious intermediate in the reaction from II to IV, the presence of III is not apparent from the spectral changes shown in Figure 1. Evident for the existence of III is compelling, however, as it can be separated by column chromatography, it has an electronic spectrum intermediate between those of II and IV, and separated samples of III cleanly react in acidic aqueous solution (with isosbestics near 576 and 420 nm) to generate IV. The charges on III and IV would suggest that the latter ion, with the 2+ charge, would be eluted more rapidly than the tripositive III. We observed elution in the reverse order, however, and cite the comments of Linck:[49] "The effect of the pendant protonated group on the ion-exchange properties is a quite characteristic property of this class of compounds. The column mobility is high compared to those of other ions of the same total charge." The tripositive III has just such a protonated, pendant ethylenediamine ligand, so its more rapid elution is not atypical.

It is worth noting that the absorbance changes accompanying reaction 1 do not involve significant changes in the intensity of the ligand field bands, while reaction 2 causes a sharp decrease in band intensity (Figure 1), consistent with a lessening of distortion caused by the bidentate ethylenediamines. Hydrolysis of the monodentate ethylenediamine (reaction 3) would not be expected to significantly relieve distortion away from a pseudooctahedral geometry, and reaction 3 causes only a minor decrease in the intensity of the ligand field bands.

The stereochemistries of these four ions (I → IV) is only partially known; I and II share a cis configuration, but there are five possible geometric isomers for $[Cr(en)(en\text{-}H)F(H_2O)_2]^{3+}$ (III) (four of these retain the *cis*-$Cr(F)(H_2O)$ moiety, with one possible *trans*-$Cr(F)(H_2O)$ isomer). We have no experimental evidence to distinguish between these products. There are two possible geometric isomers for the eventual product, $[Cr(en)F(H_2O)_3]^{2+}$ (a facial and a meridional isomer, based on the three coordinated waters), and either (or both) could be formed from *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ with strict retention of configuration about the Cr(III) center. Interestingly, the spectrum of the $[Cr(en)F(H_2O)_3]^{2+}$ generated here is similar to the spectrum reported by Linck[50] (Table III) for the $[Cr(en)F(H_2O)_3]^{2+}$ ion obtained upon extended aquation of *trans*-$[Cr(en)_2F(H_2O)]^{2+}$. Linck did not speculate on the stereochemistry of that ion, but stereoretentive hydrolysis of *trans*-$[Cr(en)_2F(H_2O)]^{2+}$ would generate only the facial isomer of IV.

The kinetic data presented here offer few surprises. As Garner determined,[41] aquation of the F^- ion proceeds through acid-independent and acid-catalyzed paths, corresponding to aquation of *cis*-$[Cr(en)_2F_2]^+$ and its conjugate acid, *cis*-$[Cr(en)_2F(HF)]^{2+}$, respectively. As observed during the aquation of *trans*-$[Cr(en)_2FX]^{n+}$ (X = F,[50] H_2O[49]), amine aquation of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ is not acid-catalyzed. Activation parameters are within

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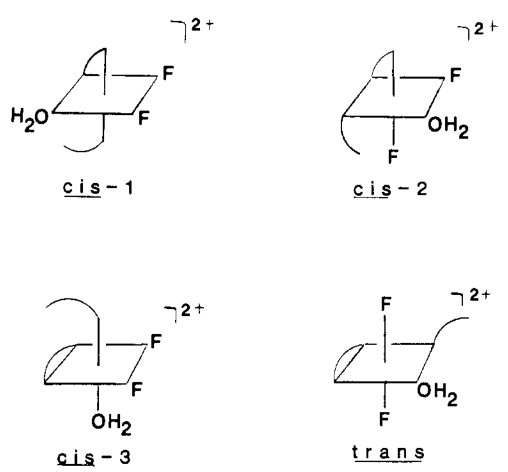

Figure 5. Possible geometric isomers for $[Cr(en)(en{-}H)F_2(H_2O)]^{2+}$.

the range expected for the observed reactions.

Photochemical Reactions. In contrast to Garner's preliminary conclusion,[41] *cis*-$[Cr(en)_2F_2]^+$ is shown to be photoreactive, undergoing photoinduced amine labilization with an efficiency ($\phi = 0.35 \pm 0.04$) characteristic of Cr(III)–amine complexes. Unfortunately, the detailed stereochemistry of the resulting $[Cr(en)(en{-}H)F_2(H_2O)]^{2+}$ ion is not known. There are four possible geometric isomers for $[Cr(en)(en{-}H)F_2(H_2O)]^{2+}$ (Figure 5); three of them retain the *cis*-CrF_2 moiety, and one has a *trans*-CrF_2 configuration. Amine labilization of *trans*-$[Cr(en)_2F_2]^+$ leads to *trans*-$[Cr(en)(en{-}H)F_2(H_2O)]^{2+}$,[11,30,49] with an electronic spectrum (Table III) that cannot be confused with the spectrum of V, allowing a straightforward assignment of cis for V.

Discrimination among the possible cis complexes is less clear, but it is tantalizing to note that when the solution containing V is made basic (vide supra), the resulting conjugate base does not undergo any perceptible ring closure, which would lead to the regeneration of either *cis*- or *trans*-$[Cr(en)_2F_2]^+$. Ethylenediamine ring closing was noted,[49] even in acidic solution, for the $[Cr(en)(en{-}H)F_2(H_2O)]^{2+}$ ion generated upon thermal aquation of *trans*-$[Cr(en)_2F_2]^+$; a configuration with trans fluorides and cis H_2O ligands was suggested for this ion. Evidence of such ring closure in V was sought, as both acidic and basic solutions of V were gently heated (40 °C) for several hours; the acidic solutions are quite stable under these conditions, while the alkaline solutions undergo a slow, uncharacterized decomposition. At a minimum, this suggests that these two $[Cr(en)(en{-}H)F_2(H_2O)]^{2+}$ ions have different isomeric structures. Examination of Figure 5 shows that some ring closing would be possible for three of the four isomers of $[Cr(en)(en{-}H)F_2(H_2O)]^{2+}$ but that the *cis*-**3** isomer has a trans configuration for the monodentate ethyenediamine and the H_2O/OH^- site; ring closure would be impossible for this isomer.

We were unable to produce sufficient quantities of VII to study its properties, and our assignment of its composition must be considered tentative. Its formation from V is accompanied by a red shift in the electronic spectrum, a decrease in the intensity of the spectrum, and no measurable loss of fluoride ions. It also elutes more slowly than the dicationic starting material, consistent with a tripositive ion. The other possible product consistent with the observed red shift in the spectrum is $[Cr(en)F_2(H_2O)_2]^+$, but such a monopositive species would not be expected to elute so slowly. We cannot rule out a photoinduced isomerization, however.

Interpretation of Photoinduced Reactions. The photochemical behavior of *cis*-$[Cr(en)_2F_2]^+$ is consistent with both the semiempirical rules of Adamson[4] and the additive angular overlap model of Vanquickenborne.[5] In the former model, the axis of lowest ligand field strength is either of the identical F–N axes, and labilization of the ligand of higher ligand field strength would indicate amine labilization, consistent with the observed formation of V. Use of the Vanquickenborne model for complexes with D_{4h} holohedral symmetry requires the assignment of the unique N–N axis as the z axis, with the two equivalent fluorides in the xy plane. In this configuration the photoreactive state is the singly degenerate $^4B_{2g}$, which yields the strong-field wave function: $(xz, yz, x^2 - y^2)$. Following the standard practice of assuming that ethylenediamine has the same ligand field parameters as NH_3, we calculate the relative bond strengths for the lowest ligand field excited state:

$$I^*(Cr{-}N)_{ax} = 2\sigma_{ax} = 14370 \text{ cm}^{-1}$$

$$I^*(Cr{-}N)_{eq} = (5/4)\sigma_{eq} = 8980 \text{ cm}^{-1}$$

$$I^*(Cr{-}F)_{eq} = (5/4)\sigma_{eq} + 3\pi_{eq} = 14640 \text{ cm}^{-1}$$

Thus, one would predict labilization of an amine in the equatorial (xy) plane, trans to a fluoride ligand. Stereoretentive photosubstitution at this site would then generate isomer *cis*-**1** (Figure 5) of $[Cr(en)(en{-}H)F_2(H_2O)]^{2+}$; stereomobility is a common feature of Cr(III)–amine photochemistry,[3] however, so such an argument cannot be used with any confidence to assign the configuration of the primary photoproduct. One can predict, with confidence, that amine photolabilization should occur, consistent with the observed photoreactivity.

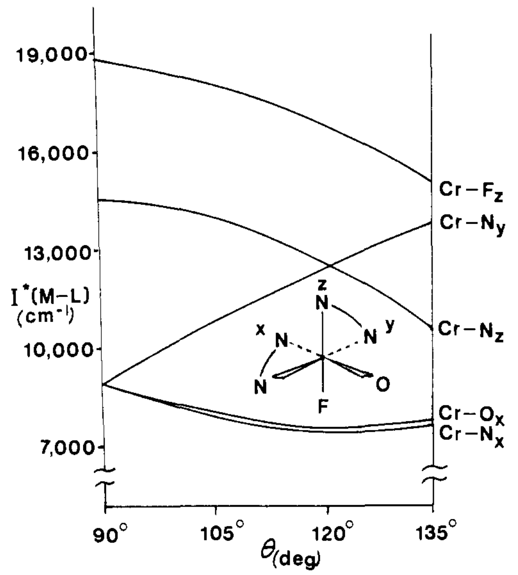

Figure 6. Changes in the bond indeces, $I^*(M{-}L)$, as a function of θ for the $^1B_{1g}$ state of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$. The graph shows that the prediction of labilization along the x axis (N–Cr–O) is not dependent on the specific value of θ.

Photolysis of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$. Experimental difficulties prevented the determination of reliable quantum yields for amine release induced by photolysis of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$, but qualitative observations indicate the photosensitivity of this ion is typical of a Cr(III)–amine complex. Adamson's model predicts that ligand field photolysis will cause labilization of the amine trans to the fluoride; while amine labilization is observed, we have no evidence of which site is photolabilized.

Use of Vanquickenborne's model becomes more difficult for complexes with less than D_{4h} holohedral symmetry. The *cis*-$[Cr(en)_2F(H_2O)]^{2+}$ ion has three distinct ligand–metal–ligand axes (an F–N, an O–N, and an N–N axis). Such an ion has D_{2h} holohedral symmetry, and Vanquickenborne has extended his D_{4h} model to account for the photochemical behavior of such ions.[51] In this model, the photoreactive state is set as $^4B_{1g}$ by orienting the complex so that the axis containing the ligands with the largest ligand field σ parameters is the z axis, while the ligands with lowest σ parameters define the x axis (Figure 6). Population of $^4B_{1g}$ requires ligand field excitation of an electron from the d_{xy} orbital to a mixture of the e_g-derived orbitals:

$$xy \rightarrow (\sin\theta)(x^2 - y^2) + (\cos\theta)(z^2)$$

where θ is introduced to describe the appropriate mixing of the

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(51) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1981**, *20*, 110.

$x^2 - y^2$ and the z^2 orbitals in the photoreactive state. Unfortunately, determination of the numerical value of θ is not straightforward, as it depends on the relative values of the σ parameters for all six ligands and the repulsion parameters, B and C, and requires a complete numerical state calculation.[51] Fortunately, θ is constrained to lie between $\pi/2$ and $3\pi/4$, and for *cis*-$[Cr(en)_2F(H_2O)]^{2+}$, there is little ambiguity in the interpretation of the calculation.

The equations used to determine the relative strengths of the Cr-ligand bonds (the bond indices) in the photoreactive states are[51]

$$I^*(ML_z) = 2\sigma_z + (2 - \cos^2\theta)\pi_z$$

$$I^*(ML_y) = 3\sigma_y + [2 - \cos^2(\theta - \pi/3)]\pi_y$$

$$I^*(ML_x) = 3\sigma_x + [2 - \cos^2(\theta + \pi/3)]\pi_x$$

The values of the bond indices clearly depend on the value of θ, but it turns out that the exact value of θ has little effect on the predicted photochemistry of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$. As shown in Figure 6, the weakest Cr-ligand bonds are the Cr-OH_2 and the Cr-N bonds (on the x axis) throughout the posssible range for θ. The indices for these two ligands are so similar that it may be overextending the model to choose between them; at their maximum separation, when $\theta = 2\pi/3$, $I^*(M\text{-}OH_2) = 7440\ cm^{-1}$ and $I^*(M\text{-}N_x) = 7180\ cm^{-1}$. For very small values of θ (between 90 and 92.7°), the index for the Cr-OH_2 bond is slightly less than that of the Cr-N bond, while, throughout most of the permissible region for θ (92.7-135°), the Cr-N bond has the lower bond index.

These calculations imply that either photoinduced Cr-N or Cr-OH_2 bond cleavage would be expected. While this analysis clearly rules out photoinduced Cr-F bond cleavage, the lack of detailed stereochemical information about the photoreaction prevents a critical evaluation of the theoretical model. Photoinduced water release could only be detected if isomerization to *trans*-$[Cr(en)_2F(H_2O)]^{2+}$ occurred; the spectrum of this ion is known to have a peak at about 457 nm,[31] and we could find no evidence of such a band. Stereoretentive water exchange would, of course, not have been detectable. Thus, the observed amine release is consistent with the Vanquickenborne model, but information on the stereochemistry of the photoinduced amine release would provide a more demanding test of the model.

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Contribution from the Woods Hole Oceanographic Institution, Howard Hughes Medical Institute, Woods Hole, Massachusetts 02543,
and Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Temperature-Jump Relaxation Study of the Zn^{2+}-Chlorophenol Red System

Joseph Bidwell[†] and John Stuehr*[‡]

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A temperature-jump relaxation study was carried out on the system Zn^{2+}-chlorophenol red in an attempt to locate the octahedral/tetrahedral conversion involving the aquo ion. A single relaxation time (50-100 μs) was observed. The detailed concentration and pH dependences were consistent with a series of coupled protolysis/hydrolysis/proton-exchange steps. The observed relaxation time corresponded essentially to the reactions $ZnOH^+ + H^+ \rightleftharpoons Zn^{2+}$ and $ZnOH^+ + HIn \rightleftharpoons Zn^{2+} + In^-$, for which the forward rate constants were 2.2×10^{10} and $1.0 \times 10^8\ M^{-1}\ s^{-1}$, respectively. These are comparable to analogous rate constants in other proton-transfer reactions. We conclude that any structural change involving Zn^{2+} does not occur to an extent that permits kinetic detection.

Introduction

In recent years our laboratory has carried out a series of rapid kinetic studies involving divalent metal and ligands such as amino acids[1] and nucleotides.[2,3] Work to date has primarily focused on the metal ions Ni^{2+}, Cu^{2+}, and Mg^{2+}.

Some years ago we carried out a temperature-jump relaxation study involving the complexation kinetics of Zn^{2+} with glycine.[4] The rate constant for the formation of the $Zn(gly)^+$ complex (two coordination sites bound) was "normal". That is, its value was consistent with the rate of displacement of solvent molecules from the primary coordination sphere of the metal ion. An unusual feature of that study was that the formation of the second (bis) complex seemed to be associated with a slow interconversion; we tentatively attributed this to a structural change involving the metal ion. Although there have been other kinetic studies involving Zn^{2+} by *T*-jump[5,6] and ultrasonic methods,[7,8] no "normal" *bis* complexation rate has been observed for ligands of coordinating ability of 2 or more. Recent Raman IR data[9] and statistical interpretation[10] of Zn^{2+}-binding constants support the concept of an octahedral-tetrahedral structural change for the Zn^{2+} aquo ion. Nevertheless, despite several attempts to detect (and one report[11] of) the kinetics of the structural change in aqueous Zn^{2+}, it has to date eluded actual observation.

More recently, we have turned our attention to the complexation kinetics of Zn^{2+} with other ligands[12] via temperature-jump spectroscopy. When "blanks" were tested (solutions lacking one component of the metal ion-indicator-ligand system), the blank consisting of Zn^{2+} and indicator often showed a relaxation effect in the 10^{-4}-s time region over the pH range 6-7. Under optimal conditions this effect had a very large amplitude (Figure 1). We felt it was necessary to know the cause of this effect prior to continuing the complexation studies with Zn^{2+}. In addition, there was the possibility that this could be the long-sought structural change postulated in aqueous Zn^{2+}. For these reasons, we carried out this detailed study of the Zn^{2+}-chlorophenol red system.

[†] Howard Hughes Medical Institute.

[‡] Case Western Reserve University.

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