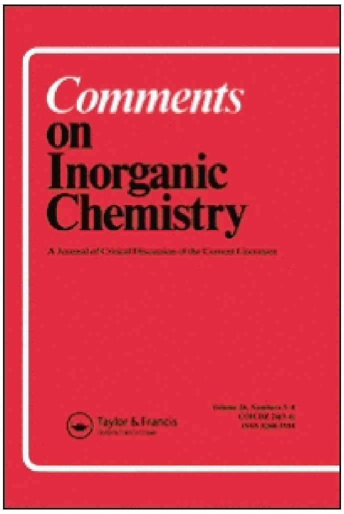

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Stereochemistry and Steric Effects in the Photosubstitutions of Chromium(III) Complexes, and Their Utility as Probes of Mechanism

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Stereochemistry and Steric Effects in the Photosubstitutions of Chromium(III) Complexes, and Their Utility as Probes of Mechanism

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A feature of chromium(III) photoaquation reactions which is unparalleled in the photochemistry of any other transition metal ions is the high degree of stereochemical change that occurs concomitant with most of these photosubstitutions. This stands in stark contrast to the nature of the ground state thermal substitutions, which, in aqueous solution, are amongst the most stereoretentive of transition metal kinetic processes. Some of the evidence behind these claims is discussed, some theoretical rationalizations presented, some problems of experimental verification and interpretation outlined and some ideas for further study are offered. The significance of these results for the mechanistic pathways of Cr(III) photochemistry is discussed, related to other photophysical results and a working hypothesis to guide future work is offered.

Key Words: *stereochemical change, photosubstitution, photoaquation, photoanation, associative, dissociative, excited state, intersystem crossing, chromium, complex*

INTRODUCTION AND OBJECTIVES

The photosensitivity to light of Cr(III) complexes was noted at least seventy years ago,[1] systematic studies began about thirty years

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later,[2] and the topic has developed into one of the more extensively studied areas of transition metal photochemistry. Several aspects of the subject have been reviewed.[3] Beyond the intrinsic interest of the behaviour exhibited by such compounds, the important reasons for this are the large variety of relatively thermally stable complexes that can be prepared, their interesting and fairly well-understood absorption and emission spectroscopy,[4] the comparative efficiency of their photochemical reactions and the fact that many of these molecules emit under room temperature solution conditions. The latter feature permits simultaneous study of the photochemistry and the quenching and emission lifetime behaviour of at least one of the excited states involved. Also of great importance was the early suggestion,[5] controversial,[6] that the photochemistry of mixed-ligand Cr(III) complexes obeyed a rule of loss of the strong field ligand on the axis of weakest overall ligand field. This proposal stimulated a great deal of the work that followed.

Despite considerable research effort, however, there is still uncertainty about many of the details of excited state participation in these important, archetypal processes. This reflects the subtlety and complexity of the problems involved, which means that many of the experimental results can be interpreted in more than one way. The purpose of this Comment is to try to bring into focus the importance of the information we have on the stereochemistry of Cr(III) photoaquation reactions, to set out the role it has played in establishing the mechanism of Cr(III) photoreactions and to emphasize that it is a useful and crucial component of the total body of evidence that must be considered in understanding the photoreaction mechanisms of these complexes. As a historical antecedent, consider the value of stereochemical studies in establishing the mechanistic details of nucleophilic substitution of organic compounds, a process with which much Cr(III) photochemistry shows a parallel.

Note that the study of the stereochemical aspects of Cr(III) photochemistry has been pursued by relatively few research groups. The author hopes to show that much challenging work remains to be done and that there remain opportunities for new workers in the area as well as for the application of new techniques and theories. The ultimate goal is, of course, to understand the subject at a level that allows us to predict quantitatively the photochemistry of any desired complex. This can not yet be done, but we could now claim to be able to anticipate, semiquantitatively, results for most types of complex in aqueous solutions.

In the following account we will avoid taking a historical approach and will occasionally neglect some of the detail and complications which arise in real experimental systems where they tend to obscure the general and important conclusions. The first objective will be to establish a working overview of the subject.

EMPIRICAL OBSERVATIONS OF CHROMIUM(III) PHOTOSTEREOCHEMISTRY

Octahedral complexes of Cr(III) have a quartet ground state arising from the t_{2g}^3 electronic configuration and many undergo efficient photosubstitution reactions on ligand field irradiation. In general these processes occur with wavelength independent quantum yields that show only very small temperature dependencies.[3d] Quenching experiments have shown[3d,7] that the reactions occur via two pathways. The first of these we will refer to as the quartet pathway. This is unquenchable and occurs on a ps or sub-ps timescale[8]; it therefore competes with population of the metastable doublet excited state. Furthermore, it appears to be competitive with vibrational relaxation.[9] The second, doublet pathway, is quenchable in parallel with the phosphorescence from the doublet state, and the photoproduct(s) deriving from this route appears with the doublet lifetime, which is often in the microsecond time domain in room temperature aqueous solution.

For non-octahedral hexacoordinate complexes, which are usually C_{4v} or D_{4h} in symmetry,[10] the question of the nature of the ligand(s) labilized comes to the fore. Examples can be found where the same or different ligands are substituted in the thermal and in the photochemical processes, and the latter observations have now been systematized and rationalized theoretically to a large extent. Tables I and II contain a summary of some observations of the dominant photoreaction modes for representative complexes. In addition to the major and minor reaction modes listed in the tables, there often occur details of wavelength and temperature depend-

TABLE I

Photosubstitution yields in *trans*- and *cis*-$CrXYL_4^{n+}$ ions[a]

Complex	Predominant Product(s)	ϕ[a]	Remarks	Ref.
trans				
$CrCl_2(NH_3)_4^+$	*cis*-$CrCl(H_2O)(NH_3)_4^{2+}$	0.44	$\phi_{NH_3} = 3 \times 10^{-3}$	51
$CrCl(H_2O)(NH_3)_4^{2+}$	*cis*-$CrCl(H_2O)(NH_3)_4^{2+}$	0.40	$\phi_{Cl^-} < 4 \times 10^{-3}$ $\phi_{NH_3} = 0.02$	51
$Cr(NCS)(H_2O)(NH_3)_4^{2+}$	*cis*-$Cr(NCS)(H_2O)(NH_3)_4^{2+}$	0.42	$\phi_{NCS^-} = 0.02$ $\phi_{NH_3} = 5 \times 10^{-3}$	51
$Cr(NCS)Cl(NH_3)_4^+$	*cis*-$CrCl(H_2O)(NH_3)_4)^{2+}$	0.27	$\phi_{NH_3} = 3 \times 10^{-3}$	51
	cis-$Cr(NCS)(H_2O)(NH_3)_4^{2+}$	0.14		
$Cr(H_2O)_2(NH_3)_4^{3+}$	*cis*-$Cr(H_2O)_2(NH_3)_4^{3+}$	0.35	$\phi_{NH_3} < 0.02$	51
$CrF_2(NH_3)_4^+$	1,2-F-6-H_2O-$CrF_2(H_2O)(NH_3)_3^+$	0.24	$\phi_{F^-} = 0.008$	37
	1,6-F-2-H_2O-$CrF_2(H_2O)(NH_3)_3^+$	0.10		
$Cr(CN)_2(NH_3)_4^+$	1,2-CN-6-H_2O-$Cr(CN)_2(H_2O)(NH_3)_3^+$	0.08	$\phi_{CN^-} < 0.005$	40
	1,6-CN-6-H_2O-$Cr(CN)_2(H_2O)(NH_3)_3^+$	0.16		
$CrBr_2(en)_2^+$	*cis*-$CrBr(H_2O)(en)_2^{2+}$	0.36	≥95% *cis*	52
$CrCl_2(en)_2^+$	*cis*-$CrCl(H_2O)(en)_2^{2+}$	0.32	≥99% *cis*	52
$Cr(NCS)Cl(en)_2^+$	*cis*-$CrCl(H_2O)(en)_2^{2+}$	0.18	$\phi_{H^+} = 6 \times 10^{-3}$	53
	cis-$Cr(NCS)(H_2O)(en)_2^{2+}$	0.04	Temp. dep. ratio	
$Cr(NCS)_2(en)_2^+$	*cis*-$Cr(NCS)(H_2O)(en)_2^{2+}$	0.23, 0.18		54, 55
	$Cr(NCS)_2(H_2O)en(enH)^{2+}$	0.13, 0.07		54, 55
$Cr(NCS)F(en)_2$	*cis*-$CrF(H_2O)(en)_2^{2+}$	0.27	$\phi_{H^+} = 0.07$	56
$CrFCl(en)_2^+$	*cis*-$CrF(H_2O)(en)_2^{2+}$	0.31		57
$CrF_2(en)_2^+$	$CrF_2(H_2O)en(enH)$	0.35	$\phi_{F^-} \leq 0.08$	58
$Cr(CN)_2(en)_2^+$	$Cr(CN)_2(H_2O)en(enH)^{2+}$	0.58	$\phi_{CN^-} \leq 0.02$ Isomers unknown	59

$CrCl_2(H_2O)_2en^+$	1-Cl-$CrCl(H_2O)_3en^{2+}$ 2-Cl-$CrCl(H_2O)_3en^{2+}$	0.12 0.10		60
$CrCl_2(cyclam)^{+}$ [b]	*trans*-$CrCl(H_2O)(cyclam)^{2+}$	3.3×10^{-4}	$\phi_{H^+} < 6 \times 10^{-4}$	32
$CrCl_2(2,3,2\text{-tet})^{+}$ [c]	*cis*-$CrCl(H_2O)(2,3,2\text{-tet})^{2+}$	0.06	$\phi_{H^+} < 7 \times 10^{-3}$	32
$Cr(NH_3)_2(cyclam)^{3+}$		$<10^{-4}$	Photoinert	20, 33
cis				
$CrCl_2(NH_3)_4^+$	$CrCl_2(H_2O)(NH_3)_3^+$	0.32	$\phi_{Cl^-} = 0.15 \pm 0.05$ *cis* product	57
$CrF_2(NH_3)_4^+$	$CrF_2(H_2O)(NH_3)_3^+$	0.46	$\phi_{F^-} \leq 0.06$ 1,2-F_2-6-H_2O = 2:1 1,6-F_2-2-H_2O some 1,2-F_2-3-H_2O	37
$CrCl_2(en)_2^+$	$CrCl_2(H_2O)en(enH)^{2+}$	0.13	$\phi_{Cl^-} = 0.02$	21
α-$CrCl_2(trien)^+$	*cis*-$CrCl(H_2O)(trien)^{2+}$	0.10		61
$Cr(CN)_2(en)_2^+$	$Cr(CN)_2(H_2O)en(enH)^{2+}$	0.51	$\phi_{CN^-} = 0.09$	59
$CrF_2(tren)^+$	α-$CrF(H_2O)(tren)^{2+}$	0.21		62
$Cr(NH_3)_2(cyclam)^{3+}$	*cis*-$Cr(H_2O)(NH_3)(cyclam)^{3+}$	0.15		46

[a] Quantum yield for dominant reaction modes at room temperature on irradiation into lowest quartet L.F. Band.

[b] cyclam = 1,4,8,11-tetraazacyclotetradecane.

[c] 2,3,2-tet = 1,4,8,11-tetraazaundecane.

TABLE II

Photosubstitution yields for $CrX(NH_3)_5^{2+}$ and *trans*-$CrX(NH_3)(en)_2^{2+}$ ions

Complex	Band Irradiated,[a] Quantum Yield				Config. of Product of NH_3 Loss	Ref.
	L_2, ϕ_{NH_3}	L_2, ϕ_X	L_1, ϕ_{NH_3}	L_1, ϕ_X		
$CrCl(NH_3)_5^{2+}$	0.38	0.007	0.36	0.005	*cis*	62
$CrBr(NH_3)_5^{2+}$	0.37	0.011	0.35	0.009	*cis*	63
$CrNCS(NH_3)_5^{2+}$	0.46	0.030	0.48	0.021	*cis*	64, 65
$CrF(NH_3)_5^{2+}$	0.43		0.43	0.0042	85% *cis*	29, 66
$CrCN(NH)_3)_5^{2+}$	0.33	<0.0005	0.33	>0.0005	2/3 *cis*	39
	L_2, ϕ_{NH_3}	L_2, ϕ_{en}	L_1, ϕ_{NH_3}	L_1, ϕ_{en}		
t-$CrCl(NH_3)(en)_2^{2+}$	0.30	0.10	0.34	>0.001	*cis*	27
t-$CrNCS(NH_3)(en)_2^{2+}$			0.2	0.3	*cis*	67
t-$CrF(NH_3)(en)_2^{2+}$	0.28	0.16	0.27	0.14	*cis*	29

[a] L_1 and L_2 represent the lowest and next highest ligand field quartet bands.

ence of reaction mode ratios which are important and informative. A few such details are included in Table II but they complicate matters considerably and are deferred for later consideration. An important feature of the photochemistry of Cr(III) revealed by studies of these complexes is the essentially complete stereochemical change which accompanies photosubstitution in a large number of complexes. Throughout this article the term stereochemical change is used in a mechanistic sense. That is, it corresponds to a mechanism in which the substituting group enters the coordination sphere trans to the leaving group. Depending on the circumstances this may or may not result in a change of molecular stereochemistry, but this is considered irrelevant.

The quenching behaviour of mixed ligand complexes is quite variable. Some systems photosubstitute in a manner which is 100% quenchable; others show partial quenchability of reaction modes and in one instance, *trans*-$Cr(NCS)F(en)_2^+$, differential quenching of modes, varying with wavelength and temperature, has been reported.[11] With this overview, it is time to consider a simple model that accounts for many of these observations.

HOW TO UNDERSTAND AND PREDICT Cr(III) PHOTOCHEMISTRY

As is well known, an octahedral complex has three equivalent planes in which electronic excitation energy can reside when it is excited to its lowest quartet ligand field excited state. That is, the triply degenerate, lowest energy $^4T_{2g} \leftarrow {}^4A_{2g}$ transition of Cr(III), which corresponds to a change in strong field electronic configuration from t_{2g}^3 to $t_{2g}^2e_g^1$, is equivalent to a 45° rotation of charge density in one of three orthogonal planes,[12] namely $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{xz} \rightarrow d_{x^2-z^2}, d_{yz} \rightarrow d_{y^2-z^2}$. The latter two upper state orbitals are linear combinations of d_{z^2} and $d_{x^2-y^2}$. Theoretically, this population of a sigma antibonding orbital in the excited state will labilize equally the four ligands in the excitation plane, leading to Cr–L bond elongation, exactly as found experimentally[13] for $Cr(NH_3)_6^{3+}$. At the same time there is, in the same plane, a vacant t_{2g} orbital which can interact with a substituting nucleophile. Both effects will operate to favour substitution chemistry from this excited state, and simple calculations[14] suggest huge rate constant enhancements compared with the ground state chemistry.

For a non-octahedral six-coordinate complex, the situation is altered by the fact that one or two of the possible planes of excitation will lie lowest in energy and be preferentially populated by excitation and/or non-radiative decay processes such as internal conversion. If one considers that Kasha's rule applies, then photochemistry is expected to originate only from the lowest energy quartet excited state. This always corresponds to the plane(s) containing the ligand(s) of smallest ligand field strength.

These features underly the mechanism of Cr(III) photosubstitution via the lowest quartet excited state, and have been elaborated by Vanquickenborne and Ceulemans[15] (VC) into an angular overlap model that predicts the identity of the ligand preferentially lost in mixed-ligand complexes and arrives at a symmetry rule based rationale for the photostereochemical behaviour of these systems.

Their analysis shows that the ligand lost preferentially is that trans to the weakest field ligand, and although the data reviewed by them fitted this well, exceptions have since been found,[16] mainly to do with steric effects on leaving ability of the various ligands. This topic is somewhat off the present purpose, however. The symmetry rules show that the substituting ligand enters the coordination sphere trans to the leaving ligand. This trans entry of the substituting ligand, which was first proposed based on experimental studies, is nicely rationalized in the VC model. The model also makes clear, as did earlier work of Zink,[17] that the remaining t_{2g}^2 cone of electron density confines the ligand motions leading to substitution to the plane of excitation of the complex, an important feature of the substitution pathway which is discussed in detail later.

The course of this process for the archetypal example $CrCl(NH_3)_5^{2+}$, including a simple pictorial representation of the reasons behind the symmetry rule, is shown in Fig. 1. It is based on VC's proposal of a reaction via a trigonal bipyramidal intermediate. The first step shows the outcome of rotation of charge on to the metal ligand bond axes in one arbitrarily selected plane of the lowest ^4E_g state, which leads to a quartet excited state of the complex, species 1. Because of the presence of the weak field

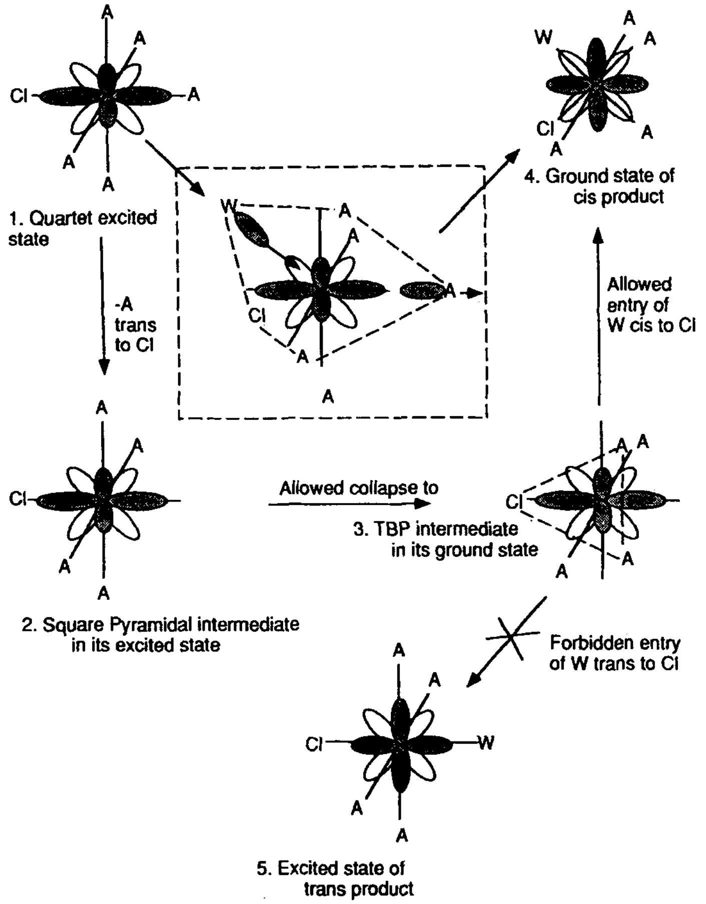


FIGURE 1 Pictorial representation of Vanquickenborne–Ceulemans theory of Cr(III) ligand labilization and photostereochemistry. Legend: W = H_2O; A = NH_3. The ammonia ligand trans to Cl is preferentially labilized and leads in an allowed fashion to the ground state of *cis*-$CrCl(H_2O)(NH_3)_4^{2+}$ product. In contrast, solvation to the trans iomer is forbidden as it leads to the excited state of this product. The boxed inset shows an equivalent route involving a Lewis base attacking at the vacant t_{2g} orbital with substitution proceeding via an asymmetric pentagonal bipyramidal intermediate.

chloride ligand, the sigma antibonding orbital populated has increased d_{z^2} character, and the ammonia trans to chloride is preferentially dissociated[18] leading to a square pyramidal (SP) intermediate, species 2. This can rearrange in an allowed process to a lower energy trigonal bipyramidal intermediate (TBP), species 3, having chloride in the equatorial position and, for this system, in its ground electronic state. Subsequent solvent attack on this TBP intermediate at the two edges cis to chloride may then follow by an allowed process leading to the ground state of *cis*-$CrCl(H_2O)(NH_3)_4^{2+}$, species 4. In contrast, entry of solvent trans to chloride would lead to the electronically excited state of the trans product, species 5, and is therefore forbidden.

This simple picture explains a great deal of Cr(III) photochemistry and photostereochemistry, is exceedingly useful and, at the same time, easy to apply and to understand. The reader who takes the time to apply it to the systems of Tables I and II will find only a few divergent examples. Explanations for some of these will be discussed later, while others, such as cis-α-$Cr(trien)Cl_2^+$ are left as exercises!

In the author's opinion, however, the VC model can not be correct in detail. Activation volumes for loss of neutral ligands from such cationic complexes are consistently negative where known, and because they are not complicated by electrostriction effects this compellingly indicates reaction via associative transition states.[19] Moreover, in one instance, evidence[20] for a seven-coordinate intermediate of microsecond lifetime has been obtained.

VC report that, though they tried, it was not possible to obtain similar theoretical predictions within a framework involving seven-coordinate species. Analysis of such a pathway is inhibited by our ignorance of the true transition state geometry as well as the greater difficulty of the calculations. Nevertheless, in the author's view, it remains legitimate to construct a diagram similar to Fig. 1, but in which the whole substitution process occurs via an *asymmetric* pentagonal bipyramidal species in which there are long bonds to the entering and leaving ligands; such an intermediate has been shown in the boxed inset of Fig. 1. In this seven-coordinate scheme, it is not so definite why the favoured ligand labilized is that trans to the chloride ligand, and why the substituting ligand should enter trans to the leaving ligand. Nevertheless, pictorially and intuitively, it seems reasonable that the same electronic driving forces will operate to control the outcome of a substitution process independent of the exact sequence of bond breaking and bond formation. We have tried to show how nucleophile attack on the vacant t_{2g} orbital is facile, while interaction of the ammonia lone pair with the occupied e_g^* orbital would favour loss of the ammonia trans to Cl. In summary this model fits the data better and works pictorially, permitting a lot of useful data interpretation, even though it currently lacks a firm theoretical basis.

STEREOCHEMISTRY AND LIGAND SUBSTITUTION MODE

An interesting feature of Cr(III) photochemistry is that geometric configuration of a diacidotetrammine complex often determines the nature of the ligand labilized along the lines implicit in the above model. The first demonstration of this showed[21] that the *trans*-$CrCl_2(en)_2^+$ mainly loses chloride while the cis isomer loses ethylenediamine. Many other examples to support this kind of behaviour have since been found, a fair proportion of these being the work of Zinato and Riccieri, and these are included in Tables I and II.

Of particular interest because of their semblance of different behaviour are the acidoaquo systems, which are unusual in exhibiting trans to cis photoisomerization. This could arise by an intramolecular rearrangement process, but the phenomenon is not observed in, for example, analogous *trans*-diacidotetrammine species. This is a clue that what is occurring is water ligand photoexchange with trans entry of the substituting water molecule. This is supported by direct measurements of water exchange in the analogous aquoammine compounds[22] and by analogy with the ligand photodissociation behaviour in aqueous media of the analogous trans dmf-acido complexes, which lose dmf to form acidoaquo products,[23] accompanied by complete stereochemical change.

STEREOCHEMICAL CHANGE IN Cr(III) PHOTOSUBSTITUTION

Trans-diacidotetram(m)ine complexes were the systems that first revealed the stereochemical change accompanying the photosubstitution.[24] For many systems the accrued evidence is that the degree of this process is very high, approaching 100% in several systems investigated and summarized in Table I. It was the completeness of the stereochemical change associated with these photoaquations that prompted the suggestion[25] that the substitution process was concerted, analogous to the Walden inversion, and possibly general for d^3 photosubstitution.

Surprisingly, the process can even occur in a crystalline system. A study[26] of *trans*-$[CrBr_2(en)_2]Br.H_2O$ showed photoaquation in the solid state with a room temperature quantum yield about equal to that in solution. The compound underwent the same reaction to a smaller extent even at 77 K. The product was found to be *cis*-$CrBr(H_2O)(en)_2^{2+}$. In contrast the anhydrous salt was photoinert.

Analogous solution results have been obtained for compounds that are models for the acidopentammines. The early results on acidopentammines were confusing because of the lack of information regarding the initial location of the ammonia ligand aquated in the main reaction mode. This ambiguity was partially avoided in studies of compounds of the type *trans*-$CrX(NH_3)(en)_2^{2+}$, where X = NCS, Cl and F. The chloro compound[27] lost mainly ammonia and the product was the cis chloroaquo isomer (100 ± 3%), entirely in accord with the model explained above. Moving beyond the photostereochemical aspects, however, studies of the wavelength and temperature dependence of the ammonia and ethylenediamine loss modes, showed that the proportion of en loss[28] increased on irradiation into the higher energy ligand field band and there was a greater temperature dependence of the yields when irradiating at lower energy.

With that complex, quenching studies were not possible, but a study[11] of the analogous *trans*-$Cr(NCS)F(en)_2^+$ showed similar wavelength dependence of quantum yields and further that the en mode and the thiocyanate mode (analogous to the NH_3 mode in the first complex) were quenched to different extents. Specifically the quantum yield of en and the fraction of the en mode that was unquenchable both increased at higher irradiation energy. Our interpretation of this data and of similar wavelength dependencies (e.g., Ref. 27) is that, over and above the known doublet involvement in the photochemical pathways, there is more than one quartet state photoactive in these non-O_h systems and that these states are not in equilibrium. This represents a departure from the Kasha rule that only the lowest excited state of a given multiplicity reacts, and we will return to this aspect in the later discussion of the photophysical implications and needed theory.

In addition to these complexities, there are also examples of complexes which do not show complete stereochemical change on photoaquation, mainly involving fluoride and cyanide as ligands. Examples are their acidopentammines, where 15 and 30% trans-acidoaquotetrammine product is found, respectively. Interpretation of the significance of these results is obscured by the lack of information as to the proportion of ammonia loss that occurs cis and trans to the acido ligand. For this reason, we compared[29] *trans*-$\mathrm{CrF(NH_3)(en)_2^{2+}}$ photochemistry to that of the fluoropentammine. The former molecule loses mainly ammonia to give cis-aquofluoro product with a smaller contribution of en loss which has an unknown stereochemistry, as shown in the upper part of Fig. 2. The comparison with experiment for $\mathrm{CrF(NH_3)_5^{2+}}$ required us to correct for the fact that ethylenediamine is a better leaving ligand than ammonia, which was done based on leaving group abilities estimated from the photochemistry[30] of the complexes $\mathrm{Cr(en)_{(3-x)}(NH_3)_{2x}^{3+}}$, which gave $k_{\mathrm{en}}/k_{\mathrm{NH_3}} = 2.8$. After applying this correction, the comparison,[31] summarized in the lower part of Fig. 2, then indicated that the 15%/85% trans/cis product ratio found for the pentammine arose as follows; ammonia trans to fluoride was lost 81% of the time, giving rise, in the model, to cis-aquofluoro product. Meanwhile the 19% loss of ammonia cis to fluoride must have yielded a 4:1 ratio of trans and cis aquofluoro product to account for the overall product stoichiometry. As will be discussed in detail later, both equatorial and axial ammonia loss can occur from the lowest ^{4}E excited state, which corresponds to excitation in either of the two orthogonal planes containing fluoride. It can be seen that the component of the equatorial ammonia loss that leads to trans product (80%) has to involve ste-

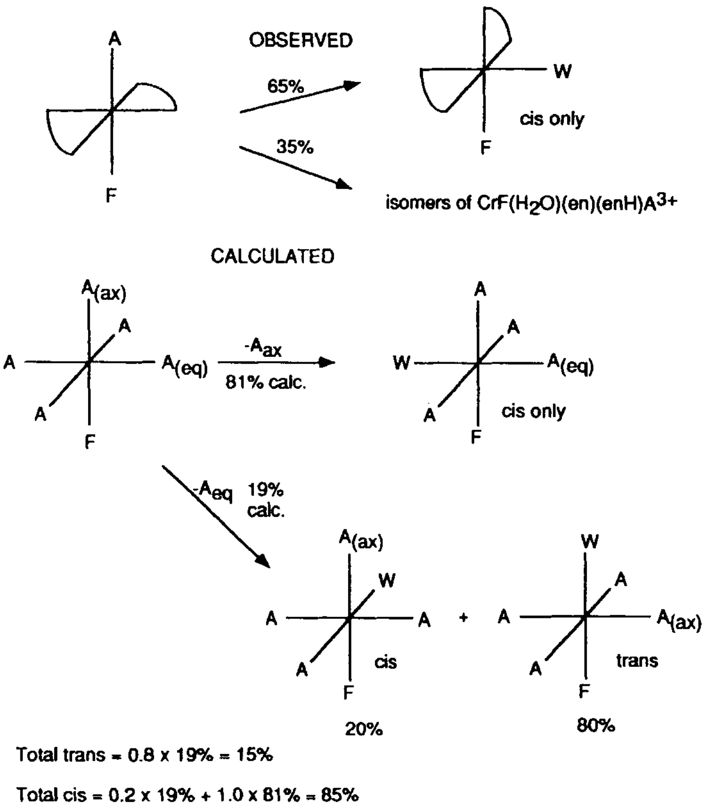


FIGURE 2 Comparison of $CrF(NH_2)(en)_2^{2+}$ and $CrF(NH_3)_5^{2+}$ photochemistry.

reochemical change but for that leading to cis isomer, no conclusion can be drawn. It could be produced both by retentive substitution and by edge displacement. Nevertheless it is clear that both ammonia loss modes occur with stereochemical change even if the equatorial one *may* be less than completely so. A similar study of *trans*-$Cr(CN)(NH_3)(en)_2^{2+}$ should be equally informative but has not yet been undertaken.

The existence of this stereochemical change suggests the question, what happens to the photochemistry if the ligand imposes steric constraints that prevent it?

PHOTOINERTNESS AND STEREOCHEMICAL CONSTRAINTS

Data relevant to this question was first obtained by Kutal and Adamson[32] who found that incorporation of the cyclam ligand in the equatorial plane of *trans*-$Cr(Cl)_2(cyclam)^+$ inhibits photochemical reaction. The quantum yield of chloride aquation was reduced to less than 0.001 *and the photoproduct produced was in the trans configuration.* The effect of the macrocyclic ligand on the stereoretentive ground state thermal reactions was much smaller. Also, in contrast, the analogous 2,3,2-tet complex, in which there is no complete ring in the equatorial plane of the complex, shows normal photochemical activity accompanied by stereochemical change although with a reduced yield compared with unconstrained analogues. Table I also includes additional examples that have since been reported. Most interesting are the cyclambisammines. The trans compound is completely photoinert, while the cis isomer photoaquates ammonia[33] with a quantum yield of 0.15, the reaction occurring via an intermediate of microsecond lifetime that has been suggested to be seven coordinate. These complexes both show a positive volume of activation of about 7 $cm^3\ mol^{-1}$ at room temperature for the major photoprocess depopulating the doublet state. This, together with spectroscopic[34] and activation energy data,[35] supports a model whereby the quenchable reaction occurs via thermally activated reverse intersystem crossing and reaction originating from the excited quartet state.

Most important of all in the present context is that these results support the claim that stereochemical change is not just a normal accompaniment of Cr(III) photoaquation, but is a *requirement* of the reaction via the excited state.

Comparison of the *trans*-$Cr(Cl)_2(cyclam)^+$ behaviour with data for ligand field band photochemistry of cobalt(III) complexes[3a] invites further speculation. These d^6 complexes have analogously low quantum yields; the stereochemistry is complex but, more often than not, retentive. The comparison suggests that blocking of the usual pathway of photoreaction by the ligand constraint in *trans*-$Cr(Cl)_2(cyclam)^+$ has revealed a residual, inefficient retentive pathway parallel to that for Co(III) complexes, and which is normally hidden under the efficient pathway. This retentive reaction mode could well be the signature of the excited state occupation of a sigma antibonding orbital, having similar characteristics in both metal ions. In contrast, a vacant t_{2g} orbital, present in the Cr(III) excited quartet states, provides a route for an efficient associative substitution with a high degree of stereochemical change.

STEREOCHEMICAL CHANGE ASSOCIATED WITH LIGAND LOSS FROM THE EQUATORIAL PLANE

The previous discussion shows that stereochemical change accompanying labilization of an axial ligand from a D_{4h} or C_{4v} complex is a well-established phenomenon. The outcome of labilization of a ligand in the equatorial plane is less clear-cut, because the four in-plane ligands are the same and therefore the position of the leaving ligand is unknown. Observation of a particular product stereochemistry then does not necessarily allow any conclusion about whether stereochemical change occurred or not.

Even worse, the often-used term "equatorial labilization" is ambiguous. Does it refer to the location of the ligand being lost or does it identify the plane in which labilization is considered to be occurring? We will take the first meaning. Then in theory there are really two circumstances which can lead to loss of an equatorial ligand and this has not always been recognized in discussions of the phenomenon.

To illustrate the two cases, we assume the applicability of the VC model. The first situation is where excitation is into one of the two degenerate planes containing the *z* axis, shown in Fig. 3. This can lead, usually as a minor mode, to loss of an equatorial ligand. If accompanied by stereochemical change this is revealed by generation of a product with different stereochemistry than that found for the analogous stereoretentive (thermal) reaction. This type of process has been implicated in the *trans*-difluoro and dicyano systems, for example. In the second process, by contrast, the equatorial plane is labilized. Loss of one of the equatorial ligands, indicated by an asterisk in Fig. 3, followed by trans entry of a water molecule, then leads to the same product as stereoretentive substitution. The stereochemistry of the product is therefore silent

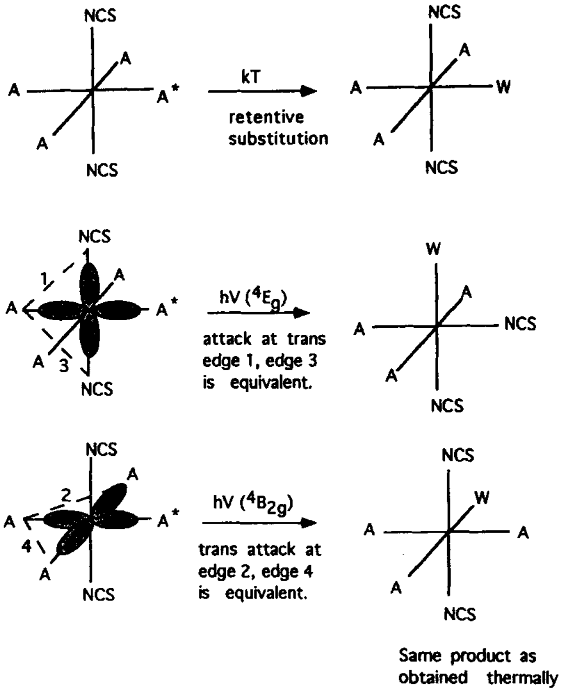


FIGURE 3 The stereochemical ambiguity of equatorial ligand loss for $Cr(NCS)_2(NH_3)_4^+$.

on the question of whether stereochemical change is associated with this process.

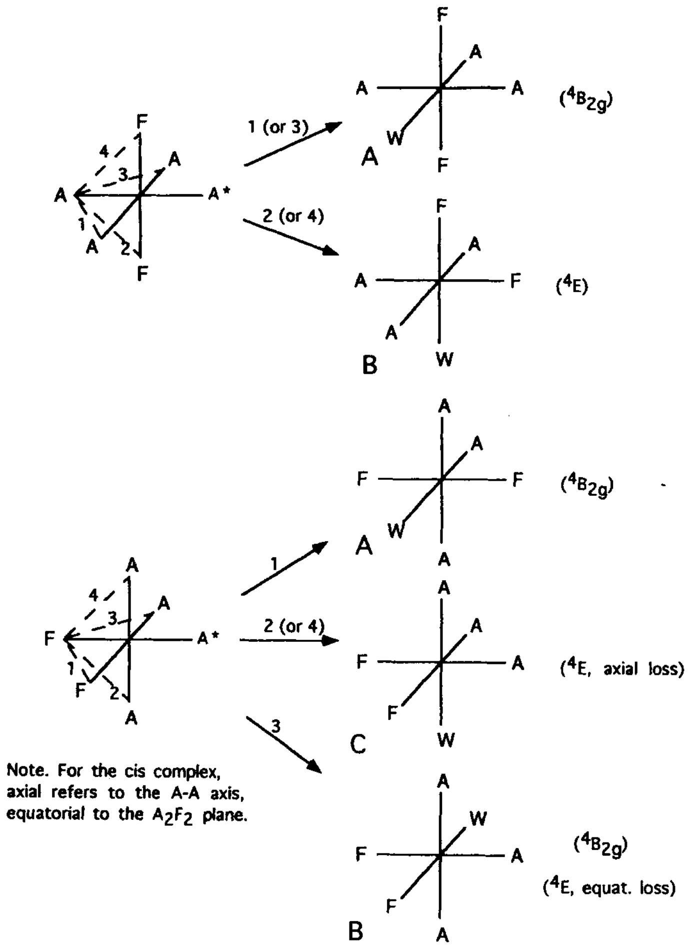
To attempt to clarify whether this second mode of equatorial ligand loss is accompanied by complete stereochemical change or not, we have synthesized[36] the compound *trans*-$Cr(CN)_2$(2,3,2-tet)$^+$. Our optimistic expectation had been that it might be photoinert, a result which would have unambiguously implied that stereochemical change was also a *requirement* of ligand loss from the ^4B state. We find, however, a yield of about 0.09 for proton uptake which we have shown corresponds to loss of and protonation of a terminal amine (en) ligand rather than cyanide loss. We are attempting currently to identify the photoproducts and their stereochemistry in order to understand from which electronic state(s) this photochemistry probably arises. If it is from the lowest lying

$^4B_{2g}$ state, the implication would be that the photoreaction is occurring in the equatorial plane and is stereoretentive; if from the ^4E_g state, it is expected to occur with stereochemical change and lead to the monodentate protonated amine aquo product with cis cyano ligands.

THEORETICAL APPROACHES

Stereochemical change has been explained in the model of VC as resulting from allowed and forbidden collapse of SP to TBP intermediates and a further symmetry restriction on attack by entering nucleophile on the TBP species. This stands in contrast to the earliest suggestion that the stereochemical change arises merely because the substituting ligand enters the coordination sphere trans to the leaving ligand in a photochemical edge-displacement process. In an effort to compare these two ideas, a study[37] of the photochemistry of *trans*- and *cis*-$CrF_2(NH_3)_4^+$ ions was undertaken, with the stereochemical predictions shown in Fig. 4. The products shown are those that arise from unrestricted edge-displacement at the indicated edges; the state and position designations in parentheses indicate how they would arise in the VC model. The results for the trans compound are consistent with either model, but for the cis they support the predictions of the VC model. In particular, reaction of the lowest quartet state of the cis isomer should not lead to any fac-WFF product whereas the unrestricted edge-displacement model suggests that this would be the major product. Experiment showed that only small amounts of this product were formed. While this does not require all the detail of the VC predictions to be true, the results do prove that the edge-displacement process is constrained to occur in the plane of excitation of the molecule. That is, for reaction of the lowest $^4B_{2g}$ state of the cis isomer, which has its sigma antibonding orbital in the A_2F_2 plane, the fac product can arise only by trans entry of a water ligand on an edge of the octahedron orthogonal to the plane of excitation, as shown in Fig. 4.

For these systems, the VC model can also account qualitatively for the observed wavelength dependence of yields in both isomers although it must be admitted that the variations observed were



Note. For the cis complex, axial refers to the A-A axis, equatorial to the A_2F_2 plane.

FIGURE 4 Predictions of edge-displacement model and VC theory for *trans*- and *cis*-$CrF_2(NH_3)_4^+$.

within the experimental uncertainties. Using the isomer labelling of Fig. 4, isomer B is the product predicted for reaction from the lowest ^4E state of the trans compound and an experimental value of B/A of 2.5 was found for low energy irradiation (577 nm). The small proportion of isomer A can be explained as the sole product expected by reaction from the higher lying $^4B_{2g}$ state, which might also be populated to some extent. For irradiation to higher energy (436 nm), the fraction of product A produced increases so that B/A is now only 2.2.

For the cis isomer, low energy irradiation gave B/A of 1.2 and a small amount of product C (C/A = 0.22). The first two are consistent with predictions for the $^4B_2$ state which lies at slightly lower energy in the cis complex. The C produced can be explained in terms of some reaction via the higher lying ^4E state. Consistent with this is that, on irradiation at higher energy, an increase in the proportion of products C (C/A = 0.5) and B (B/A = 1.4) is found and agrees with expectations for greater participation of the higher ^4E state. For both isomers then, the product yield variations were in accord with expectations for reaction of both quartet states, with greater participation of the higher state at higher energies. Again this indicates that in these systems, Kasha's rule is infringed.

There arose in these results a problem for the then existing VC theory in that the major predicted pathways from the lowest quartet states of *trans*- and *cis*-$CrF_2(NH_3)_4^+$ lead to the same TBP intermediate in its excited electronic state. If it reacts while electronically excited, it leads to product B, while if it decays to its ground state before reacting, it should form product A. While these are the products formed, the proportion is not the same for the two isomeric complexes; the putative intermediate seems to have a memory of its origin. In order to rationalise this and other results, VC have elaborated their theory [38] to include an analysis of the Jahn–Teller distortions expected for the TBP intermediates. Where the three equatorial ligands in the TBP species are not all the same, the crossing point between the upper and lower electronic surfaces is offset from equilateral triangular geometry. The fate of the excited state SP intermediate initially produced then depends on whether or not the crossing region between the upper and lower energy surfaces lies on its pathway of decay via the TBP geometry and also depends on the position of the system's entry point to the upper state surface. This neatly rationalises the observed behaviour for the difluoro systems. The reader is referred to the original paper for further explanation and details. But while the model accounts nicely for the experimental observations described above, it continues to affront the evidence for seven-coordinate transition states.

The data for the analogous cyano[39] and dicyano[40] systems is also interesting, as they also show complex photostereochemistry, albeit without measured wavelength dependence.[41] Photolysis of cyanopentammine leads to *cis*- and *trans*-aquocyanotetrammine products in a 2:1 ratio, but this result can not be easily interpreted as the trans isomer could arise either by stereoretentive replacement of the trans NH_3, violating the stereochemical rule usually observed, or it could arise by loss of a cis ammonia with stereochemical change. A study of a system like *trans*-$Cr(CN)(NH_3)(en)_2^{2+}$ would help unravel this problem. The diacido complex is more informative, as ammonia loss from the trans leads to the meridional trans-dicyanoaquo (B′, equivalent to B, Fig. 4) and cis-dicyanoaquo (A′, equivalent to A, Fig. 4) in a ratio B′/A′ = 0.5, close to the opposite behaviour from the difluoro complexes. The results are consistent with each other in that the lowest quartet state here is now $^4B_{2g}$ which should lead to isomer A′, while the upper ^4E state gives B′. For the two systems, the calculated $^4E/^4B_2$ splittings are almost equal at about 0.26 μm^{-1} but are opposite in sign. They are sufficiently large that there would be negligible equilibrium population of the upper state at room temperature. How to understand this, together with the quenching data and the known involvement of the doublet state, is a problem dealt with in a later section.

PHOTOSTEREOCHEMISTRY OF OTHER PHOTOSUBSTITUTIONS

All the processes stereochemically studied to date have been photosolvations. However, Wasgestian and co-workers have found[42] that photoanation can also occur in concentrated solutions of appropriate nucleophiles and does so in competition with aquation from both quartet and doublet states. Does this process also occur with stereochemical change? We have recently undertaken[43] a study of this question using the complex *trans*-$CrCl(NH_3)(tn)_2^+$, which we predict should photoaquate ammonia almost exclusively. Our data to the present supports this expectation and shows that on addition of 3 M NCS^- to the solution, photoanation does occur.

As the product, we find a single chromatographic peak at a retention time consistent with a $Cr(NCS)Cl(tn)_2^+$ product. We are currently working to prove that cis and trans isomers of this material would be separated under the chromatographic conditions used and to establish the geometric configuration of the photoanation product.

PROBLEMS, AMBIGUITIES AND COMPLICATIONS

Many of the problems and ambiguities that arise in the stereochemical work and its interpretation have been mentioned already. Here we want only to add a couple more.

In complexes with bidentate or polydentate ligands the question arises as to what kinds of restrictions are imposed on the photochemical pathways by steric factors. We have already dealt at length with the most dramatic of these effects in the discussion of cyclam complexes. As a different kind of example, however, we have tried to analyse the photostereochemistry of trisbidentate complexes such as $Cr(en)_3^{3+}$ and $Cr(tn)_3^{3+}$ which can be considered as homologues of $Cr(NH_3)_6^{3+}$. Note that the bidentate ligand does not impose any fundamental constraint on the photochemistry of such complexes. It can readily detach from the metal at either end and protonate to form a monodentate coordinated species. It has been shown, in fact, that en is a significantly better leaving ligand than ammonia while tn is significantly worse. We have attributed[44] this to the strain present in five-membered rings and the stability of six.

The concern here is with a different aspect; can an entire bidentate ligand migrate in order to allow the trans entry of the substituting ligand? Figure 5 illustrates the problem as it arises in analysing the photostereochemical predictions for Λ-$Cr(en)_3^{3+}$. In any one of the three possible planes of excitation there are two kinds of N coordination site. Choosing the plane of excitation to be that of the paper, sites A and B correspond to a ligand with one N in this plane and the other N out-of-plane. C and D correspond to a ligand with both N atoms in plane.

For photochemical substitution of A, one trans edge, edge 2, is blocked by the in-plane bidentate ligand, but the other, edge 1, is

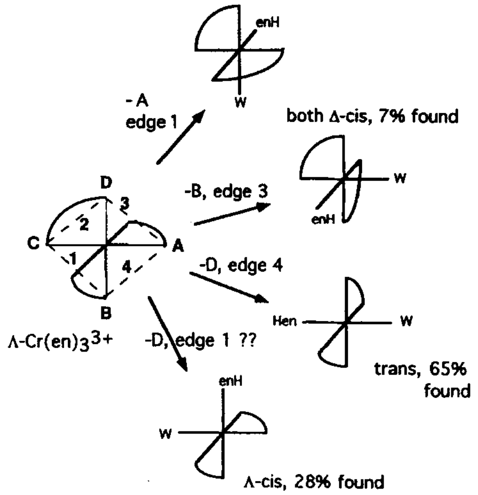


FIGURE 5 Photostereochemistry of Λ-Cr(en)$_3^{3+}$ and the ligand migration issue.

free. Entry of water here (accompanied by migration of coordinator B through rotation of the ligand around its out-of-plane attachment) is a facile process which leads to the cis product with the Δ-configuration. The same product is predicted for loss of B by trans attack at edge 3. Cimolino and Linck[45] found 7% of this product for Cr(en)$_3^{3+}$. For loss of D, trans attack could occur at edge 1 or 4. The latter is conventional, with coordinator A being replaced by water and moving round to the site previously held by D, to give trans product (65% found).

The questionable process is displacement of D by attack at edge 1. This requires that as D dissociates, the complete bidentate ligand allows its remaining attachment site, C, to migrate to the site vacated by D. This would lead to Λ-cis product of which 28% was found. The question is whether or not this is reasonable. We wished to obtain additional evidence for the occurrence of this process in complexes of bidentate ligands. (Of course the reader who has become a true believer in the model will already be convinced!).

An approach to this question, though considerably less than perfect, was our comparison[46] of the photochemistry of *cis*-Cr(cyclam)L-L^{3+} with L-L equal to diammine and ethylenediamine. The first complex loses ammonia with a quantum yield of

0.15 to give exclusively the cis aquoammine product. Similarly the en analogue lost one end of the en ligand with a yield of 0.09 and the aquo(enH) product was again the cis isomer. The photochemistry of both was therefore as expected for the normal trans entry of water ligand at the only free edge trans to the leaving ligand that allows substitution with preservation of the cis conformation of the cyclam ligand. In addition, the yields are similar and the inference is that the migration of the attached end of the en ligand is possible although apparently somewhat less facile than migration of a monodentate ligand. What of course is missing is a clear demonstration that the final N coordination site is the one initially labilized, and this remains as a challenge to us and others to achieve. The problem is difficult synthetically, structurally and analytically.

We have more recently obtained[16b] further indirect evidence for the process. The main photoreaction mode of *trans*-$Cr(CN)_2(tn)_2^+$ is loss of tn to form the monodentate protonated tnH^+-aquo product. Chromatographic product analysis combined with kinetic evidence indicates that this product has the two cyanide ligands trans to one another. This in turn implies that the product arises by substitution in the equatorial plane, and assuming this follows the usual trans attack pathway, the whole tn ligand must migrate. The alternative would be that equatorial labilization is for some reason stereoretentive. This is unlikely, and inconsistent with the other evidence presented earlier, although it would be an interesting theoretical challenge if true.

MECHANISTIC SIGNIFICANCE OF PHOTOSTEREOCHEMICAL RESULTS

Much of chromium photochemistry is known to occur via the doublet state, being quenchable and occurring with the doublet lifetime, and the biggest argument in the whole field, still going on, has been about the detailed pathway of this process. The problem has been tackled using kinetic evidence, spectroscopic findings, temperature dependence and medium studies of emission lifetime and intensity, volumes of activation for the doublet lifetime and deuterium isotope effects on doublet lifetime. The consensus of this evidence now weighs against direct reaction of the doublet state and in favour of either reverse intersystem crossing and reaction via the quartet state or tunnelling to a ground state transition state for reaction.

There is stereochemical and product distribution evidence, although not as much as there could be, that bears directly on these debates and which, in the author's opinion, has been sadly neglected in some discussions of the overall evidence. Several complexes have been shown to give rise to the same products and product stereochemistries when irradiated directly into the doublet or into the quartet state, suggesting a common intermediate for the two routes. The most striking and compelling experiment[47] is with *trans*-$Cr(NCS)(CN)(NH_3)_4^+$ which shows three reaction modes. All three are quenched in parallel with the doublet emission intensity, and the same percentage of all three reactions, 25%, is unquenchable. The photoproduct ratios are identical for the quenchable pathway via the doublet and the unquenchable fraction originating in the quartet state. The two pathways therefore involve a common intermediate. The photophysical evidence mentioned earlier and reviewed and extended very competently in a recent paper[35] supports reverse intersystem crossing as the major route depopulating the doublet. The evidence is therefore consistent with all the photochemistry having its immediate origin in the excited quartet state(s).

What has not received sufficient emphasis is the stereochemical aspect of this behaviour. As has been pointed out earlier, there is a reasonable theoretical understanding in terms of quartet reactivity of the stereochemical change observed. This photostereochemistry is the same, for example, for $Cr(en)_3^{3+}$ for the unquenchable and quenchable routes.[45] For $Cr(tn)_3^{3+}$ some complexities including a small wavelength dependence of the cis/trans product ratio in the red edge of the first ligand field band were reported,[9] but the photostereochemical results were similar. It is really hard to believe that this would occur by chance in several different complexes if the mechanism were reaction of two different excited states, a doublet with no vacant t_{2g} orbital[48] and ground state geometry, and a quartet with an occupied e_g and vacant t_{2g} orbital and a strongly Jahn–Teller distorted geometry.

The author also finds unsatisfactory the second proposal, that both pathways lead to product by tunnelling to a ground state intermediate or transition state for reaction. The ground state reactions are normally stereoretentive, so we are asked to believe that two states of quite different geometry and electronic configuration tunnel to the same transition state and furthermore one that is quite different in its reactions and stereochemical behaviour from the usual electronic ground state transition state. If, on the other hand, all that is being said is that the electronically excited states evolve to a non-electronically excited intermediate analogous to the TBP species or its seven-coordinate equivalent, then the proposal is really just a subset of the VC theory. In the author's view the latter is then infinitely superior as it offers methods for prediction of the reaction modes and stereochemistry and provides a basis for understanding photostereochemistry and wavelength dependencies at a sophisticated level such as was discussed for the trans and cis $CrF_2(NH_3)_4^+$ systems, for example. The tunnelling model is sterile by comparison.

CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

There is now a good basis of understanding of Cr(III) photochemistry including its stereochemistry and the effect of ligand constraints on the behaviour. Many problems remain to be solved, however. On the theoretical level we need to solve the difficult problem of a working model of reaction via associative attack which will explain both the reaction modes and stereochemistry. The analysis analogous to that presented recently in terms of Jahn–Teller effects in the TBP intermediates in their electronically excited and ground states needs extension to more realistic intermediates also, although the value of the existing simple pictures is undeniable.

On the experimental side several specific issues have already been identified in the previous discussion. Further data on stereochemical behaviour as a function of temperature and pressure is desirable. Do all stereoisomers show the same activation energies and have the same volumes of activation? What are the effects of solvent? The stereochemistries of the ground state thermal reactions are known to change with solvent. The only photostereochemical data appear to be our early study[50] that indicated stereochemical change for $Cr(RNH_2)_5Cl^{2+}$ in water/acetone mixtures. More studies are needed. The continued investigation of the effect of ligand constraints is also desirable. Other items on the list are a better experiment to demonstrate migration of a bidentate ligand, unambiguous studies of the stereochemistry of equatorial labilization and, if it does not occur entirely with stereochemical change, exploration of the factors that influence this phenomenon. Further, direct proof that more than one quartet excited state reacts is needed and that the photostereochemistry and reaction mode is truly as predicted by theory. Can much photosubstitution chemistry be studied for other d^3 systems? Finally, does stereochemical change occur in the fast ground state substitution chemistry of octahedral d^2 and/or d^4 complexes as might be expected from parallels with the excited quartet state electronic configuration? (This will be a tough question to answer because of the lability of these systems.)

A WORKING HYPOTHESIS FOR Cr(III) PHOTOCHEMISTRY

To close, it is good to have a working model to guide experiments. With only a moderate amount of speculation, one can be offered that rationalizes the photophysical and photochemical observations available. Reaction occurs from the electronically excited quartet states via a seven-coordinate intermediate of asymmetric pentagonal bipyramidal geometry. The ligand lost is that in the plane of excitation that is originally trans to the weakest field ligand and the substituting ligand enters the coordination sphere trans to the leaving ligand. As described in the VC theory, the system evolves smoothly from the excited electronic quartet state through to the ground state of the product. As a corollary, the predictions of leaving group need to be modified if steric effects are important in restricting the motions required or if other factors operate to favour loss of a particular ligand. Thus ligands with the same LF strength are not all equally labilized.[49] Leaving group sequences might be established to accommodate this complication, e.g., our work shows that, for steric reasons, there is a leaving group ability sequence en > NH_3 > tn.

The confusing aspects of the photophysics can be understood only if viewed in a kinetic rather than a conventional spectroscopic context applied to an isolated molecule. We take it as given that the quartet states are reactive and so much so they have a ps or sub-ps lifetime in room temperature solution media.[8,9] As indicated earlier, theory and experiment suggest that both ^4E and $^4B_2$ states react in wavelength dependent proportions that are not consistent with a Boltzmann eqilibrium between them, and also for the pathway via the lowest doublet state, reverse intersystem crossing has to populate both states in the same, or very similar, non-Boltzmann proportions. How can all this be? The author proposes the answer is to recognise the importance to these processes of the interactions with the solvation environment. It is well-established that the energy barrier to depletion of the doublet state, for example, is markedly dependent on solvent or medium and this has recently been interpreted[33] in terms of influences on reverse intersystem crossing.

Consider a supermolecule consisting of the excited complex and its immediate solvation sphere, which can include counter ions as well as solvent. For the fast reaction occurring in competition with intersystem crossing, selection of the plane of excitation and hence reaction can be influenced, even determined, by the perturbation owing to a close (colliding) solvent molecule or other nucleophile at the instant the photon is absorbed in a type of photoselection process. Whether or not "^4E or ^4B state" results is a function of the solvent interactions with the complex and their energetics, and not related simply to the spectroscopy of an isolated molecule. We have put the state symbols in quotes here to emphasize that the states involved likely have little or no real existence. Once excited, the interaction of the nucleophile with the excited state is so strong that a seven-coordinate species is formed on the timescale of the nuclear motions involved.

In a parallel manner, the processes that originate in the doublet can be similarly influenced. If a doublet state molecule has, in close proximity to it, a strongly interacting nucleophile, then this will alter the energies of the supermolecule doublet and quartet states, leading to a smaller activation barrier for reverse intersystem crossing and facilitating the process. How this could occur as a result of raising of the energy of the doublet state is indicated by the energy level diagram in Fig. 6. The process envisaged could be called "nucleophile-assisted reverse intersystem crossing" and will lead to the same seven-coordinate transition states as correspond to nucleophile association to the "^{4}B and ^{4}E states". The proportion will again be influenced by the site of nucleophile approach to the doublet state molecule. Since the geometry and solvation of the doublet and ground states are very similar, it is better understood how the proportions of "^{4}B and ^{4}E states" produced could be essentially the same from the two routes and different from the Boltzmann proportion calculated from the isolated

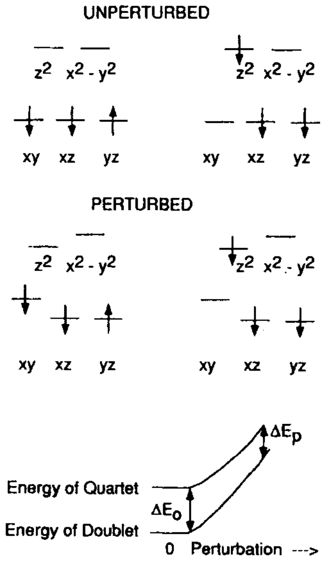


FIGURE 6 Qualitative illustration of perturbation of one electron levels and "nucleophile-assisted reverse intersystem crossing". Collision of a nucleophile such as H_2O on a 45° line in the xy plane will raise the energy of the one electron orbitals to different extents, d_{xy} being raised most in energy while $d_{x^2-y^2}$, d_{z^2} and d_{xz}, d_{yz} will rise by lesser amounts. As shown, this will raise the energy of the doublet state more than the energy of certain quartet states; shown is the situation for a quartet state with a vacant d_{xy} orbital. The lower part of the diagram shows how the energies of these states will vary with closeness of approach of the nucleophile and how, although the absolute energies of the states both increase, the barrier to doublet/quartet reverse intersystem crossing could be lowered by such a collision.

molecule spectroscopy. This could be said to be returning to a model of direct doublet reaction, but there is more to it than that, and hence the introduction of the terminology "nucleophile-assisted reverse intersystem crossing". In the first place all of the seven-coordinate transition states resulting may not go on to products, some returning to ground state molecules. Moreover the vacant t_{2g} orbital present in the quartet states and absent in the lowest doublet appears to be an essential feature of the photosubstitution which gives rise to the stereochemical change observed, and which is not to be expected from the doublet state electronic configuration.[48]

CLOSING COMMENT

This article has represented an attempt at synthesis of what we know about Cr(III) photochemistry into a self-consistent model that will enable others to understand and predict Cr(III) photobehaviour. It was not intended as a comprehensive review and the author apologizes to the many whose contributions have not been mentioned. The emphasis has deliberately been on the stereochemical aspects and on developing simple predictive procedures and concepts such as are found, for example, in organic photochemistry. Hopefully some of the ideas presented will be judged reliable and suitable enough to form the basis for undergraduate presentations of the subject. Inevitably a great deal of the photophysical background has been left out, and the interested reader is referred to the reviews cited[4] which cover this well.

The author hopes that the article will be of interest and will stimulate new workers to tackle some of the outstanding challenges.

Acknowledgments

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