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FLUORO-DIAMINE COMPLEXES OF CHROMIUM(III)

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CONTENTS

ABBREVIATIONS

bipy = bipyridine
chxn = *trans*-1,2-diaminocyclohexane
cpt = *trans*-1,2-diaminocyclopentane
en = ethylenediamine
phen = 1,10-phenanthroline
pn = 1,2-propanediamine
py = pyridine
tn = 1,3-propanediamine

A. INTRODUCTION

For a complete review of the chemistry of amine complexes of Cr(III) through 1969 the reader is referred to the work of Garner and House [1].

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The current review is concerned with the investigations that have been carried out using fluoro complexes of Cr(III) since about 1960. For the most part the complexes discussed in this review have incorporated en, pn or tn as the bidentate ligands since these have been the more extensively studied complexes.

The small highly-basic fluoro ligand forms a strong bond to the Cr(III) center which remains intact in the absence of acid. In the presence of acid two different reactions can occur: (1) ligand unwrapping (Cr–N bond breaking) and (2) F^- loss. Which reaction dominates is a function of $[H^+]$. Thus a variety of products are to be expected upon acid hydrolysis of these complexes.

In addition these fluoro complexes serve as ideal model compounds to evaluate the current theories of Cr(III) photochemistry, as well as to further emphasize the differences between similar complexes of Co(III) and Cr(III).

B. SYNTHETIC METHODS

For complete reviews of the general synthetic methods used for the preparation of Cr(III) complexes, the reader is referred to the work of Garner and House [1] or Chang [2] and the references listed therein. Vaughn [3] has described the synthetic routes utilized for the preparation of a number of Cr–F amine complexes.

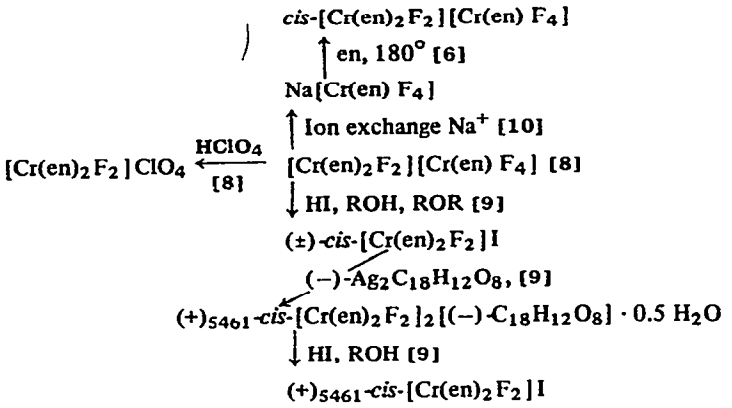
Fluoro-containing complexes can be prepared via many different routes, but the most commonly used approaches are: (a) direct reaction of $CrF_3 \cdot 3.5\ H_2O$ with the appropriate anhydrous diamine; (b) reaction of a dilute aqueous hydrofluoric acid solution of $CrCl_3 \cdot 6\ H_2O$ with the desired diamine; (c) reaction of *trans*-$[Cr(py)_4F_2]^+$ with the desired diamine in boiling 2-methoxyethanol; (d) anation of *cis*- or *trans*-$[Cr(AA)_2F(OH_2)]^{2+}$ with the appropriate ligand in methyl alcohol; (e) dehydration of *trans*-$[Cr(AA)_2F(OH_2)]X_2$ at elevated temperatures; and (f) substitution of a labile ligand in non-aqueous media which results in solvent coordination.

Routes of limited utility are: (a) reactions involving thermal deamination of *tris*-$[Cr(AA)_3]X_3$ complexes [4]; (b) reactions involving Cr(II) as a starting material [5]; and (c) reactions using diperoxo complexes as starting materials [6].

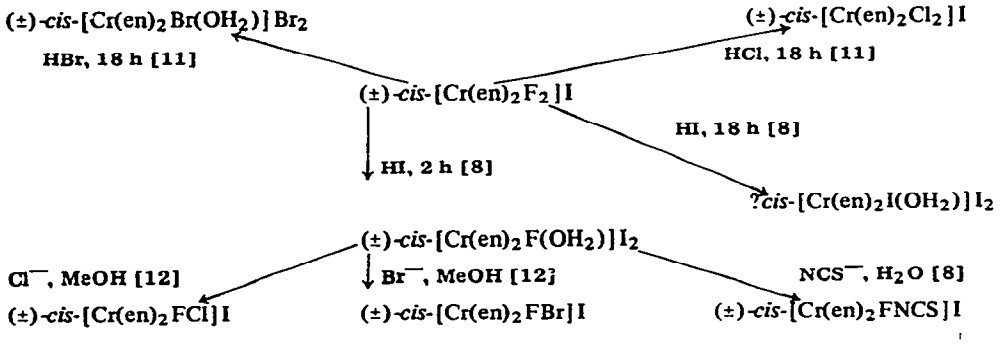
(i) Direct reaction of $CrF_3 \cdot 3.5\ H_2O$ and the anhydrous diamine, AA (AA = en, pn, tn or chxn)

The general preparative sequence can be illustrated by the reaction

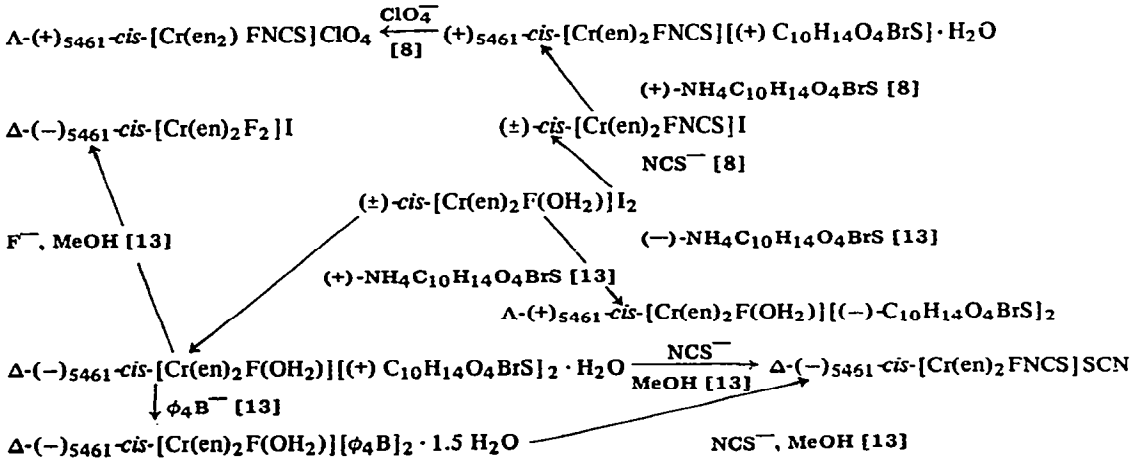
$$3\ en + 2\ CrF_3 \cdot 3.5\ H_2O \rightarrow [Cr(en)_2F_2][Cr(en)F_4] + 7\ H_2O \qquad (1)$$



Flow Chart 1. Some reactions of $[Cr(en)_2F_2][Cr(en)F_4]$.



Flow Chart 2. Some reactions of *cis*-$[Cr(en)_2F_2]I$.

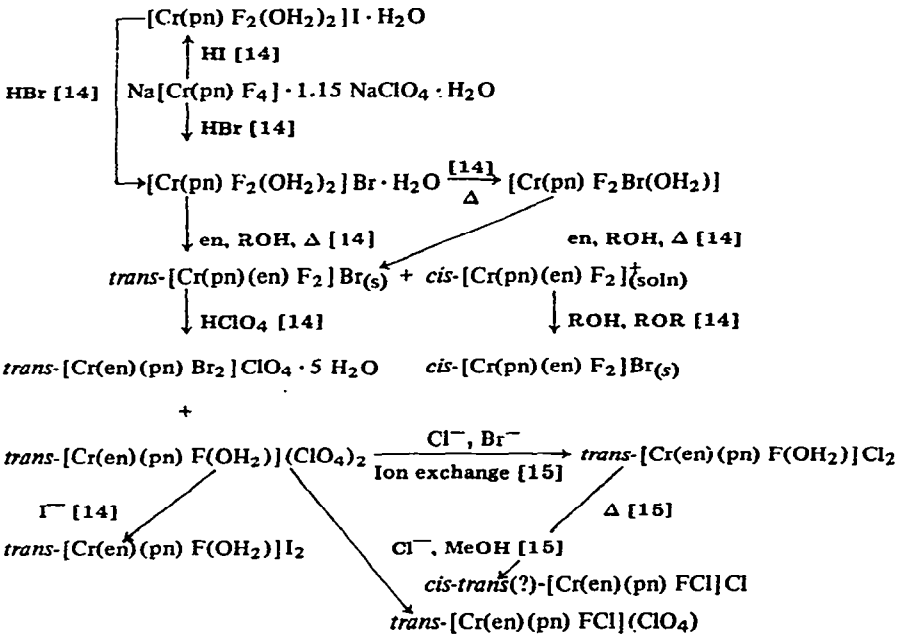


Flow Chart 3. Some reactions of *cis*-$[Cr(en)_2F(OH_2)]I_2$.

When AA is en or pn, the cation of the reaction product $[Cr(AA)_2F_2]^+$, involves a *cis* arrangement of the two fluoro ligands; and when AA is tn or chxn, the fluoro groups are *trans* to one another due presumably to increased crowding of the chelate ring [7].

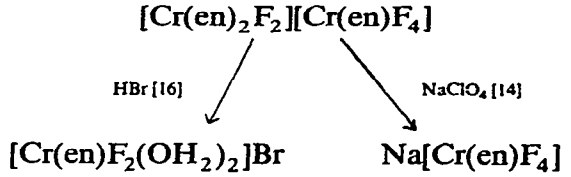
Flow charts 1, 2 and 3 illustrate the structure proof for the cation, some reactions of the cation, and some reactions of the synthetically important cation *cis*-$[Cr(en)_2F(OH)_2)]^{2+}$.

The anion of the complex $[Cr(AA)F_4]^-$ can be isolated by ion exchange techniques [10] or by precipitation as the sodium salt [14]. Flow chart 4 illustrates the utility of $[Cr(AA)F_4]^-$ as a starting material for the preparation of other Cr–F complexes.



Flow Chart 4. Complexes derived from $[Cr(pn)F_4]^-$.

Essentially the same sequence of reactions has been carried out using $[Cr(pn)F_2(OH_2)_2]Br$ as the starting material and 1,3-propanediamine as the added bidentate ligand [15]. For the preparation of some propanediamine *trans*-1,2-diaminocyclohexane complexes, see the work of Vaughn and Marzowski [14].



The complex $[Cr(en)F_2(OH_2)_2]Br$ arises via Cr–F bond breaking in the anion and not by Cr–N bond rupture in the cation. The cation reacts slowly in concentrated HI or HBr with F^- ion release to yield *cis*-$[Cr(en)_2F(OH_2)]^{2+}$. The isomer distribution in $[Cr(en)F_2(OH_2)_2]^+$ has not been definitely established; however, preliminary indications are that the two fluoro ligands are *trans* to each other. Final conformation must await the results of the X-ray structural determination which is underway.

(ii) Reactions in buffered solutions

There are two routes currently used to prepare *trans*-difluoro isomers of Cr(III). Direct reaction of a soluble Cr(III) salt with the appropriate diamine in aqueous solution results in the formation of oxo- and hydroxo-containing species rather than the desired product. This is a result of the very strong bond Cr(III) forms with oxygen donors in comparison to those formed with nitrogen donors. The problem of the oxygen donor has been solved by working in a highly buffered amine–amine salt solution or by working in non-aqueous solvents.

The first of these methods, developed by Dahme [17] was utilized to prepare *trans*-$[Cr(en)_2F_2]^+$ by treating an aqueous hydrofluoric acid solution of $CrCl_3 \cdot 6\,H_2O$ with excess aqueous ethylenediamine. Fluoride anation occurs during the reaction to yield the *trans*-difluoro complex rather than the *tris* en complex. This method has also been utilized to prepare the corresponding pn [18], tn [19], and *trans*-1,2-diaminocyclohexane complexes [20].

However, if the reaction is run under the same conditions using the weaker acid, acetic acid, rather than hydrofluoric acid, the products obtained depend on the bidentate ligand used. The major products when en or pn was used as the bidentate ligand were the corresponding *tris* complexes, whereas when 1,3-propanediamine was used the product was the *trans*-diacetate [21].

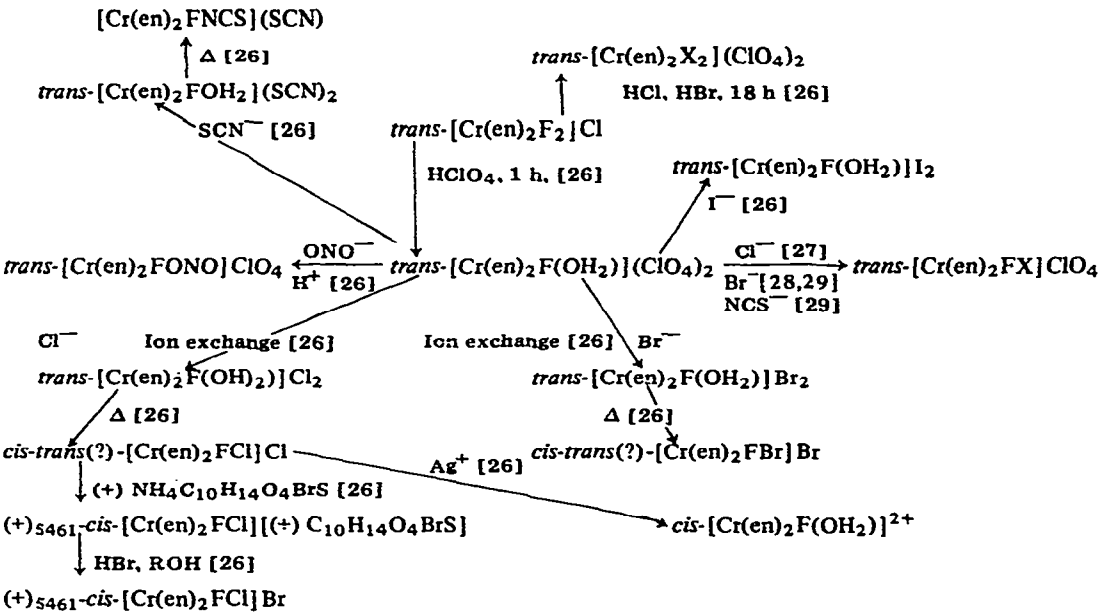
(iii) Reactions in 2-methoxyethanol

The other method for the preparation of *trans*-difluoro isomers of Cr(III), developed by Glerup et al. [22], utilizes reactions of a solution of *trans*-$[Cr(py)_4F_2]^+$ with the appropriate ligand in boiling 2-methoxyethanol. The Cr–F bond is stable in the absence of strong acids and remains intact during the preparative reaction. It would appear that the chelate effect, rather than any large differences in Cr–N bond strength, is the driving force for the substitution of the four equitorial pyridine ligands. *Trans* complexes containing: en; (±) pn; (−) pn; tn; (−) cyclohexanediamine; tris-(2-aminoethyl)amine; 1,4,8,11-tetraazaundecane; and 1,5,8,12-tetraazadodecane have been prepared. Complexes of 1,4,7,10-tetraazadecane, 1,10-

phenanthroline, and 2,2′-bipyridyl are reported to have a *cis* arrangement of the fluoro ligands [22].

Others have used this same reaction to prepare *trans*-difluoro complexes of 2-picolyamine (α form) [23] and β,β',β''-triaminotriethylamine [24]. It has been possible to prepare *trans*-difluoro complexes which contain S,S-stilbenediamine and S,S-2,4-pentanediamine using this method [25].

The importance of the *trans*-difluoro complexes is that they provide an easy, direct route to the *trans*-FX and *cis*-FX complexes. The very strong Cr–F bond is easily cleaved in the presence of a strong acid to yield the corresponding $F(OH_2)^{2+}$ complex which can be easily isolated. Flow chart 5 illustrates the preparative utility of *trans*-F_2 complexes.



Flow Chart 5. Complexes derived from *trans*-$[Cr(en)_2F_2]^+$.

(iv) Anation reactions in methyl alcohol

Complexes of the type $[Cr(AA)_2FX]^{n+}$ (AA = en, tn) can be easily prepared by reacting the corresponding fluoro aquo complexes with the appropriate ammonium salt in methyl alcohol [27]. It is not necessary that the fluoro aquo complex be more than slightly soluble in the methyl alcohol. In fact some complexes have been prepared by this method, by reacting a slurry of the starting material and the ammonium salt to produce the desired product [28,29]. However, such a method requires rather large solubility

differences between the reactant and product so one can cleanly separate the desired product.

The starting material usually employed is the fluoro aquo perchlorate or iodide so as to avoid the complication of an additional coordinating anion. The method is stereoretentive in that *cis* starting materials yield *cis* products and *trans* starting materials yield *trans* products.

The original investigation using this method for Cr–F complexes [27] utilized room temperature reactions; however, *trans*-$[Cr(en)_2FBr]^+$ could not be isolated from the reaction mixture. Others [28,29] found that this product can be easily obtained by carrying out the reaction at elevated temperatures.

The advantages of this method are: (1) direct anation in the absence of a strongly coordinating solvent; and (2) anation under conditions that leave the Cr–F bond intact.

(v) Dehydration reactions

The dehydration of *trans*-$[Cr(en)_2F(OH_2)]X_2$ ($X = Cl^-, Br^-, I^-, SCN^-$) is of interest since the reaction was the basis for the original preparation of *cis*-FX isomers [26]. That the reaction produces *cis* isomers has been proved beyond a reasonable doubt since the product of the dehydration was resolved into *d*,*l* forms [26]. However, the isomer distribution in the product has not been established. The *trans*-$[Cr(en)_2FCl]ClO_4$ complex does not isomerize to the *cis* form at the temperature necessary for the dehydration of the *trans*-$F(OH_2)$ complex. This would suggest that the dehydration process could involve a five-coordinate trigonal bipyramidal intermediate rather than a square pyramidal intermediate followed by an isomerization step. When the complex *trans*-$[Cr(tn)_2F(OH_2)]X_2$ is dehydrated, the major, if not the only, product of the reaction is *trans*-$[Cr(tn)_2FX]X$ [30].

(vi) Substitution reactions in a coordinating solvent

A synthetic route which has not been exploited to its fullest potential is the solvolysis of the starting material in a coordinating non-aqueous solvent. Such a method requires a soluble salt with a weak Cr–X bond, which can be easily cleaved in the non-aqueous solvent, or if the Cr–X bond is strong the formation of a very weak acid, a weak base, or insoluble salt must be possible. The hardest requirement to meet is that the salt be soluble, although it is possible in some cases to utilize compounds which have small but finite equilibrium solubilities.

A solvent which has been utilized for this purpose is liquid HF. Solvolysis of $[Cr(bipy)_2(C_2O_4)]^+$ and $[Cr(phen)_2(C_2O_4)]^+$ in $HF_{(l)}$ produces the corre-

sponding *cis*-F_2 compounds [31]. In this case the driving force for the replacement of the oxalate ring probably is the formation of two strong Cr–F bonds, as well as the formation of the weak acid $H_2C_2O_4$. The reaction results in the rupture of two strong Cr–O bonds causing the loss of the five-membered oxalate ring.

It is also possible to increase the F^- concentrations of $HF_{(l)}$ by adding HgF_2 to the system and at the same time to utilize the Hg^{2+} ion as an anion scavenger. This was done in the following reaction [31]

$$cis\text{-}[Cr(o\text{-phen})_2Cl_2]^+ + HgF_2 \xrightarrow{HF_{(l)}} cis\text{-}[Cr(o\text{-phen})_2F_2]^+ + HgCl_2 \qquad (2)$$

The weakness of the Cr–Br bond was exploited by Wong and Kirk [32] in order to prepare *cis*- and *trans*-FNH_3 complexes. The reaction of *trans*-$[Cr(en)_2FBr]ClO_4$ with liquid ammonia containing a little ammonium perchlorate results in Cr–Br bond breaking followed by Cr–NH_3 bond formation. The Cr–F bond remains intact during the reaction which yields *cis*- and *trans*-$[Cr(en)_2FNH_3]^{2+}$. The approximate isomer ratio found (*cis*:*trans* = 60:40), is near to that expected for a trigonal bipyramidal intermediate. The important point in this synthesis is that the reaction goes with extensive stereo change whereas most aquation reactions of Cr(III) complexes go with little or no stereo change. A similar reaction has been carried out using *trans*-$[Cr(tn)_2FBr]ClO_4$ as the starting material, and in this case, the product of the reaction appears to be the *trans* isomer [33]. If this is true, we have another example of the rather large differences that exist between en and tn complexes of Cr(III).

C. ELECTRONIC SPECTRA

The visible electronic spectra of fluoro complexes of Cr(III) which result from spin-allowed transitions can be easily explained in terms of current theory. In the presence of an octahedral ligand field the Russell–Saunders free ion ground state term, ^4F, is split into the $^4A_{2g}$, $^4T_{2g}$, and $^4T_{1g}(F)$ states while the high energy ^4P state is not split by the field. Since the system contains only three *d*-type electrons, the non-degenerate $^4A_{2g}$ state is the ground state. Thus, one would expect in order of increasing energy the following three spin-allowed transitions to occur: $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$, and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$. The $^4T_{2g}(F)$ state is exactly 10 Dq above the $^4A_{2g}$ state since energy must be conserved and there is no high-energy state of the proper symmetry to mix with the $^4T_{2g}(F)$ state and change its energy. The separation of $^4A_{2g}$ and $^4T_{1g}(F)$ states is not as straightforward since the $^4T_{1g}(F)$ state mixes with the $^4T_{1g}(P)$ state. The mixing of the $^4T_{1g}$ states manifests itself by lowering the energy of $^4T_{1g}(F)$ and raising the

energy of the $^4T_{1g}(P)$. The Racah parameter B, which has a value of 918 cm^{-1} for Cr(III) [34], is reduced by 10% in the complex anion CrF_6^{3-}.

Since the third spin-allowed transition, $^4A_{2g} \rightarrow {}^4T_{1g}(P)$, is shifted to higher energies due to mixing of the two $^4T_{1g}$ excited states, the expected transition is sometimes obscured by another transition which results from the transfer of charge from the ligand to an acceptor orbital centered on the chromium. In the case of CrF_6^{3-} all three transitions are observed.

Substitution of one of the ammine ligands in $[Cr(NH_3)_6]^{3+}$ by a fluorine donor results in a lowering of the symmetry and in changes in the electronic spectrum. The complex $[Cr(NH_3)_5F]^{2+}$ can be assumed to have a local site symmetry of C_{4v} if only the CrN_5F core is considered. The ground state is not split by the lowering of the symmetry, but since C_{4v} symmetry cannot tolerate degeneracies greater than two, the ^4T states are split. In the lower C_{4v} symmetry, the A_{2g} state transforms as B_1, the $T_{2g}(F)$ is split into the B_2 and E states, and T_{1g} splits into the A_2 and E states. It is to be anticipated that these splittings should produce two additional spin-allowed transitions. In the case of $[Cr(NH_3)_5F]^{2+}$, the anticipated additional bands are not found; rather, the spectrum consists of two bands centered at 27,300 cm^{-1} and 19,900 cm^{-1} [35]. However, $[Cr(NH_3)_5Cl]^{2+}$ does show splitting [36,37] of the $^4T_{2g}(O_h)$ with a transition at 19,400 cm^{-1} and a shoulder at 22,100 cm^{-1}. A single transition was found at 26,600 cm^{-1} for this complex, indicating that the splitting of the $^4T_{1g}(P)[O_h]$ state was too small to observe.

In a similar fashion, complexes of the type $[Cr(AA)_2FNH_3]^{2+}$, where AA is either ethylenediamine, en, or 1,3-propanediamine, tn, have a local site symmetry of C_{4v} which is independent of the geometrical arrangement of the monodentate ligands. The electronic spectra of *cis*- and *trans*-$[Cr(en)_2FNH_3]^{2+}$ and *trans*-$[Cr(tn)_2FNH_3]^{2+}$ show no evidence of the splitting of the excited states [32,33].

Likewise, theory predicts that the CrN_4F_2 core complexes with two different local site symmetries (*trans*-D_{4h} and *cis*-C_2) should exhibit splitting of the excited states with the splitting in the *trans* complex twice that found for the *cis* isomer [38]. In the cases of *trans*-$[Cr(en)_2F_2]^+$ [26,39] and *trans*-$[Cr(tn)_2F_2]^+$ [19,22] such a splitting is observed whereas the effect is absent in *cis*-$[Cr(en)_2F_2]^+$ [5].

Table 1 contains the spectral data for some fluoro-containing complexes of Cr(III).

D. POLARIZED SPECTRA

If a single crystal is irradiated with polarized, rather than unpolarized, monochromatic light, then only those transitions whose dipole moment

TABLE I

Electronic spectral data for some Cr–F complexes

Complex	Solvent	λ_{max}, ϵ	λ_{min}, ϵ	λ_{max}, ϵ	λ_{max}, ϵ	Reference
$[Cr(NH_3)_5F]^{2+}$	0.1 M $HClO_4$	366 (20.4)		503 (41.7)		35
		369 (21.9)		500 (42.6)		40
$[Cr(en)_2F_2][Cr(en)F_4]$	H_2O	384 (45.5)		528 (85.0)		9
$[Cr(pn)_2F_2][Cr(pn)F_4]$	H_2O	380 (63.0)		524 (98.0)		14
cis-$[Cr(en)_2F_2]^+$	0.1 M $HClO_4$	375 (37)	431 (11)	519 (75)		5
	H_2O	378 (39.5)		516 (75.5)		9
cis-$[Cr(pn)_2F_2]^+$	acetone	370 (88.6)		530 (88.6)		15
	H_2O	375 (33.5)		517 (45.0)		14
cis-$[Cr(phen)_2F_2]^+$	H_2O	420 sh (69.2)	455 (16.6)	522 (46.5)		22
cis-$[Cr(en)_2FCl]^+$	H_2O	387 (42.8)		518 (62.4)		26
	H_2O	383 (41.9)	441 (17.4)	520 (72.4)		12
cis-$[Cr(en)_2FBr]^+$	H_2O	381 (37.6)		512 (61.2)		26
	H_2O	376 (42.1)	433 (22.3)	515 (72.9)		12
cis-$[Cr(en)_2F(OH_2)]^{2+}$	H_2O	372 (32.9)	429 (16.2)	502 (74.8)		12
	H_2O	373 (32.4)	426 (16.1)	503 (74.2)		8
	1.5 M H_2SO_4	376 (35.1)		507 (70.2)		19
	0.1 M $HClO_4$	378		506		26
cis-$[Cr(tn)_2F(OH_2)]^{2+}$	1.5 M H_2SO_4	376 (30.8)		511 (27.0)		19
cis-$[Cr(en)_2FNCS]^+$	H_2O	373 (50)		500 (104)		8
cis-$[Cr(en)_2FNH_3]^{2+}$	0.1 M $HClO_4$	360 (34.4)		494 (64.9)		32
trans-$[Cr(en)_2FCl]^+$	H_2O	381 (27.4)		460 (21.5)	553 (19.8)	27
	H_2O	381 (27.6)		460 (21.1)	551 (19.3)	28
	H_2O	381 (25.8)		459 (20.6)	553 (18.7)	19
trans-$[Cr(en)_2FBr]^+$	H_2O	385 (30.1)		466 (23.2)	563 (22.7)	28
trans-$[Cr(en)_2F(OH_2)]^{2+}$	H_2O	371 (31.2)		454 (25.6)	519 (24.2)	26
	H_2O	368 (29.6)		458 (24.0)	519 (22.5)	19
trans-$[Cr(en)_2FNCS]^+$	H_2O	375 (33.9)		509 (41.2)		29
trans-$[Cr(en)_2FNH_3]^{2+}$	0.1 M $HClO_4$	356 (24.1)		490 (45.7)		32
trans-$[Cr(en)_2FONO]^+$	H_2O	498 (32.0)				41

Complex	Solvent	λ_{max}, ϵ	λ_{min}, ϵ	λ_{max}, ϵ	λ_{max}, ϵ	Reference
trans-$[Cr(tn)_2FCl]^+$	H_2O	386 (31.8)		461 (20.0)	564 (19.6)	19
		368		460	564	30
trans-$[Cr(tn)_2FBr]^+$	H_2O	390 (34.9)		465 (20.1)	378 (22.4)	19
	H_2O	387		467	575	30
trans-$[Cr(tn)_2F(OH_2)]^{2+}$	H_2O	375 (37.8)		460 (22.4)	533 (20.9)	19
	H_2O	375		460	534	30
trans-$[Cr(tn)_2FNH_3]^{2+}$	0.2 M $HClO_4$	368 (31.9)		500 (45.9)		33
trans-$[Cr(NH_3)_4F_2]^+$	H_2O	354 (10.0)	478	552 (12.1)		42
trans-$[Cr(en)_2F_2]^+$	H_2O	350 (14.5)	400 sh (12.8)	466 (21.1)	525 (16.3)	43
		351 (14.4)	397 (13.2)	465 (21.0)	530 sh (16.5)	22
trans-$[Cr(pn)_2F_2]^+$	H_2O	351 (15.2)	400 (13.9)	467 (23.1)	530 sh (17.0)	22
	H_2O	348 (15.8)	397 (15.0)	466 (23.0)	522 sh (17.5)	14
trans-$[Cr(tn)_2F_2]^+$	H_2O	360 (16.4)	397 (16.8)	462 (20.9)	542 (16.5)	19
	H_2O	360	394	464	542	30
		360 (16.3)	398 (16.5)	468 (20.7)	538 (16.8)	22
trans-$[Cr(chxn)_2F_2]^+$	H_2O	354 (18.1)	397 (17.3)	467 (26.9)	530 sh (19.5)	22
trans-$[Cr(\pm cpt)_2F_2]^+$	H_2O	349 (25.9)			504 (27.4)	44
Mixed ligand complexes						
trans-$[Cr(pn)(en)F_2]^+$	H_2O	350 (16.0)	395 (14.6)	456 (22.4)	525 sh (18.0)	14
trans-$[Cr(pn)(tn)F_2]^+$	H_2O	353 (26.9)	390 (20.0)	464 (26.1)	525 sh (17.6)	14
	H_2O	355 (27.6)	395 sh (20.9)	465 (27.1)	530 sh (18.9)	15
trans-$[Cr(en)(pn)F(OH_2)]^{2+}$	H_2O	368 (37.6)		456 (31.0)	519 (28.5)	14
	0.1 M $HClO_4$	369 (33.3)		458 (27.2)	518 (27.8)	15
trans-$[Cr(pn)(tn)F(OH_2)]^{2+}$	H_2O	367 (52.7)		460 (40.7)	515 (35.4)	14
cis-$[Cr(pn)(chxn)_2F_2]^+$	H_2O	377 (41.3)			518 (63.3)	14
cis-$[Cr(pn)(en)F_2]^+$	H_2O	377 (26.8)			515 (40.6)	15
trans-$[Cr(pn)(en)FCl]^+$	H_2O	378 (31.2)		458 (22.6)	549 (20.4)	15
cis-$[Cr(pn)(en)FCl]^+$	H_2O	385 (39.0)			512 (57.5)	15
cis-$[Cr(pn)(en)FBr]^+$	H_2O	384 (35.2)			518 (52.4)	15
cis-$[Cr(pn)(tn)FCl]^+$	H_2O	375 (37.7)			523 (43.0)	15
cis-$[Cr(pn)(tn)FBr]^+$	H_2O	382 (34.6)			513 (49.7)	15

TABLE 1 (continued)

Complex	Solvent	λ_{max}, ϵ	λ_{min}, ϵ	λ_{max}, ϵ	λ_{max}, ϵ	Reference
Complexes containing partially unwrapped ligands						
trans-$[Cr(en)(enH)(OH_2)F_2]^{2+}$	0.75 M H_2SO_4	366 (18.1)		410 sh (10.0)	518 (40.6)	19
	0.4–0.7 M $HClO_4$	365 (18.6)		410 sh (10.0)	519 (40)	43
trans-$[Cr(en)(enH)(OH_2)_2F]^{3+}$	1.5 M H_2SO_4	380 (28.5)			515 (45.8)	19
	2.0–2.5 M HCl	378 (29.4)			512 (47.3)	43
Monodiamine complexes						
$[Cr(en)F_4]^-$	0.1 M $HClO_4$	410 (14.5)		571 (32.9)		45
	H_2O	412 (18.5)		572 (34)		10
$[Cr(pn)F_4]^-$	H_2O	408 (19.1)		573 (36.4)		14
$[Cr(en)(OH_2)_2F_2]^+$	0.1 M $HClO_4$	372 (11.4)		415 sh (8.3)	544 (35.2)	16
	0.15 M H_2SO_4	382 (12.1)		410 sh (10.0)	545 (36.2)	19
	H_2O	371 (12.5)		410 sh (10.1)	543 (37.0)	43
$[Cr(tn)(OH_2)_3F]^{2+}$	0.15 M H_2SO_4	390 (33.2)		535 (41.5)		19
$[Cr(pn)F_2(OH_2)_2]^+$	0.1 M $HClO_4$	373 (11.9)	415 sh	545 (36.1)		14
	0.1 M $HClO_4$	373 (12.2)	415 sh	545 (35.0)		15
Other complexes						
cis-$[Cr\{N(CH_2-CH_2-NH_2)_3\}F_2]^+$	H_2O	378 (56.8)	438 (32.5)	528 (116.5)		22
cis-$[CrF_2$(1,4,7,10)tetraazadecane$]^+$	H_2O	374 (56.2)	432 (27.8)	523 (120.6)		22
trans-$[CrF_2$(1,4,8,11)-tetraazadecane$]^+$		348 (16.2)		453 (22.5)	522 (16.0)	22
trans-$[CrF_2$(1,5,8,12)-tetraazadodecane$]^+$	H_2O	354 (23.3)	427 sh (24.2) plateau 390–400 (17.3)	460 (37.2)	530 sh (17.4)	22
α-cis-$[Cr(C_6H_8N_2)_2F_2]^+$	H_2O	373 (50.2)	430 (12.7)	519 (99.2)		23
	H_2O	373 (49.9)	430 (12.3)	519 (98.8)		23
$[Cr(NH_2C_2H_5)_4F_2]^+$	0.1 M HCl	356 (16.3)	408 (14.5)	494 (22.4)		22
$[Cr(H_2NC_3H_7)_4F_2]^+$	0.1 M HCl	356 (17.5)	413 (16.1)	502 (26.1)		22
$[Cr(H_2NC_3H_5)_4F_2]^+$	0.1 M HCl	353 (18.3)	415 (16.0)	509 (27.3)		22

vectors are oriented in the same way as the electric vector of the incident beam will be allowed. In general, the necessary condition for this to occur is that the symmetry of the complex be lower than cubic.

The polarized single-crystal electronic spectra of *trans*-$[Cr(en)_2F_2]ClO_4$ [46] and *trans*-$[Cr(en)_2F(OH_2)](ClO_4)_2$ [47] have been measured. In the case of *trans*-$[Cr(en)_2F_2]ClO_4$, a complex which is centrosymmetric, the intensity of the *d–d* transitions must be largely due to vibronic coupling. Proceeding as before, the local site symmetry of *trans*-$[Cr(en)_2F_2]^+$ (D_{4h}) results in the following electronic states:

$$^4A_{2g} \rightarrow {}^4B_{1g}, \quad {}^4T_{2g}(F) \rightarrow {}^4B_{2g} + {}^4E_g, \quad {}^4T_{1g}(F) \rightarrow {}^4A_{2g} + {}^4E_g.$$

Therefore, the following spin-allowed electronic transitions would be expected on the basis of symmetry alone:

$$^4B_{1g} \rightarrow {}^4B_{2g}, \quad {}^4B_{1g} \rightarrow {}^4E_g, \quad {}^4B_{1g} \rightarrow {}^4A_{2g}.$$

The representations of the electronic dipole integrals in D_{4h} are given as

	$^4B_{1g} \rightarrow {}^4B_{2g}$	$^4B_{1g} \rightarrow {}^4E_g$	$^4B_{1g} \rightarrow {}^4A_{2g}$
$\int \psi_e' z \psi_e \, d\tau$	A_{1u}	E_u	B_{2u}
$\int \psi_e'(x, y) \psi_e \, d\tau$	E_u	A_{2u}, B_{2u}	E_u

However, consideration of the normal vibrational modes of the first excited states reveals that there are no vibrational modes of A_{1u} or B_{2u} symmetry to couple with the ground electronic states.

Thus, the vibronically allowed transitions are

$^4B_{1g} \rightarrow {}^4B_{2g}$ (*xy* polarization)

$^4B_{1g} \rightarrow {}^4E_g$ (both polarizations)

$^4B_{1g} \rightarrow {}^4A_{2g}$ (*xy* polarization)

In order for the terms $\parallel$ and $\perp$ polarizations to have their complete meanings, it is necessary that the crystal structure and hence the orientation of the F–Cr–F axis with respect to the crystal axes be known. In the absence of structural data, it is possible to derive meaningful information from a measurement of the polarized spectra if the arrangement of the complex in the crystal is such that the directions of the extinction corresponds to being $\parallel$ and $\perp$ to the C_4 axis of the crystal. This happy situation arises in both *trans*-$[Cr(en)_2F_2]ClO_4$ and *trans*-$[Cr(en)_2F(OH_2)](ClO_4)_2$.

Measurement of the single-crystal polarized electronic spectrum of *trans*-$[Cr(en)_2F_2]ClO_4$ revealed transitions at 18,500, 21,700, 25,300, and 29,300 cm^{-1} with a shoulder at 41,000 cm^{-1} for what would appear to be essentially *x*, *y*-polarization. In the approximately $\parallel$ polarization, the bands at 21,700

and 29,300 cm^{-1} were almost, but not completely, absent. Thus, the bands at 21,700 and 29,300 cm^{-1} can be reliably assigned to $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4B_{1g} \rightarrow {}^4A_{2g}$. The other transitions can now be assigned, and these are shown below [46].

$$^4B_{1g} \rightarrow {}^4E_g[{}^4T_{2g}(F)]\ 18,500\ cm^{-1}$$

$$^4B_{1g} \rightarrow {}^4B_{2g}[{}^4T_{2g}(F)]\ 21,700\ cm^{-1}$$

$$^4B_{1g} \rightarrow {}^4E_g[{}^4T_{1g}(F)]\ 25,300\ cm^{-1}$$

$$^4B_{1g} \rightarrow {}^4A_{2g}[{}^4T_{1g}(F)]\ 29,300\ cm^{-1}$$

$$^4B_{1g} \rightarrow \begin{cases} {}^4A_{2g}[{}^4T_{1g}(P)] \\ {}^4E_g \end{cases} 41,000\ cm^{-1}\ \text{sh.}$$

It is to be noted that the splitting of the third cubic band ($^4T_{1g}(P)$) was not well resolved and that in the splitting of the first cubic band the ^4E_g state is about 3000 cm^{-1} below the $^4B_{2g}$.

The polarized single-crystal spectrum of the non-centrosymmetric complex *trans*-$[Cr(en)_2F(OH_2)](ClO_4)_2$ exhibits only splitting of the first two cubic bands. Unlike *trans*-$[Cr(en)_2F_2]ClO_4$, *trans*-$[Cr(en)_2F(OH_2)](ClO_4)_2$ revealed no evidence of the splitting of the $^4T_{1g}(P)$ band. Since the complex is non-centrosymmetric, it is anticipated that the purely electronic selection rules might operate in this case and that the vibronic mechanism would not be important. Calculations similar to those previously described using a local site symmetry of C_{4v} and purely electronic selection rules indicate that only the two ^4E bands are allowed in the $\perp$ polarization and none in the $\parallel$ polarization, an effect which is not in accord with the experimental spectrum. Bands were found at 19,140 cm^{-1} ($\perp$), 19,300 cm^{-1} ($\parallel$), 22,530 cm^{-1} ($\perp$), 27,490 cm^{-1} ($\perp$), and 27,800 cm^{-1} ($\parallel$). Such a band pattern has been explained by treating the two different axial ligands not as individual ligands but as an average ligand pair. Such a treatment not only allows one to change the local site symmetry to D_{4h}, but it also requires the operation of the vibronic mechanism to destroy the center of symmetry.

Another approach to the problem has been to use a local site symmetry of C_{4v} in conjunction with the vibronic mechanism. However, the predictions of this approach do not agree with the experimental facts.

Using a symmetry of D_{4h} and a vibronic mechanism, the following band assignments have been made [47]:

$$^4B_{1g} \rightarrow {}^4E_g[{}^4T_{2g}(F)]\ 19,140\ cm^{-1}\ (\perp),\ 19,300\ cm^{-1}\ (\parallel)$$

$$^4B_{1g} \rightarrow {}^4B_{2g}[{}^4T_2g(F)]\ 22,530\ cm^{-1}$$

$^4B_{1g} \rightarrow {}^4E_g[{}^4T_{1g}(F)]$ 27,280 cm^{-1}

$^4B_{1g} \rightarrow {}^4A_{2g}[T_{1g}(F)]$ 27,490 cm^{-1}

The ordering of the energy levels is the same as that reported for *trans*-$[Cr(en)_2F_2]^+$, but the separation of the ^4E_g and $^4A_{2g}$ states derived from the splitting of the second cubic band is much less than that found for the *trans* complex.

E. KINETIC STUDIES

Kinetic studies of fluoro-containing complexes, although rather limited, are important for three reasons: (a) many acid hydrolysis reactions involve both Cr–X (X is the leaving group) and Cr–N bond breaking; (b) if the photochemistry of Cr–F complexes is to be understood, the nature of the thermal aquation and photochemical products must be known; and (c) useful comparisons can be made with the corresponding Co(III) complexes.

One of the earliest studies was that of Fehrmann and Garner [48] who determined the rates of F^- ion release from (±)-*cis*-$[Cr(en)_2F_2]^+$ as a function of pH. The aquation reaction which was found to be acid-catalysed was apparently one of the first, if not the first, example of acid-catalysed fluoride ion release with Cr(III) complexes. Similar behavior had been reported earlier for the corresponding Co(III) complex [49].

Acid-catalysed fluoride ion release can be explained by invoking the scheme below:

$$(\pm)\text{-}cis\text{-}[Cr(en)_2F_2]^+ + H^+ \rightleftharpoons (\pm)\text{-}cis\text{-}[Cr(en)_2F_2H]^{2+} \quad (3)$$

$$(\pm)\text{-}cis\text{-}[Cr(en)_2F_2H]^{2+} + H_2O \xrightarrow{k} (\pm)\text{-}cis\text{-}[Cr(en)_2FOH_2]^{2+} + HF \quad (4)$$

When the reaction is studied under pseudo-first-order conditions at constant pH, the rate is given as rate $= k\{(\pm)\text{-}cis\text{-}[Cr(en)_2F_2]^+\}$, an expression from which k can be easily evaluated. The major product of the aquation was the *cis*-$F(OH_2)^{2+}$ complex, and no evidence was found for Cr–N bond breaking. At higher values of the pH, base hydrolysis did occur with increased rates, but it was not possible to estimate the rate constants for this reaction.

One rather odd feature of the acid hydrolysis reaction is that after about 50% of the total fluoride has been released there is an uptake of ionic fluoride from the solution. It has been suggested that this uptake could occur because the chloroacetate ion from the buffer acts as a bridging ligand to produce polynuclear complexes which then take up the F^- ion from the solution.

Although ligand unwrapping (Cr–N bond breaking) had been found previously in Cr(III) complexes [50] Pyke and Linck [43] were apparently the

first to observe this effect with Cr–F complexes.

If *trans*-$[Cr(en)_2F_2]^+$ is allowed to aquate in 0.1 M $HClO_4$ for less than two half-lives, the major product is the partially unwrapped species $[Cr(en)(enH)(H_2O)F_2]^{2+}$. Continued aquation (4–6 half-lives) resulted in two additional products, $[Cr(en)(OH_2)_2F_2]^+$ and a complex mistakenly identified as *cis*-$[Cr(en)_2F(OH_2)]^{2+}$.

It was originally proposed that the major path for the aquation of *trans*-$[Cr(en)_2F_2]^+$ was directly to the unwrapped species with the *cis* isomer and $[Cr(en)(OH_2)_2F_2]^+$ being formed via subsequent reactions of the primary product. However, such a scheme requires that the partially unwrapped and protonated en ligand dissociate a proton and reclose in acidic solution. Subsequent work [19] has shown that the complex identified as *cis*-$[Cr(en)_2F(OH_2)]^{2+}$ is actually *trans*(?)-$[Cr(en)(enH)(OH_2)_2F]^{3+}$.

In contrast to the acid hydrolysis of *cis*-$[Cr(en)_2F_2]^+$, the acid hydrolysis of *trans*-$[Cr(en)_2F_2]^+$ was not acid catalysed over the range of $[H^+]$ studied (0.04–0.57 M). The nature of the products would appear to be due to the great strength of the Cr–F bond rather than the weakness of the Cr–N bond.

The acid hydrolysis of *trans*-$[Cr(en)_2F_2]^+$ has also been studied at 50°C over the $[H^+]$ range 0.15–6.0 M [19]. In 4.0–6.0 M $HClO_4$ solutions at 50°C *trans*-$[Cr(en)_2F_2]^+$ is converted to *trans*-$[Cr(en)_2F(OH_2)]^{2+}$ at rates which depend on $[H^+]$. However, due to side reactions of comparable rates it is impossible to say if the dependence of the rate on $[H^+]$ is strictly first order.

At lower acid concentrations (< 0.5 M), the reaction yields a mixture of products which were time- rather than $[H^+]$-dependent. Thus, at $[H^+] < 0.5$ M where the rate of F^- ion release is less than the rate of disappearance of the reactant, the products were *trans*-$[Cr(en)(OH_2)_2F_2]^+$, *trans*-$[Cr(en)(enH)(OH_2)F_2]^{2+}$, and *trans*-$[Cr(en)(enH)(OH_2)_2F]^{3+}$. The third product is important since it indicates Cr–F bond breaking in the unwrapped species.

At hydrogen ion concentrations > 4.0 M, the rate of fluoride ion release is a function of acid concentration. Thus, the overall rate law for the destruction of *trans*-$[Cr(en)_2F_2]^+$ must contain terms which are both dependent on, and independent of, $[H^+]$.

Hydrolysis of *trans*-$[Cr(en)_2FCl]^+$ in 0.15 M $HClO_4$ at 50°C for 15 min produced five products which could be separated by ion exchange chromatography [19]. These products were: (1) an impurity in the starting material which could be eluted with 0.15 M H_2SO_4 [$\sim 0.3\%$ of the total Cr(III)]; (2) *trans*-$[Cr(en)(OH_2)_3F]^{2+}$ ($\sim 7.0\%$); (3) *trans*-$[Cr(en)(enH)(OH_2)FCl]^{2+}$ ($\sim 7.0\%$); (4) *trans*-$[Cr(en)_2(OH_2)F]^{2+}$ (39%); (5) *trans*-$[Cr(en)(enH)(OH_2)_2F]^{3+}$ (29%), and unreacted starting material.

Linck [51] has investigated the acid hydrolysis of *trans*-$[Cr(en)_2FCl]^+$, *trans*-$[Cr(en)_2FBr]^+$, *trans*-$[Cr(en)_2F(OH_2)]^{2+}$, and *trans*-$[Cr(en)_2NCSBr]^+$ at various acid concentrations and temperatures. In 0.01 M $HClO_4$ at 25°C, *trans*-$[Cr(en)_2FCl]^+$ aquates to yield four of the five products previously reported for the same reaction in 0.15 M $HClO_4$ at 50°C. The product $[Cr(en)(OH_2)_3F]^{2+}$, which arises as a result of the aquation of *trans*-$[Cr(en)(enH)(OH_2)_2F]^{3+}$, was not found in the studies done at 25°C. However, the general acid hydrolysis scheme found at 25°C was identical to that found by previous investigators at 50°C.

A consideration of the products formed from the acid hydrolysis of *trans*-$[Cr(en)_2FCl]^+$ reveals that the reaction must involve two separate paths [51]. One of these paths must involve Cr–Cl bond breaking and the other, ligand unwrapping or Cr–N bond rupture. At 25°C the ratio of the first-order rate constants for Cl^- loss and Cr–N bond breaking is essentially 4:1.

Linck [51] has stated that Cr–N bond breaking is not sensitive to the *trans* directing influence of the 1,6 ligands in complexes of the type *trans*-$[Cr(en)_2YX]^{n+}$. Cr–X bond breaking in these complexes dominates Cr–N bond rupture when Y is a good activating ligand (F^-), but Cr–X bond breaking and Cr–N bond rupture are competitive when Y is a poor activating group (NCS^-). In *trans*-$[Cr(en)_2F_2]^+$ one finds only Cr–N bond breaking; but in *trans*-$[Cr(en)_2FCl]^+$, where F^- is a better *trans* director than Cl^-, Cl^- loss exceeds Cr–N bond breaking by a factor of 4:1. Similarly, in *trans*-$[Cr(en)_2FBr]^+$, where Br^- is a much poorer *trans* director than F^-, the reaction involves only Br^- loss.

In the case of the aquation, for short times, of *trans*-$[Cr(en)_2F(OH_2)]^{2+}$ in 0.1 M $HClO_4$ at various temperatures, the sole product was the partially unwrapped species [51]. The secondary aquation product $[Cr(en)(OH_2)_3F]^{2+}$ formed at long times did not involve Cr–F bond breaking.

Experimentally it has been found, for complexes of the type *trans*-$[Cr(en)_2FX]^+$ that, Cr–N bond breaking dominates F^- loss at $[H^+] < 0.5$ M, but at higher acid concentrations Cr–F bond breaking is more important than ligand unwrapping [19,43].

F. 1,3-PROPANEDIAMINE COMPLEXES

The substitution of 1,3-propanediamine for ethylenediamine in Cr–F complexes produces drastic changes in the behavior of the complexes on acid hydrolysis [19]. For example, *trans*-$[Cr(tn)_2F_2]^+$ or *trans*-$[Cr(tn)_2F(OH_2)]^{2+}$ reacts with aqueous acids to yield as the primary hydrolysis products *trans*-$F(OH_2)^{2+}$ or *trans*-$(OH_2)_2^{3+}$ with no Cr–N bond breaking. The reaction of the *trans*-difluoro complex shows a first-order dependence on $[H^+]$

and is second-order overall while the *trans*-FX ($X = Cl^-$, Br^-) complexes are first-order overall and independent of $[H^+]$.

Secondary reaction products were found after the *trans*-difluoro complex had undergone hydrolysis in 0.15 M $HClO_4$ for 7 days at 50°C [19]. These products were $[Cr(tn)(OH_2)_3F]^{2+}$ and *cis*-$[Cr(tn)_2OH_2F]^{2+}$. A third hydrolysis product, *cis*-$[Cr(tn)_2(OH_2)_2]^{3+}$, was detected when the acid concentration was raised to 2.0 M. Thus, even at long reaction times ligand unwrapping to form a "one-ended" tn ligand did not occur; nor in the cases of the *trans*-FCl or FBr complexes did Cr–N bond breaking complicate the mechanistic studies.

The rates of halide ion loss from the FCl and FBr complexes do not appear to be greatly affected by the size of the chelate rings, unlike the rates of halide ion loss from the Co(III) complexes where large differences have been found. Thus, it would appear that the differences in ring strain in the activation step for the en and tn complexes of Cr(III) are small and cannot account for the differences in reaction rates.

TABLE 2a

Acid hydrolysis of some Cr–F complexes

Reactant	Product	$[H^+]$
cis-$[Cr(en)_2F_2]^+$	*cis*-$[Cr(en)_2(OH_2)F]^{2+}$	0.1 $HClO_4$
	?*cis*-$[Cr(en)_2(OH_2)F]^{2+}$	0.1 HNO_3
	cis-$[Cr(en)_2(OH_2)F]^{2+}$	0.01–0.10 $HClO_4$
	?*cis*-$[Cr(en)_2(OH_2)F]^{2+}$	0.01 HNO_3
	?*cis*-$[Cr(en)_2(OH)F]^+$	6–8 pH
trans-$[Cr(en)_2F_2]^+$	?*trans*-$[Cr(en)(enH)(OH_2)F_2]^{2+}$	0.4–0.2
		0.1
		0.04–0.27
		0.1
		0.04–0.57
		0.1
trans-$[Cr(en)_2F_2]^+$	?*trans*-$[Cr(en)(enH)(OH_2)F_2]^{2+}$	0.15
		0.50
		2.0
*tran*s-$[Cr(en)_2F_2]^+$	*trans*-$[Cr(en)_2(OH_2)F]^{2+}$	0.15
		0.50
		2.00
		4.00
—		6.00

Couldwell and House [52] have suggested that the greater reactivity of the 1,3-propanediamine complexes compared to that of the en complexes of Co(III) may be due to the increased stability of the twist boat conformation of the tn rings with respect to the chair conformation of the en rings.

The reasons that Cr–N bond breaking occurs with *trans*-$[Cr(en)_2FX]^+$ (X = Cl, Br), at rates roughly comparable to X^- loss, and does not occur in the tn system until late in the hydrolysis are not well understood. Such differences could possibly reflect differences in solvation in the transition state with the protonated en complex being more efficiently solvated than the corresponding tn complex. It is to be noted that only *trans* isomers of Cr(III) en complexes undergo ligand unwrapping at appreciable rates and that if Cr–N bond breaking does occur in *cis*-FX complexes, the rates are very low. Thus, ligand unwrapping would appear to involve steric factors rather than differences in Cr–N bond strengths.

The kinetic data for the acid hydrolysis of some Cr–F complexes are summarized in Table 2.

Temperature	$k \cdot 10^5$ sec^{-1}	μ	E_a	Reference
25	0.53	0.1	23	48
25	1.4	0.15 $NaNO_3$	~14	48
41	1.1–3.1	0.01–0.1	23	48
41	2.0	0.063 $NaNO_3$		48
41	(0.9–17)	0.003–0.1		48
25	1.26–1.21	1.0 $NaClO_4$		43
25	1.65	0.12		43
37.5	6.61–6.68	1.0		43
37.5	9.03	0.12		43
43.7	14.37–14.75	1.0		43
43.7	19.61	0.12		43
50.0	20	2.0		19
50.0	17	2.0		19
50.0	4	2.0		19
50.0	7	0.15		19
50.0	9	0.50		19
50.0	32	2.0		19
50.0	89	4.0		19
50.0	224	6.0		19

Table 2a (continued)

Reactant	Product	$[H^+]$
trans-$[Cr(en)_2FCl]^+$	*trans*-$[Cr(en)(enH)(OH_2)FCl]^{2+}$	0.15
trans-$[Cr(en)_2FCl]^+$	*trans*-$[Cr(en)_2OH_2F]^{2+}$	0.15
trans-$[Cr(en)_2FCl]^+$	$[Cr(en)(enH)(OH_2)FCl]^{2+}$	0.01
	$[Cr(en)_2F(OH_2)]^{2+}$	0.01
		0.01
		0.01
		1.0
		1.0
		0.1
trans-$[Cr(en)(enH)(OH_2)F_2]^{2+}$	*trans*-$[Cr(en)(OH_2)_2F_2]^+$	1.50
trans-$[Cr(en)(enH)(OH_2)F_2]^{2+}$	*trans*-$[Cr(en)(enH)(OH_2)_2F]^{3+}$	1.50
trans-$[Cr(en)(enH)(OH_2)FCl]^{2+}$	*trans*-$[Cr(en)(enH)(OH_2)_2F]^{3+}$	0.15
trans-$[Cr(en)(enH)(OH_2)_2F]^{3+}$	blue $[Cr(en)(OH_2)_3F]^{2+}$	2.0
		2.0
trans-$[Cr(en)(OH_2)_2F_2]^+$	blue $[Cr(en)(OH_2)_3F]^{2+}$	0.15
		0.30
		1.54
		0
trans-$[Cr(en)_2NH_3F]^{2+}$	$[Cr(en)(enH)NH_3(OH_2)F]^{3+}$	pH 3.1–3.6
trans-$[Cr(en)_2NH_3F]^{2+}$	*trans*-$[Cr(en)_2(OH_2)F]^{2+}$	pH 3.1–3.6
trans-$[Cr(en)_2FCl]^+$	*trans*-$[Cr(en)(enH)(OH_2)FCl]^{2+}$	
trans-$[Cr(en)_2FCl]^+$	*trans*-$[Cr(en)_2F(OH_2)]^{2+}$	
trans-$[Cr(en)_2FBr]^+$	*trans*-$[Cr(en)_2F(OH_2)]^{2+}$	0.1
		1.0
		0.1
		1.0
		0.1
		1.0
trans-$[Cr(en)_2F(OH_2)]^{2+}$	$[Cr(en)(enH)(OH_2)_2F]^{3+}$	0.1
		0.1
		1.0
trans-$[Cr(en)_2F(OH_2)]^{2+}$	$[Cr(en)(enH)(OH_2)_2F]^{3+}$	0.15
		0.50
		1.00
		2.00
		4.00
		6.00

Temperature	$k \cdot 10^5$ sec^{-1}	μ	Reference
50.0	>10	0.15	19
50.0	<70	0.15	19
18.4	2.3		51
25.0	6.2		53
25.0	6.4		51
25.0	5.8		51
25.0	4.6		51
25.0	4.1		51
36.0	26		51
50.0	4.7	2.25	19
50.0	1.3	2.25	19
50.0	<20	0.15	19
50.0	9.3	2.0	19
50.0	10.3	2.0	19
50.0	12.8	0.7	19
50.0	14.3	0.3	19
50.0	32.0	1.54	19
50.0	222	0	19
20	1.5	0.04 ($KClO_4$)	54
20	0.30	0.04 ($KClO_4$)	54
25	1.2		51
25	4.85		51
17	1.82	0.11	51
17	1.68	1.0	51
25.5	57	0.11	51
25.5	52	1.01	51
37.7	223	0.1	51
37.7	196	1.0	51
25.1	2.56	0.12	51
35.3	10.7	0.15	51
35.3	8.0	1.04	51
50.0	39.0	2.0	19
50.0	39.0	2.0	19
50.0	41.0	2.0	19
50.0	39.0	2.0	19
50.0	23.0	4.0	19
50.0	7.2	6.0	19

TABLE 2b

1,3-propanediamine complexes

Reactant	Product	$[H]^+$	Temperature	$k_{obs} \cdot 10^4$ (sec^{-1})	$k_2 = k_{obs}/[H^+]$	μ	Reference
trans-$[Cr(tn)_2F_2]^+$	*trans*-$[Cr(tn)_2F(OH_2)]^{2+}$	0.51	50.0	1.40	2.7	2.0	19
		1.0	50.0	2.65	2.6	2.0	19
		1.5	50.0	3.78	2.7	2.0	19
		2.0	50.0	5.05	2.5	2.0	19
		1.0	35.0	0.39	0.39	2.0	19
		2.0	35.0	0.80	0.40	2.0	19
		0.51	65.0	9.4	18.4	2.0	19
		1.0	65.0	17.9	17.5	2.0	19

TABLE 2c

Reactant	Product	$[H^+]$	Temperature	$k_{obs} \cdot 10^3$	μ	Reference
trans-$[Cr(tn)_2FCl]^+$	*trans*-$[Cr(tn)_2F(OH_2)]^{2+}$	0	50.0	1.35	2.0	19
		0.50	50.0	1.39	2.0	19
		1.00	50.0	1.28	2.0	19
		1.50	50.0	1.33	2.0	19
		2.00	50.0	1.30	2.0	19
		2.00	40.0	3.96	2.0	19
		2.00	45.0	6.6	2.0	19
		2.00	60.0	27.0	2.0	19
trans-$[Cr(tn)_2FBr]^+$	*trans*-$[Cr(tn)_2F(OH_2)]^{2+}$	0	25.0	1.21	1.0	19
		0.10	25.0	1.20	1.0	19
		0.50	25.0	1.18	1.0	19
		1.00	25.0	1.16	0	19
		0.10	30.0	1.96	1.0	19

G. PHOTOCHEMISTRY

The photochemistry of fluoro-containing complexes of Cr(III) has received considerable attention, since these complexes provide ideal model systems in which to study the various photochemical rules and theories. The "rule" in question is that of Adamson [55] which states: "The axis having the weakest average ligand field will be the one labilized." The theories are the so-called σ-bonding/molecular orbital approach [56] and the theory of Vanquickenborne and Ceulemans [57,58].

One of the earliest studies of the photolysis of Cr–F ethylenediamine complexes was that of Pyke and Linck [56] who investigated the photoaquation of *trans*-$[Cr(en)_2F_2]^+$.

If aquation does take place from the lowest-lying-quartet excited state ($^4T_{2g}(F)$ for a complex with true O_h symmetry), then for the tetragonally distorted complex *trans*-$[Cr(en)_2F_2]^+$ of local site symmetry, D_{4h}, the $^4T_{2g}(F)$ state will be split, and the e_g orbitals which were degenerate in O_h become non-degenerate. Both e_g orbitals are σ-antibonding in nature, but the one lower in energy, which can be either predominantly $d_{x^2-y^2}$ or d_{z^2} in nature, is the orbital of importance. In the ground state a molecular orbital of predominantly $d_{x^2-y^2}$ character is said to be the lower of the two [46], although this has been a matter of considerable dispute.

When 0.015 *M* acidic solutions of *trans*-$[Cr(en)_2F_2]^+$ were photolysed with a monochromatic source centered at 5200 Å (the $^4B_{1g} \rightarrow {}^4E_g$ transition is about 5300 Å), one dominant photoproduct, $[Cr(en)(enH)H_2OF_2]^{2+}$, was obtained. This same product was found in the products of the acid hydrolysis of *trans*-$[Cr(en)_2F_2]^+$. Isolation and characterization of this complex were done in solution, and the stereochemistry has not been confirmed. The dominant photoproduct is consistent with the σ-bonding/molecular orbital model which predicts bond stretching and breaking in the *xy*-plane instead of F^- ion release. In this particular complex the axis with the weakest average ligand field is the F–Cr–F axis, and F^- ion release would be anticipated from Adamson's "rule". No *trans*-$[Cr(en)_2F(OH_2)]^{2+}$ was detected in the reaction products.

Manfrin et al. [59], who have investigated the photolysis of acidic solutions of *trans*-$[Cr(en)_2F_2]^+$ as a function of the wavelength of the photolysis source, have reported different photoproducts. These were: (1) $[Cr(en)(enH)(OH_2)F_2]^{2+}$, the major and anticipated product; and (2) $[Cr(en)_2(OH_2)F]^{2+}$, a product formed in low quantum yield. The major product is claimed to have a different isomeric composition than the product obtained via thermal aquation.The product of the thermal aquation is assumed to involve a *trans* arrangement of the two fluoro ligands although this has not been established beyond a reasonable doubt. Manfrin et al. [59], concluded

that a significant portion of (1) must contain an isomer which involves the two fluoro ligands being *cis* to one another. In 1980 Pyke and Linck [60] reported the results of a reinvestigation of this system. The dominant photoproduct was (1) $[Cr(en)(enH)(OH_2)F_2]^{2+}$ which is the same product obtained from the thermal aquation. Minor photolysis products were (2) an isomer of (1), and (3), *cis*-$[Cr(en)_2F(OH_2)]^{2+}$. The geometry of (2) has not been cstablished, but it appears that (1) would account for about 80% of the product given by $[Cr(en)(enH)(OH_2)F_2]^{2+}$. These results have been interpreted as being consistent with the original suggestion that in the photolysis of *trans*-$[Cr(en)_2F_2]^+$ the net stereochemistry is retained. However, these results in themselves do not imply that the water substitution process is stereoretentive.

Photolysis of an acidic solution of *trans*-$[Cr(en)_2FCl]^+$ at 5200 Å resulted in five fractions which could be separated by ion exchange chromatography [53]. These fractions were: (1) *trans*-$[Cr(en)_2FCl]^+$; (2) $[Cr(en)(enH)(OH_2)FCl]^{2+}$; (3) *trans*-$[Cr(en)_2F(OH_2)]^{2+}$; (4) *cis*-$[Cr(en)_2F(OH_2)]^{2+}$; and (5) $[Cr(en)(enH)(OH_2)_2F]^{3+}$ with *cis*-$[Cr(en)_2F(OH_2)]^{2+}$ being the dominant product.

Products (2), (3), and (4) are of interest, since (2) indicates Cr–N bond breaking in the *xy*-plane and (4) is consistent with Cl^- labilization.

Wirth and Linck [53] have proposed that as one goes from the *trans*-$[Cr(en)_2F_2]^+$ complex where the dominant photoproduct involved ligand unwrapping and hence Cr–N bond breaking in the *xy*-plane to the *trans*-FCl complex, the energy separation between the σ-antibonding levels changes in such a way that the predominantly d_{z^2} orbital moves closer to the $d_{x^2-y^2}$ orbital. Hence, in the FCl complex both levels are populated upon photolysis to the extent that Cr–N and Cr–Cl bond breaking are competitive. Thus, the loss of Cl^- from this complex which is not in accord with the axial labilization rule is allowed.

The presence of (3) presents somewhat of a problem since it is formed in low quantum yield ($\phi = 0.02$–0.045) at 3°C in 0.01 M $HClO_4$ and not at all at 23°C. The original investigators rationalized the presence of the *trans*-$F(OH_2)^{2+}$ complex as being due to the fact that labilization along the F–Cl axis proceeded with a 10% retention of the net stereochemistry.

Wong and Kirk [61] have proposed an alternative explanation to account for the production of the major portion of the *trans*-$[Cr(en)_2F(OH_2)]^{2+}$ formed during the photolysis of *trans*-$[Cr(en)_2FCl]^+$. Their experimental data suggest that because of the ease of Cl^- loss from the FCl^+ complex, coupled with the difficulty of making reliable thermal aquation corrections, a large fraction of the observed *trans*-$[Cr(en)_2F(OH_2)]^{2+}$ product arises not as a result of the photolysis, but as a result of simple thermal aquation of the starting material.

In the case of photolysis of acidic solutions of *trans*-$[Cr(en)_2(NCS)NH_3]^{2+}$ at 4790 Å, the main reaction product involved proton uptake with about 40% of the total released base being NH_3 [54]. These results imply the formation of a species with a partially unwrapped en ligand. This result is consistent with the σ-bonding molecular orbital model but not the "rule".

If the NCS^- ligand in *trans*-$[Cr(en)_2(NCS)NH_3]^{2+}$ is replaced by Cl^- and the above experiment repeated [61], the dominant mode of the photoaquation was complete $Cr-NH_3$ bond breaking to yield *cis*-$[Cr(en)_2OH_2Cl]^{2+}$. This result is in agreement with both the σ-bonding molecular orbital model as well as the predictive rules.

Photolysis of acidic solutions of *trans*-$[Cr(en)_2FNH_3]^{2+}$ at 4360 Å resulted in three fractions which could be separated by ion exchange chromatography [61]. These were: (1) *trans*-$[Cr(en)_2F(OH_2)]^{2+}$; (2) *cis*-$[Cr(en)_2(OH_2)F]^{2+}$; and (3) unreacted starting material *trans*-$[Cr(en)_2FNH_3]^{2+}$; however, because of experimental difficulties no attempt was made to isolate products of charge 3+. The partially unwrapped species $[Cr(en)(enH)NH_3OH_2F]^{3+}$ was not detected although it would be an anticipated reaction product. In this particular case the wavelength of the photolysis, 4360 Å, was selected so that axial labilization could be studied without undue complications resulting from secondary photolytic reactions.

The results of the photolysis show a high quantum yield for proton uptake and essentially no F^- ion loss. The dominant mode of proton uptake is NH_3 loss, and the quantum yield for this process is a function of neither the temperature nor the wavelength used for the irradiation. Although the $Cr-NH_3$ bond breaking was independent of temperature and the wavelength used, the reaction which involves Cr–en bond breaking is temperature-dependent at 5460 Å and is wavelength-independent at higher temperature, shorter wavelengths. Product (2), *cis*-$[Cr(en)_2F(OH_2)]^{2+}$, accounts for greater than 97% of the observed photoproduct arising from NH_3 loss.

The σ-donor molecular orbital theory would predict Cr–N bond breaking with en loss from *trans*-$[Cr(en)_2FNH_3]^{2+}$ which is exactly the opposite to what was found.

It was originally proposed [62] that the ionic nature of the Cr–F bond was responsible for this behavior; however, it now appears that the model of Vanquickenborne and Ceulemans [57,58], "ligand field model", provides an attractive explanation for the behavior of this complex as well as for several other Cr(III)–F complexes upon photoaquation. Essentially this theory places emphasis on the excited-state bond energies rather than the concept of an axis of labilization as the dominant factor in determining what ligands will be lost. Fortunately, the theory also provides a way of calculating the excited-state bond energies in a rather easy way.

The question of the relative *d* orbital energy ordering in complexes of the

type $[Cr(en)_2FX]^{n+}$ has been central to a discussion of Cr(III) photochemistry. In the development of the MO/σ donor theory, the lowest lying antibonding MO was thought, from measurements of the polarized single crystal spectrum of *trans*-$[Cr(en)_2F_2]^+$ [46], to be predominately $d_{x^2-y^2}$ in nature. It was then necessary to allow the energy of the d_{z^2} orbital to lower to account for the loss of Cl^- from *trans*-$[Cr(en)_2FCl]^+$ [53].

If the z axis of the distorted octahedron is taken as the axis which contains the fluoro ligand, then the d orbital ordering is given as

$$d_{xy} < d_{xz}, \quad d_{yz} \ll d_{x^2-y^2} < d_{z^2} \quad [62,63,64].$$

As pointed out by Vanquickenborne and Ceulemans [65] promotion of an electron by photolysis from the ground state to the first excited quartet state does not correspond to $(d_{xz}, d_{yz}) \rightarrow (d_{x^2-y^2})$ transition.

When the symmetry of the complex is lowered from O_h to D_{4h} (*trans*-$[Cr(en)_2F_2]^+$) or $C_{4v}([Cr(NH_3)_5F]^{2+})$, the $^4T_{2g}(F)$ splits to $^4B_2$ and ^4E, but only the energy of the ^4E which corresponds to the $xy \rightarrow x^2 - z^2$ and $yz \rightarrow y^2 - z^2$ transitions in first-order perturbation theory is lowered while the energy of $^4B_2$ does not change.

The end result of this treatment is that, in the case of *trans*-$[Cr(en)_2FNH_3]^{2+}$, the axial ammine should be labilized twice as much as any of the equatorial ligands. In the case of *trans*-$[Cr(en)_2F_2]^+$, Cr–N bond breaking rather than F^- loss is observed because the ground state Cr–F bond energy is considerably larger than the ground state Cr–N bond energy, not because the first excited quartet state corresponds to the $(xz, yz) \rightarrow (x^2 - y^2)$ transition. The photoactive ^4E state which is comprised of the $(x^2 - z^2)$ and $(y^2 - z^2)$ orbitals is 75% z^2, and 25% $x^2 - y^2$ in character. If the $^4E(^4T_{2g})$ interacts with the $^4E(^4T_{1g})$ via second-order interaction, the dz^2 contribution decreases from 75% to about 71% because in this case $E(z^2) > E(x^2 - y^2)$. Such a change will increase in-plane labilization but, as stressed by Vanquickenborne and Ceulemans [65], not to the extent that in-plane labilization will dominate axial labilization.

Calculations [66] for *trans*-$[Cr(en)_2FNH_3]^{2+}$ based on the model of Vanquickenborne and Ceulemans indicate that the splitting of the first cubic term, $^4T_{2g}(F)$, to the ^4E and the $^4B_2$ states results in the ^4E being 1360 cm^{-1} below the $^4B_2$. This ordering of the first two excited states is in agreement with that found for *trans*-$[Cr(en)_2F_2]^+$ from measurements of the polarized spectra [46]. Additional calculations [66] indicate that the ^4E state should have about 73.0% d_{z^2} character. Further calculations of excited-state bond energies indicate that the ^4E state should involve mainly loss of NH_3 while the $^4B_2$ state will favor loss of en.

The above calculations qualitatively predict the results of the photolysis of *trans*-$[Cr(en)_2FNH_3]^{2+}$ at 5400 Å which resulted in a 4:1 loss of NH_3

versus en. Photolysis at shorter wavelengths never resulted in en loss becoming the dominant photoprocess probably due to competitive internal conversions from $^4B_2$.

Although the ligand field model correctly predicts NH_3 loss over that of ethylenediamine, the question of whether the model [58] correctly accounts for the stereochemistry of the observed products has been raised [66].

Photolysis of acidic solutions (pH = 3) of *trans*-$[Cr(en)_2FNCS]^+$ at five wavelengths ranging from 5780 to 3660 Å resulted in three products which could be separated by ion exchange chromatography [67]. These three products were: (1) *trans*-$[Cr(en)_2FNCS]^+$; (2) $[Cr(en)(enH)(H_2O)(F)(NCS)]^{2+}$; and (3) *cis*-$[Cr(en)_2F(OH_2)]^{2+}$. Products (1)–(3) confirm that Cr–F bond breaking did not occur but that Cr–N bond breaking (en or NCS^-) is the dominant mode of photoaquation.

Calculations based on the model of Vanquickenborne and Ceulemans predict the ^4E state to be 2300 cm^{-1} (28 kJ) below the $^4B_2$ excited state. Further, the model predicts the ^4E state to have about 76.4% d_{z^2} character. In terms of excited-state bond energies, the model predicts NCS^- loss, followed by en loss, followed by F^- loss in the ^4E state. Thus, the ^4E favors Cr–NCS bond breaking over F^- loss, and this is in accord with the experimental facts [67].

The σ-donor model, however, incorrectly predicts the major products to involve en loss, and Adamson's rule incorrectly predicts NCS^- loss but not the loss of en.

The origin of the Cr–en bond breaking presents a problem in that at the lowest temperature studied (10°C) and at long wavelengths (> 5460 Å) some Cr–en bond breaking was found. To account for the Cr–en bond breaking under these conditions Kirk and Wong [67] have proposed a model which involves at least two different excited states which are not in thermal equilibrium. If the lower of these two states is populated at 5460 Å and the second populated only by thermal activation, then the Cr–en bond breaking can be explained.

H. X-RAY STRUCTURAL STUDIES

Despite the rather extensive kinetic data, the detailed photolysis studies, and the importance of single crystal polarized spectral data, very few crystallographic studies have been carried out using Cr–F complexes.

In 1974 Babel [68] reported the structure of $BaLiCrF_6$ which involved an octahedral arrangement of the F^- ligands around the Cr(III) center. The Cr–F distance was found to be 1.90(3) Å.

The crystal structure of *trans*-difluoro(1,4,8,11-tetraazaundecane) chromium(III) was reported by Bang and Pederson [69] in 1978. This *meso*

structure involved an R,S conformation of the chelate rings resulting from dissymmetry introduced by the two inner asymmetric nitrogens. This R,S conformation remained intact even in basic solution. The two Cr–F distances in this molecule were not identical, one being 1.85 Å and the other 1.90 Å. The Cr–N distances varied from 2.06 to 2.08 Å. The F–Cr–F angle was 178.0(7)°. The oxygen atoms of the perchlorate were disordered and the position of the chloride atoms appears to rule out the possibility of hydrogen bonding from oxygen to nitrogen.

Recently the crystal structure of *trans*-$[Cr(tn)_2FNH_3](ClO_4)_2$ has been determined [33] and found to involve a chair-twist boat conformation of the two chelate rings. All Cr–N distances range from 2.086(5) Å to 2.080(6) Å, and the Cr–F distance of 1.872(3) Å is close to the value reported for CrF_6^{3-}. The chair-twist boat conformation for the two chelate rings is thought to arise via a non-bonded repulsive interaction between the fluoro ligand and the axial hydrogen atoms on the nitrogens of one of the rings.

The H_3N–Cr–F angle was 179.0(2)° which is essentially the angle found for F–Cr–F in the tetraazaundecane complex.

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