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Photolysis of *trans*-$[Cr(en)_2NH_3F]^{2+}$, $[Cr(NH_3)_5F]^{2+}$, and *trans*-$[Cr(en)_2FCl]^+$

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Received April 7, 1977 AIC70255A

The photolyses of *trans*-$[Cr(en)_2NH_3F]^{2+}$ (A) and $[Cr(NH_3)_5F]^{2+}$ (B) in acidic aqueous solution in the wavelength range 365–536 nm and 10–20 °C gave rise to base loss as the predominant photoprocess. The data on A show that loss of ammonia is preferred over ethylenediamine under all conditions studied. The overall yields and their variations with temperature and wavelength for the two complexes are very similar, supporting a division of the total ammonia yield from B into analogous axial and equatorial components. This reveals that the predominant loss of ammonia from B is from the position trans to the fluoride ligand. Ammonia loss from A leads to 99% *cis*-aquofluoro product, whereas B leads to 15% trans and 85% cis. Again assuming parallel behavior of the compounds, equatorial loss of ammonia from B must therefore be associated with stereochemical change. If fluoride is accepted to be a strong σ and π donor, then the results are shown to be in disagreement with predictions of the molecular orbital/σ-donor models of Cr(III) photochemistry.

Introduction

In 1967 Adamson[1] proposed that the photosubstitution reactions of chromium(III) complexes on irradiation into the lowest quartet absorption band could be predicted as preferential loss of the strong field ligand on the weakest field axis with an overall quantum yield about that for an octahedral complex of the same average ligand field. Irradiation into higher energy states was predicted to lower the discrimination.

For a number of complexes roughly this behavior has been observed to hold, but for $[Cr(NH_3)_5X]^{2+}$ the data are ambiguous since no, or inadequate, data on the original position of the leaving ammonia is available. Also some clear exceptions exist. Linck and co-workers found that $[Cr(en)_2F_2]^+$ lost mainly ethylenediamine,[2] $[Cr(en)_2FCl]^+$ lost mainly chloride,[3] and $[Cr(en)_2(NCS)_2]^+$ lost thiocyanate and ethylenediamine[4] in a 2:1 ratio. They proposed that the σ-donor strength,[2] not the overall ligand field strength of the ligands, determined the axis of labilization and ligand lost. Also, together with others,[5,6] they recognized the possible role of π bonding in the excited state in stabilizing a π-donor ligand against substitution. This renders the rules applicable but reduces their predictive power because of the interplay of conflicting and uncertain parameters. Adamson et al.,[7] furthermore, found the sterically constrained *trans*-$[Cr(cyclam)Cl_2]^+$ to photolyze with ϕ only 3×10^{-4}, supporting a proposal[8] that stereochemical change might be a requirement of Cr(III) photosubstitution. The rules can be restated to incorporate these aspects[8] and, given judgement and knowledge of the necessary parameters, can be of predictive utility. In parallel, Zink has published theoretical (MO) papers[6,9,10,11] dealing with the nature of labilization for doublet and quartet states, the d_{z^2} character in the lowest quartet excited state at ground-state geometry, and the nature of the ligand lost from a labilized axis.

To be able to obtain data on the nature of labilization, reactivity, and stereochemistry of reaction for various excited states of model compounds, we have synthesized[12] *trans*-$[Cr(en)_2NH_3X]^{n+}$ for X = F^-, Cl^-, NCS^-, and H_2O as signposted models for the analogous pentaammines. A preliminary study[13] of the isothiocyanato compound showed that for the lowest excited quartet the base released in photolysis was only about 40% ammonia. Therefore this compound, and by analogy $[Cr(NH_3)_5NCS]^{2+}$, did not entirely follow the original rules. It fits the σ-donor version if isothiocyanate is a slightly weaker σ donor than ammonia and a reasonably good π donor, but unfortunately good spectral data to support this is not presently available. The MO theory was also consistent with the results.

More recently we have published an account[14] of the photochemistry of the chloro analogue. In this compound the ratio of ammonia to ethylenediamine was wavelength and temperature dependent suggesting participation of two states in the photochemistry, but on irradiation into the ^4E state the reaction mode was exclusively ammonia loss to give essentially *cis*-$[Cr(en)_2H_2OCl]^{2+}$ consistent with the rules mentioned above as well as the σ-donor/molecular orbital theories.

The purpose of the present paper is to describe a study of the fluoro analogue. In view of the results obtained for other fluoro compounds,[2,3] this compound might be expected to be somewhat unusual, and also it was interesting to see whether the photochemistry of this compound would fit within the framework of any of the existing models.

The nature of the stereochemistry of Cr(III) photoreactions is a topic which has recently been the subject of some dispute.[2–4,14–16] Since it was predicted by the models that a considerable proportion of the photoreaction of *trans*-$[Cr(en)_2NH_3F]^{2+}$ should consist of ethylenediamine aquation, it was hoped that a comparative study of the stereochemistry of *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $Cr(NH_3)_5F^{2+}$ would provide information on the stereochemistry of photoaquation subsequent to equatorial (in-plane or *xy*-plane) labilizations. The isomer nature of the product of *trans*-$[Cr(en)_2FCl]^+$ was also reinvestigated since it has been reported[3] to photolyze to yield significant amounts of *trans*-$[Cr(en)_2FH_2O]^{2+}$.

Experimental Section

cis- **and** *trans*-$\mathbf{[Cr(en)_2NH_3F](ClO_4)_2}$. These were prepared and characterized as described in a previous paper.[12] The compounds were purified by repeated fractional crystallization and checked by measurement of the molar absorptivities of the ligand field absorption bands. The purity, particularly the presence of residual cis compound in the trans, was finally checked by ion-exchange chromatography. This showed that the isomer purity of the trans compound used for the photochemical study was better than 99%.

$[Cr(NH_3)_5F](ClO_4)_2$ was prepared as described by Kyuno, Kamada, and Tanaka[17] and purified by repeated fractional crystallization. *trans*-$[Cr(en)_2FCl]ClO_4$ was prepared as described by Wirth, Bifano, Walters, and Linck.[18]

Other aspects of the experimental procedures have been previously published, generally[14] and in detail.[19]

Results

Thermal Reactions of the Complexes. As a necessary prerequisite to the photochemical investigations information on the thermal lability of the compounds was required. The thermal aquation of $[Cr(NH_3)_5F]^{2+}$ has been investigated by Linhard and Weigel[20] and more recently by Jones and Phillips.[21] The earlier study indicated that the first step involved loss of ammonia but the later work indicated that fluoride loss was the preferred mode in the primary step while ammonia loss resulted mainly or exclusively from secondary reactions. Jones and Phillips found the rate of fluoride aquation to be independent of $[H^+]$ between pH 1 and 10, with a rate constant of 3.5×10^{-6} s^{-1} at 45 °C and an apparent activation energy of 25.0 kcal mol^{-1}. At 20 °C the rate constant, $1.2 \times 10^{-7}\ s^{-1}$, is so small that thermal reaction is completely negligible under the conditions of the photochemical investigations.

Data on the thermal reactions of *trans*-$[Cr(en)_2FCl]^+$, investigated by Wirth and Linck,[3] indicate that the major reaction mode is chloride loss to produce *trans*-$[Cr(en)_2H_2OF]^{2+}$, with a first-order rate constant of 6.2×10^{-5} s^{-1} at 25 °C. Ethylenediamine loss also occurs, but much more slowly.

trans-$[Cr(en)_2NH_3F]^{2+}$ was found to aquate thermally with proton uptake. The first-order (to at least 6%) rate constant for decomposition in the pH range 3.1–3.6 and ionic strength 0.04 ($KClO_4$) was found to be $4.3 \times 10^{-6}\ s^{-1}$ at 11 °C and $1.8 \times 10^{-5}\ s^{-1}$ at 20 °C; these values yield an apparent activation energy of 26 kcal/mol. At 20 °C, about 15% of the proton uptake was found to correspond to release of ammonia. No attempt was made to determine the rate of fluoride aquation, but by comparison with similar fluoro complexes, e.g., $[Cr(NH_3)_5F]^{2+}$ [20,21] and *trans*-$[Cr(en)_2F_2]^+$,[22] fluoride loss is expected to be much smaller than proton uptake.

The possible reaction modes for *trans*-$[Cr(en)_2NH_3F]^{2+}$ are analogous to those for the chloro analogue,[14] namely

$$trans\text{-}[Cr(en)_2NH_3F]^{2+}\ (R) \xrightarrow{H^+} [Cr(en)(enH)NH_3H_2OF]^{3+}\ (P) \quad (1a)$$

$$P \xrightarrow{H^+} [Cr(en)NH_3(H_2O)_2F]^{2+} + enH_2^{\ 2+} \quad (1b)$$

$$R \xrightarrow{H^+} [Cr(en)_2H_2OF]^{2+} + NH_4^+ \quad (2)$$

$$R \xrightarrow{H^+} [Cr(en)_2NH_3H_2O]^{3+} + F^- \quad (3)$$

Ion-exchange chromatography showed that the product of reaction 2 was *trans*-$[Cr(en)_2H_2OF]^{2+}$ and no cis product or $[Cr(en)NH_3(H_2O)_2F]^{2+}$ bands were observed. Reaction 1b is likely to be slow relative to 1a and since many monodentate protonated ethylenediamine species are now known to be fairly stable, these results indicated that the main thermal reactions are eq 1a and 2. The approximate rate constants at 20 °C are $k_{1a} = 15 \times 10^{-6}\ s^{-1}$ and $k_2 = 3 \times 10^{-6}\ s^{-1}$.

These rate measurements show that the thermal reactions of *trans*-$[Cr(en)_2NH_3F]^{2+}$ are fairly slow so that the thermal corrections required in the photochemical work are small and can be precisely applied using the approximate rate constants obtained in this cursory examination.

Photolysis of *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$. Photolysis of *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$ in acidic solutions occurs with increase in the pH of the solution. At 546 nm and 20 °C, the quantum yields for proton uptake for the two complexes were found to be 0.41 and 0.43, respectively. For the former complex about 65% of the proton uptake was due to ammonia loss and, at 20 °C, this ratio was approximately the same at 436 and 366 nm. The fluoride yield was not measured for either complex but by analogy with similar fluoro complexes[2,3] can be expected to be small at the wavelengths investigated.[23]

Product Stereochemistry. For studies of the stereochemistry of the reaction products, *trans*-$[Cr(en)_2NH_3F]^{2+}$ was photolyzed at 436 nm, while $[Cr(NH_3)_5F]^{2+}$ was photolyzed at 366, 436, and 546 nm. For the former complex, the emphasis was on the stereochemistry of axial labilization (NH_3 loss) and the wavelength was chosen to minimize secondary photoreactions; for $[Cr(NH_3)_5F]^{2+}$, the emphasis (vide infra) was on the stereochemistry of equatorial labilization, and irradiations at different wavelengths allow a comparison of the trans/cis product ratios for $[Cr(NH_3)_5F]^{2+}$ photolysis with the axial/equatorial labilization ratios observed for *trans*-$[Cr(en)_2NH_3F]^{2+}$ photolysis. When solutions of these two complexes were photolyzed to the extents necessary to yield adequate product for ion-exchange analysis and spectral characterization of the species of interest, three products were resolvable from the *trans*-$[Cr(en)_2NH_3F]^{2+}$ mixture and five from the $[Cr(NH_3)_5F]^{2+}$ mixture.

Bands II and III of the chromatogram of the photolyzed *trans*-$[Cr(en)_2NH_3F]^{2+}$ mixture were *cis*-$[Cr(en)_2H_2OF]^{2+}$ and *trans*-$[Cr(en)_2NH_3F]^{2+}$, respectively, identified from the UV–visible spectra of collected fractions. The concentration of the species corresponding to band I was too low for spectral examination, but the elution time was the same as that for an observed product of thermally aquated *trans*-$[Cr(en)_2NH_3F]^{2+}$ and for an authentic sample of *trans*-$[Cr(en)_2H_2OF]^{2+}$. Band I can therefore be identified, at least in part, as the latter. It should be noted that under the conditions used for photolyzing samples of *trans*-$[Cr(en)_2NH_3F]^{2+}$ for chromatographic work, no resolvable secondary product was observed. Also note that the expected $[Cr(en)(enH)NH_3H_2OF]^{3+}$ product would be eluted only at high concentrations of eluent (≥1.5 M ammonium sulfate), a condition found to cause a significant rise in the baseline of the chromatogram, probably due to increased leaching of absorbing resin impurities. Hence no attempt was made to characterize the tripositive complex product(s).

Bands III, IV, and V of the chromatogram of the $[Cr(NH_3)_5F]^{2+}$ mixture were spectrally examined and by comparison with known spectra[17,18,24] could be assigned to *trans*-$[Cr(NH_3)_4H_2OF]^{2+}$, *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$, and $[Cr(NH_3)_5F]^{2+}$, respectively.

The concentrations of the species corresponding to bands I and II were too low for spectral analysis. These last are likely due to secondary photolysis as they are proportionately smaller at lower conversions and their ion-exchange elution characteristics suggest that they are easily eluted dipositive ions, likely candidates being the isomers of $[Cr(NH_3)_3(H_2O)_2F]^{2+}$.

In the absence (or near absence) of secondary photolysis, the trans/cis product ratios may, in principle, be directly determined from the ion-exchange chromatograms. Unfortunately, however, the fluoride-containing products of *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$ gave rise to difficulties as shown by a comparison of the quantities of products determined from the integrated chromatogram peaks (A) and the moles expected from the measured quantum yields (B),[3,25,26] shown in Table I. For the *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$ products, the ratio A/B (which may be viewed as a relative sensitivity of the detection system for the products) is on average about 0.8. In contrast, this ratio was always close to 1.00 for the products of other chromium(III) complexes. These results indicate that there occurred either incomplete oxidation of the fluoro complexes or partial formation of species which are not as highly absorbing as CrO_4^{2+}, an example being CrO_3F^-, which has a molar absorptivity of about 1800 L mol^{-1} cm^{-1} at 370 nm[27] (cf. ϵ_{370} 4500 L mol^{-1} cm^{-1} for CrO_4^{2-}). The cited species is apparently reasonably stable in water.[28]

However, despite the above problems with absolute determinations, approximate trans/cis product ratios may be determined under the assumption that for a particular ion-exchange chromatogram the sensitivity is the same for a given pair of acido–aquo isomers. Such ratios are presented in Table II for the photoproducts of *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$. The uncertainty in the values may be inferred from the magnitude and range of the (A/B) values, Table I, to be no greater than 20%. For the $[Cr(NH_3)_5F]^{2+}$ products, the apparent trans/cis ratio is approximately temperature and wavelength independent, but there appears to be some correlation with the number of moles of product analyzed in a particular run; at 546 nm, the trans/cis ratio is 0.24 for 18 μmol of product, 0.21 for 11 μmol, and 0.18 for 4 μmol. Extrapolation of these three points to the limit of 0 μmol yields

Table I. Calibration Data for the Ion-Exchange Determination of Photoproducts of Some Cr(III) Complexes

Complex	Trial	μmol of product: From band areas (A)	μmol of product: Expected[a] (B)	A/B	% conversion[b]
trans-$[Cr(en)_2NH_3F]^{2+}$ [c]	1	5.4	6.6	0.82	10.1
	2	5.9	7.8	0.76	13.1
$[Cr(NH_3)_5F]^{2+}$ [d]	1	3.6	4.2	0.86	7.0
	2	2.8	3.8	0.74	6.3
	3	3.8	4.4	0.86	7.3
	4	3.6	5.1	0.71	8.4
	5	2.7	4.0	0.68	7.0
	6	3.6	4.3	0.84	7.1
	7	15.6	18.5	0.84	15.4
	8	14.4	18.2	0.79	15.2
	9	7.6	10.5	0.72	17.6
trans-$[Cr(en)_2FCl]^+$	1	4.9	4.7	1.04	6.8
	2	6.8	6.7	1.01	11.1
$[Cr(NH_3)_5Cl]^{2+}$	1	4.3	4.5	0.94	7.5
	2	6.6	6.7	0.99	11.0
	3	3.0	2.9	1.03	4.8
trans-$[Cr(en)_2Cl_2]^+$	1	4.4	4.4	1.00	7.3
	2	6.2	6.3	0.98	10.5

[a] Calculated from the light flux, quantum yield, and irradiation time but not corrected for inner-filter effects or secondary photolysis. For the last three complexes, the quantum yields used were from ref 3, 25, and 26, respectively. [b] Percentage conversion based on measured quantum yields. [c] For this complex, the comparison is between μmol of *cis*- and *trans*-$[Cr(en)_2H_2OF]^{2+}$ found and calculated from the measured corrected quantum yield for ammonia loss. [d] For this complex, the comparison is between the total μmol of all primary and secondary photolysis products and is calculated from the measured corrected quantum yield for proton uptake.

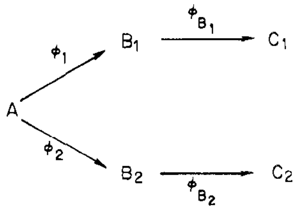
a value of 0.16 for the trans/cis ratio. This is similar to the average value of 0.18 obtained for the runs at low conversions (trials 1–6, Table II); in the following discussion no emphasis is placed on the exact value.

In contrast to the relative high trans/cis product ratios found for $[Cr(NH_3)_5]^{2+}$, the two trials for *trans*-$[Cr(en)_2NH_3F]^{2+}$, Table II, show uncorrected ratios of only 0.047 and 0.037 and, once corrected for thermal production of the trans product, yield 0.012 and 0.005, respectively. The variability of these last values is due to the difficulty in matching the temperature profiles of the thermal and photolysis runs—the *trans*[Cr-$(en)_2H_2OF]^{2+}$ formed thermally corresponds to only 0.3% decomposition. For the purpose of later discussions, a value of 0.01 ± 0.005 for the trans/cis product ratio will be used.

Corrections for Secondary Photolysis. A knowledge of the trans/cis product ratios suffices to correct the measured quantum yields for inner filtering during photolysis, but to correct for secondary photolysis, quantum yields for the photoreactions of the primary photoproducts are required. For the fluoro complexes considered here, exact values were impossible to obtain because of the uncertainties in the chromatographic determination of the products. Since the corrections are expected to be generally small, however, estimated values suffice. For the products of $[Cr(NH_3)_5F]^{2+}$ photolysis, *trans*-$[Cr(NH_3)_4H_2OF]^{2+}$ is likely to undergo photoexchange of water as the predominant mode and a quantum yield for NH_3 loss, Φ_{NH_3}, of zero may be assumed; *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$ is likely to lose NH_3 and a quantum yield similar to that for *cis*-$[Cr(en)_2H_2OCl]^{2+}$, namely, 0.2, may be assumed. For the products of *trans*-$[Cr(en)_2NH_3F]^{2+}$ photolysis, the *trans*-$[Cr(en)_2H_2OF]^{2+}$ can be neglected since its concentration is always low; of the two major photoproducts, *cis*-$[Cr(en)_2H_2OF]^{2+}$ should be similar in photoreactivity to *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$ and again a quantum yield of 0.2 for proton uptake, Φ_{H^+}, is assumed; Φ_{H^+} for the second product, $[Cr(en)(enH)NH_3H_2OF]^{3+}$, is also assumed to be 0.2 while Φ_{NH_3} is assumed to be 0.1. Although the absorption spectrum of the $[Cr(en)(enH)NH_3H_2OF]^{3+}$ product is not known, a reasonable assumption is that it is the mean of those for *cis*-$[Cr(en)_2H_2OF]^{2+}$ and *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$.

For convenience, the parameters used for the correction of the crude quantum yields are collected and presented in Table III.

Corrections of the crude quantum yields for transmission changes, inner-filter effects, and secondary photolysis were made as described before,[14] except that the reaction scheme, for both fluoro complexes, is



The corrected quantum yields are given in Table IV. In all cases the corrections amount to <2% and any errors due to uncertainty in the parameters for the corrections are very small.

Included in Table IV are estimated values of the quantum yields for axial (Φ_{ax}) and equatorial (Φ_{eq}) ammonia loss for $[Cr(NH_3)_5F]^{2+}$. These values were derived under the assumption, discussed later, that Φ_{ax} is the same as for *trans*-$[Cr(en)_2NH_3F]^{2+}$.

Discussion

Reaction Modes in Photolysis of *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$. The quantum yield data, Table IV, show that both *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$ show similar large quantum yields for proton uptake. No evidence was obtained for any significant fluoride loss,[23] in agreement with expectations based on studies of other fluoro complexes. For

Table II. *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$ Photoproduct Isomer Ratios

Complex	Trial	λ,[a] nm	T, °C	(Trans/cis)$_{measd}$[b]	(Trans/cis)$_{cor}$[c]	% conversion[d]
trans-$[Cr(en)_2NH_3F]^{2+}$	1	436	10	0.047	0.012	
	2		10	0.037	0.005	
$[Cr(NH_3)_5F]^{2+}$	1	366	10	0.17_4		6.8
	2		20	0.19_8		7.1
	3	436	10	0.15_1		7.3
	4		20	0.19_3		8.4
	5	546	10	0.17_8		7.0
	6		20	0.18_3		6.3
	7		10	0.233		15.4
	8		10	0.232		15.2
	9		10	0.206		17.6

[a] Wavelength of irradiation. [b] Measured product ratio; no corrections for thermal reactions. [c] Corrected for thermal production of trans product. (No cis product appears from the thermal reactions.) [d] Calculated from the measured quantum yields.

Table III. Molar Absorptivities of $[Cr(NH_3)_5F]^{2+}$, *trans*-$[Cr(en)_2NH_3F]^{2+}$, and Their Major Photoproducts at the Wavelengths of Irradiation and the Photolysis Quantum Yields for the Products

Complex	ϵ_{366}	ϵ_{436}	ϵ_{546}	Φ_{H^+}[a]
trans-$[Cr(en)_2NH_3F]^{2+}$	23.0	21.2	12.8	–
cis-$[Cr(en)_2H_2OF]^{2+}$	30.0	16.0	37.3	0.2
$[Cr(en)(enH)(NH_3)H_2OF]^{3+}$ [c]	22	11	29	0.2
$[Cr(NH_3)_5F]^{2+}$	20.5	12.2	19.0	–
cis-$[Cr(NH_3)_4H_2OF]^{2+}$	13.1	5.2	20.0	0.2
trans-$[Cr(NH_3)_4H_2OF]^{2+}$ [b]	27	12	20	0

[a] Assumed quantum yield for proton uptake as discussed in text. [b] Estimated from published spectrum.[18] [c] Estimated as discussed in text. $\Phi_{NH_3} = 0.10$ is assumed for this product (or product mixture).

trans-$[Cr(en)_2NH_3F]^{2+}$ the data on the directly determined ammonia yields enabled division of the proton uptake into that due to ammonia loss and that due to production of a monodentate protonated ethylenediamine species. No direct evidence was obtained for this latter species, but it can be inferred indirectly from the absence of any unusual postirradiation proton uptake or release and is supported by detailed studies of other ethylenediamine compounds.

The data reveal that ammonia loss is the predominant reaction mode at all temperatures and wavelengths studied and that the quantum yield is relatively insensitive to conditions. In contrast the remainder, due to ethylenediamine aquation, is quite temperature sensitive at 546 nm and shows wavelength variations in yield.

Ion-exchange chromatography of the products showed that the product arising from ammonia aquation was $[Cr(en)_2H_2OF]^{2+}$ and a quantitative study of the stereochemistry of the product, Table III, showed that it was at least 97% cis and, after correction for the *trans*-$[Cr(en)_2H_2OF]^{2+}$ produced by thermal aquation of ammonia, most probably at least 99% cis. This result is similar to data obtained in other studies of the stereochemistry of the products of axial labilization.[8,14] This result is further discussed later, together with the results for $[Cr(NH_3)_5F]^{2+}$, Table II, where the product of ammonia aquation was found to be a mixture of about 15% *trans*- and 85% *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$ (at 0% conversion).

Temperature and Wavelength Dependence of Quantum Yields. The results in Table IV show that for *trans*-$[Cr(en)_2NH_3F]^{2+}$ the quantum yield of ammonia loss shows little or no temperature variation at the two wavelengths studied, while the quantum yield for ethylenediamine is quite temperature dependent at 546 nm but not at 436 nm. Plots of log Φ vs. $1/T$ yield apparent activation energies (kcal mol^{-1}, 99% confidence level) of 11 ± 7 and 1 ± 3 at 546 nm and −1 ± 4 and 0.4 ± 2 at 436 nm for ethylenediamine and ammonia aquation, respectively.

Comparison of the data for the two complexes, *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$, reveals similar magnitudes, wavelength and temperature dependences of the quantum yields for proton uptake. On the assumption that the two complexes are similar enough in spectroscopic parameters and excited-state properties that the axial yields of ammonia would be the same, it is possible to divide the overall ammonia yield from $[Cr(NH_3)_5F]^{2+}$ into an equatorial and axial component. Table IV shows the values calculated by this method. The derived quantum yields show very similar trends to those already discussed for *trans*-$[Cr(en)_2NH_3F]^{2+}$. This is due in part, of course, to the carry over of the axial ammonia yield values, but nevertheless the striking similarity in the temperature and wavelength dependence of the quantum yields supports the assumption made in their derivation.

Comparison with Theory. Even a cursory examination of the data reveals that it does not fit easily into the framework of the current models. The background information available on behavior of analogous fluoro complexes, combined with the predictions of the σ-donor/MO theories based on currently available spectroscopic parameters for F^-, NH_3, and en, would lead one to predict ethylenediamine loss from *trans*-$[Cr(en)_2NH_3F]^{2+}$ and equatorial ammonia loss from $[Cr(NH_3)_5F]^{2+}$ as the predominant reaction modes. We now consider the possible reasons for the departure from these predictions, whether it is a genuine failure of the theories or is simply due to anomalous behavior of these compounds.

The observations of differing wavelength dependences for the axial (NH_3) and equatorial (en) photoaquation modes of *trans*-$[Cr(en)_2NH_3F]^{2+}$ suggest that reaction must be originating from at least two types of excited state. In an earlier paper describing the photochemistry of the analogous compound *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ we proposed a model in which the two lowest vibrationally equilibrated quartet states, $^4E^0$ and $^4B_2{}^0$, corresponding respectively to relaxation with axial and equatorial bond extension, were thought to give rise to different reactivity patterns. This suggestion was attractive at least in part because these reactivity patterns were then consistent with predictions of the molecular orbital theory. For $[Cr(en)_2NH_3F]^{2+}$ such support is not available since the predictions of molecular orbital theory appear contrary to our observations. Furthermore, recent work by Kane-Maguire and co-workers[29] and also by Forster and co-workers[30] suggests alternative mechanisms to account for wavelength dependence of quantum yields. First Kane-Maguire and co-workers[29] have proposed a variation in intersystem crossing efficiency with excitation energy, coupled with the possibility of reaction by both vibrationally equilibrated and nonequilibrated species. More recently Forster and co-workers[30] have suggested that preselection of particular solvation environments by variation in wavelength of excitation may play a role. We therefore

Table IV. Quantum Yields for *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$

Complex	λ, nm	T, °C	Φ_{H^+}[a]	Φ_{ax}[b]	Φ_{eq}[c]	Φ_{eq}/Φ_{H^+}
trans-$[Cr(en)_2NH_3F]^{2+}$	546	10	0.320 ± 0.002 (3)	0.254 ± 0.004 (4)	0.07 ± 0.005	0.22
		20	0.408 ± 0.009 (10)	0.267 ± 0.005 (6)	0.14 ± 0.01	0.34
	436	10	0.428 ± 0.010 (3)	0.268 ± 0.009 (2)	0.16 ± 0.01	0.38
		20	0.426 ± 0.005 (3)	0.275 ± 0.010 (2)	0.15 ± 0.01	0.35
	366	20	0.435 ± 0.005 (2)	0.276 ± 0.010 (2)	0.16 ± 0.01	0.37
$[Cr(NH_3)_5F]^{2+}$	546	10	0.348 ± 0.004 (8)	0.25	0.10	0.29
		20	0.433 ± 0.010 (3)	0.27	0.16	0.37
	436	10	0.409 ± 0.003 (3)	0.27	0.14	0.34
		20	0.442 ± 0.006 (3)	0.28	0.16	0.36
	366	20	0.430 ± 0.004 (3)	0.28	0.15	0.35

[a] Quantum yield for H^+ uptake; $\phi \pm S$, where S is the standard deviation for the set of measurements; the numbers in parentheses indicate the number of measurements. [b] Quantum yield for axial labilization. For *trans*-$[Cr(en)_2NH_3F]^{2+}$ this is for loss of NH_3 while for $[Cr(NH_3)_5F]^{2+}$ it is for loss of the NH_3 on the H_3N–Cr–F axis. The latter values are taken to be the same as for B under the same conditions. [c] Quantum yield for equatorial labilization. For *trans*-$[Cr(en)_2NH_3F]^{2+}$ this is for solvation of one end of an ethylenediamine ligand to yield a monodentate enH^+ species. For both complexes Φ_{eq} is taken to be $\Phi_{H^+} - \Phi_{ax}$. These values are necessarily less precise than the other values.

begin by considering the more general kinetic requirements suggested by our data and leave attempts to identify the states involved until later.

The facts to be explained for *trans*-$[Cr(en)_2NH_3F]^{2+}$ are as follows: (1) ethylenediamine aquation shows an apparent activation energy at 546 nm but not at 436 nm; (2) ammonia aquation shows essentially zero apparent activation energy at either wavelength. This requires there to be a low-lying state (A), reached by excitation at 546 nm, but not at 436 nm, which leads to ammonia aquation, but not to all of the ethylenediamine aquation, at least some of which must arise from a state (B), reached from state A, leading to an apparent activation energy of 11 kcal mol^{-1}. The absence of any negative apparent activation energy for the ammonia aquation process, which proceeds with a significant yield, then either requires a very high quantum yield of ethylenediamine from state B, which is not observed ($\Phi \simeq 0.15$ at 436 nm), or alternatively requires state B to aquate ammonia with about the same efficiency as state A. The data also require that molecules reaching state B do not significantly return to state A but, if deactivated without reaction, return directly to the ground state. Otherwise the scheme again implies a nonzero activation energy for ammonia and for ethylenediamine aquation at 436 nm. The only unusual feature suggested here is the requirement of deactivation of state B directly to the ground state, rather than through state A.

Having arrived at this general two-state model one can now consider the question of the nature of these states. Following a scheme parallel to that found by Kane-Maguire et al.[29] for $[Cr(en)_3]^{3+}$, state A would correspond to moderately vibrationally excited molecules produced by absorption, either before or after intersystem crossing but before thermalization. These would have to lead to the specific ammonia aquation reaction arising from state A. State B would then correspond to molecules thermalized to the doublet state and subsequently reacting. This reaction could be either from the doublet state or from a thermally equilibrated quartet state arising from reverse intersystem crossing. On this picture, to be consistent with the data, the 11 kcal activation energy observed for ethylenediamine aquation would either have to arise from the absorption process (in which case one might expect to see large temperature effects on the absorption spectrum) or be an activation energy for intersystem crossing. It cannot correspond to the doublet/quartet spacing and be an activation for reverse intersystem crossing as this would not explain the observed distribution of yields and activation energies. The interpretation seems somewhat unlikely, particularly as it ascribes the more specific reaction to a vibrationally excited species and the less specific mode to an equilibrated species.

The Forster model[30] cannot be eliminated or supported on the basis of our data, and we therefore for now leave it as an open question as to whether selective excitation is playing a role in our observations.

Considering our original proposal in this light, state A would be $^4E^0$ and state B would be $^4B_2{}^0$ (the superscript 0 is used to indicate vibrational equilibration). The results then point to an efficiency of about 0.25 for ammonia photoaquation and close to zero for ethylenediamine arising from $^4E^0$ and efficiencies of 0.27 and 0.15 for ammonia and ethylenediamine from $^4B_2{}^0$. These values are not uniquely defined by the data and can be varied to some extent from these values, remaining inside the experimental error limits. However, it is unambiguous that the low-energy state reached at 546 nm loses ammonia preponderately, namely, ≥0.25:0.07 or ≥4:1. In contrast excitation to higher energies results in increased, but not even predominantly, ethylenediamine aquation.

These conclusions are in complete disagreement with the predictions of the σ-donor/molecular orbital theories if, as has been suggested often in the literature, fluoride is a better σ and π donor than amine nitrogen. Thus on the σ-donor model one anticipates equatorial labilization and ethylenediamine aquation for the lowest quartet state. Similarly the molecular orbital theory predicts the wave function of the ^4E state to be predominantly $d_{x^2-y^2}$ in character (our calculation using $\Delta\sigma(F,N) = 433$ cm^{-1}, $\Delta\pi(F,N) = 2017$ cm^{-1}, obtained for *trans*-$[Cr(en)_2F_2]^+$ by Rowley[31] gives a value of approximately 71%) again predicting equatorial labilization. The models also predict that fluoride would be stabilized in the excited state by its π-donor ability; this is the only prediction supported by our observations.

Since the σ-donor/molecular orbital theory has been supported by much of the experimental work prior to this study, one should not abandon it without examining the initial assumption that fluoride is a better σ and π donor than nitrogen, from which the false predictions arise. This may in fact be quite uncertain. Several papers quote $\Delta\sigma$, $\Delta\pi$ parameters in the range 270–600 cm^{-1} and 1700–2000 cm^{-1},[31-33] respectively, derived from a single-crystal study of *trans*-$[Cr(en)_2F_2]^+$, thus consistently supporting the high donor strength of fluoride. Completely inconsistent with these values, however, Rowley calculates from data for $[Cr(NH_3)_5F]^{2+}$, $\Delta\sigma = -843$ cm^{-1}, $\Delta\pi = -195$, in the opposite sense. At first sight this suggests a difference in ligand behavior between the mono- and difluoro compounds. In view of this discrepancy we obtained the original spectrum[34] of $[Cr(NH_3)_5F]^{2+}$ and on the basis of the band polarizations observed[34] we conclude that Rowley interchanged the $^4A_2/^4E^b$ energy ordering; when we properly sequence the levels $^4E^a < {}^4B_2 < {}^4E^b < {}^4A_2$, an order that parallels that for *trans*-$[Cr(en)_2F_2]^+$, then we obtain $\Delta\sigma = 300$ cm^{-1}, $\Delta\pi = 1700$ cm^{-1}, in good agreement with the values derived from the spectrum[31] of difluorotetraammine. The spectroscopic evidence is then consistent and supports the idea that fluoride is a good σ and π donor.

However, Lever et al.[35] some time ago questioned the validity of using $\Delta\sigma$ and $\Delta\pi$ parameters as indicators of the bonding in complexes. Specifically in respect of Cr–F bonding they presented arguments that the bonding was ionic and that the t_{2g}/e_g orbital splittings observed were consistent with perturbations by a highly polarizing small negative ion. If this is correct, and the Cr(III)–F bond is a strong ionic bond, this may provide a reprieve for the σ-donor/molecular orbital theory. If the empirically derived splittings of the t_{2g} and e_g orbitals in the di- and monofluoro complexes are electrostatic in nature, then the excited states may have molecular orbital occupancies different than implied by simple molecular orbital calculations, and it may be that in the lowest quartet state the d_{z^2} orbital is preferentially occupied by the excited electron, giving axial labilization as a result of the overall weak ligand field of fluoride. This would represent a return to the original rules[1] for the fluoride ligand.

Not only does this provide a possible rationale for the preferential loss of ammonia from *trans*-$[Cr(en)_2NH_3F]^{2+}$ but it can also be made consistent with the data on *trans*-$[Cr(en)_2F_2]^+$ and *trans*-$[Cr(en)_2FCl]^+$.

First, remember that, for a complex showing a small departure from octahedral symmetry, such as these, the lowest energy quartet transition (^4E) corresponds to a 45° rotation of charge around either the x or y axis, i.e., d_{x^2}, d_{y^2} to $d_{z^2-x^2}$, $d_{z^2-y^2}$ so that the "axial labilization" also includes "equatorial labilization", though presumably smaller. If fluoride is a weak ligand but a very poor leaving group and if one assumes further that the excited state reacts competitively in that if loss of the preferentially labilized ligands is slow, loss of a good leaving group, not on the "labilized axis", may successfully compete with deactivation, it is then possible to rationalize consistently the photochemistry of these three compounds.

Thus all three are to be considered examples of predominantly axial labilization. In *trans*-$[Cr(en)_2NH_3F]^{2-}$ and *trans*-$[Cr(en)_2FCl]^+$ the ammonia or chloride leaves the labilized axis in competition with a reluctant fluoride. In *tran*-$[Cr(en)_2F_2]^+$ the poor leaving group ability of fluoride allows ethylenediamine loss to successfully compete.

The above analysis reveals that the only consistent picture that accounts for all the data on the reactivity of the lowest quartet states of the three fluoro complexes *trans*-$[Cr(en)_2F_2]^+$, *trans*-$[Cr(en)_2FCl]^+$, and *trans*-$[Cr(en)_2NH_3F]^{2+}$ is that F^- is a weak, ionic ligand but a poor leaving group. To deny this leads to the conclusion that *trans*-$[Cr(en)_2NH_3F]^{2+}$ is a major exception to the theories.

If the Cr–F bond is quite ionic, with a large force constant, then this could result in the $^4E^0$ level lying above $^4B_2{}^0$, owing to a greater loss of potential energy by relaxation in the equatorial plane. This could provide an explanation for $^4B_2{}^0$ relaxing directly to the ground state, rather than through ^4E. If this were to be correct then the 11-kcal activation energy discussed earlier would correspond to the energy required to reach the crossing point of the $^4B_2$ and ^4E potential energy curves.

Stereochemistry of Axial and Equatorial Labilization. The ion-exchange chromatographic results for *trans*-$[Cr(en)_2NH_3F]^{2+}$ show that axial labilization (ammonia loss) leads to *cis*-$[Cr(en)_2H_2OF]^{2+}$. Because of the difficulties with assignment of stereochemistries, no attempt was made to identify the particular products of ethylenediamine loss for this compound.

Comparison of the above results for axial loss with the isomer analysis data for $[Cr(NH_3)_5F]^{2+}$ forms a basis for gaining some information on the stereochemistry of equatorial labilization in the latter compound. The similarity in the temperature and wavelength dependence of the total amine quantum yields for the two compounds, the similar photochemical behavior of analogous pairs of ethylenediamine and ammine compounds, and the similarity of the spectroscopic parameters Dq(en) and $Dq(NH_3)$, as well as $\Delta\sigma,\Delta\pi$(en-F) and the analogous $\Delta\sigma,\Delta\pi(NH_3F)$ suggest similar labilizations and reactivities for the excited states of *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$. We think these are good reasons to expect that the axial ammonia yields in the two compounds will be much the same. Furthermore, in view of the cis stereochemistry of the product of axial ammonia loss from *trans*-$[Cr(en)_2NH_3F]^{2+}$ and for axial ligand loss in a large number of other compounds, it is expected that axial ammonia loss in $[Cr(NH_3)_5F]^{2+}$ would also lead to *cis*-aquofluoro product. On the basis of these assumptions it follows that the trans product found for $[Cr(NH_3)_5F]^{2+}$ must arise from the equatorial reaction mode. This mode constitutes about 40% of the total reaction, Table IV, so that the stereochemistry of the products of equatorial reaction is about 37% trans and 63% cis, with an uncertainty of 10% due to the uncertainties in the chromatography, but possibly more if the assumptions made above are invalid. At 546 nm and 10 °C the drop in the percentage of trans product expected from the halving of the equatorial reaction mode is not observed. As noted, the experimental uncertainties are large enough to have obscured this change.

These results on the stereochemistry of equatorial labilization do not permit any new conclusions about the nature of the transition states since, again allowing for experimental error and for the fact that real transition-metal reactions rarely follow statistical predictions of isomer ratios, these results are consistent with both dissociative and associative paths. One important conclusion can be reached, however; these observations are consistent with the equatorial reaction occurring by the same edge displacement pathway as has been suggested to be required for axial labilization[8] but are definitely *not* consistent with aquation with retention of configuration.[3,36]

Because of the report[3] of a significant amount of *trans*-$[Cr(en)_2H_2OF]^{2+}$ in the photoproducts of *trans*-$[Cr(en)_2FCl]^{2+}$, we reinvestigated this molecule. Our results were quite variable, the percent trans ranging from 3 to 10% depending on temperature, photolysis time, and percentage conversion. The compound is thermally fairly labile, producing the trans compound as one of the products and we found it impossible with this system to make completely reliable thermal corrections. We conclude that the complex might photolyze to produce some *trans*-$[Cr(en)_2H_2OF]^{2+}$, but our data do not support a figure as high as the reported 8–10%. Furthermore we believe it a very difficult compound on which to make such measurements reliably and that the data on more thermally stable compounds should be given greater significance.

Acknowledgment. The authors gratefully acknowledge the financial assistance of the National Research Council of Canada and University of Victoria Faculty Research Fund. C. F. C. Wong is grateful for a University of Victoria Scholarship.

Registry No. A, 58410-71-2; B, 19443-25-5; *trans*-$[Cr(en)_2FCl]^+$, 42476-29-9; *trans*-$[Cr(en)_2H_2OF]^{2+}$, 28101-89-5; *cis*-$[Cr(en)_2H_2OF]^{2+}$, 34431-44-2; $[Cr(NH_3)_5Cl]^{2+}$, 14482-76-9; *trans*-$[Cr(en)_2Cl_2]^+$, 14403-88-4; $[Cr(en)(enH)(NH_3)H_2OF]^{3+}$, 63977-20-8; *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$, 43008-00-0; *trans*-$[Cr(NH_3)_4H_2OF]^{2+}$, 40029-19-4.

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