substitution on $\mathrm{Ni(OH_2)_6^{2+}}$,[39] and they are consistent with a dissociative mechanism. In contrast, the ΔV^* values for reaction of $\mathrm{Cl^-}$,[37] $\mathrm{NCS^-}$,[38] and $\mathrm{Br^-}$[40] with $\mathrm{Fe(OH_2)_6^{3+}}$ are -5, -1, and -19 $\mathrm{cm^3\ mol^{-1}}$, respectively, and are consistent with an associative mechanism.

In conclusion, the comparison of ligand-substitution rate constants with varying ligands and the water solvent exchange rate seems more consistent with dissociative activation for substitution on $\mathrm{Fe(OH_2)_5(OH)^{2+}}$ and associative activation for $\mathrm{Fe(OH_2)_6^{3+}}$.

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Registry No. $\mathrm{Fe(OH_2)_6^{3+}}$, 15377-81-8; $\mathrm{Fe(OH_2)_5OH^{2+}}$, 15696-19-2.

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Photoaquation of *trans*- and *cis*-$\mathrm{[Cr(NH_3)_4F_2]^+}$

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The photoaquation of *trans*- and *cis*-$\mathrm{[Cr(NH_3)_4F_2]^+}$ in acidic aqueous medium at 22 °C leads to efficient ammonia aquation ($\phi = 0.36$ and 0.45, respectively, for irradiation in the lowest quartet state) with minor yields of fluoride. The quantum yields or quantum yield ratios show small wavelength dependencies. The observed products from *trans*-$\mathrm{[Cr(NH_3)_4F_2]^+}$ were 1,6-difluoro-2-aquotriamminechromium(III) (*mer* FWF) and 1,2-difluoro-6-aquotriamminechromium(III) (*mer* WFF) in a 1:2.5 ratio, while the cis compound yielded these two products in a 1:1.5 ratio, with the addition of small, wavelength-dependent amounts of 1,2-difluoro-3-aquotriamminechromium(III) ion. The results for the trans compound are consistent with both the edge displacement model of photostereochemistry and a recent theory invoking dissociative, symmetry-restricted photoreaction. In contrast the results for the cis compound do not fit at all well with the edge displacement model but are consistent with the symmetry-restricted, dissociative model, despite some difficult ambiguities which arise in its application.

Introduction

The development of theoretical models[1-7] for the photochemical modes of reaction of chromium(III) and other metal complexes and recently their photostereochemistry[8] has been and continues to be a vigorous area of research. Of at least equal importance is the continued and further exploration of the behavior of actual systems under a variety of conditions to provide a background of data to explore validity of the theories. In particular emphasis should be on the need to provide data which will test and discriminate between the models with the maximum stringency wherever possible.

For a large number of the chromium complexes studied to date the different models give very similar predictions, so the data, although interesting and valuable in their own right, do not provide the desired discrimination. A satisfying exception has been the data on fluoroammine complexes of chromium(III); it was an early elegant study[2] of *trans*-$\mathrm{[Cr(en)_2F_2]^+}$ that first showed that, while many complexes underwent the photoreaction mode predicted by Adamson's rules,[1,5] this was not universal. More recently a comparison[9] of the photochemistry of $\mathrm{[Cr(NH_3)_5F]^{2+}}$ and *trans*-$\mathrm{[Cr(en)_2NH_3F]^{2+}}$ has provided a test of the recent Vanquickenborne and Ceulemans (VC) models.[7,8] These satisfactorily accounted for the reaction modes but gave correct predictions of the photostereochemistry only if it was assumed[10,11] that the theory could be extended to allow reaction of the postulated five-coordinate trigonal-bipyramidal intermediate in an electronically excited state.

For extension of the range of compounds studied and hopefully for further useful background data, a study of the photoreaction modes and stereochemistry of *trans*- and *cis*-$\mathrm{[Cr(NH_3)_4F_2]^+}$ has been undertaken and is reported here. The photochemistry of the analogous *trans*-$\mathrm{[Cr(en)_2F_2]^+}$ has been the subject of a dispute[2,12] over whether or not the photo and thermal products of ethylenediamine aquation are identical and therefore over the stereoretentivity of the process. The analogous amine compounds with their fewer, more readily identifiable product isomers offered an excellent potential for clear-cut product isomer analysis, and therefore a more definite verdict as to whether the photoaquation of the equatorial ammonia is, by analogy, stereoretentive as originally suggested.[2] These compounds in addition provide an opportunity of a further test of the VC theory of photostereochemistry.

Experimental Section

Preparation of Complexes. Both *trans*- and *cis*-$\mathrm{[Cr(NH_3)_4F_2]^+}$ were most conveniently prepared by fluoride anation[13,14] in acidified

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methanol, although the method of Schäffer and Glerup[15] for the trans compound and reaction of *cis*-$[Cr(NH_3)_4(C_2O_4)]^+$ with 48% HF for the cis compound both gave acceptable yields.

trans-$[Cr(NH_3)_4F_2]ClO_4$ was prepared and recrystallized as described.[14] The violet product was washed with methanol and recrystallized from aqueous perchlorate solution; the yield was 70%. Chromatography showed the compound to be free from elutable impurities except for two peaks corresponding to known resin-catalyzed decomposition products. The UV–visible spectrum [λ_{max}, nm (ϵ_{max}, L mol^{-1} cm^{-1}): 357 (11.4), 404 (11.1), 490 (15.3), 540 (13.8)] was in good agreement with literature values.[13,15]

For the cis compounds, 5.0 g of *cis*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$[16,17] and 2.0 g of NH_4F in 50 mL of distilled acidified methanol were stirred at 30 °C for 6 h. The product was filtered off, washed with methanol, and recrystallized from aqueous perchlorate medium; the yield was 35%. The UV–visible spectrum [λ_{max}, nm (ϵ): 380 (18.0), 527 (41.7)] was in good agreement with literature values.[15] Chromatographic analysis revealed contamination by *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$ and other compounds which interfered and were not removed by repeated recrystallizations. The subsequent quantitative work had therefore to be carried out by using chromatographically purified solutions.

Chromatographic Techniques. Elution chromatography for both purification and qualitative and quantitative analyses utilized a thermostated column 20 cm in length and 8 mm in diameter of Hamilton HC8X cation-exchange resin, eluted first with 0.15 M followed by 1.0 M sodium sulfate solutions, both 10^{-3} M in $HClO_4$. A modified Technicon AutoAnalyser was used to react the eluted complexes with 1 M sodium hydroxide and 0.5% (w/v) hydrogen peroxide. A complete chromatogram could be recorded by monitoring the chromate absorbance at 370 nm.

Calibration curves measured by using both standard chromate and *trans*-$[Cr(NH_3)_4F_2]^+$ gave linear plots for moles of chromium vs. peak area over the range 0.1–2 μmol.

It was observed that the starting fluoro complexes, and to some extent the product peaks, were subject to irreproducible resin-catalyzed decomposition, primarily loss of fluoride. Some experiments were carried out to assess the uncertainties arising thereby; these involved leaving samples stationary on the top of the column for varying periods prior to elution and quantitative determination of the decomposition products.

Identification of Chromatographic Peaks. Identification of the chromatographic peaks was based primarily on the elution times which were very reproducible. It was also possible, on peaks containing sufficient material (1.5–0.5 μmol), to collect the elution peak, obtain its UV–visible spectrum (10-cm cell, Cary 17, 0–0.1 absorbance range) and, by determination of the chromium content of the solution (alkaline peroxide oxidation and chromate absorption at 370 nm), obtain the ϵ_{max} values. Any spectral changes on addition of base to the solution were also observed. The small size of the product peaks led to significant variability in the ϵ values, although the λ_{max} values were more reproducible. Analysis for nitrogen and fluoride, although attempted, was too irreproducible to be useful.

Product Analysis and Quantum Yield Measurements. Isomer analysis of the photolysis products was carried out on 4.0×10^{-2} M solutions of *trans*-$[Cr(NH_3)_4F_2]^+$ in 1.02×10^{-3} M $HClO_4$ or (5–7) $\times 10^{-3}$ M chromatographic fractions of *cis*-$[Cr(NH_3)_4F_2]^+$ in 1.02×10^{-3} M $HClO_4$ along with the 0.5 M Na_2SO_4 eluant, photolyzed at 436 and 577 nm and 366 and 577 nm, respectively. For the trans compound conversions ranged from 6–8%, but for the cis compound 10–15% conversions were required. In addition to these experiments isomer analysis was carried out on solutions of each compound that had been thermally decomposed in acid aqueous solutions at 50–60 °C and in some cases at 20 °C. Approximate rate constants were measured by using proton uptake.

Quantum yield measurements on similar solutions were carried out by use of the ΔpH method with an Ingold LOT electrode and Metrohm pH meter reading to 0.001 pH unit. The measured proton uptakes were periodically checked by back-titration to the original pH with use of standard acid, and agreement within 4% was observed in all such experiments.

Depending on the wavelengths of interest both ferrioxalate[18] actinometry and reineckate[19] actinometry were used, together with continuous monitoring of the intensity with use of a Philips 150 CV phototube observing 8% of the beam. Balzers interference filters, in conjunction with a 1000-W mercury lamp (Illumination Industries, CA), were used as the light source.

In the quantum yield experiments conversions were less than 2% for measurements on the trans compound and were in the range 6–8% for the cis compound.

Results

Thermal Decomposition. Mainly for an assessment of the possible importance of thermal reactions a brief study was made of the thermal decompositions of both difluorotetraammine isomers by using both the ΔpH method at pH 3 and ion-exchange chromatography.

Over the range studied first-order behavior was observed for the trans isomer, with a rate constant at 49 °C of 9.3×10^{-6} s^{-1} (average of two runs differing by 5%). This rate constant corresponds to $k_{NH_3} + {}^1/_2k_{F^-}$ since at pH 3 only about 50% of the fluoride is protonated.

From the chromatographic data for the thermal reaction at 20 °C the observed moles of product allow an estimate of 4×10^{-7} s^{-1} for the rate constant. Only two significant products were observed: 1,6-difluoro-2-aquotriamminechromium(III) ion and *trans*-$[Cr(NH_3)_4H_2OF]^{2+}$ in a ratio corresponding to k_{NH_3}/k_{F^-} of about 0.8. These compounds are both produced by resin-catalyzed decomposition so that, although a correction has been applied, an uncertainity in this ratio of up to 25% remains.

A ΔpH study of chromatographically purified solutions of the cis isomer containing approximately 10^{-2} M complex in 0.5 M Na_2SO_4/10^{-3} M $HClO_4$ yielded the value 8.4×10^{-6} s^{-1} (50 °C) (average of two runs differing by 10%). The chromatographic analysis of similar solutions thermalized at 50 °C to about 10% decomposition revealed three products, 1,2-difluoro-6-aquotriammine (*B*), 1,2-difluoro-3-aquotriammine (*C*), and *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$ (*Z*). The identification of these is discussed later. In addition three small peaks, about 40% total of the main product peaks, appeared very early in the chromatogram. These seem likely to be sulfate anation products which might correspond to a loss of product of this magnitude.

In reasonable agreement with the ΔpH value, the overall rate constant based on $B + C + Z$ was 1×10^{-5} s^{-1} (two, differing by 8%) with $(B + C)/Z = 1.4 \pm 0.2$ and $B/C = 0.24$. It is not possible to make any reliable corrections for the possible losses of *B*, *C*, and *Z* by anation. Since it might well be selective, it could lead to fairly large changes in the observed product ratio. The excellent agreement of the overall rate constant with that observed for $B + C + Z$ gives a little assurance, however, that the incurred errors may not be too serious. It is unfortunate that possible anation of product is such a potential problem here as reliable rate constant ratios for k_{NH_3}/k_{F^-} and $(k_{NH_3})_{eq}/(k_{NH_3})_{ax}$ and their corresponding activation energy differences would be of considerable interest.

A more extensive and precise kinetic study of both systems would be very useful, although difficult. For our purposes the results show that for both isomers thermal reactions are, at 20 °C, sufficiently slow to be negligible in the photochemical study.

Quantum Yield Measurements. Quantum yields for photolysis at 577 and 436 nm for the trans and 577 and 366 nm for the cis isomer, at pH 3 and 20 °C, are given in Table I,

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Table I. Overall Quantum Yields and Product Isomer Ratios for Photoaquation of *trans*- and *cis*-$[Cr(NH_3)_4F_2]^+$

t, °C	λ_{irrad} (state),[a] nm	ϕ_{H^+}[b]	ϕ_{F^-}[c]	B/A[d]	C/A[d]
			Trans		
5	577 ($^4E_{ga}$)	0.34 (3)	0.008 (3)	2.5 ± 0.2 (4)	≤0.03 (4)
5	436 ($^4E_{gb}$)	0.41 (3)	0.005 (2)	2.2 ± 0.3 (2)	≤0.03 (2)
			Cis		
20	577 ($^4B_2$)	0.45 (2)	<0.06 (3)	$1.2_5 \pm 0.1_2$ (3)	0.22 ± 0.04 (3)
20	365 (^4E_b)	0.47 (2)	<0.05 (3)	1.4_4 ± 0.05 (3)	0.50 ± 0.02 (3)

[a] These assignments are based on the observed spectral bands combined with conventional calculations[7] of the $^4E_a/^4B_2$ and $^4E_b/^4A_2$ splittings. [b] Figures in parentheses are the numbers of determinations based on the ΔpH method with reineckate actinometry. The standard deviation of the pooled data set was 0.011. [c] Values for fluoride based on chromatographic observations of the amounts of *trans*- and *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$ present (see text). [d] Error limits given are the standard deviations for each chromatographic data set: A = 1,6-difluoro-2-aquotriamminechromium(III) ion/*mer* FWF; B = 1,2-difluoro-6-aquotriamminechromium(III) ion/*mer* WFF; C = 1,2-difluoro-3-aquotriamminechromium(III) ion/*mer* WFF. For the chromatographic runs on the trans compound the percent photolysis was always less than 5%. For the cis, due to the dilute solutions used, it ranged from 10 to 17%.

together with the chromatographically determined product ratios. Note that the proton uptake yields correspond to ammonia loss plus half of any fluoride.

The fluoride quantum yields given in the table were based, for the trans isomer, on the amount of *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$ found, thus relying on the unlikelihood of any *trans*-aquofluoro arising from photochemical loss of fluoride. For the cis isomer, both *trans*- and *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$ might be produced. The quantum yields given are therefore based on the total of these and probably represent upper limits as small amounts of cis product likely arise from resin decomposition.

Table I shows that the main photolysis process for both isomers is ammonia aquation.

Product Isomers of the Photo and Thermal Reactions. Ammonia loss from *trans*- and *cis*-$[Cr(NH_3)_4F_2]^+$ leads to difluoroaquotriamminechromium(III) which may exist as three geometric isomers, while fluoride loss may lead to *trans*- and *cis*-fluoroaquotetraammine, respectively. The latter isomers were readily identified by comparison of the retention times with those of known samples, as well as from a photolyzed solution of $[Cr(NH_3)_5F]^{2+}$ where both are known products, previously identified by collection of the chromatographic peaks and measurement of their UV–visible spectra.

The assignment of the difluoroaquotriammines presented greater problems as known samples of these complexes were not available. The analysis was therefore based on the reproducible retention times of the peaks, which were each completely resolved from all others, and on expectations for the thermal and photochemical reaction products. Collection of the peaks, spectral analysis, and [Cr] determination yielded UV–vis spectral data for each isomer, but since the compounds are new and no closely comparable systems are well characterized, the spectral data are of limited usefulness in identification. Chemical analysis for N and F, although attempted, did not yield reproducible, useful data for the sample sizes available (0.5–1.5 μmol) but in any event would not have assisted with isomer identification.

To begin at our final conclusions, the overall elution order observed with 0.15 M followed by 1 M sodium sulfate (pH 3) was: 1,6-difluoro-2-aquotriamminechromium(III) (*mer* FWF), *trans*-$[Cr(NH_3)_4F_2]^+$, 1,2-difluoro-6-aquotriammine (*mer* WFF), 1,2-difluoro-3-aquotriammine (*fac* WFF), *cis*-$[Cr(NH_3)_4F_2]^+$, an identified minor species, X, apparently an isomer of $[Cr(NH_3)_3(H_2O)_2F]^{2+}$, *trans*-$[Cr(NH_3)_4H_2OF]^{2+}$, and *cis*-$[Cr(NH_3)_4H_2OF]^{2+}$. All these peaks except *trans*-$[Cr(NH_3)_4F_2]^+$ could be seen in the chromatogram of a thermalized, photolyzed solution of *cis*-$[Cr(NH_3)_4F_2]^+$, and all were resolved from one another.

The identification was based on the following experiments.

1. A thermally decomposed solution of *trans*-$[Cr(NH_3)_4F_2]^+$ gave rise to two product chromatographic peaks, which could be assigned as *mer* FWF and *trans*-fluoroaquotetraammine, the latter being a known identified species. This assumes that the ammonia aquation observed is stereoretentive, consistent with the usual situation for chromium(III) thermal reactions in aqueous media.

2. A photolyzed solution of *trans*-$[Cr(NH_3)_4F_2]^+$ gave rise to four peaks; both *trans*- and *cis*-fluoroaquotetraammine were present in small amounts, the former largely from resin-catalyzed decomposition (it increased dramatically with standing of the sample on the column) and the latter from photolysis (it increased proportionally to the photolyses time). The two remaining major products were the previously observed *mer* FWF and a new peak for *mer* WFF with only a barely discernible amount of *fac* WFF being produced. Experience has shown that axial ligand loss generally occurs with stereochemical change,[8] accounting for the *cis*-fluoroaquo product from fluoride loss of ammonia. Loss of ammonia, if stereoretentive, would lead only to *mer* FWF. The observation of the second ammonia loss product requires stereochemical change, and the theories to be discussed later suggest that the second product is much more likely to be *mer* WFF than *fac* WFF.

3. A thermally reacted solution of *cis*-$[Cr(NH_3)_4F_2]^+$ gave peaks corresponding to *cis*-aquofluoro and to the peaks assigned earlier as *mer* WFF and *fac* WFF. The identification of *mer* WFF is consistent with experiment 2 above, and the remaining peak identifies the third difluoroaquotriammine, *fac* WFF. The observed peaks are therefore consistent with stereoretentive aquation of fluoride and axial and equatorial ammonia.

4. A photolyzed solution of *cis*-$[Cr(NH_3)_4F_2]^+$ gave rise to small amounts of *trans*- and *cis*-fluoraquo, major amounts of *mer* FWF and *mer* WFF, and a smaller amount of *fac* WFF.

In summary, all three difluorotriammine isomers are observed, consistent with expectation.

The thermal observations identify *mer* FWF uniquely and identify the pair *mer* WFF and *fac* WFF. The photochemical data confirm the first assignment and support the given sequence for the latter two isomers as the only reasonable one.

The given sequences are also consistent with the known elution characteristics of such complex ions. Monocations elute prior to dications, as observed here. *trans*-Difluoro species will elute before the cis species, and compounds in which a water ligand replaces an ammonia will elute faster than the ammine analogue. Finally the facial WFF isomer, with its greater dipole moment, is expected to elute last of the group, but prior to *cis*-$[Cr(NH_3)_4F_2]^+$. The order given is completely consistent with these conditions.

The spectral data obtained by collecting the chromatographic peaks followed by chromium determination lead to the following results where the molar absorptivities are only accurate to about ±25% [λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}), λ_{min} (ϵ), λ_{max} (ϵ)]: *mer* FWF, 405 (9), 455 (5), 536 (19); *mer* WFF, 390 (20), 453 (5), 534 (24); *fac* WFF, ..., 445 (9), 550 (33). In addition a splitting of the second ligand field band in *mer* FWF was observed.

Further spectral data were obtained by adding base to each of the above fractions. In all cases an increase in ϵ, to 35 for *mer* FWF and WFF and to 45 L mol^{-1} cm^{-1} for *fac* WFF, and a shift of the first ligand field band to about 555 nm was observed. The red shift in base is consistent with the presence of one of more aquo ligands, since hydroxo has a smaller *Dq* value than water. Also since hydroxo and fluoro are similar ligands, the similar λ_{max} and ϵ_{max} values for the first ligand field band in the two meridional hydroxo analogues is consistent with the assignment, as is the greater ϵ_{max} for the more asymmetric *fac* isomer. Similar ϵ_{max} differences have been observed for the *mer* and *fac* triaquotriammine analogues.[20]

The observed molar absorptivities are smaller, and the splittings are larger for trans isomers, also consistent with the above, and the most asymmetric isomer, *fac* WFF, has the greatest ϵ_{max}. Our efforts to predict the λ_{max} values by using ligand field calculations and published ligand field parameters led to almost identical predictions for all isomers, so no help is forthcoming from these.

Although no single piece of evidence presented above provides by itself proof of the correctness of the sequencing of the difluoroaquotriammine isomers in the chromatogram, the cumulative weight of the evidence is conclusive. There can be no doubt about the identification of *mer* FWF or that the remaining pair of monocation peaks are *mer* FWF and *fac* WFF. Although the arguments for the sequencing of the latter beg the results of this study, there can again be little doubt that to reverse the assigned order would result in an anomalous ordering of elution times, unusual spectral properties, and unusual photolysis processes.

The product isomers of the thermal reactions have already been discussed. Table I gives a summary of the photochemical observations; the uncertainties quoted are based on estimates of the uncertainties due to resin-catalyzed decomposition. Some runs showed evidence for this; others gave identical yields of product independent of whether or not the sample was allowed to remain on the column for a period prior to elution. Product X was found to arise from resin-catalyzed decomposition of product and formed a useful monitor of its importance in any particular experiment.

Wavelength Dependence of Quantum Yields. The predominant photoreaction mode of trans-$[Cr(NH_3)_4F_2]^+$ is ammonia loss, Table I, with an overall quantum yield which increases on irradiation to shorter wavelengths. The observed main products of this reaction are *mer* FWF and *mer* WFF in a 30:70 ratio which may become more equal at shorter wavelengths, but the variation of which is within the 15% uncertainity of the data. The amount of *fac* WFF produced was very small, though real, but it could have arisen from the secondary photolysis of the primary products.

The main photoproduct of the minor fluoride aquation process is expected to be *cis*-aquofluoro, of which a small but reproducible amount, not arising from resin-catalyzed decomposition, was observed, corresponding to the quantum yields quoted in Table I. Any *trans*-aquofluoro produced by photolysis would be obscured by the fairly large resin-produced peak. Consequently, the fluoride yields, if in error for this reason, could be somewhat higher; the data suggest they could not be more than about 50% greater. The variability of the results for *cis*-aquofluoro was about ±20%, so the observed decrease to shorter wavelength is significant, as is the increase in the ammonia yield.

In contrast the cis compound exhibits wavelength independence of the quantum yield for the major ammonia aquation process and also is slightly more photoactive than the trans compound. The main products are again *mer* FWF and *mer* WFF, but with the significantly different ratio 45:55. This ratio may show an opposite wavelength dependence to the trans compound, but again it is within the experimental uncertainty of the results. A significant amount of *fac* WFF is produced, 9% of the total, increasing to 17% on irradiation at short wavelength. The small fluoride yields quoted are given as upper limits as they are based on the total *trans*- and *cis*-aquofluoro product observed and some may have come from the resin.

Secondary Photolysis. The molar absorptivity of *trans*-$[Cr(NH_3)_4F_2]^+$ is rather low compared with some of its photoproducts. Also relatively high conversions were required in the work on the cis compound. It is therefore appropriate for both compounds to recognize the possibility of problems due to secondary photolysis.

This may be done on the basis of the spectral data given earlier in this section for the main products, together with the assumption of equal quantum yields for starting compounds and products, and a published treatment of such errors.[20,21] Experience suggests that quantum yields for loss of ammonia and fluoride would be lower for products than for the starting materials, so these calculations will yield upper limits.

For the quantum yield measurements on the trans compound conversions were less than 2%, so any secondary photolysis was also ≤2%. For the chromatographic work, where conversions ranged from 6–8% the estimated upper limit product losses, for 577 and 436 nm, respectively, are *mer* FWF ≤ 6% and 5%, *mer* WFF ≤ 9% and 5%, and *fac* WFF ≤ 13% and 6%.

For the quantum yield measurements on the cis compound conversions were up to 8%, corresponding to errors up to 4%. For the chromatographic work conversions ranged to 16%, giving errors for 577 and 365 nm, respectively, of *mer* FWF ≤ 5% and 5%, *mer* WFF ≤ 9% and 9%, *fac* WFF ≤ 14% and 19%.

These calculations show that the most significant problems occur with the more strongly absorbing *fac* WFF isomer. Bear in mind that the real effects may be much smaller than these. Since generally they are within the uncertainty of the chromatographic analyses, they have not been included in the error limits given in Table I. More importantly there need be no concern that the observed trends of the product distribution are seriously affected by secondary photolysis.

Discussion

Thermal Reactions. Although the study of the thermal reactions of *trans*- and *cis*-$[Cr(NH_3)_4F_2]^+$ was peripheral to the main purpose of this work and therefore restricted in its scope, a comment on the findings is justified. Generally it has been found that acidoamminechromium(III) complexes thermally aquate the acido ligand. In several instances, however, fluoro complexes have been shown to be exceptions.[23,24] This present study shows that, for these difluorotetraammines also, ammonia loss is a major process.

For the cis isomer, where aquation of two stereochemically different ammonias can occur, the isomer analysis data show that, on the assumption of stereoretentivity, at 50 °C the axial ammonia is 4 times as labile as the equatorial ammonia. This result suggests that perhaps the fluoride ligand is cis labilizing in the compound.

Photolysis Modes: Comparison with Models. The photolysis data on *trans*-$[Cr(NH_3)_4F_2]^+$ is particularly important in light of its analogy to *trans*-$[Cr(en)_2F_2]^+$, the system which first supported the suggestion[2] that the simple photolysis rule,[1] loss of the strong field ligand in the weak field axis, was not all embracing. Instead the labilization was related to the σ-donor

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Table II. Calculated Splittings and Excited-State Bond Energies (μm^{-1}) for *trans*- and *cis*-$[Cr(NH_3)_4F_2]^+$

Trans[a]	
$^4B_{2g} - {}^4E_{ga} = 2\Delta\pi - {}^3/_2\Delta\sigma = 0.273$	
$^4A_{2g} - {}^4E_{gb} = 2\Delta\pi + {}^3/_2\Delta\sigma = 0.408$	
$^4E_{ga}$	$I^*(Cr{-}NH_3) = 1.15$ $I^*(Cr{-}F) = 1.50$
$^4B_{2g}$	$I^*(Cr{-}NH_3) = 0.90$ $I^*(Cr{-}F) = 1.87$
Cis[a]	
$^4B_2 - {}^4E_a = -0.136$	
$^4A_2 - {}^4E_b = -0.204$	
$^4B_2$	$I^*(Cr{-}NH_3, eq) = 0.90$ $I^*(Cr{-}NH_3, ax) = 1.44$ $I^*(Cr{-}F) = 1.46$
^4E_a	$I^*(Cr{-}NH_3, ax) = 0.91$ $I^*(Cr{-}NH_3, eq) = 1.16$ $I^*(Cr{-}F) = 1.66$

[a] $\epsilon\sigma_{NH_3} = 0.718\ \mu m^{-1}$, $\epsilon\pi_{NH_3} = 0\ \mu m^{-1}$; $\epsilon\sigma_{F^-} = 0.763\ \mu m^{-1}$, $\epsilon\pi_{F^-} = 0.17\ \mu m^{-1}$.

strength of the ligands. Also, and more important for this work, it was suggested that the photochemical and thermal reaction products were the same and that equatorial labilization was therefore stereoretentive. A recent reinvestigation[12] has called these conclusions into question.

Also a recent theory of the photo reaction modes[7] and photostereochemistry[8] of chromium(III) complexes would predict nonstereoretentive equatorial ammonia loss in the trans complexes, but the theory is not well established experimentally. A study[10] of the photostereochemistry of $[Cr(NH_3)_5F]^{2+}$ led to results which were in conflict with the theory unless it admits the possibility of reaction via electronically excited five-coordinate intermediates. It was therefore desirable to study further molecules, as unambiguous as possible, to explore the validity of the theory, and to provide data for further developments.

A serious complication to be faced in any comparison of photochemical observations with theory is our continuing uncertainty as to the identity and detailed nature of the reactive excited states. Quenching experiments have established[25] excited quartet state participation for a number of compounds, and reaction via the doublet has also been demonstrated by the same experiments although whether the doublet itself reacts remains an open question.[26,27]

Both complexes studied here show evidence for participation of more than one excited state; the trans isomer has a wavelength-dependent NH_3/F^- ratio, and the cis isomer shows a variation of the *fac* WFF/*mer* FWF ratio with wavelength. Such observations and the implied multiple-excited-state participation are now commonplace. In the following discussion we assume that the two lowest quartet states $^4B_2$ and ^4E_a are the reactive states participating and that the doublet reactivity is unimportant. This is suggested by the theoretical models, by the experiments[28] on differential quenching in the analogous $[Cr(en)_2(NCS)F]^+$, and by luminescence studies.[27]

Table II gives the calculated state splittings for the $^4T_2$ and $^4T_1$ states in the two isomers, leading to the level ordering $^4E_{ga} < {}^4B_{2g} < {}^4E_{gb} < {}^4A_{2g}$ for the trans and $^4B_2 < {}^4E_a < {}^4A_2 < {}^4E_b$ for the cis isomer. The lowest two quartets in the cis isomer are close together in energy while there is twice the calculated splitting in the trans isomer.

Table II shows also the bond-strength predictions for the lowest quartet states based on the theory. For the trans isomer both quartets favor ammonia loss due to the lower excited-state ($Cr{-}NH_3$) bond energy. Since the higher lying (Franck–Condon energies) $^4B_{2g}$ state has a weaker ammonia bond and stronger fluoride bond, a greater degree of participation of $^4B_{2g}$ photoreaction upon shorter wavelength excitation would be consistent with the observed increase in the ϕ_{NH_3}/ϕ_{F^-} ratio. The observations for the trans compound are therefore completely consistent with predictions of VC theory for a model of ^4E_g reaction with wavelength-dependent participation of $^4B_{2g}$. Photophysical or quenching studies which might help prove such a mechanism would be very useful though difficult since the anticipated effects would be small.

The cis compound is also predicted to lose ammonia predominantly or exclusively from both low-lying quartet states in agreement with observations. The lowest state, $^4B_2$, is predicted to lose equatorial ammonia, while the ^4E_a state, if it reacted, should lose axial ammonia. Furthermore the states are close enough in Franck–Condon energy that, if they relax with similar Stokes shifts and are sufficiently long-lived, they would likely be interconverting at room temperature. Loss of both kinds of ammonia ligand might therefore be anticipated, with any wavelength dependence a moot point, complicating the discussion of the stereochemical results. The observed constancy of the quantum yield with wavelength might suggest single-state participation or such interconversion, but the wavelength dependence of the product ratio suggests multiple-excited-state participation without complete equilibration. The interpretation of the stereochemical data in terms of the models is therefore obscured by the uncertainty regarding axial vs. equatorial ammonia loss and its possible wavelength dependence. Nevertheless some conclusions can be drawn.

Photostereochemistry. For both complexes the major photoaquation mode was ammonia loss, and Table I shows the product isomer ratios found for the ammonia loss products. The minor fluoride mode could lead to either *cis*- or *trans*-$[Cr(NH_3)_4H_2OF]^{2+}$, and the analysis was complicated by the stereoretentive resin-catalyzed decomposition of the appropriate starting material. Thus we were able to show that photolysis of *trans*-$[Cr(NH_3)_4F_2]^+$ definitely led to *cis*-aquofluoro, but except that it was not major, nothing could be said about any trans product. Hence complete information on the photostereochemistry of this mode could not be obtained. Similar problems, though less severe, occurred in our study of the cis isomer. Comparison of the amounts of the two isomers produced by the column and by photochemistry suggests that both *cis*- and *trans*-$[Cr(NH_3)_4H_2OF]^{2+}$ are produced in small amounts photochemically. Fortunately the photostereochemistry of the minor fluoride mode is of no import for present purposes.

The ammonia loss products from *trans*-$[Cr(NH_3)_4F_2]^+$ give a clear answer to one of the main questions of this study, the nature of the photostereochemistry of equatorial labilization. Note that *mer* FWF and *mer* WFF are produced in a ratio of a little over 2:1 at both wavelengths. Negligible *fac* WFF is produced, and the minor amounts observed could have arisen from secondary processes.

It will be obvious that *mer* WFF can be formed only by a stereomobile photoaquation of *trans*-$[Cr(NH_3)_4F_2]^+$. Owing to the indistinguishability of the ammonia ligands, *mer* FWF could be produced by either stereoretentive or mobile processes. Although this creates an inherent uncertainty in the exact degree of photostereomobility it must lie in the range 70–100%; the photoaquation is not stereoretentive, and it could be completely stereomobile. For the analogous *trans*-$[Cr(en)_2F_2]^+$, which should behave similarly, our results provide strong

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support for the claims[12] that the photo and thermal products are different and that the photoaquation of ethylenediamine is not stereoretentive.

It was suggested[5] that the photostereomobility observed for Cr(III) complexes corresponded to attack by the entering ligand trans to the leaving ligand, this being equivalent to an edge displacement process via a seven-coordinate transition state. Subsequent studies of axial, and more recently of equatorial photosubstitution,[10] have been consistent with this proposal.

For *trans*-$[Cr(NH_3)_4F_2]^+$ the edge displacement model predicts statistically 50% *mer* FWF/50% *mer* WFF. It may be expected that, if preference exists, the fluoride ligand is the more inclined to migrate preferentially in order to maximize its separation from the entering water molecule. Such a preferential migration of fluoride is consistent with the higher than statistical proportion of *mer* WFF found. Also no *fac* WFF product would be expected for this photoreaction. These conclusions are independent of any uncertainties about the excited states involved in the photochemistry and are in good agreement with our observations.

The VC theory of photostereochemistry[8] recognizes symmetry restrictions on the collapse to a trigonal bipyramid (tbp) of the five-coordinate intermediate left after dissociation of the leaving ligand and further symmetry restrictions on the subsequent attack on the tbp intermediate by the entering ligand. While the theory accounts nicely for many of the observations on photostereochemistry subsequent to axial ligand loss,[8] it did not in its original form[8] account readily for the data[10] on equatorial ligand loss. To do so it was necessary to allow for the possibility of reaction of the tbp intermediate while in an electronically excited state.[10] Since this modification introduces an uncertainty as to the proportion of the total reaction which may occur via this route, the theory unfortunately loses much of its predictive capability and consequently its ability to be rigorously tested. Vanquickenborne and Ceulemans have very recently published[11] a treatment of the loss of an equatorial ligand from *trans*-$[CrL_5F]^{2+}$ which agrees with the earlier conclusions.

Following a similar approach to that of Vanquickenborne and Ceulemans[11] Figure 1A shows the orbital correlation diagram and Figure 1B the predicted stereochemistry for the aquation of the $^4B_{2g}$ and ^4E_g states of *trans*-$[Cr(en)_2F_2]^+$. Only the orbital correlation diagrams have been given; these have been shown to give the same predictions as the state diagrams.[8,11] The ordering of the orbitals of the trigonal bipyramidal (tbp) intermediates was based on calculations using published equations[7] and the ϵ_σ and ϵ_π parameters of Table II. (That we make use of a model invoking five-coordinate intermediates should not imply to the reader that we believe the processes are dissociative.)

The loss of ammonia (x axis) from the $^4E_g[(xy)(yz)(z^2 - x^2)]$ component of the lowest quartet excited state of *trans*-$[Cr(NH_3)_4F_2]^+$ will lead to the $^4B_2[(xy)(yz)(x^2)]$ state of the square pyramidal (sp) intermediate shown in Figure 1A. This can rearrange by the allowed F–Cr–F bending to produce the tbp intermediate with two equatorial fluorides in its $^4B_2$-$[(xy)(yz)(z^2 - x^2)]$ excited state. To the extent to which the latter reacts before electronic relaxation to its ground state it will aquate to *mer* WFF because of the cis attack selection rule[8,10,11] on the entering aquo ligand, Figure 1B. Note that this selection rule is opposite to that derived previously,[8,11] owing to the reversed energy sequence of the in-plane d orbitals where there are two equatorial fluorides. Any proportion that deactivates to the electronic ground state prior to reaction will give rise to *mer* FWF, as also shown in Figure 1B. Thus for the ^4E_g derived pathway the expected products would be a fixed ratio of *mer* FWF/*mer* WFF determined by the proportion of excited- to ground-state reaction.

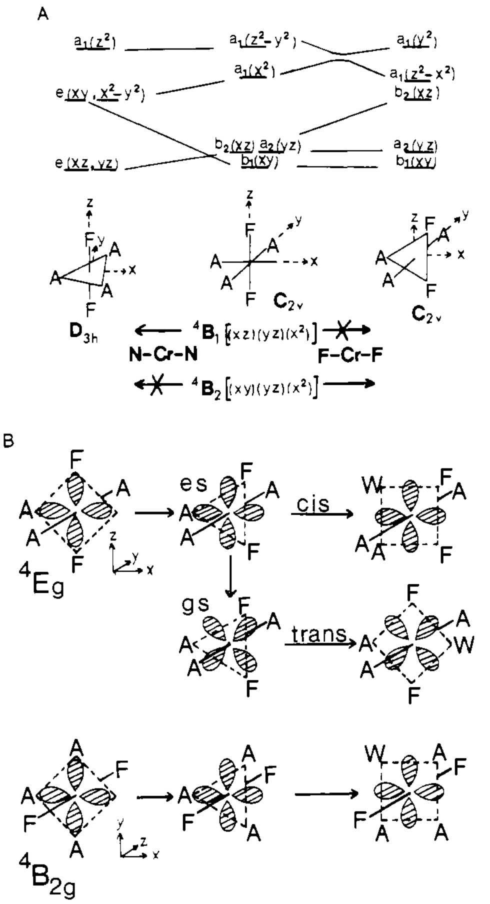

Figure 1. (A) *trans*-$[Cr(NH_3)_4F_2]^+$. Orbital correlation diagram between the square pyramidal intermediate with two basal fluorides and the trigonal bipyramidal intermediates with two axial fluorides and two equatorial fluorides. This parallels the analysis of ref 11 but for the inverse ordering of the in-plane d orbitals for this situation of two equatorial fluoride ligands. This is based on angular overlap calculations using published equations[7] and the ligand field parameters of Table II. (B) VC theory[8,11] predictions for *trans*-$[Cr(NH_3)_4F_2]^+$ photostereochemistry: A = NH_3, F = F^-, W = H_2O, es = excited state, gs = ground state. For clarity in both Figures 1 and 2 only the occupied σ^* orbital has been depicted; the vacant orbital lies in the same plane at 45°, and the allowed distortion corresponds to in-plane movement of the ligands toward the vacant orbital and away from the filled orbital and the third ligand. The lower lying ^4E_g state loses x-axis ammonia to yield the sp intermediate species shown. This undergoes allowed F–Cr–F bending to give in its excited state ($d_{z^2-x^2}$ populated) the tbp intermediate with two equatorial fluorides which reacts such that cis attack of the entering water molecule correlates with the ground state of the product, *mer* WFF. Deactivation to the ground state (d_{xz} populated) allows trans attack of water to give the ground state of *mer* FWF. The $^4B_{2g}$ state loses ammonia to give a sp intermediate species which, by allowed N–Cr–N bending, leads to the doubly degenerate tbp intermediate with axial fluorides. This reacts to give *mer* FWF only.

In contrast, loss of x-axis ammonia from the $^4B_{2g}$ state of *trans*-$[Cr(NH_3)_4F_2]^+$ will lead to the $^4B_1[(xz)(yz)(x^2)]$ state of the sp intermediate, Figure 1A. This undergoes allowed N–Cr–N bending to produce the degenerate ground state of the tbp intermediate with two axial fluorides, which aquates by reaction in the equatorial plane exclusively to *mer* FWF, Figure 1B. Neither state gives rise in theory to facial WFF.

Our observations of both *mer* WFF and *mer* FWF as products are consistent with these rationalizations. If the possibility of reaction of both the electronically excited and its ground-state tbp intermediate is denied, then the theory becomes inconsistent with the data. It is worth emphasizing that the theory has lost some of its predictive power and that for this compound, thus far, it is not superior to the edge displacement model.

It differs from the latter, however, in its further predictions. The predicted stereochemistries of reaction of the ^4E and $^4B_{2g}$ derived tbp intermediates are different; for given solvent, temperature, etc., a presumably fixed ratio of *mer* WFF/*mer* FWF from ^4E_g and *mer* FWF alone from $^4B_{2g}$. Hence, on irradiation to shorter wavelength, if increased $^4B_{2g}$ participation does take place, a large proportion of *mer* FWF should be observed. The data in Table I might reveal such a trend. If the reaction at 577 nm reveals the product ratio for pure ^4E_g reaction and if the increased ammonia quantum yield at 436 nm were entirely due to $^4B_2$ reaction, then the *mer* WFF/*mer* FWF ratio should change from 2.5 to 2.1. This is in good agreement with our data. Unfortunately the trends observed are within the experimental uncertainty and can therefore not be taken as proving the operation of the symmetry rules.

For *cis*-$[Cr(NH_3)_4F_2]^+$ one of the products, facial WFF, Table I, is definitely produced in a wavelength-dependent proportion, indicating once more participation of more than one excited state and complicating the analysis of the data. The interpretation of the product isomer data in terms of the photostereochemistry is further complicated for this complex by the possibility of loss of both equatorial ammonia and axial ammonias.

For loss of equatorial ammonia, the reaction mode expected for the lowest quartet state, Table II, the edge displacement model predicts statistically 25% *mer* FWF, 25% *mer* WFF, and 50% *fac* WFF. Any preferential migration of fluoride would increase the proportion of *mer* FWF relative to the other isomers. The predictions are quite different from the observations, most notably in the small amounts of *fac* WFF observed but also in the fact that the ratio *mer* WFF/*mer* FWF is greater, not less than 1. If loss of an axial ammonia occurred, it should lead statistically to 50% *mer* WFF and 50% *fac* WFF with any preferential fluoride migration increasing *fac* WFF. Recognition of this possible additional photolysis mode does not therefore allow the edge displacement model to explain the small amounts of facial isomer observed, although it could explain the enhanced *mer* WFF. Also it is consistent with the increase in the *mer* WFF/*mer* FWF and *fac* WFF/*mer* FWF ratios observed on irradiation at 365 nm, where ^4E state may react and enhance axial ammonia loss. The edge displacement model does not, however, allow a completely satisfactory explanation of the observations.

It is not a simple matter to apply the VC theory to *cis*-$[Cr(NH_3)_4F_2]^+$ as the symmetries encountered are low and the allowed processes and conserved symmetries are therefore not obvious. Remember that in the starting complex the true symmetry is only C_{2v}, but conventionally this is approximated as D_{4h} by considering only the average σ- and π-donor strengths on the *x* and *y* axes. As soon as dissociation and rearrangement occur this assumption breaks down and the original d-orbital set tends to lose its clear identity.

For the lower energy $^4B_2$ state $[(xz)(yz)(x^2 - y^2)]$, the predicted reaction mode is loss of equatorial ammonia. The sp intermediate $^4A'[(xz)(yz)(x^2 - y^2)]$ will rearrange by the allowed bending of the N–Cr–F axis, with conservation of a plane of symmetry, to the excited $^4B_2[(xz)(yz)(x^2 - y^2)]$ state of the tbp intermediate with two equatorial fluorides; see Figure 2A,B. This excited state, the same as that derived from the ^4E_g state of *trans*-$[Cr(NH_3)_4F_2]^+$, will then aquate as before with a cis (to ammonia) selection rule to yield *mer* FWF and, if deactivated prior to reaction, will aquate with a trans selection rule to yield *mer* FWF, Figure 2B.

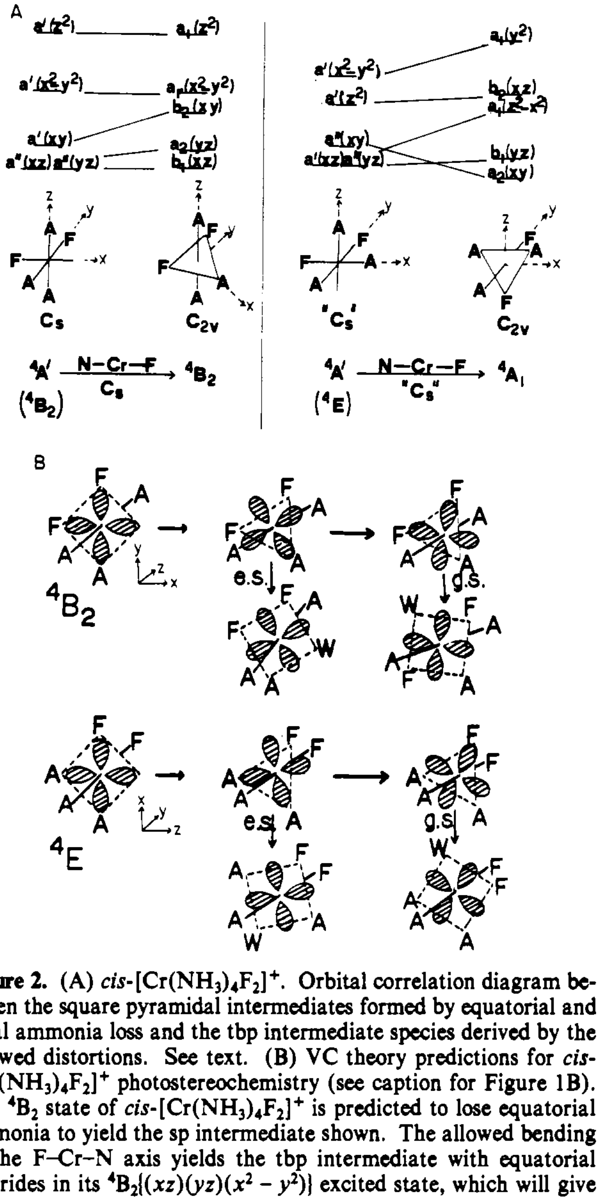

Figure 2. (A) *cis*-$[Cr(NH_3)_4F_2]^+$. Orbital correlation diagram between the square pyramidal intermediates formed by equatorial and axial ammonia loss and the tbp intermediate species derived by the allowed distortions. See text. (B) VC theory predictions for *cis*-$[Cr(NH_3)_4F_2]^+$ photostereochemistry (see caption for Figure 1B). The $^4B_2$ state of *cis*-$[Cr(NH_3)_4F_2]^+$ is predicted to lose equatorial ammonia to yield the sp intermediate shown. The allowed bending of the F–Cr–N axis yields the tbp intermediate with equatorial fluorides in its $^4B_2\{(xz)(yz)(x^2 - y^2)\}$ excited state, which will give rise to a mixture of *mer* WFF and *mer* FWF depending on the proportion of excited- to ground-state reaction. The ^4E state is predicted to lose axial ammonia to yield the sp intermediate with one axial and one equatorial fluoride which rearranges by F–Cr–N bending to give the tbp intermediate with one axial and one equatorial fluoride in its $^4A_1\{(xy)(yz)(xz)\}$ excited state. Excited-state reaction occurs with a trans selection rule to give *mer* WFF and ground-state reaction with a cis selection rule to give *fac* WFF.

The higher lying ^4E state, $[(xy)(xz)(z^2 - y^2)/(xy)(yz)(z^2 - x^2)]$, is predicted to lose axial ammonia to yield a sp intermediate species $^4A'[(xz)(yz)(z^2)]$ of C_s symmetry. In the subsequent rearrangement by allowed F–Cr–N bending to produce the tbp intermediate with one axial and one equatorial fluoride, there is no conserved symmetry element; the remaining symmetry plane is destroyed. Since, however, this rearrangement occurs in the *xz* plane without significant involvement of the *y* axis ligands, Figure 2B, it may be approximated that this plane of symmetry, and hence C_s symmetry, is conserved throughout the process. This leads to the orbital correlation diagram in the lower part of Figure 2A which shows that the tbp intermediate is produced in its $^4A_1[(xy)(yz)(xz)]$ excited state. This excited state, to the extent to which it reacts prior to deactivation to the $^4B_2$ ground state, is predicted to yield some mixture of *mer* WFF ($^4A_1$ reaction) and *fac* WFF ($^4B_2$ reaction), Figure 2B.

If such a theory of reaction modes and stereochemistry is correct, if both quartets react, and if increased ^4E reaction does occur to shorter wavelengths, then the following aspects of the data can be explained: (i) the small proportion of *fac* WFF observed, (ii) the increase in *fac* WFF on shorter wavelength excitation, and (iii) the observation of an increase in *mer* WFF/*mer* FWF at shorter wavelength. The theory therefore provides a satisfactory qualitative rationalization of the data. There are too many uncertainties to pursue a quantitative analysis.

It is unfortunate that no information is available on the extent of axial vs. equatorial ammonia loss and its wavelength dependence, as this would facilitate a clearer analysis and a better test of the theory. Nevertheless the theory accounts better for the data than the edge displacement model, most notably in explaining the small yields of *fac* WFF. The latter observation is the only one to date that provides any real evidence for the importance of symmetry restrictions over and above the constraints imposed by the original edge displacement proposal.

A further major aspect of the observations has been neglected till now. Attention was drawn to the equivalency of the excited-state tbp intermediates derived from the lowest quartet states of *trans*- and *cis*-$[Cr(NH_3)_4F_2]^+$ via which the major proportion of the photochemistries appears to occur. This tbp intermediate leads to *mer* WFF from its excited state and *mer* FWF from its ground state. Only if it is allowed that reaction can occur to differing extents from the electronically excited and ground states of this tbp intermediate for the two systems is it possible to explain the differing meridional isomer ratios. If not, or if it is required that these two states be in Boltzmann equilibrium prior to reaction, then a problem exists for the VC theory. Further if reaction via only the ground state of the tbp intermediate is expected, then only *mer* WFF would be produced. It seems that our data absolutely requires, in the context of the VC theory, reaction via electronically excited intermediates together with ground state and that, for some reason, the ratio of excited- to ground-state reaction may depend on the origin of the tbp intermediate species.

The superiority of the VC theory over the edge displacement model should not be interpreted as supporting a dissociative model for Cr(III) photochemistry. It may well be that the steric course of the reaction is predisposed by the symmetry requirements for an idealized five-coordinate process, but it remains very likely that both the leaving group and entering group are simultaneously in the picture, and this offers other mechanisms to explain differing product ratios from the lowest quartet reactions of the cis and trans complexes. There is some experimental evidence to show that Cr(III) photoreactions may be associative.[29] The VC theory should be considered a useful technique rather than a picture of reality.

In summary, it has been shown that ammonia photoaquation from *trans*-$[Cr(NH_3)_4F_2]^+$ is stereomobile, that the stereochemistry of photolysis of this complex is consistent with both the edge displacement model and the VC theory, that the cis complex photostereochemistry provides the first evidence of the operation of the VC type symmetry rules, and that, by accepting the participation of both $^4B_2$ and ^4E excited states in photochemistry, the VC model gives a reasonably good account of the photochemical reaction modes and stereochemistries of both molecules. Since the same intermediate is involved in the major mode for the two complexes, the different photochemistries emphasize that the mechanism is unlikely to be truly dissociative.

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Registry No. *trans*-$[Cr(NH_3)_4F_2]^+$, 31253-66-4; *cis*-$[Cr(NH_3)_4F_2]^+$, 58864-86-1; *mer* FWF, 75010-87-6; *mer* WFF, 75045-11-3; *fac* WFF, 75045-12-4.

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Enthalpy Changes in Oxidative Addition Reactions of Organic Iodides with *trans*-Chlorocarbonylbis(trimethylphosphine)iridium(I)

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Titration calorimetric methods have been used to determine enthalpies of the oxidative addition reaction of *trans*-$[IrCl(CO)(PMe_3)_2]$ with I_2, HI, CH_3I, C_2H_5I, *n*-C_3H_7I, *i*-C_3H_7I, $C_6H_5CH_2I$, $CH_3C(O)I$, and $C_6H_5C(O)I$ in 1,2-dichloroethane. Heats of solution of selected metal complexes and iodo compounds have been determined. These results were used to calculate $\Delta H°$ values for the oxidative addition reactions. Combination of the $\Delta H°$ values and heats of formation of the appropriate compounds has made it possible to calculate $\Delta H°$ for the β-elimination reaction of an ethyl complex, CO insertion into the $Ir-CH_3$ bond, and the isomerization of an isopropyl to an *n*-propyl complex. A relative scale of bond energies, $D(Ir-R) - D_1(Ir-I)$ has been determined based on the data obtained in this study. The general trend in $D(Ir-R)$ is $H > CH_3 \approx I \approx CH_3C(O) > C_2H_5 > n\text{-}C_3H_7 > i\text{-}C_3H_7 > CH_2C_6H_5$.

To date, no thermochemical information has been available concerning the oxidative addition reaction of organic halides with d^8 metal centers. Kinetic, synthetic, and structural studies have made reactions of the Vaska-type complexes *trans*-$[IrCl(CO)L_2]$ (L = tertiary phosphine), the best characterized model system for this class of reactions.[1-9] In general, the oxidative addition reaction has been very important in the development of organometallic chemistry since it is widely encountered in stoichiometric or catalytic syntheses which are mediated by transition-metal complexes.[2,4,5] Thermochemical

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