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Photochemistry and Photophysics of Chromium(III) Complexes

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Contents

Sandy Kirk obtained his B.Sc. and Ph.D. degree in physical chemistry from the University of Edinburgh in 1959 for work on the gas-phase decomposition of hydrogen peroxide and alkyl hydroperoxides. He was introduced to photochemistry during a 2-year postdoctoral position with Gerald Porter at UBC, Vancouver. After joining the University of Victoria in 1961, he entered the developing field of inorganic photochemistry in 1967 via summer work in 1967 with Arthur Adamson and a Humboldt Fellowship with Hans Schläfer in 1968–69. Since that time his research has focused on the primary processes, excited-state participation, and stereochemical aspects of the photochemistry of coordination complexes. In recent years he has collaborated on solid-state spectroscopy with Hans Güdel in Bern, Switzerland.

I. Introduction

The photochemistry of Cr(III) complexes has been a central theme of inorganic photochemistry from the inception of the area in the early 1960s and interest continues to the present day. Some of the problems identified at the outset, for example, the identity of the reactive excited states, are still actively being investigated and do not seem to have been completely resolved despite considerable research effort.

There have been many previous reviews related to Cr(III) photochemistry, photophysics, and spectroscopy. Early examples focused on the reaction modes observed in homo- and heteroleptic complexes and the successes and failures of competing photochemical models in predicting those modes.[1−4] These reviews also dealt with the nature of the reactive excited states and the stereochemistry of the photoreactions, while another review introduced a group-theoretical model for fast (“prompt”) photoprocesses.[5] The topics of more recent specific reviews relevant to Cr(III) photochemistry have been potential applications for polypyridyl Cr(III) complexes,[6] wavelength dependence of quantum yields over narrow spectral ranges,[7] an analysis of possible photochemical intermediates,[8] mechanistic implications of pressure-dependence studies,[9] applications of picosecond spectroscopy,[10,11] stereochemical and electronic contributions to doublet state relaxation channels,[12,13] comparison of thermal and photochemical mechanisms,[14] rate constants for excited-state quenching,[15] stereochemistry and steric effects[16] and solvent effects[17] as probes of mechanism, photochemistry of cyanometalates,[18] developments of orbital models,[19,20] and primary photochemical processes.[21] Recent general reviews have dealt with the structure and reactivity of metal-centered excited states,[22] the photophysics of Cr(III) complexes,[23] and the photochemistry of cyanoam(m)ine complexes.[24]

The present review is based on literature searches up to and including December 1998. It will draw on the information and ideas of the reviews mentioned above but try not to repeat their efforts. The focus will rather be to review recent literature not covered above, to try to fill perceived gaps in the coverage to date, and to draw attention to areas which would merit further investigation.

II. Background Spectroscopy and Photophysics

On the basis of studies in low-temperature glasses and crystals, the absorption and emission spectroscopy of Cr(III) is well understood[23] and there is a

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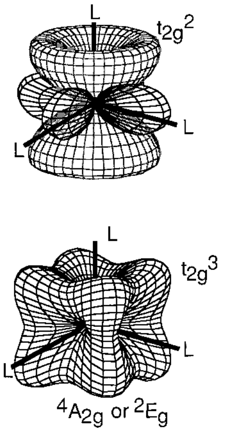

Figure 1. Electron density distributions for the ground state, $^4A_{2g}$, and the lowest doublet, ^2E_g, and quartet, $^4T_{2g}$, excited states of an O_h Cr(III) complex. For clarity, the vacant t_{2g} orbital in the $^4T_{2g}$ state is omitted. Its lobes lie in the same plane as, and bisect, those of the e_g* singly occupied orbital shown.

consensus on the fundamental properties of the lowest excited states under these conditions. Excitation into the triply degenerate lowest excited quartet state, $^4T_{2g} \leftarrow {}^4A_{2g}$, corresponds to promotion of an electron from the ground-state t_{2g}^3 configuration to the e_g* level, specifically to one of the component[25] one-electron transitions $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{xz} \rightarrow d_{z^2-x^2}$, and $d_{yz} \rightarrow d_{z^2-y^2}$. In effect this constitutes a rotation of charge distribution by 45° in one or another of the three orthogonal planes containing the ligands. The resulting electron density distribution in the Franck–Condon state is compared with the ground- and doublet-state t_{2g}^3 electron density distributions in Figure 1. Because of the antibonding electron density on two of the Cr–L bonding axes in the quartet excited state, relaxation will occur to a new geometry; a tetragonal distortion is suggested by the electron distribution, but some theories[5,26] have allowed for the possibility of trigonal distortions.

For a few complexes there is sufficient structure in the absorption spectrum that it can be analyzed to establish the energy of the thermalized quartet excited state and the excited-state distortions created by occupation of an e_g* orbital. For $Cr(NH_3)_6^{3+}$, for example, analysis of the vibrational components in the $^4T_{2g} \leftarrow {}^4A_{2g}$ 6 K absorption spectrum of $[Cr(NH_3)_6](ClO_4)_2Cl{\cdot}KCl$ assigns[27] the center of the spin–orbit split 0–0 lines as 501.1 nm, placing the vibrationally relaxed quartet state 19 956 cm^{-1} above the ground state. Successful analysis of the observed vibrational progressions in terms of a_{1g} and e_g components showed that the vibrationally relaxed excited quartet state has tetragonal symmetry corresponding to a 2 pm shortening of the axial Cr–N bonds and a 12 pm lengthening of the equatorial Cr–N bonds.

In contrast, the structured spectrum and the small Stokes shift associated with absorption and emission involving the lowest ^2E_g state[23] show that it has essentially ground-state geometry and bonding. It is important to note that in this excited state, each of the t_{2g} orbitals is singly occupied,[28] precluding any Jahn–Teller distortions.

For heteroleptic complexes containing ligands with significantly different ligand-field strengths, similar considerations apply but the lower symmetry splits the O_h lowest $^4T_{2g}$ and ^2E_g states into $^4E/^4B_2$ and $^2A_1/^2B_1$ components, respectively. The directions and magnitudes of the former splittings are detailed elsewhere[4,23] and will be used later. For the important case of tetragonal splitting caused by incorporation of a single ligand or two trans ligands of smaller ligand-field strength, the lowest quartet state is the ^4E component, corresponding to localization of the antibonding electron density on the metal–ligand axes in the *xz* or *yz* plane. For such complexes, the lowest doublet state is a component of $^2E(O_h)$ which retains the one-electron occupancy numbers for each t_{2g} orbital. For some complexes of fluoro or hydroxo ligands with their strong π-donor characteristics, however, the ^2E component of the $^2T_{1g}(O_h)$ state can be the lowest doublet.[28] This gives broader absorption and emission spectra with greater sensitivity to medium effects.[23]

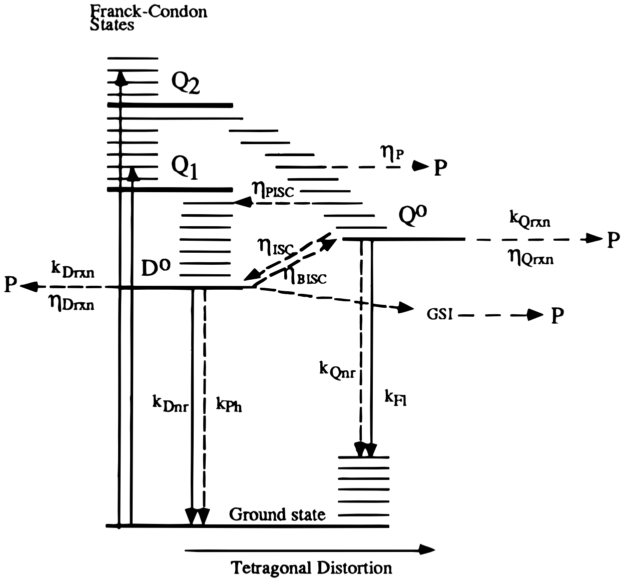

Figure 2. Energy level diagram and excited-state kinetic scheme for Cr(III) complexes. Legend: P = photoproduct, ISC = intersystem crossing, PISC = prompt intersystem crossing, BISC = back intersystem crossing, D° and Q° = thermally equilibrated lowest excited doublet and quartet states, respectively, Qrxn = reaction from Q°, Drxn = reaction from D°, GSI = photochemical intermediate in its ground electronic state, η = efficiency of any process. The figure shows four possible routes for product formation, including a prompt process from the quartet state with efficiency, η_P, competitive with vibrational and solvent shell relaxation, which is depicted by a sloping ladder of energy levels. Also shown are fluorescence, phosphorescence, and doublet and quartet nonradiative decay. ISC, BISC, and formation of a GSI have been represented by sloping arrows for clarity, but these really involve a combination of horizontal and vertical processes.

For octahedral complexes, the above spectroscopy can be summarized in the energy level/kinetic processes diagram of Figure 2. Excitation into the lowest ligand-field or higher Franck–Condon states followed by internal conversion populates the thermally equilibrated lowest quartet excited state, Q°, and, by intersystem crossing, also the lowest doublet excited state, D°. In Figure 2, ISC is shown as occurring both by the conventional route via Q°, ISC, and also in competition[29–31] with vibrational relaxation, P(rompt)ISC. In low-temperature solids, the thermalized quartet and doublet states can both be emissive. In situations where both emit, it is possible to measure the energy of the doublet state from the coincidence of the 0−0 band in absorption and emission and to estimate the energy of the quartet state as the mean of the absorption and emission spectral band maxima. The energy of the doublet state is independent of the ligand-field strength but varies with the nephelauxetic parameter of the ligands, while the quartet-state energy increases with ligand-field strength. Consequently, the excited doublet/quartet state spacing increases with ligand-field strength.[22,23] For a series of complexes in the solid state at a given low temperature, this leads to fluorescence from weak-field complexes, phosphorescence from high-field complexes, and phosphorescence accompanied by delayed fluorescence for complexes of intermediate field.

In contrast to this clear picture for low-temperature solid-state systems, little information is available regarding the properties of the thermalized lowest excited quartet state in room-temperature solutions, i.e., under normal photochemical conditions. A procedure[32] for estimating the energy of this state, the "5%-absorption" criterion, has its origin in the low-temperature spectroscopic studies; its applicability in room temperature solutions is unknown but somewhat doubtful. Fluorescence or delayed fluorescence has been searched for in room-temperature solution studies by many workers, and only one report[33] remains viable. Consequently, little is known about the energy of the thermalized quartet excited state in solution and the reported rise time for doublet phosphorescence, <1 ps, implies that this state may have only a fleeting existence.[34] Regarding its chemical reactivity, however, doublet quenching experiments have clearly shown that photochemistry occurs from the quartet state as there is often an unquenchable component of reaction. It is not generally known to what extent this reaction occurs in competition with vibrational and solvent-shell relaxation but the subpicosecond time scale for ISC[34] and the observations of the wavelength dependence of intersystem crossing yields suggest it may compete. Note finally that theoretical models for the reaction mode and photostereochemistry based on the assumption of excited quartet state reactivity[4,35,36] have enjoyed a remarkable degree of success in explaining[1,2,16,24] experimental observations.

In contrast to our ignorance about the energy and lifetime of the thermalized excited quartet state in solution, there is a superabundance of information[23] regarding the lowest doublet-state energy, the phosphorescence decay lifetime and the apparent activation energy for the decay lifetime in various media.[37] For most complexes, part or all of the photochemistry is quenched by quenchers of the doublet state. There are three extant mechanisms for this doublet photochemistry: (i) direct reaction of the doublet state (Drxn), (ii) back (reverse) intersystem crossing (BISC) followed by quartet reaction (Qrxn), (iii) tunneling to an electronically ground-state intermediate (GSI) for reaction. All three routes are shown in Figure 2, and the problem of which processes actually occur for different complexes has been a major concern of much recent research. The kinetics of the processes shown in Figure 2 are discussed in full detail[23] in a recent review. On the basis of this and other schemes,[38,39] expressions can be written for the unquenchable, ϕ_{unq}, and quenchable, ϕ_{q}, quantum yields of reaction and for the total quantum yields of reaction on quartet and doublet irradiation, ϕ_{Qirrad} and ϕ_{Dirrad}, respectively. These are expressed in terms of the efficiencies, η_i, of the various processes of Figure 2, where $\eta_i = k_i/\Sigma k_i$ and the sum applies for all the rate constants depleting a particular species

$$\phi_{\mathrm{unq}} = \eta_{\mathrm{P}} + (1 - \eta_{\mathrm{PISC}} - \eta_{\mathrm{P}})\eta_{\mathrm{Qrxn}} \tag{1}$$

$$\phi_{\mathrm{q}} = \{\eta_{\mathrm{PISC}} + (1 - \eta_{\mathrm{PISC}} - \eta_{\mathrm{P}})\eta_{\mathrm{ISC}}\}(\eta_{\mathrm{Drxn}} + \eta_{\mathrm{GSI}} + \eta_{\mathrm{BISC}}\eta_{\mathrm{Qrxn}})/(1 - \eta_{\mathrm{ISC}}\eta_{\mathrm{BISC}}) \tag{2}$$

$$\phi_{\mathrm{Qirrad}} = \phi_{\mathrm{unq}} + \phi_{\mathrm{q}} \tag{3}$$

$$\phi_{\mathrm{Dirrad}} = (\eta_{\mathrm{Drxn}} + \eta_{\mathrm{GSI}} + \eta_{\mathrm{BISC}}\eta_{\mathrm{Qrxn}})/(1 - \eta_{\mathrm{ISC}}\eta_{\mathrm{BISC}}) \tag{4}$$

Analogous expressions containing the relevant efficiencies in the numerator apply for the quantum yields of prompt and delayed fluorescence, phosphorescence, and nonradiative decays.

A notable feature of Cr(III) photochemistry is the stereochemical change that usually accompanies photosubstitution,[2,16,24,40,41] particularly for loss of the axial ligand in complexes with D_{4h} or C_{4v} symmetry. Early studies of *trans*-Cr(cyclam)Cl_2^+ showed[42,43] the molecule to be almost photoinert, and this has been taken as evidence that stereochemical change may be a requirement of the photochemical reaction. The stereochemical change has been modeled theoretically[4,36] in terms of dissociative ligand loss from the quartet state followed by symmetry-allowed reactions of the resulting five-coordinate intermediates. The dissociative aspect of the theory is in conflict with volume of activation evidence[39,44,45] for an associative pathway in these photoreactions. Efforts to develop the theory in a context of seven-coordinate intermediates have not been successful. Nevertheless, a pictorial associative model that may retain the essence of the theory and yet reconcile these discrepancies has been proposed.[16] Both the dissociative and associative versions are reproduced pictorially in Figure 3 for convenience in following the later discussions of reaction modes and stereochemistry of photosubstitution, and the figure caption provides detail on the processes involved. Experimentally, Cr(III) photostereochemistry corresponds to a simple edge displacement confined to the plane of labilization in an excited quartet state. In the model, this confinement arises because of the t_{2g}^2 cone of electron density on either side of the labilization plane, Figure 1, which clearly disfavors any out-of-plane motions of the Lewis base ligands. This photostereochemical model can be extended to accommodate the situations where more than one quartet excited state is reactive or where the allowed reaction pathway passes through the excited state of the trigonal bipyramidal (tbp) intermediate.

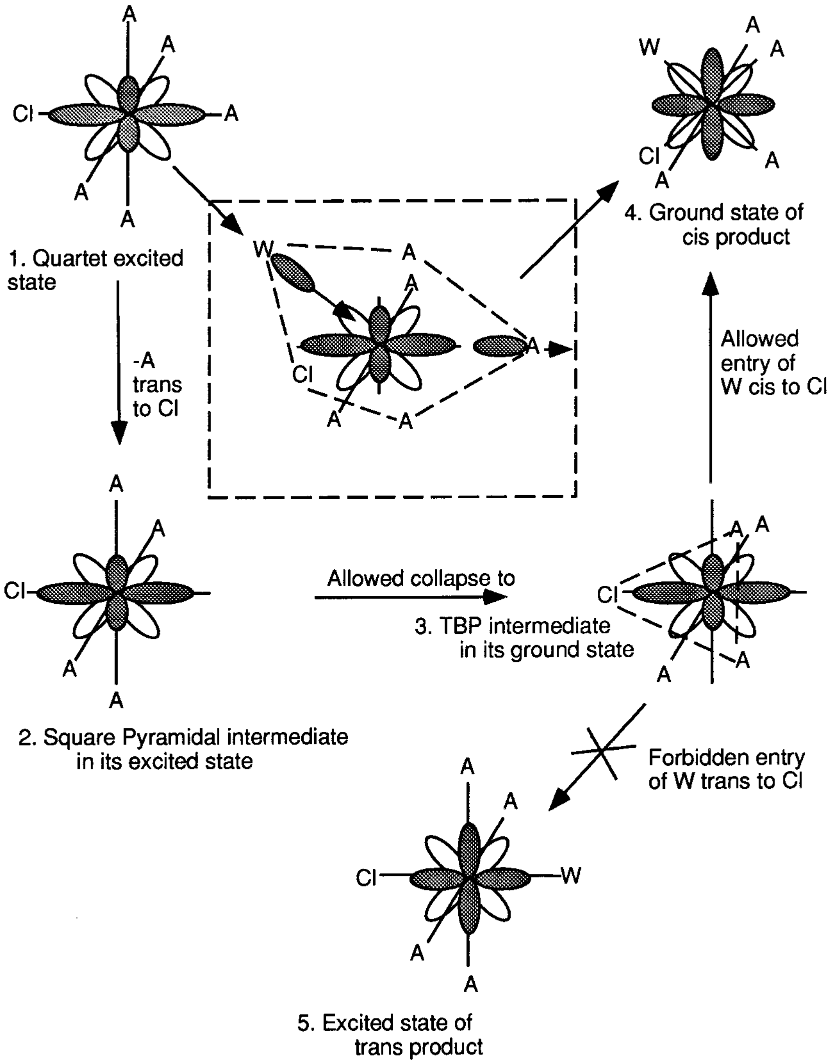

Figure 3. Pictorial representation of Vanquickenborne–Ceulemans theory of Cr(III) photostereochemistry. Legend: W = H_2O; A = NH_3. The lowest excited state shown at the top left has electron density located in the *xz* (or *yz*) plane, labilizing all four ligands in this plane. Because of the presence of the weaker field chloride ligand, the antibonding electron density is concentrated on the *z* axis, which causes the ammonia ligand trans to Cl to be preferentially labilized. The resulting square pyramidal (sp) intermediate collapses to a trigonal bipyramidal (tbp) intermediate in the symmetry-allowed fashion shown. For this ground state of the tbp intermediate, entry of a water ligand cis to chloride is an allowed process that leads to the ground state of *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. In contrast, entry of water trans to the chloride ligand is forbidden, as it leads to the excited state of *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. The boxed inset shows an equivalent seven-coordinate route proceeding via an asymmetric pentagonal bipyramidal intermediate. For some ligand combinations, it is expected that the tbp intermediate, **3**, will be produced in its electronically excited state which has the opposite orbital occupancy from that shown; clearly this shows the opposite symmetry rules for ligand entry and favors formation of the trans product.

The stereochemical work quoted above concentrated on labilization of an axial ligand from the lowest ^4E state in tetragonal complexes. A focus of work in the review period has been to explore the corresponding situation for two other situations: labilization of an equatorial ligand from the ^4E state and photosubstitution in tetragonal complexes for which $^4B_2$ is the lower energy component of the split $^4T_{2g}(O_h)$ state. Also of great interest has been the use of macrocyclic ligands to control photoreactivity and to explore their effect on photophysical properties.

The interest in the absorption and emission spectroscopy of Cr(III) complexes continues unabated. Some studies post-dating the Forster review have examined and analyzed sharp line doublet emission spectra as a means to obtain ligand-field parameters.[46−62]

III. Photochemical Reaction Patterns

A. Substitution Processes

Table 1 presents a survey of the recent studies of photosubstitution of homoleptic Cr(III) complexes. The table reveals an intense focus on N_6 systems over the review period. Among those included are a number of important complexes containing two different amine ligands, which can be considered as homoleptic only to the extent that the ligand-field strengths of the ligands present are reasonably similar.

Hexam(m)ine complexes of Cr(III) have been found to photoaquate an am(m)ine ligand with essentially wavelength-independent quantum yields that are as high as 0.5. Note that for several complexes listed in

Table 1. Photosubstitution Studies on Homoleptic Cr(III) Complexes

complex	λ_{irrad}	ϕ	%D[a]	comment	ref
$Cr(NH_3)_6^{3+}$	436	0.47		$\Delta V^{\ddagger}(\phi) = -7$ cm^3 mol^{-1}	44
	347(Q2)		74	%D from conductivity detection	157
	530(Q1)		80		
	436	0.44	74		82
	458(Q1)	0.43		$\Delta V^{\ddagger}(\phi) = -6$ cm^3 mol^{-1}	39
	646(D)	0.44		$\Delta V^{\ddagger}(\phi) = -6$ cm^3 mol^{-1}	
$Cr(meam)_6^{3+}$	436	0.42		5 °C	259
Δ-$Cr(en)_3^{3+}$	365−685	0.37		28% Δ-*cis*, 7% Λ-*cis*, 65% *trans*-$Cr(en)_2(enH)(H_2O)^{4+}$	64
$Cr(en)_3^{3+}$	514(Q1)	0.42	68	%D from emission and chemistry on D/Q irradiation	38
	669(D)	0.45	64		
	404(Q)	0.37			63
	669(D)	0.59			
	347, 530		69	%D from conductivity detection	157
$Cr(sen)^{3+}$	355	0.10			184
	436	0.099(6)	70	22 °C	210
	675	0.074(2)			
$Cr(pn)_3^{3+}$	436	0.39		15 °C	259
Cr(*trans*-chxn)$_3^{3+}$	436	0.37			259
$Cr(tn)_3^{3+}$	366	0.18		$\phi\{Cr(tn)_2(H_2O)_2^{3+}\} = 0.04$	260
	347		78	%D from conductivity detection	157
	365, 436, 540	0.14	78	found 60% *trans*-$Cr(tn)_2(tnH)(H_2O)^{4+}$	82
	366	0.21		found 80% *trans*-$Cr(tn)_2(tnH)(H_2O)^{4+}$	70
$Cr(tn)_2(NH_3)_2^{3+}$	436	0.34	85	for trans isomer	198
	436	0.24		for cis isomer	
$Cr(tn)(NH_3)_4^{3+}$	436	0.36	83		198
$Cr(ditn)_2^{3+}$	436	0.16			259
cis-$Cr(cyclam)(NH_3)_2^{3+}$	365	0.2		trans isomer photoinert	192
	646(D)	0.15		$\Delta V^{\ddagger}(\phi) = 0.6$ cm^3 mol^{-1}	200, 203
	477(Q1)	0.15		$\Delta V^{\ddagger}(\phi) = 0.6$ cm^3 mol^{-1}	
	347(Q2)	0.14			
	366	0.16			261
$Cr(cyclam)(en)^{3+}$	436	0.21			259
	436	0.09			261
$Cr([9]aneN_3)_2^{3+}$	355, 436	$\leq$0.001			184, 259
$Cr(TAE[9]aneN_3)^{3+}$	355	0.27			184
$Cr(TAP[9]aneN_3)^{3+}$	355	0.01			184
$Cr(bpy)_3^{3+}$	313	0.13	98	pH 9.5, pH dependent; λ independent	215
$Cr(phen)_3^{3+}$	404(Q1)	0.005		pH > 9; λ independent	123
$Cr(acac)_3$	730	0.011		ϕ constant 730 → 350 nm, increases in UV with maximum at 250 nm	66
	366	0.011			
	250	0.039			
$Cr(NCS)_6^{3-}$	546	0.26		$\Delta V^{\ddagger}(\phi) = 2.1$ cm^3 mol^{-1}	45
$Cr(CN)_6^{3-}$	365	0.11	0	$\Delta V^{\ddagger}(\phi) = 2.7$ cm^3 mol^{-1}	45

[a] Percentage of photoreaction via the doublet state.

Table 1, e.g., $Cr(NH_3)_6^{3+}$, $Cr(en)_3^{3+}$, $Cr(tn)_3^{3+}$, and *cis*-$Cr(cyclam)(NH_3)_2^{3+}$, the quantum yield is the same for doublet and quartet irradiation, though for $Cr(en)_3^{3+}$ there is some disagreement.[38,63] For most of the complexes where it has been studied, between 70% and 80% of the reaction occurs with the doublet lifetime and is quenchable by species such as hydroxide ion or $Cr(ox)_3^{3-}$. It was shown[64] for Δ-$Cr(en)_3^{3+}$ that the stereochemistry of the photoproducts was the same upon irradiation into the doublet or quartet state, indicating reaction via an intermediate or transition state common to both pathways. For $Cr(NH_3)_6^{3+}$, the volume of activation is -6.0 cm^3 mol^{-1} for both doublet and quartet irradiation, consistent with an associative mechanism for the photoaquation, while for *cis*-$Cr(cyclam)(NH_3)_2^{3+}$ both excitations give $\Delta V^{\ddagger} = 0.6$ cm^3 mol^{-1}. For the anionic complexes listed, interpretation of the positive $\Delta V^{\ddagger}$ values is complicated by the changes in solvent electrostriction associated with aquation of a negatively charged ligand but the authors concluded[65] that the values indicated a dissociative interchange mechanism for these photoaquations.

Steric effects can influence quantum yields in major ways, as shown by the variations found for the $Cr(tn)_x(NH_3)_{6-2x}^{3+}$ systems, attributed to the stability of the six-membered chair ring formed by the tn ligand, the photoinertness seen for $Cr([9]aneN_3)_2^{3+}$, and the contrast in photoreactivity between $Cr(TAE[9]aneN_3)^{3+}$ and $Cr(TAP[9]aneN_3)^{3+}$. Note also the contrast between the photoreactive cis and the photoinert trans isomers of $Cr(cyclam)(NH_3)_2^{3+}$. There now exist a number of photoinert N_6 cage complexes, not included in Table 1, the properties of which will be presented in the later section devoted to mechanistic studies. The mechanistic significance of these observations, as well as the extensive studies of photophysical and solvent effects, is similarly deferred to later sections. Several homoleptic complexes containing bidentate ligands do not undergo efficient ligand substitution processes but instead show photoracemization or isomerization.

A study[66] of the thermal and photochemical ligand substitution in $Cr(acac)_3$ in 50% water/ethanol solvent showed parallel UV−vis absorption changes for

Table 2. Photosubstitution Studies on Heteroleptic Complexes

complex	λ_{irrad}	ϕ(main mode)	comment	ref
$Cr(NH_3)_5(H_2O)^{3+}$	546	0.20(NH_3)	90% cis product $\phi(H_2O$ exchange$) = 0.08$	14
trans-$Cr(NH_3)_4(H_2O)_2^{3+}$	546	0.31(isom)	$\phi = 0.025(NH_3)$; 0.001(ret. exch.)[c]	14
cis-$Cr(NH_3)_4(H_2O)_2^{3+}$	546	0.14(isom)	$\phi = 0.06(NH_3)$; 0.06(ret. exch.)[c]	14
fac-$Cr(NH_3)_3(H_2O)_3^{3+}$	546	0.15(isom)	$\phi = 0.05(NH_3)$; 0.04(ret. exch.)[c]	14
mer-$Cr(NH_3)_3(H_2O)_3^{3+}$	546	0.12(ret. exch.)[c]	$\phi = 0.06$(isom); 0.01(NH_3)	14
trans-$Cr(NH_3)_2(H_2O)_4^{3+}$	546	0.07(ret. exch.)[c]	$\phi = 0.05$(isom); 0.004(NH_3)	14
cis-$Cr(NH_3)_2(H_2O)_4^{3+}$	546	0.18(ret. exch.)[c]	$\phi = 0.002(NH_3)$	14
$Cr(NH_3)(H_2O)_5^{3+}$	546	0.06(exch.)	no NH_3 loss	14
trans-$Cr(tn)_2(tnH)(H_2O)^{4+}$	366	0.25		70
cis-$Cr(tn)_2(tnH)(H_2O)^{4+}$	366	0.29		70
trans-$Cr(tn)_2(H_2O)_2^{3+}$	366	0.37(isom)	$\phi = 0.01$(tnH); 0.01(ret. exch.)[c]	70
cis-$Cr(tn)_2(H_2O)_2^{3+}$	366	0.20(isom)	$\phi = 0.006$(tnH); 0.03(ret. exch.)[c]	70
trans-$Cr(NH_3)_4(H_2O)Cl^{2+}$	546	0.42	trans → cis isom.	71
trans-$Cr(NH_3)_4(dmf)Cl^{2+}$	546	0.31(dmf)	*cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ product	71
		0.017(Cl^-)		
		0.007(NH_3)		
$Cr(NH_3)_5(py)^{3+}$		0.2(py)		102
		0.16(NH_3)	mainly *cis*-$Cr(NH_3)_4(py)(H_2O)^{3+}$	
$Cr(NH_3)_5(NCS)^{2+}$	488	0.002(NCS^-)	$\Delta V^{\ddagger} = -9.8$ cm^3 mol^{-1}	44, 45
		0.420(NH_3)	$\Delta V^{\ddagger} = -6.4$ cm^3 mol^{-1}	
$Cr(NH_3)_5I^{2+}$	546	0.28(NH_3)	8 °C, $\phi_{I^-} \approx 0$	83
$Cr(NH_3)_5CN^{2+}$	495	0.33(NH_3)	$\phi_{CN^-} < 0.0005$	90
			74% via doublet	157
trans-$[Cr(en)_2Br_2]Br{\cdot}H_2O$	436	~0.26	solid-state aqn.; cis product	73
trans-$Cr(tn)_2(NH_3)Cl^{2+}$	436	0.34	aqn & NCS^- anation; cis products $\phi(Cl^-) < 0.003$	80
cis-$Cr(phen)_2Cl_2^+$		0.01	ϕ enhanced by deoxyguanosine	84
trans-$Cr(tn)_2F_2^+$	546	0.18(tn)	B/A ≈ 1[a]	87
		0.34(F^-)	product 90% cis	
cis-$Cr(cyclam)F_2^+$	514	0.28(F^-)	*trans*-$Cr(tet\text{-}a)F_2^+$ is photoinert	88
$Cr(NH_3)_4F_2^+$	577	0.34(NH_3)	*trans*; B/A = 2.5; C/A < 0.03[a] λ dependent	148
	577	0.45(NH_3)	*cis*; B/A = 1.2; C/A = 0.2[a] λ dependent	
$Cr(NH_3)_4(CN)_2^+$	480	0.33(NH_3)	*trans*; A/B = 2[a]	93, 94
	480	0.25(NH_3)	*cis*; C/B = 2[a] (1.2 for Q2 irradiation)	
trans-$Cr(tn)_2(CN)_2^+$	458	0.052(tnH)	$\phi(CN^-) = 0.035$ at 436 nm	225
		0.023(CN^-)		
trans-$Cr(2,3,2\text{-}tet)(CN)_2^+$	436	0.09(tetH)	15 °C; stereoretentive?	109, 110
trans-$Cr(NH_3)_4(CN)(NCS)^+$	505	0.062(CN^-)	same proportion of photoproducts for quenchable (75%) and unquenchable (25%) reaction	97
		0.02(NCS^-)		
		0.25(NH_3)		
$Cr([9]aneN_3)(NCS)_3$	488	0.05(NCS^-)		106
$Cr(tn)(CN)_4^-$	408	0.04	useful quencher	199
$Cr(py)(CN)_5^{2-}$	400	0.08(py)		262
		0.011(CN^-)	product 90% cis?	
$Cr(CN)_5(H_2O)^{2-}$	436	0.045	pH = 5.8	263
$Cr(CN)_5(OH)^{3-}$	436	0.091	pH = 14, ϕ was λ dependent	263
	462	0.063[b]	$\phi = 0.058$ at 278 K	101
	254	0.14[b]	$\phi = 0.17$ aerated	
$Cr(CN)_4(N_3)(OH)^{3-}$	436	0.062[b]	pH 12	101
	254	0.35[b]	pH = 13; $\phi = 0.34$ aerated	
$Cr(CN)_3(H_2O)_3$	436	0.07[b]	pH = 5.8	263

[a] A = 1,6-X_2-2-H_2O = *trans-mer*; B = 1,2-X_2-6-H_2O= *cis-mer*; C = 1,2-X_2-3-H_2O = *fac*. [b] Measured for disappearance of starting complex. [c] Stereoretentive water exchange.

the thermal and photoreactions, corresponding to substitution of a single acac ligand by water or hydroxide ion, depending on the pH. The quantum yield was independent of pH and irradiation wavelength within the range 350−730 nm, where at the longer wavelengths at least one-third of the excitation should be directly into the doublet state. Studies of the temperature dependence of the quantum yield of substitution for 546 nm irradiation gave an apparent activation energy of 15.5 ± 0.4 kJ mol^{-1}, much smaller than the thermal activation energy of 104 ± 1 kJ mol^{-1}. On irradiation into the 250 nm region, no redox intermediates could be detected, and the enhanced yield in this region was, therefore, attributed to reaction from a ligand-localized $\pi\pi^*$ excited state that did not efficiently internally convert to the ligand-field states. An explanation was offered in terms of the reduction in the ring bond order from 3 to 2 which favors ring distortion away from planarity on $\pi \rightarrow \pi^*$ excitation along with the effect of the consequent reduced electron density at the carbonyl oxygens, which decreases their coordinating ability.

Table 2 presents a summary of the recent studies of photosubstitution of heteroleptic complexes. A few cyanoam(m)ine examples have been included for completeness and convenience of reference in the later discussion, but note that the behavior of these complexes has been reviewed[24] in detail elsewhere. Also included but reviewed previously[14] are the extensive studies of $Cr(NH_3)_x(H_2O)_{6-x}^{3+}$ complexes.

The work reviewed earlier[1,2,4] established a pattern of reactivity of mixed-ligand complexes that was fairly well-described by the angular overlap model (AOM).[4,35,36] In this model, reaction is assumed to arise from the lowest excited quartet state, generally ^4E. In the labilized plane, the ligand with the lowest excited-state metal−ligand bond strength is preferentially dissociated. These metal−ligand bond strengths can be calculated based on the empirical σ and π parameters obtained from absorption and emission spectra interpreted in terms of the two-dimensional spectrochemical series.[67] For many systems the result corresponds to loss of the strong-field ligand from the weak-field plane, but exceptions occur for strongly π-interacting ligands such as fluoride and cyanide. The observed wavelength dependences of quantum yields are often consistent with increased involvement at shorter wavelengths of the next higher quartet state, usually $^4B_2$, which often has a different predominant reaction mode. The ^4E and $^4B_2$ bands overlap, so it is not possible to irradiate specifically into each component. Generally, the photostereochemistry is consistent with mechanistic stereochemical change and therefore with the labilization plane, edge displacement model, Figure 3.

The data in Table 2 for complexes studied since the earlier reviews reveal the interest in exploring the extent to which the above ideas are supported by the behavior of complexes containing am(m)ine and aqua, fluoro, cyano, and pyridino ligands. Table 2 also encapsulates explorations of the extent to which the electronic predispositions embodied in the above model are modified by other factors such as leaving-group abilities of the ligands, competition between different leaving ligands, and steric factors. The ensuing discussion roughly follows the order of the complexes listed, which is based on charge type and increasing ligand-field strength, but modified so that related complexes are grouped together.

The extensive studies of photoaquation, $^{18}OH_2$ exchange, and isomerization in the $Cr(NH_3)_x(H_2O)_{6-x}{}^{3+}$ complexes[14,68,69] and some of their 1,3-propanediamine analogues[70] have established that substitution of a water ligand competes very strongly with aquation of an ammonia ligand. Hence, some of the complexes that would be predicted to lose ammonia by the AOM instead substitute water preferentially. Examples are *cis*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$ and *fac*-$Cr(NH_3)_3(H_2O)_3$. This photosubstitution occurs most frequently with stereochemical change and, therefore, appears as if it were a photoisomerization. However, the quantum yield for water exchange is always greater than the quantum yield for "isomerization". This nicely parallels the reported photoaquation[71] of DMF from *trans*-$Cr(NH_3)_4(DMF)Cl^{2+}$ which gives *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ as its product. Likewise *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ "photoisomerizes"[71] with $\phi = 0.42$, presumably via the same substitution mechanism. Similar behavior has been found[70] for the first few members of the mixed tn/H_2O complexes, as listed in Table 2. The Moensteds concluded that (i) water ligands were the predominant leaving groups, (ii) the reactivity was predominantly in the plane containing the largest number of water ligands (the weakest field plane), and (iii) the stereochemistry of the products indicated entry of the substituting water ligand trans to the leaving ligand. An associative pentagonal bipyramidal transition state reached by and therefore common to both doublet and quartet excited states was favored and justified on energetic and ligand-field grounds.

A system that photoaquates ammonia with stereochemical change[72] in accord with the AOM is $Cr(NH_3)_5(NCS)^{2+}$; both ammonia and thiocyanate photoaquation have negative volumes of activation,[44] supporting the associative pathway for both reaction modes. Intriguingly, viscosity studies[45] on this and other complexes have shown strong evidence for cage effects in Cr(III) photoreactions as quantum yields decrease at higher glycerol concentrations. However, observation of a cage effect is not necessarily inconsistent with associative reaction. An increase in solvent viscosity or formation of outer-sphere complexes can also be expected to hinder solvent substitution in a photoreaction that must compete with excited-state decay processes.

Other work that agrees with the expectations of the AOM are a study of solid-state photoaquation and of solution photoanation. Thus, solid *trans*-$[Cr(en)_2Br_2]Br\cdot H_2O$ exposed to light changes color from green to red,[73] which results from substitution of the crystal water into the coordination sphere with stereochemical change to give *cis*-$[Cr(en)_2(H_2O)Br]Br_2$. The anhydrous salt is photostable unless it is irradiated in moist air. Remarkably, this photoreaction occurs with a quantum yield, $\phi = 0.26$, that is essentially the same as the solution value.

The first photoanation study[74] was carried out early in the history of Cr(III) photochemistry and focused on thiocyanate anation of $Cr(H_2O)_6{}^{3+}$ and $Cr(NH_3)_5(H_2O)^{3+}$. The first-order dependence of quantum yield on thiocyanate concentration, together with comparison of the thermal and photochemical yields, favored a mechanism involving ion-pair formation followed by photochemical outer-sphere/inner-sphere ligand exchange. A subsequent study[75] of azide and thiocyanate anation of $Cr(DMSO)_6{}^{3+}$ in DMSO solution was considered to support an associative mechanism for the process. Shortly after, Wasgestian and co-workers investigated the competition in chloride[76,77] and thiocyanate[78] solutions between photoaquation and photoanation of $Cr(NH_3)_6{}^{3+}$. With chloride, the total reaction quantum yield remained constant with increasing chloride concentration but the extent of photoanation increased at the expense of photoaquation, showing that the two processes were competitive. This was true both in acidic and alkaline solutions, the doublet state being completely quenched in the latter. The competition between Cl^- (and Br^-) and H_2O was the same for both routes, and for an assumed intersystem crossing yield of 0.7, the reaction efficiencies via the doublet and quartet states were the same, 0.45. Analogous behavior was found using thiocyanate,[78] although here a total yield increase found with increasing thiocyanate concentration was attributed to some photoredox reactions arising from outer-sphere electron transfer from thiocyanate ion to Cr(III). It has also been reported[79] that in the presence of excess KCN, $Cr(CN)_2(H_2O)_3NO$, and $Cr(H_2O)_5NO^{2+}$ react thermally to yield a tricyano species that is stable thermally but undergoes photoanation to $Cr(CN)_5NO^{3-}$.

The question of the photostereochemistry of such photoanations has recently been addressed using the molecule *trans*-$Cr(tn)_2(NH_3)Cl^{2+}$, which photosubstitutes ammonia[80] exclusively. This photobehavior represents a successful demonstration of the predictive value of the AOM, modified to recognize that the leaving-group abilities of the am(m)ine ligands[81,82] lie in the order en > NH_3 > tn, which then predicts a strong preference for ammonia labilization in the molecule. As free thiocyanate is added to an aqueous solution of *trans*-$Cr(tn)_2(NH_3)Cl^{2+}$, photoanation begins to compete with photoaquation but the total photosubstitution quantum yield remains constant. Chromatographic analysis of the $Cr(tn)_2(NCS)Cl^+$ product resulting from photoanation showed it to be the cis isomer, with an undetectable amount of trans, showing that stereochemical change is also associated with photoanation.

A study[83] of photoaquation of $Cr(NH_3)_5I^{2+}$ completes the series of halopentammines and has shown that the molecule photoaquates ammonia efficiently, $\phi = 0.28$. Measurement of any iodide photoaquation mode was difficult. This was partly because of thermal aquation of iodide by the starting material but more seriously because the $Cr(NH_3)_4(H_2O)I^{2+}$ photoproduct, presumably the cis isomer, aquates iodide 30 times more rapidly than the starting complex. This mandated measuring the time course of the iodide concentration before, during, and after photolysis, with fitting of the resulting curve to the complete differential equations for the system using the Simplex method. The best fit for the data was for $\phi(I^-) \approx 0$. This result is contrary to the AOM, which predicts that in the lowest ^4E excited state, the Cr−I bond has the weakest excited-state bond strength by about 20 kJ mol^{-1}.

The photoaquation of *cis*-$Cr(phen)_2Cl_2^+$ leads to both *cis*-$Cr(phen)_2Cl(OH_2)^{2+}$ and *cis*-$Cr(phen)_2(OH_2)_2^{3+}$ products,[84] and the quantum efficiency for the loss of starting material at pH 7 is 0.010 under argon and 0.0026 under oxygen. The presence of deoxyguanosine increases the rate of loss as much as 2-fold under argon, but only the rate of diaqua product formation is enhanced by the nucleoside. This effect was attributed to reductive quenching of the *cis*-$Cr(phen)_2Cl_2^+$ excited state by the base. In the presence of calf-thymus DNA, photolysis yielded unidentified covalent adducts with the nucleic acid. In experiments using polyribonucleosides, a preference was found for binding to the purines.

Fluoro complexes have played an important role in the development of Cr(III) photochemistry. The weak ligand-field strength of the fluoride ligand arises because of the opposing effects of its σ- and π-donor strengths, and the π-donor capability results in π-stabilization of the Cr−F bond in the quartet excited state. Thus, the photochemical aquation of one end of the ethanediamine ligand from *trans*-$Cr(en)_2F_2^+$ was an important early observation[85] suppporting the molecular-orbital photochemical models. The fact that the stereochemistry of its photo and thermal products appeared[86] to differ stimulated studies on more tractable analogues. Listed in Table 2 is the quantum yield data for *trans*- and *cis*-$Cr(NH_3)_4F_2^+$. The ammonia photoaquation mode observed is as predicted by the AOM, although there is no evidence regarding the proportion of loss of the axial versus equatorial ammonia ligands in the cis isomer. The listed photoproducts, specifically the absence of significant amounts of fac product from the cis isomer, provided the first evidence that supports the angular overlap model of photostereochemistry over a simple random edge-displacement process. The essential difference is that in the former, the motion of the involved ligands is confined to the plane of excitation. To explain the product stereochemistry, it was necessary to assume that the putative five-coordinate tbp intermediate could substitute solvent in its excited state as well as in its ground state. This photostereochemistry has now been reinterpreted in terms of the Jahn−Teller behavior of these five-coordinate intermediates as described in the sections on theoretical developments and photostereochemistry.

Many recent studies have focused on the changes in photochemistry that may be induced by steric effects involving the ligands. Surprisingly *trans*-$Cr(tn)_2F_2^+$ photoaquates[87] not tn but F^- as the dominant mode. This is an impressive change in properties arising because of an extra methylene group in the ring but can be understood in terms of differing leaving-group abilities for the various amine ligands. Thus, studies[81,82] of the $Cr(en)_x(NH_3)_{6-2x}{}^{3+}$ and $Cr(tn)_x(NH_3)_{6-2x}{}^{3+}$ series confirmed that while en is a much better leaving ligand than NH_3, tn is much worse, probably because of the stability of the six-membered, chair conformation ring it forms when coordinated to Cr. The study of the $Cr(tn)_x(NH_3)_{6-2x}{}^{3+}$ series[82] also indicated that ligand loss from the plane of excitation is competitive, i.e., the presence of an ammonia ligand in the plane of labilization reduced photoaquation of tn from the same plane. An even worse leaving ligand is cyclam, and Table 2 shows that that *cis*-$Cr(cyclam)F_2^+$ also aquates[88] fluoride efficiently as does an earlier example[89] $Cr(tren)F_2^+$. In contrast, the *trans*-Cr(tet-a)F_2^+ complex with its sterically rigid in-plane N_4 coordination is photoinert.[88]

Some parallels with this behavior can be found in mixed cyanoam(m)ine complexes. Cyano complexes have been extensively studied[90−100] by the Perugia group of Riccieri and Zinato and co-workers. Zinato has written an excellent review[24] of their synthesis, properties, spectroscopy, thermal kinetics, photochemistry, and photophysics. Listed in Table 2 are a few examples chosen to illustrate some of the phenomena mentioned above. The importance of these complexes is that, cyanide being a stronger-field ligand than am(m)ine, the lowest excited state in most of the *trans*-$Cr(N)_4(CN)Y^+$ isomers is the $^4B_2$ state for which the AOM predicts labilization of the ligand(s) in the equatorial plane. $Cr(NH_3)_5CN^{2+}$ and *trans*-$Cr(NH_3)_4(CN)_2^+$ fit the expectations nicely by photoaquating[93] ammonia exclusively, although clearly in the former compound there is an ambiguity about the position of the ammonia aquated. Compared with *trans*-$Cr(NH_3)_4(CN)_2^+$, the molecule *trans*-$Cr(tn)_2(CN)_2^+$ has a very much smaller amine aquation yield and a much larger quantum yield for cyanide, consistent with the poor leaving-group ability of tn. As Table 2 shows, the cyanide quantum yield increases for shorter wavelength irradiation. The trend to enhanced cyanide yields persists in $Cr(tn)(CN)_4^-$, where the AOM-predicted amine loss is not observed and merely a relatively inefficient loss of cyanide ligand is seen. The relative photostability of $Cr(tn)(CN)_4^-$, coupled with its low ionic charge, its high-energy absorption bands, and the near-IR emission from its long-lived doublet state, all make this molecule an excellent candidate for use as a quencher. Note that, in contrast to $Cr(tn)(CN)_4^-$, even $Cr(NH_3)(CN)_5^{2-}$ aquates ammonia[100] to a greater extent than cyanide, consistent with the AOM predictions. Interestingly, and as a final example of the complexities possible, *trans*-$Cr(NH_3)_4Cl(CN)^+$ has a very large cyanide quantum yield,[98] $\phi = 0.32$. This was attributed to an excited-state trans effect arising from the interactions of the π-donor chloro and π-acceptor cyano ligands through the Cr d orbitals in the excited state.

Some mixed aquacyano complexes have also been included in Table 2. No water exchange yields have been measured for these species, which are often difficult to study because of concurrent thermal reactions. Small yields for the disappearance of starting material have been found for $Cr(CN)_5(H_2O)^{2-}$, $Cr(CN)_5(OH)^{3-}$, and $Cr(CN)_3(H_2O)_3$. For the pentacyano complexes, this arises by photoaquation of cyanide to give a tetracyano product, $Cr(CN)_4(H_2O)_2^-$ or $Cr(CN)_4(OH)_2^{3-}$, that rapidly thermally aquates a second cyanide ligand to give the more stable tricyano complex. This behavior has been confirmed for $Cr(CN)_5(OH)^{3-}$ and extended to $Cr(CN)_4(N_3)(OH)^{3-}$ in a recent extensive study[101] of these systems. The $Cr(CN)_4(N_3)(OH)^{3-}$ was synthesized by azide substitution of a cyanide ion starting with $Cr(CN)_5(OH)^{3-}$ and is believed to be the cis-isomer based on kinetic grounds together with its UV and IR spectra. Consistent with the earlier work, cyanide yields were shown to be twice the yield for disappearance of starting material for both complexes. The final products were identified as $Cr(CN)_3(H_2O)_{3-x}(OH)_x^{x-}$ and $Cr(CN)_2(N_3)(H_2O)_{3-x}(OH)_x^{x-}$, respectively. For $Cr(CN)_5(OH)^{3-}$ it was shown that when the temperature was lowered to 278 K, the cyanide yield dropped to 1.38 cyanides per complex molecule lost, consistent with a reduced rate for the secondary thermal reaction to release cyanide ion from the photoproduct. The cyanide photoaquation mode observed for both complexes is consistent with the AOM predictions, although there is uncertainty in the appropriate parameter values for azide.

Another interesting ligand is pyridine; it is a π acceptor like cyanide but as its bonding strength to Cr is smaller, it may be better suited to reveal information about the role of π-bonding in the excited-state chemistry. Consistent with this expectation, in the complex $Cr(NH_3)_5(py)^{3+}$, the observed preference for photoaquation of the weaker-field py over ammonia can be attributed to the weakening of both the Cr−py σ- and π-bonding in the excited state.[102] This is the first pentammine to show preferential loss of the weaker-field ligand, and the result is in accord with the predictions of the AOM[4] and some early models.[103−105] The observation also confirmed the π-acceptor nature of the pyridine ligand, which had been disputed. This, therefore, provides an example of the use of photochemical properties to infer ligand characteristics. The complex was also unusual in showing different py/NH_3 quantum yield ratios of ∼1 and ∼2 for the unquenchable and quenchable contributions to reaction, respectively. Finally, excitation into the py ligand-localized absorption band gave an efficiency of 0.7 for population of the Cr-localized LF states. The stereochemistry of the product from ammonia loss was partly trans, again an unusual result analogous to that for the fluoropentammine series. This interesting system is further discussed in the sections on mechanistic studies and photostereochemistry.

A complex that combines these two π-acceptor ligands, $Cr(py)(CN)_5^{2-}$, photoaquates pyridine in accord with the AOM, along with minor yields of cyanide. Both yields are reduced in DMSO. None of the photochemistry is quenchable with $Co(sep)^{3+}$, which quenches the phosphorescence. The photochemistry, therefore, originates in the quartet states and is influenced by solvent effects, attributed to hydrogen bonding or protonation of cyanide and the influence of solvent orientation toward anionic complexes.

A series of $Cr([9]aneN_3)X_3$ complexes with X = Br, F, CN, and NCS were prepared,[106] but unfortunately only the last was sufficiently soluble to permit photochemical experiments. In DMSO, DMF, or acetonitrile solutions irradiated at 488 nm, $Cr([9]aneN_3)(NCS)_3$ photosolvates thiocyanate ligand, with $\phi = 0.05$. This is not the AOM-predicted mode but that is not surprising given the photostability of the $[9]aneN_3$ ligand. The molecule phosphoresces at 753 nm with a decay lifetime[106,107] of about 50 μs, and in oxygen-saturated acetone solution, quenching by oxygen generates singlet oxygen with an efficiency of 0.48. The molecule was used as a sensitizer[108] in a study of reversible energy transfer with $Cr(CN)_6^{3-}$ as the acceptor in degassed DMSO solutions. The reverse energy transfer was about 50−65% efficient, and the measured rates gave a calculated energy barrier for the back transfer of between 10.5 and 12 kJ mol^{-1}, consistent with the spectroscopically derived doublet energy difference of about 10 kJ mol^{-1} for the two complexes.

In summary, these studies show that a large number of complexes do conform to the predictions of the AOM which are based on ligand σ and π parameters. However, the nature of the leaving ligand cannot be reliably predicted over a very wide range of ligand types and structures. This may sometimes reflect problems with the AO parameter values, but other factors that seem to be important are (i) the leaving ability of the ligand relative to those of the other ligands in the plane of excitation, (ii) σ and π interactions between ligands in the plane of excitation, (iii) steric aspects, e.g., rigidity of a ligand occupying all positions in an equatorial plane. It is interesting that despite these reservations regarding prediction of the labilization mode, for most of the complexes discussed here, there is good adherence to the stereochemical expectations of the AOM.

The last factor in the above list is illustrated by the observed photoinertness of *trans*-Cr(cyclam)L_2^{n+} complexes for L = Cl, NH_3, F (actually for tet-a), and CN to be discussed later. The photoinert nature of these complexes has supported the idea that stereochemical change may be a universal requirement of Cr(III) photosubstitution reactions. The situation seems clear for complexes in which labilization is in a plane containing the weak-field axis (^4E states). Products observed are those consistent with stereochemical change, and apparently incorporation of a ligand that prevents the necessary rearrangement turns off the photochemistry. However, for complexes reacting via the ^4B state, the situation is much less clear.

The study of *trans*-Cr(2,3,2-tet)$(CN)_2^+$ included in Table 2 was undertaken to try to clarify this issue. It was anticipated that the lowest $^4B_{2g}$ state should preferentially aquate a primary amine ligand. The idea was that if stereochemical change was required in this process, then the molecule should be photoinert as the remaining ligand rings prevent the necessary trans entry of a water ligand. Experimentally, however, the molecule aquated an amine ligand[109,110] with $\phi = 0.09$ to give a photoproduct that could be recoordinated to the starting complex with its trans cyano ligands, implying a stereoretentive photoaquation. The ligand mode but apparently not the stereochemistry fit the AOM. The discussion of possible explanations for this result is left to the photostereochemistry section.

Finally, an unusual photoreaction[111] of the (thiooxalato-*O,S*)bisethylenediamineCr(III) complex is mentioned here because the primary step is a ligand photoaquation. Photolysis of $Cr(en)_2(SC_2O_3)^+$ in acidic aqueous solution leads to release of H_2S and formation of $Cr(en)_2ox^+$ product. The mechanism proposed involves photoaquation of thiooxalate to give a monodentate thiooxalate intermediate. Protonation of the ligand then promotes hydrolysis of the C−S bond to generate H_2S and monodentate oxalate, which then recoordinates to Cr(III). Consistent with this mechanism, the quantum yield was pH-dependent, increasing from 0.080 at pH 5.0 to 0.160 at pH 2.8.

B. Photoisomerizations

Many Cr(III) photosubstitution reactions occur with stereochemical change, and although some authors have referred to this merely as photoisomerization accompanying substitution, the evidence just discussed shows that this usually results from the symmetry-controlled concerted substitution process illustrated in Figure 3. The water exchange with stereochemical change seen[1,68,70,112] in aquaam(m)ine complexes mimics simple isomerizations. However, the concern of this section is to deal with the other photoisomerizations that are found and to explore their mechanisms. The main examples found are photoracemization and related *fac*/*mer* isomerizations in complexes with unsymmetrical bidentate ligands. The literature survey did not unearth any studies of photochemical linkage isomerization.

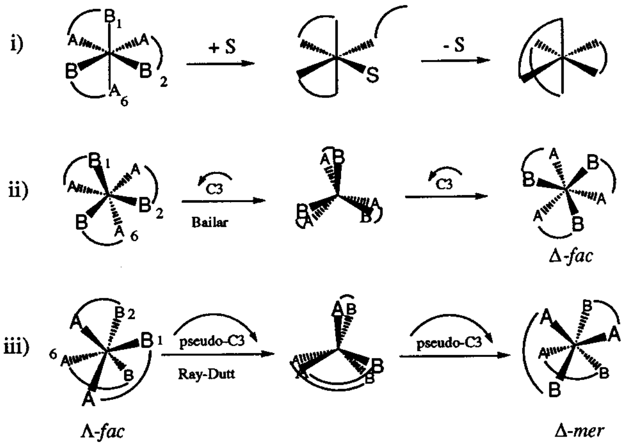

Figure 4. Mechanisms for photoracemization and isomerization. All three mechanisms shown begin with the Λ-*fac* isomer. The 1, 2, and 6 positions have been labeled to assist the viewer in relating the different orientations shown. (i) Bond rupture leading to six-coordinate intermediates with recombination to starting material statistically can lead to all possible outcomes. (ii) Bailar twist around C_3 axis gives racemization without isomerization. (iii) Ray−Dutt twist around pseudo-C_3 axis gives simultaneous racemization and geometric isomerization.

Early studies established the common occurrence of photoracemization, and various authors have considered the mechanisms. As shown in Figure 4, the contenders are (i) detachment of one end of a bidentate ligand and recoordination, (ii) a Bailar twist, or (iii) a Ray−Dutt twist. The first mechanism can be dissociative or associative, and the transition state leading to the intermediate shown can have different geometries. This gives a number of possibilities for the extent of photoracemization and photoisomerization for the unsymmetric ligand case. Consequently, in Figure 4, the identities of the ligand atoms in the intermediate(s) and product(s) have not been specified for mechanism a. The statistical ratios for products based on equal probabilities of all bond breaks and recombinations have been tabulated[113] for all the mechanisms in the bond-rupture category. Figure 4 shows that the Bailar twist leads to racemization alone, while the Ray−Dutt twist leads to isomerization accompanied by racemization.

A summary listing of observed photoracemization quantum yields is given in Table 3. A substitutional mechanism was proposed[114] for photoracemization of $Cr(ox)_3^{3-}$ based on wavelength-dependence, temperature-dependence, and solvent-dependence results in ethanol/water mixtures and comparison of the thermal and photochemical behaviors. Both the deuterium isotope effects and the extents of oxalate exchange with ^{18}O from $H_2{}^{18}O$ were parallel for the thermal and photoracemizations. In contrast, photoracemization was not acid-catalyzed, was less solvent dependent, and had an apparent activation energy of only 13 kJ mol^{-1} compared with 72 kJ mol^{-1} for the thermal reaction. These similarities and differences were explained by a mechanism involving photochemical generation of the intermediate,

Table 3. Photoracemization Quantum Yields

complex	λ_{irrad}, nm	ϕ	comment[a]	ref
$Cr(ox)_3^{3-}$	420	0.045	4 °C in 30 mol % ethanol	114
	570	0.041		
	697	0.034	$E_a(\phi) = 13$ kJ mol^{-1}	
$Cr(ox)_3^{3-}$	420	0.110	25 °C, ϕ reduced in DMSO/H_2O mixtures	115
$Cr(acac)_3$	365, 405, 434, 546, 577	$(6.3, 4.5, 4.9, 5.4, 4.5) \times 10^{-3}$	±5%, λ independent, in chlorobenzene; $E_a(\phi) = 10$ kJ mol^{-1}	116
$Cr(atc)_3$	577	$(7.6 \pm 1) \times 10^{-4}$	$\Delta \rightarrow \Lambda$ *fac*/*fac* rac.	113
		$(9 \pm 3) \times 10^{-4}$ estd	$\Lambda \rightarrow \Delta$ *fac*/*fac* rac.	
		$(12 \pm 3) \times 10^{-4}$	$\Delta \rightarrow \Lambda$ *mer*/*mer* rac.	
		$(35 \pm 4) \times 10^{-4}$	$\Lambda \rightarrow \Delta$ *mer*/*mer* rac.	
		$(10 \pm 1) \times 10^{-4}$	Δ retentive $f \rightarrow m$ isom.	
		$(4 \pm 0.6) \times 10^{-4}$	Λ retentive $f \rightarrow m$ isom.	
		$(47 \pm 5) \times 10^{-4}$	Λ-*fac* → Δ-*mer*	
		$(6 \pm 0.6) \times 10^{-4}$	Δ-*mer* → Λ-*fac*	
			ϕs are λ dependent	
$Cr(phen)_3^{3+}$	350(CT)	0.016	86% quenchable	117
	457.9(LF)	0.015		
	457.9	0.0372	$\phi = f(\mu$, pH, T, [Cr])	119
	465.8	0.0292		
	488	0.0299		
	514.5	0.0177		
$Cr(phen)_2ox^+$	350, 502	0.21	unquenchable? $E_a(\phi) = 5.8$ kJ mol^{-1}	117
$Cr(phen)(ox)_2^-$	600	0.081 ± 0.003	25 °C, $\phi = f(I, [Cr])$	127
$Cr(tfa)_3$	546	$(24 \pm 3) \times 10^{-4}$	*fac*/*fac* rac.	128
		$(38 \pm 3) \times 10^{-4}$	*mer*/*mer* rac.	
		$(12 \pm 3) \times 10^{-4}$	retentive $f \rightarrow m$ isom.	
		$(2.4 \pm 0.6) \times 10^{-4}$	retentive $m \rightarrow f$ isom.	
		$(36 \pm 9) \times 10^{-4}$	*fac* → *mer* rac.	
		$(7.1 \pm 1.7) \times 10^{-4}$	*mer* → *fac* rac.	
mer-$Cr(tfa)_3$	546	$(18 \pm 0.3) \times 10^{-4}$	*mer* → *fac* isom., in ethanol	130, 140
	408	$(21 \pm 1) \times 10^{-4}$		
	366	$(17 \pm 2) \times 10^{-4}$		
$Cr(en)_3^{3+}$	>400, broad	0.015	measured against extensive photoaquation	131
Λ-*fac*-Cr(S-tryp)$_3$	488	0.03	Λ-*fac* → Δ-*fac* only	132

[a] rac. = racemization. isom. = isomerization.

$Cr(ox)_2(ox^-)(H_2O)^{3-}$, having a monodentate oxalate, as occurs in the nonacid-catalyzed thermal pathway. A further study[115] of the solvent dependence of this photoracemization, backed by NMR measurements of the solvent cage composition in DMSO/water mixtures, supported this mechanism. It was found that DMSO preferentially solvated the complex but that there was a decrease in the photoracemization yield associated with DMSO solvation despite it being a good ligand. This was explained in terms of a cooperative effect of the solvent molecules in the dechelation of the complex, because of stabilization of the monodentate oxalato ligand through H bonding to H_2O.

Photoracemization of $Cr(acac)_3$ in chlorobenzene solvent was found[116] to be 10-fold less efficient than that found above for $Cr(ox)_3^{3-}$ but again showed a small apparent activation energy of 10 kJ mol^{-1}. The authors considered both bond-rupture and twist mechanisms to be possible.

A study[113] of all four diastereoisomers of tris[(+)-3-acetylcamphorato]Cr(III) complex, $Cr(atc)_3$, showed they could be interconverted thermally at over 100 °C or photochemically with quantum yields of about 10^{-3} on visible or UV irradiation. HPLC analysis of the products obtained on photolysis at 577, 350, and 254 nm and thermalization at 134 °C enabled measurement of 8 of the 12 quantum yields connecting the four diastereomers, with the remainder being estimated from photostationary state data. The quantum yields obtained for irradiation at 577 nm are shown in Table 3. They show that racemization is less important than isomerization and that the most efficient process involves Λ to Δ racemization accompanied by fac to mer isomerization. Comparison of the quantum yields with the statistical ratios expected for the various mechanisms shown in Figure 4 presented a number of difficulties, but the authors concluded that the data, particularly for the Δ-*fac* isomer, were best fit by a bond-rupture mechanism leading to a square pyramidal intermediate with the monodentate ligand in the axial position. In this analysis, the authors did not consider the phenomenon of stereochemical change in Cr(III) photoprocesses, which had been discovered a few years earlier but had not received general recognition.

On irradiation of $Cr(phen)_3^{3+}$ at wavelengths ≥350 nm, photoracemization is the dominant photoreaction. Quenching experiments with iodide ion implicated the lowest excited quartet state as a reactive state.[117] This conclusion was supported by the results of a photoracemization study on the oxalatobis(1,10-phenanthroline)chromium(III) ion.[117] Subsequent doublet quenching studies[118] of $Cr(phen)_3^{3+}$ showed that although I^- is about 100 times more effective a quencher than SCN^-, both ions quench the phosphorescence completely, along with 95% of the photoracemization, which therefore involves the system reacting via the doublet. The nonquenchable fraction of the photoracemization quantum yield, which can be attributed to reaction from quartet excited states, is wavelength-dependent in the range 458−514 nm, and this was taken[119] to indicate a dependence of the intersystem crossing yield on the initial vibronic state populated. A wavelength dependence of intersystem crossing yield in the red-edge of the first ligand-field band was also established for the complex $Cr(bpy)_3^{3+}$.[120] It is important to note that these studies showed that intersystem crossing is competitive with vibrational relaxation of the quartet state. Of interest also is the partial photoresolution observed for $Cr(phen)_3^{3+}$ on irradiating with circularly polarized light[121] or in a medium containing chiral anions.[122]

Although no specific study of photoracemization was involved, also relevant are the detailed studies of the thermal and photoreactions of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$. The substitutional mechanism via an aqua-substituted intermediate was supported by detailed studies of $Cr(phen)_3^{3+}$ photoreaction as a function of pH and temperature in the presence and absence of doublet-state quenchers.[123] The authors argued that since most of the reaction occurs via the doublet state, a twist mechanism would not be expected because this state is not distorted with respect to the ground state. Also, the photoracemization is pH-dependent, which would not be expected for a twist mechanism. They concluded that the photoreaction and photoracemization were competitive processes involving an aqua-substituted intermediate.

The photochemistry and photophysics of $Cr(bpy)_3^{3+}$ [124] and $Cr(phen)_3^{3+}$ [125] following pulse excitation at 347 nm were studied and compared in pH 2.3−11.0 aqueous media by conductivity and optical detection methods. For both complexes the quantum yield for net polypyridyl ligand loss increased with hydroxide ion concentration: for $Cr(phen)_3^{3+}$ to a maximum of 0.08 at pH 11.0. This reaction was ascribed to attack of hydroxide ion on a six-coordinate aquamonodentate intermediate which could either recoordinate with racemization or lose polypyridyl ligand with formation of diaqua product. This is supported by the factor of 2 relating the quantum yields of 0.08 found for net polypyridyl photoaquation in base and 0.038 found for photoracemization in acid, since the recoordination of the aqua/monodentate polypyridyl intermediate in acid medium will lead to enantiomeric change only 50% of the time. The mechanistic conclusions of this work differ mainly from the earlier studies of polypyridyl complexes[123,126] in suggesting that the intermediate aqua/hydroxo complex is six- rather than seven-coordinate.

Photoreaction via both the quartet and doublet states was also found for $Cr(phen)(ox)_2^-$, irradiated at pH = 6 with seven different laser wavelengths in the first quartet band (514.5, 529, 575, 584, 600, 614, and 630 nm). Photoracemization was the only reaction observed. Quantum yields decreased as light intensity increased, interpreted in terms of intensity-dependent and -independent paths. The intensity-independent path was attributed to reaction from the short-lived quartet state, while the intensity-dependent path was explained in terms of formation of the usual aquamonodentate intermediate that could photolyze to the starting enantiomer by absorption of a second photon or otherwise rechelate with racemization. This pathway was quenched by iodide, was enhanced by ground-state complex concentration, and declined in importance for longer wavelength irradiation, all consistent with a route via the doublet state. The two-photon path was also subject to circular polarization selectivity, in contrast to the quartet pathway.[127]

The above studies favored photoracemization via solvento-substituted intermediates. Others have indicated that twist mechanisms may also play a role.

mer- and *fac*-$Cr(tfa)_3$ were studied in chlorobenzene, and quantum yields for all possible combinations, Table 3, of photoisomerization and/or photoracemization were obtained for irradiation at 546 nm. Since all possible products corresponding to racemization with and without isomerization were observed, it was concluded[128] that both twist and bond-rupture mechanisms were occurring. A later study[129,130] of *mer*-$Cr(tfa)_3$ in various solvents explored the wavelength dependence and excited-state participation in these reactions. Mer to fac isomerization was the dominant process observed at wavelengths ≥366 nm, but for photolysis at 254 nm, both isomerization and redox decomposition occurred, with the quantum efficiency of the latter pathway displaying a pronounced solvent dependence. The results showed there were two photoactive excited states in the complex, assigned as the ligand-field quartet, $^4T_{2g}$, and a higher lying state with appreciable ligand to metal charge-transfer character.

An initial study[30] of the loss of optical activity of chiral $Cr(en)_3^{3+}$ on photolysis did not distinguish between photoracemization and formation of achiral or stereochemically changed aquated photoproducts. However, the observations of wavelength-dependent photoreaction and phosphorescence yield quenching by hydroxide were useful in showing that intersystem crossing was competitive with $^4T_{2g}$ vibrational equilibration. In a later study,[131] photoracemization was distinguished from photoaquation and the quantum yield for the photoracemization of $Cr(en)_3^{3+}$ was found to be 0.015, independent of proton concentration in the range 0.08−1.0 M. This acid independence was considered to disfavor the bond-rupture mechanism via a one-ended basic intermediate. A quartet state twist reaction via a trigonal prismatic transition state, a Bailar twist, was proposed. It was argued that such a transition state was supported by angular overlap molecular orbital studies of Burdett.[26]

A recent investigation[132] of Λ- and Δ-*fac*-Cr(S-tryp)$_3$ has been interpreted as providing strong evidence for such a photoinduced Bailar twist. On ligand-field excitation at 488 nm, the Δ-*fac* isomer is essentially photoinert while the Λ-*fac* isomer undergoes complete conversion to Δ-*fac* with a quantum yield of 0.03. The complete photoinversion implies a key stereochemical role for the asymmetric carbon of (*S*)-tryptophan, which is consistent with molecular mechanics calculations which show Δ-*fac* to be more stable by ~30 kJ mol^{-1}. The observed optical inversion without *fac* → *mer* isomerization suggests a Bailar twist mechanism. This preference for a Bailar over a Ray−Dutt twist was considered to be consistent with the small chelate bite of 1.31 estimated for the complex. A Bailar twist should be energetically preferred[133] over a Ray–Dutt twist for chelate bite values <1.4. It would be of considerable interest to explore the excited-state participation in this photoreaction.

In summary, many authors have considered photoracemization to occur via bond-rupture intermediates with evidence in favor of reaction via both quartet and doublet states. Other work[132,134] has pointed to participation of a twist mechanism, and the suggestion[131] has been made that the quartet state may react via a twist mechanism. Such a reaction mode could be consistent[5] with a published group-theoretical approach to prompt quartet-state reactions. However, a problem with the use of chiral asymmetric bidentate ligands to distinguish between geometric and optical isomerization is that it unfortunately generates diastereoisomers, and this introduces thermodynamic driving forces into the isomerization steps. This driving force rather than a specific twist mechanism could then explain the product distributions seen. Also, none of the authors has specifically addressed the role of the stereochemical change shown in Figure 3 on the outcome of photoracemization and photoisomerization via bond-rupture intermediates. Photoracemization appears to be a subject that merits further investigation.

C. Redox Processes

Most Cr(III) complexes exhibit intense absorptions in the near UV region below about 350 nm that can be assigned as ligand to metal charge transfer (LMCT) bands. Irradiation into the LMCT bands can lead to efficient internal conversion to the ligand-field states. For complexes showing this behavior, photosubstitution reactions are seen with the same or sometimes lower quantum yields as for ligand-field irradiation.[24,135] Conversely, other complexes show redox chemistry on charge-transfer excitation, giving results that support photoreaction via a transient Cr(II) species, usually assumed to be a caged solvent-separated radical pair analogous to those seen for Co(III) complexes.[1] This radical pair species can subsequently react by two pathways. Back electron transfer can occur to give a Cr(III)-solvated product plus free ligand or complete solvolysis to $Cr^{2+}(aq)$ and free ligands may result.

Irradiation of $Cr(NH_3)_5N_3^{2+}$ at pH 1 in the ligand to metal charge-transfer band was reported to lead to redox decomposition[136] to a Cr(II) fragment and azide radical with quantum yields of 0.45 at 313 nm and 0.4 at 263 nm, whereas at longer irradiation wavelengths in the ligand-field bands, photoaquation occurs to yield $Cr(NH_3)_4(H_2O)(N_3)^{2+}$. In a subsequent study[137] of the molecule, both redox and nitrene pathways were reported and their quantum yields obtained as a function of irradiation wavelength. The formation of azide radical was inferred based on flash photolysis evidence, and 1.5 mol of nitrogen was found per mole of complex decomposed. Both photoprocesses showed threshold energies which were in agreement with previous results and proposed models,[137] and the photoactive state for both pathways was thought to be LMCT. In a later study,[138] irradiation of the same complex at 313 nm gave 1 mol of nitrogen per mole of decomposed complex and the flash photolysis results were interpreted as showing that less than 12% of the reaction could be accounted for by a photoredox mode producing azide radical. The main reaction mode was instead proposed to be cleavage of the azide $N-N_2$ bond to give the reactive $Cr(NH_3)_5N^{2+}$ nitrene intermediate. In the presence of HCl, this forms $Cr(NH_3)_5NH_2Cl^{3+}$, a known oxidant of iodide ion. By following this oxidation process as a function of HCl concentration, it was shown that its limiting quantum yield was equal to the quantum yield of decomposition of the starting complex; the main photolysis mode was, therefore, formation of the nitrene intermediate. This work also concluded there were difficulties in the earlier work with the measurement of the extent of photoredox reaction by scavenging of redox products (presumably Cr(II)) by Co(III) complexes. It appears that species derived from the nitrene pathway are also capable of reducing Co(III) complexes, and the authors recommended caution in the use of this probe technique.

Photolysis[139] of $Cr(NH_3)_5Br^{2+}$ in the LMCT region led to reduction of Cr(III) and oxidation of Br^-, producing $Br_2^{\bullet -}$ radical anions which were detected in flash photolysis studies. The redox quantum yield was again wavelength-dependent with a threshold in the second ligand-field quartet absorption band.

Irradiation at 295 and 250 nm of the charge-transfer (CT) bands of *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ resulted[99] in aquation of all three ligands. By quenching studies with $Cr(C_2O_4)_3^{3-}$ and comparison between the quantum yields on CT and LF excitation, the efficiency of conversion from the LMCT state to the LF states was estimated to be 0.6. The intrinsic LMCT photoreactivity was shown to be largely aquation of thiocyanate ion ($\phi \approx 0.09$), consistent with the $\pi(NCS^-) \rightarrow e_g^*(Cr)$ nature of the LMCT band. The other possible fate of the LMCT state, formation of $Cr^{2+}(aq)$ with aquation of all ligands, was estimated to occur about 10–20% of the time and accounted for the small yields of free ammonia and cyanide.

Study[130,140] of *trans*-$Cr(tfa)_3$ in several nonaqueous solvents also revealed redox photochemistry for irradiation at 254 nm. Both isomerization and redox decomposition occurred, but the redox quantum yield displayed a pronounced solvent dependence, the proportion increasing markedly in hydrogen-donor solvents such as ethanol and 2-propanol. The redox process was attributed to a hydrogen-atom transfer reaction between the LMCT excited state and the solvent, with subsequent thermal reactions to give free ligand and solvated chromium(II) complex. That is

$$trans\text{-}Cr(tfa)_3 \rightleftharpoons {}^*Cr(tfa)_3 \rightarrow Cr(II)(tfa)_2(tfa^\bullet) \qquad (5)$$

$$Cr(II)(tfa)_2(tfa^\bullet) \rightarrow trans\text{- or } cis\text{-}(tfa)_3 \qquad (6)$$

$$Cr(II)(tfa)_2(tfa^\bullet) + ROH \rightarrow Cr(tfa)_2 + H(tfa) + RO^\bullet \qquad (7)$$

Competing with this redox decomposition is the internal conversion to the ligand-field states responsible for isomerization. A similar study[66] of $Cr(acac)_3$ reported a 4-fold increase in the photosolvation quantum yield on 250 nm irradiation in 50% by water/ethanol solvent. The authors reported no evidence for redox products, but since the net chemistry parallels that for $Cr(tfa)_3$, it may well occur by the same redox intermediate mechanism.

Short-wavelength excitation of $Cr(bpy)_3^{3+}$ and some analogues in methanol has also been shown[141] to produce $Cr(bpy)_3^{2+}$ in competition with population of the LF doublet state. $Cr(bpy)_3^{2+}$, which absorbs at 560 nm, was considered to be formed by electron transfer to $Cr(bpy)_3^{3+}$ from a methanol molecule, which eventually forms formaldehyde stoichiometrically. By selective excitation of one Cr(III) polypyridyl to generate its Cr(II) form in a mixture of two distinguishable polypyridyls, this photoredox chemistry was used to show that the self-exchange rate constant was 4×10^9 M^{-1} s^{-1}, approximately diffusion-controlled.

Redox chemistry has also been reported[142] for Cr polypyridyl units incorporated into polymers. The materials used were $Cr(NN)_2(PAA)$ and $Cr(NN)_2(PMA)$, where NN = bpy and phen, PAA = poly(acrylic acid), and PMA = poly(methacrylic acid). Long-wavelength irradiation led to inefficient photoaquation of polypyridyl ligands, a process parallel to the thermal reaction, with quantum yields in the range $(0.4-5) \times 10^{-3}$ for the various compounds studied. On irradiation into the CT region below 350 nm, however, a new photoreaction was seen. For the two PAA complexes, transient absorption was seen in the 470 nm region in laser flash photolysis experiments. This absorption was attributed to alkyl radical Cr(III) intermediates, produced by polymer−carboxylate ligand to Cr(III) charge transfer to give a $Cr(II)polymerCOO_2^{\bullet}$ species, followed by loss of CO_2 from the acid radical and coordination to Cr of the resulting carbon-based radical. Analogous intermediates did not form with the PMA complexes, and this was considered a result of the steric effect of the methyl group.

An excited-state redox reaction has also been reported for a number of mixed-ligand cyano Cr(III) complexes and is discussed in a recent review.[18] This chemistry is of particular interest when carried out in alkaline solution in the presence of oxygen as the Cr(II) complexes generated by the primary photoredox processes of the LMCT state are oxidized to chromate by thermal reactions under these conditions. Formation of chromate by this route has been reported[143] for 265 nm photolysis of $Cr(CN)_6^{3-}$ ($\phi = 0.06$) and $Cr(CN)_5OH^{3-}$ ($\phi = 0.025$) in oxygen-saturated 1 M KOH. Chromate ion is also generated[144] by 436, 366, and 313 nm irradiation of $Cr(CN)_5NO^{3-}$ in oxygen-saturated solutions in the pH range 7−13. Here, a redox reaction was attributed to the redox reactivity of ligand-field states, but note that this is under solution conditions with a formally Cr(II) complex for which thermal oxidation to chromate also occurs.

A series of $CrA_2(NCS)_4^-$ (A = NH_3, aniline, *n*-propylamine, morpholine) and $Cr(A-A)(NCS)_4^-$ (A−A = en, tn) complexes showed[145] ligand-field absorption maxima slightly shifted to longer wavelengths in the order NH_3 < en, tn < *n*-propylamine < morpholine < aniline. On charge-transfer excitation at 254 nm, they all photosubstituted thiocyanate ion and, with exception of the aniline complex, also decomposed to yield Cr(II) and $(NCS)_2^{\bullet-}$ radical, both of which were seen in flash photolysis experiments. In air-saturated methanol, about 10% of the Cr(II) was oxidized to chromate(VI). Again, the observed quantum yields could be accounted for by a mechanism involving two fates for the LMCT state: (i) formation of labile Cr(II) and thiocyanate radical and (ii) replacement of thiocyanate by solvent. For $Cr(NH_3)_2(NCS)_4^-$, the quantum yields for these processes were 0.06 and 0.23, respectively, while for the anilino analogue they are ∼0 and 0.17.

Photoredox processes leading to formation of chromate ion have also been found[146] on 254 nm irradiation of a series of binuclear and mononuclear Cr(III) ammine complexes, namely, the $(NH_3)_5CrOHCr(NH_3)_5^{5+}$, $(NH_3)_5CrOHCr(NH_3)_4(H_2O)^{5+}$ and $(NH_3)_5CrOHCr(NH_3)_4Cl^{4+}$, $Cr(NH_3)_5(H_2O)^{3+}$, $Cr(NH_3)_5Cl^{2+}$, and $Cr(NH_3)_6^{3+}$ complexes. In chloride- or perchlorate-supporting electrolytes, chromate was found only when molecular oxygen was present. The photosubstitution was also accompanied by some cleavage and photosubstitution reactions seen only on LMCT irradiation and not from the ligand-field bands, demonstrating inefficient internal conversions and contrasting photochemical pathways to these products. From the dependence of Cr(VI) yields on chloride concentration, it was concluded that ion pairs were involved in the process. Also it was argued that since oxygen did not thermally oxidize $Cr^{2+}(aq)$ to chromate under the authors' conditions, the LMCT excited state must be directly oxidized by molecular oxygen to an oxidation state above Cr(III). When nitrate was the supporting electrolyte, molecular oxygen was not required and chromate formation was accompanied by the reduction to nitrite of 1.4−1.8 mol of nitrate per mole of chromate formed. Again, this process was assumed to involve LMCT in a complex/nitrate ion pair but now resulting in Cr(II) and NO_3 radical, followed by back reaction prior to cage escape to oxidize the Cr(II) above Cr(III) and hence eventually to Cr(VI).

Further support for these redox processes comes from studies[147] of electrogenerated chemiluminescence (ECL) in aprotic solvents. For $Cr(CN)_6^{3-}$, strong ECL which matches its phosphorescence spectrum is observed in DMF and CH_3CN when the potential of a Pt working electrode is stepped from about +2.2 to −2.0 V (vs a Ag wire quasi-reference electrode). The formation of excited-state $Cr(CN)_6^{3-}$ on stepping to the cathodic limit potential was ascribed to exergonic redox reaction between the $Cr(CN)_6^{4-}$ produced and an oxidant of solvent origin produced at the anodic limit potential. An ECL signal which matches the corresponding phosphorescence spectrum is also observed for $Cr(bpy)_3^{3+}$ in CH_3CN solution on pulsing the working electrode between +2.2 and −1.6 V.

IV. Theoretical Studies

The angular overlap model of photostereochemistry has been extended to incorporate Jahn–Teller effects that could influence the final product distribution formed from the postulated five-coordinate intermediates in the reaction pathway, Figure 3. This extension of the original model was stimulated by the observation[148] that the same excited-state five-coordinate trigonal bipyramidal (tbp) intermediate was predicted to form in the photoreaction of *trans*- and *cis*-$Cr(NH_3)_4F_2^+$ yet gave rise to different proportions of the final photoproducts, *cis-mer*- and *trans-mer*-$Cr(NH_3)_3(H_2O)F_2^+$, Table 2. To account for these product differences, it was necessary to assume[148,149] that, depending on its origin, the intermediate reacted from its excited and ground states in different proportions. Such behavior has now been reinterpreted by consideration of the Jahn–Teller excited- and ground-state potential surfaces for the square planar (sp) and tbp intermediates. Both a summary of the conclusions[150] and a detailed treatment[20] have been published, and only a summary will be presented here.

An sp CrL_5 fragment is Jahn–Teller active with respect to an e′ bending mode. This gives rise to excited- and ground-state surfaces with 3-fold symmetry which intersect at the symmetric tbp configuration as shown diagramatically for L = N in the upper part (a) of Figure 5, based on Ceuleman's[20] figure. The diagram shows the three possible sp intermediates arranged in a triangle around the central tbp species. The nitrogen atoms have been labeled and the sp intermediates oriented so that it is easy to see how, starting at the tbp configuration, an increase in one of the three equatorial N*x*–Cr–N*y* angles from 120° to 180° leads to each of the three sp species shown. The energy splitting between the excited-state surface and the ground-state surface is maximum at the sp configuration, while at the tbp configuration the two states are degenerate. The crossing point in the diagram represents the conical intersection between the ground- and excited-state surfaces.

In this theory, photodissociation of a ligand from the excited quartet state creates an excited-state sp fragment at one of the three sp entry points on the excited-state surface, chosen here as P. The antibonding electron density on the Cr–N axes causes the system to decay on the excited-state surface by a decrease in the N1–Cr–N3 angle, bringing the fragment toward the tbp configuration. At the tbp configuration, the system encounters the conical intersection with the ground-state surface; here there will be a tendency for the nuclear decay momentum to carry the molecule further toward the ground states of the two tbp intermediates, at the opposite (right) side of Figure 5a. In these ground-state sp intermediates there is no antibonding electron density at the vacant ligand site and rapid recombination with solvent will result in a product that shows mechanistic stereochemical change.

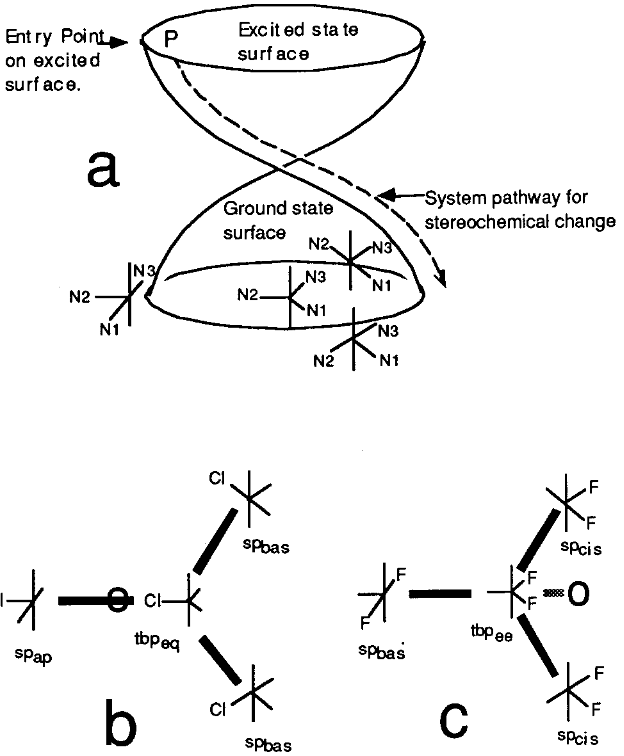

Figure 5. Jahn–Teller model of photostereochemistry via five-coordinate intermediates. Symbols: ap = apical; bas = basal; ee = equatorial–equatorial. (a) Upper and lower excited-state surfaces for the trigonal bipyramidal (tbp) and the three square planar (sp) intermediates possible for a $Cr(N)_5$ fragment. Dissociation of a ligand per Figure 3 injects the system onto the excited-state surface at one of the sp entry points, e.g., P. Decay leads to the tbp configuration, which is the degeneracy point for the excited- and ground-state surfaces. After crossing to the lower surface at this point, the nuclear momentum of the system will carry it forward to the sp transverse intermediates, leading to recoordination of solvent with mechanistic stereochemical change. (b) For a $Cr(N)_4X$ fragment where X is a weaker ligand, such as for X = Cl, the degeneracy point, O, now lies on the path from sp_{ap} to tbp_{eq}. Surface crossing and nuclear momentum again lead to the transverse sp_{bas} intermediates for which recoordination of solvent gives stereochemical change. (c) For a tbp fragment with two weaker field ligands such as $Cr(N)_3F_2$, the crossing point, O, now lies on the decay coordinate beyond the tbp_{ee} configuration. For entry at the sp_{bas} point, this leads to a more random decay to the three sp ground states and a more random distribution of products.

Introducing a heteroligand to generate a CrL_4X sp intermediate causes little change in these surfaces except that it moves the crossing point between excited- and ground-state surfaces away from tbp geometry. The direction of this shift in position depends on whether X is a stronger or weaker ligand than L. This is shown for the weak-field case in the view from above, part b of Figure 5, where the crossing point is indicated by the circle. The heavy lines indicate the distortion coordinates connecting the different species; excited states are above the plane of the paper and ground states below. Typically, photodissociation of a ligand creates the excited-state sp_{ap} fragment on the excited-state surface and the system then decays toward the tbp configuration. Since the crossing point lies on the same side of the tbp geometry as the entry point, decay brings the system directly to the crossing point where it will transfer to the ground-state surface and its momentum will cause it to form the sp_{bas} five-coordinate intermediates. On recombination with solvent, the stereochemically changed cis product results.

In contrast, if entry is at one of the other two sp entry points, sp_{bas}, the crossing point will not be reached directly and the stereospecificity will be lost as the decay distributes itself into the three available channels to ground-state tbp species. This was summarized in the rule: "In all cases where the crossing point of the upper and lower surfaces is displaced *toward* the excited-state entrance point, the preference for selective transverse tunneling is most pronounced. In cases where the crossing point of the upper and lower surfaces is displaced *away* from the entrance point, the directional selectivity is partly lost and a more random decay will be observed". The application of this model to specific systems has been quite successful, see later.

Ab initio calculations[151] on the electronic structure of the complexes $Cr(NH_3)_6^{3+}$, $Cr(NH_3)_5F^{2+}$, *trans*-$Cr(NH_3)_4Cl_2^+$, and *cis*- and *trans*-$Cr(NH_3)_4F_2^+$ have validated the basic additivity and transferability of σ and π parameters of the angular overlap theory. However, population analysis indicates that a given ligand to metal bonding does vary somewhat depending on the other ligands present. The known σ and π donor/acceptor characters of the NH_3, Cl^-, and F^- ligands were reproduced by the calculations. Good values for quartet-state energies were obtained, but the doublet-state energies were too high and their splittings presented problems. However, the calculations correctly identified *trans*-$Cr(NH_3)_4F_2^+$ as a $^2T_{1g}$ emitter and the others as ^2E emitters. Also considered was the direction of the splitting of the ^2E state in tetragonal complexes. Subsequently, the photochemistry of these molecules was considered,[150] applying the same mechanism via five-coordinate sp and tbp intermediates and calculating the energies of these intermediates based on idealized geometries. These ab initio calculations led to the correct identification of the reactive lowest excited quartet state and to the same state correlation diagrams for the isomerizations of the five-coordinate fragments as were earlier obtained from the AO ligand-field calculations. Finally, the paper presented a summary of the Jahn–Teller approach to photostereochemistry discussed above.

Whereas the calculations of state energies for $Cr(NH_3)_6^{3+}$ in the above work were carried out at ground-state geometry, another coincident study[152] calculated energies both at ground-state geometry and at the published geometry of the vibrationally equilibrated lowest quartet excited state.[27] This enabled the authors to estimate the spacing between the relaxed quartet and doublet states, which was ≥ 3300 cm^{-1}, to be compared with the estimate from the "5%-absorption" procedure of 4400 cm^{-1} and the experimental[153] apparent activation energy for doublet-state deactivation of 3800 ± 100 cm^{-1}. In the opinion of the authors, this lent credence to the doublet decay being dominated by thermally activated BISC to the quartet state. It was also noted that there was good agreement between the experimental apparent activation volume for the high-temperature process[153] depleting the doublet state of 4.3 ± 0.2 mL mol^{-1} and the theoretical estimate for BISC of 3–4 mL mol^{-1}. They did not rule out, however, the alternative of crossing to a ground-state intermediate on the basis of the results. Another significant calculation was of the spin–orbit interaction between the ^4E_g state and the upper $^2B_{1g}$ component of the ^2E_g state, which conferred 3.4% $t_{2g}{}^2e_g{}^1$ character upon the latter. Recently another density functional calculation on this molecule has appeared,[154] and in this work the geometry was allowed to optimize. The bond lengths, the sequence of d–d excitation energies, and the tetragonal distortion of the $^4T_{2g}$ excited state were well reproduced, but the calculated transition energies and vibrational frequencies differed significantly from the experimental values.

V. Mechanistic and Photophysical Studies

One of the central questions in Cr(III) photochemistry has been the role of the quartet and doublet states in the photoreactions. There is a large body of evidence for reaction via both states from quenching experiments[2,24] and observations of reaction on two different time scales[155–157] in direct photoproduct monitoring experiments. One component is subnanosecond and the other occurs with the doublet lifetime. The proportion of the doublet reaction varies from 0 to 100% for different complexes. There are also many observations of wavelength-dependent quantum yields in tetragonal complexes,[2,24,148,158] and these have often been attributed to reaction via more than one quartet state, generally reaction from ^4E with greater contributions from $^4B_2$ at shorter wavelengths,[158] as this usually rationalizes nicely the observed wavelength changes in reaction modes. Many of the studies to be discussed are related to the question of whether the reaction via the doublet occurs (i) directly, (ii) via BISC and quartet reaction, and (iii) by tunneling to a ground-state intermediate, as introduced in Figure 2.

There is also some uncertainty as to the exact route of the reaction from the quartet state. This may occur prior to vibrational and solvent-shell relaxation or from a thermally relaxed excited state. It is known[34] that the doublet state is populated within 1 ps after excitation. This could represent the lifetime of the relaxed quartet state, but the rapidity of the process makes it likely that ISC competes with relaxation. If so, then the lifetime of the relaxed quartet could be longer than this 1 ps value. However, the failure to observe fluorescence from Cr(III) complexes in room-temperature solutions still requires that, if formed, the relaxed quartet state has a short lifetime, consistent with its expected extreme reactivity.

In the next sections, the evidence bearing on these questions is reviewed. The photophysical aspects have been reviewed to 1990 elsewhere,[22,23] and only a summary is presented here.

A. Doublet-State Population

As mentioned earlier, observations of the wavelength dependence of the fraction of reaction that is quenchable by doublet quenchers and of phosphorescence yields have indicated that quartet to doublet

Table 4. Efficiency of Doublet State Population, ϕ_D

complex	ϕ_D	method[a]	ref
$Cr(NH_3)_6{}^{3+}$	0.69(4)	Q	76
	0.80(4)	CM, 347 nm	157
	0.74(4)	CM, 530 nm	
$Cr(en)_3{}^{3+}$	0.7	S	168
	0.3	AM	155
	0.64(14)	PR	38
	0.68(10)	EM	38
	0.68(6)	CM	157
$Cr(tn)_3{}^{3+}$	0.78	CM	157
$Cr(bpy)_3{}^{3+}$	0.94	S	168
	0.93(8)	PA	170
	$>$0.93	CM	124
$Cr(phen)_3{}^{3+}$	0.2	S	168
	0.95(3)	PA	170
Cr(5-Cl-phen)$_3{}^{3+}$	0.73(5)	PA	170
Cr(4,4′-Me$_2$bpy)$_3{}^{3+}$	1.04(5)	PA	170
trans-$Cr(en)_2(NCS)_2{}^{+}$	0.4	S	168
Cr([9]aneN$_3$)$_2{}^{3+}$	0.95(5)	PA	171
trans-Cr(cyclam)$(CN)_2{}^{+}$	1.1(1)	PA	171
trans-Cr([15]aneN$_4$)$(CN)_2{}^{+}$	1.08(5)	PA	171
Cr(TAP[9]aneN$_3$)$_2{}^{3+}$	1.05(5)	PA	171
$Cr(NH_3)_5CN^{2+}$	0.74(4)	CM	157
	0.73	Q	95
$Cr(NH_3)_5(NCS)^{2+}$	0.77(3)	CM	157
trans-$Cr(en)_2F_2{}^{+}$	1.0	CM	157

[a] S, from sensitized phosphorescence yield; PA, photoacoustic method; CM, monitoring of prompt and slow product formation by conductivity changes; Q, fraction of quenchable photochemistry; AM, monitoring of prompt and slow product formation by absorption changes; EM, comparison of phosphorescence intensity on doublet and quartet excitation; PR, comparison of quenchable photochemistry to photochemistry on direct doublet irradiation.

ISC may be competitive with quartet-state relaxation in many complexes. The prompt and slow processes, Figure 2, give rise to an overall doublet population quantum yield given by $\phi_D = \eta_{pisc} + (1 - \eta_{pisc} - \eta_p)\eta_{isc}$. It has often been assumed that $\phi_D = \eta_{isc}$, but this is clearly valid only when η_{pisc} and η_p are negligible. In support of the rapidity of doublet population, measurement of the rise time of doublet-state transient absorption indicated that it occurred faster than the 7 ps rise time of the laser pulse[159] and more recently, and after some controversy,[10,159−165] the value has been refined[34] to ≤1 ps; that is, the population arises with a rate constant greater than 10^{12} s^{-1}. It has also been observed that solvent rigidity may influence the intersystem crossing yield for[166] $Cr(en)_3{}^{3+}$, while a solvent deuterium isotope effect has been reported[167] for $Cr(bpy)_3{}^{3+}$.

Direct measurements of the efficiency of doublet-state population have been made, although exploration of the wavelength dependence has not generally been feasible. The available data for room-temperature solutions are summarized in Table 4. Early experiments employed comparison of direct and sensitized phosphorescence (S) and gave values[168] ranging from 0.2 for $Cr(phen)_3{}^{3+}$ to 0.94 for $Cr(bpy)_3{}^{3+}$, with a value of 0.7 for the much-studied $Cr(en)_3{}^{3+}$. Concordant measurements were obtained[38] for $Cr(en)_3{}^{3+}$, by measurement of the phosphorescence yield on quartet and doublet excitation (EM), 0.68, and from the ratio of the quenchable reaction quantum yield on quartet irradiation to the yield on doublet irradiation (PR), 0.64. In contrast, for low-temperature solid-state systems, the intersystem crossing yield is often unity[23] and the lower values for room-temperature solutions can be attributed to competition with intersystem crossing of quartet photoreaction and/or nonradiative decay to the ground state. Part of this decay process is likely to be attributable to (partial?) ligand dissociation followed by recombination to produce ground-state starting material.

A photoacoustic method (PA) for measuring these yields has been developed[169] and employed[170,171] to obtain values for several polypyridyl and some amine complexes, Cr([9]aneN$_3$)$_2{}^{3+}$, *trans*-Cr(cyclam)$(CN)_2{}^{+}$, *trans*-Cr([15]aneN$_4$)$(CN)_2{}^{+}$, and Cr(TAP[9]aneN$_3$)$^{3+}$. Comparing the sensitization and PA methods shows they give concordant values for $Cr(bpy)_3{}^{3+}$ but serious disagreement for $Cr(phen)_3{}^{3+}$. Since the several polypyridyl complexes measured by PA have ϕ_D just below unity, this focuses suspicion on the low $Cr(phen)_3{}^{3+}$ value of 0.2 from the sensitization method, which also gives a surprisingly low value for $Cr(en)_2(NCS)_2{}^{+}$. Unfortunately application of the PA method seems to be limited to photostable complexes with relatively long doublet lifetimes.

Fortunately an indirect method is also available. For Cr(III) complexes that show the same quantum yield of photochemistry on doublet and quartet irradiation, it can be inferred that the overall reaction efficiency via the doublet and quartet states is the same and the fraction of the reaction that occurs via the doublet state equals ϕ_D. From conductivity monitoring experiments,[124,125,156,157] it is 0.68 for $Cr(en)_3{}^{3+}$, in excellent agreement with the values from the direct methods. These studies also gave[157] the values 0.74 for $Cr(NH_3)_5(CN)^{2+}$ in agreement with the 0.73 value[95] from quenching experiments, 0.77 for $Cr(NH_3)_5(NCS)^{2+}$, 1.0 for *trans*-$Cr(en)_2F_2{}^{+}$, and >0.93 for $Cr(bpy)_3{}^{3+}$. Absorption monitoring of $Cr(en)_3{}^{3+}$ photoproducts[155] gave a value of 0.70 for the fraction of reaction occurring via the doublet, although the authors concluded that $\eta_{isc} = 0.3$. These results were reinterpreted[172] to support the higher value, although this reinterpretation was disputed.[173] In the final analysis, an overview of the results in Table 4 supports the 0.7 value for $Cr(en)_3{}^{3+}$ and, in turn, the equality of its quartet and doublet photochemical quantum yields, Table 1.

In summary, doublet population is an efficient process in the complexes studied, with yields generally in the range 0.7−1.0.

B. Doublet-State Deactivation Pathways

There is considerable literature on the pathways of doublet-state relaxation, and many aspects have been reviewed elsewhere.[12,13,22,23,37] In the low-temperature regime, there is a weak-coupled process having a small (<4 kJ mol^{-1}) activation energy that, on approaching room temperature, is dominated in a solvent-dependent manner[22,23,37,174] by a higher activation energy process. For many Cr(III) complexes, the emission lifetime under solution photochemical conditions shows a linear Arrhenius plot that yields an apparent activation energy for the high-temperature process leading to doublet relaxation, although there are important exceptions.[23] The linearity of the plot for many complexes implies that relaxation is dominated by a single process, and some of these show evidence[175] of isokinetic behavior with Barclay–Butler plots for data derived from different solvent media. Similar observations stimulated[95,176] a set of "emission rules" based on the high-temperature deactivation process being direct doublet reaction. These rules suggested (i) a positive correlation between the doublet lifetime of a CrL_6^{n+} complex and the ligand-field strength of L and (ii) that relatively short lifetimes would be observed for mixed-ligand complexes when the ligand that is labilized in the ground-state thermal reaction is located on the weakest-field axis.

An alternate process often considered is BISC to the quartet state. In one study,[177] a reasonable correlation was found between the estimated lowest quartet-state energy calculated by the AOM and the logarithmic doublet lifetime for a series of 16 complexes, mostly acidoam(m)ines. On the other hand, examination of a larger array of complexes, including a number of $Cr(N)_6$ types, and looking at correlation of the logarithmic doublet lifetime with the ligand-field stabilization energy (LFSE) showed[22] only crude correlations. Consequently, some authors[22,23,123] have questioned BISC as the doublet relaxation pathway for such higher-field complexes. This and other considerations have led to the proposal in an extensive series of papers[178–186] of a third possibility, crossing or tunneling to a ground-state intermediate for reaction. In this work, several approaches have been taken and the results are included in the next sections.

In the low-temperature relaxation regime, large deuterium isotope effects on the doublet lifetime are found,[23] consistent with a weak-coupled nonradiative decay involving nested potential surfaces. Also consistent with weak-coupled decay is the correlation found between the relaxation rate and the number of N–H oscillators in the complex.[187] In contrast, for photoactive complexes, the high-temperature relaxation process shows very small or zero isotope effects, and this suggests that a strong-coupled process such as doublet reaction, BISC, or surface-crossing to a GSI is operative. Interestingly, for some complexes in which steric constraints prevent photoreaction, the large deuterium isotope effects persist up to room temperature and the apparent activation energy for the decay is larger than for reactive isomers.

The choice between the BISC and GSI pathways of doublet decay has been explored[13,181,182,184–186] by two approaches: (i) study of complexes in which there is a large Q/D spacing because of strong-field ligands such as bpy, phen, and CN^- and (ii) incorporation of ligands which apply stereochemical perturbations and/or constraints on the complex. In the first approach, it was found that several complexes had large and variable estimated barriers to BISC but the doublet relaxed with much smaller and very similar apparent activation energies such that there was at best only slight correlation with the calculated barrier. Several of the complexes had unexpectedly short lifetimes. The second approach has resulted in the preparation of a number of very interesting complexes with macrocyclic ligands.

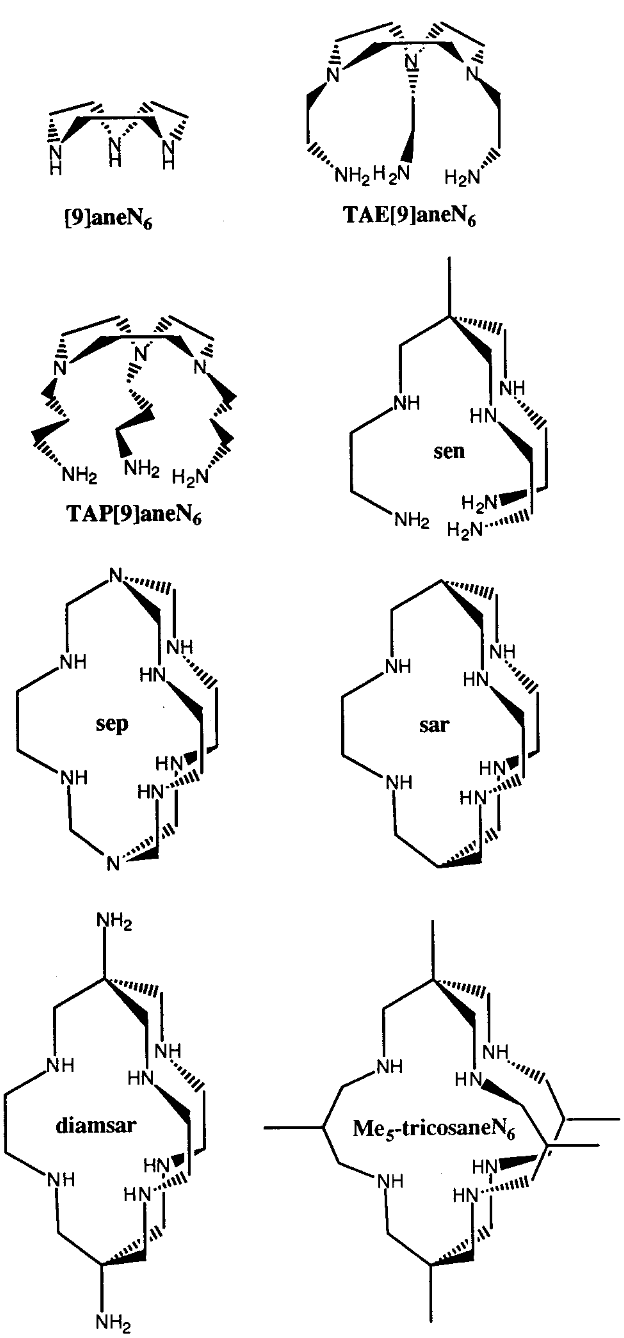

Figure 6. Macrocyclic ligand structures.

To facilitate this discussion, Figure 6 shows the structures of a variety of the macrocyclic ligands used and Table 5 summarizes some of the literature data on deuterium isotope effects.

The first macrocyclic complex studied was $Cr(sep)^{3+}$, and it was synthesized[178] to test the proposition that chemical reaction controlled the high-temperature doublet lifetime. The complex, which is photoinert, showed a doublet lifetime of 10 μs in DMF at 0 °C compared with 6.2 μs for the photoactive $Cr(en)_3^{3+}$. The similarity of these lifetimes certainly argues against control of the doublet lifetime by chemical reaction, although an even longer lifetime for the photoinert cage complex might have been expected. The complexity of the photophysical behavior of these

Table 5. Medium and Isotope Effects on Doublet Lifetimes

complex	$\tau(\mu s)$, solid		$\tau(\mu s)$, solution	ref
	77 K	RT	RT (T, K)	
$[Cr(NH_3)_6](ClO_4)_3$	35	27	2.2 (297)	207
$[Cr(ND_3)_6](ClO_4)_3$	600	538	3.1 (297)	207
$[Cr(en)_3](ClO_4)_3$	54	17	1.7 (297)	207
$[Cr(D\text{-}en)_3](ClO_4)_3$	290	28	1.8 (297)	207
trans-$Cr(cyclam)(NH_3)_2^{3+}$	180 (DMSO)		55 (293)	192
trans-$Cr(D\text{-}cyclam)(ND_3)_2^{3+}$	3720 (DMSO)		165 (293)	192
cis-$Cr(cyclam)(NH_3)_2^{3+}$	73	19 (293)	1.7 (293)	192
cis-$Cr(D\text{-}cyclam)(ND_3)_2^{3+}$	1580	65 (293)	2.1 (293)	192
$Cr([9]aneN_3)_2^{3+}$	400		30.2 (298)	184
$Cr(D\text{-}[9]aneN_3)_2^{3+}$	3.03 ms		30.2 (298)	184
$Cr(TAE[9]aneN_3)^{3+}$	114		4×10^{-3} (estd)	184
$Cr(D\text{-}TAE[9]aneN_3)^{3+}$	1.0 ms		4×10^{-3} (estd)	184
$Cr(TAP[9]aneN_3)^{3+}$	265		179 (298)	184
$Cr(D\text{-}TAP[9]aneN_3)^{3+}$	4.3 ms		850 (298)	184
$Cr([9]aneN_3CH_2^-)_2^{3+}$	50		7×10^{-5} (estd)	184
$Cr([9]aneN_3CH_2^-)_2^{3+}$	114		1×10^{-5} (estd)	184
$Cr(sep)^{3+}$			4.5 (295)	178
$Cr(sar)^{3+}$	60		<0.01	188
$Cr(diamsar)^{3+}$	65		<0.01	188
$Cr(sen)^{3+}$	171, deut. 2.94 ms	13	10^{-4} (estd)	184
$Cr(Me_5\text{-}tricosaneN_6)^{3+}$	440		235, deut. 1.51 ms	190
$Cr(Me_5\text{-}D\text{-}tricosaneN_6)^{3+}$			1510	190
trans-$Cr(cyclam)(CN)_2^+$			335 (295)	193
trans-$Cr(D\text{-}cyclam)(CN)_2^+$			1500 (295)	193
trans-$Cr(tet\text{-}a)(F)_2^+$	49	42	30 (293)	88
trans-$Cr(D\text{-}tet\text{-}a)(F)_2^+$	1240	1100	234 (293)	88

cage complexes was soon augmented by the observation[188] that the equally photoinert cage complexes $Cr(sar)^{3+}$ and $Cr(diamsar)^{3+}$ had extremely short, perhaps subnanosecond, doublet lifetimes.

The thermally activated relaxation of the lowest energy doublet state was examined for both the low- and high-temperature regimes in several types of Cr(III) complexes. Study of a large variety of amine and acidoammine complexes showed[183] that in the low-temperature regime, decay involved at least two channels, only one of which was sensitive to the number of high-frequency oscillators. The other appeared sensitive to the identity of the ligating atoms. The high-temperature decay channel was studied[182] for *trans*-$Cr(N_4)X_2^{n+}$ complexes (where N_4 was a macrocyclic tetramine) including some macrocyclic complexes with pyridyl and thioether ligands. On the basis of a lack of correlation between the logarithmic doublet lifetime and the quartet/doublet energy gaps calculated using the 5%-absorption rule, it was concluded that BISC and crossing to a GSI are competitive channels, the former being important for complexes with weak-field ligands such as $X = Cl^-$ and Br^- while the latter operates for strong-field ligands such as NH_3 and CN^-. This approach was extended by incorporating methyl groups into the macrocyclic ligands to provide stereochemical perturbations, and the doublet luminescence properties of cis and trans isomers were compared. It was concluded that crossing to a GSI was responsible for the doublet decay in the ammine and cyano analogues.

The role that the stereochemistry of the ligand can play in influencing the doublet-state room-temperature solution lifetime was dramatically illustrated by a comparison[185] of the behavior of complexes $Cr(TAE[9]aneN_3)^{3+}$ and $Cr(TAP[9]aneN_3)^{3+}$. These complexes have the $[9]aneN_3$ ring coordinating three of the Cr(III) sites and three pendant arm amine ligands coordinating to the other three; the first complex has ethanediamine arms and the second 1,3-propanediamine arms. The complexes have very similar ground-state spectroscopic properties and 77 K doublet lifetimes of 114 and 265 μs, respectively, but at room temperature, the doublet lifetimes are 4×10^{-3} (estd) and 180 μs, respectively. The authors argued that this does not relate to the doublet/quartet energy gap, which is similar for the two molecules. On the basis of molecular mechanics calculations, the phenomenon was attributed to the effect on the ligand steric energy of twisting along a trigonal coordinate when coordinated to the metal ion. There is a respective 69 and 12 kJ mol^{-1} energy relaxation of the ligand steric strain in these two complexes when the ligand is twisted from octahedral toward trigonal prismatic geometry. The mechanism proposed was that in the excited doublet state, relief of ligand strain would drive such trigonal distortion, which in turn would promote d-orbital mixing, reduce the doublet- to ground-state energy spacing, and facilitate rapid nonradiative decay to the ground state.

This theme was pursued[184] in a study of the molecule $Cr(sen)^{3+}$, an analogue of $Cr(en)_3^{3+}$ with a neopentyl cap bonded in a facial position, Figure 6. The crystal structure of the molecule showed enlargement of the bond angles in the neopentyl cap consistent with ligand strain induced on coordination to Cr(III). The complex had a quite normal 171 μs lifetime at 77 K, a 13 μs lifetime at room temperature when doped into $[Rh(sen)](ClO_4)_3$, but a solution lifetime in DMSO estimated as 0.1 ns. The dramatic reduction again was attributed to a dynamic process involving a relaxation of the trigonal strain in the doublet excited state. Molecular mechanics calculations showed that the ligand had its lowest steric energy for a twist angle of 14° on the Kepert scale[189] (for which the octahedral angle is 30°). For a series of similar am(m)ine complexes, there was a good correlation between the logarithmic doublet lifetime in solution and the ligand steric energy for a twist angle of 15°. The conclusion from these two studies was that large amplitude trigonal twists facilitate thermally activated Cr(III) doublet-state (^2E_g) relaxation. This theme has been central to recent reviews.[12,13]

Very recently two new photoinert cage complexes have been synthesized,[190] $Cr(Me_5\text{-tricosaneN}_6)^{3+}$ and $Cr(Me_6\text{-tetracosaneN}_6)^{3+}$. The first of these is the analogue of $Cr(sep)^{3+}$ but with six-membered 1,3-propanediamine rings around the periphery of the cage, as opposed to the five-membered ethanediamine rings in $Cr(sep)^{3+}$. $Cr(Me_5\text{-tricosaneN}_6)^{3+}$ has[191] a 77 K emission spectrum with a strong 0−0 band and a lifetime of 440 μs at 77 K, a near record 235 μs lifetime at 298 K, increasing to 1.51 ms on deuteration. The less symmetric $Cr(Me_6\text{-tetracosaneN}_6)^{3+}$ complex has C_i symmetry, a somewhat broader low-temperature doublet emission spectrum, and a subnanosecond doublet lifetime in solution at room temperature. The authors state[190] that neither photoreaction nor access of solvent molecules to the Cr center can be important in determining these lifetimes. They ascribe the difference between these two complexes and the others discussed above to the flexibility of the ligands and the role that this may have in promoting radiationless decay. They point out that the long-lived $Cr(Me_5\text{-tricosaneN}_6)^{3+}$ has a rigid cage; they give the twist angle as 66.5°, which, converted to the Kepert scale, is 3° more than the octahedral angle.

A particularly important series of complexes has been the trans and cis isomers of the series $Cr(cyclam)L_2^{n+}$, where L = Cl,[42,43] NH_3,[192] CN,[193] and F (here the trans isomer was of the tet-a ligand).[88] The trans isomers are all photoinert, but the cis isomers are photoreactive, Table 2. They have been important not only in indicating that stereochemical change may be a requirement of photosubstitution, but studies of the isotope effects on their doublet lifetimes have made important contributions to our understanding of the doublet decay processes. First note, Table 5, that a photoreactive complex such as $Cr(NH_3)_6^{3+}$ shows large solid-state room-temperature deuterium isotope effects on its doublet lifetime, the deuterated analogue having a 20-fold longer lifetime, but in solution the deuteration effect is reduced to a mere 40% lifetime increase. Similar behavior is shown by $Cr(en)_3^{3+}$ and *cis*-$Cr(cyclam)(NH_3)_2^{3+}$ and appears to be typical for a photoactive complex. In contrast, among the photoinert complexes, *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ shows a 3-fold room-temperature solution lifetime increase on deuteration, a 5-fold increase is found for *trans*-$Cr(cyclam)(CN)_2^{+}$ (unfortunately the cis isomer has proved difficult to synthesize), and an 8-fold increase for *trans*-$Cr(tet\text{-}a)F_2^{+}$. For deuterated *trans*-$Cr(tet\text{-}a)F_2^{+}$, the isotope effect at room temperature is much the same in the solid state and solution. Analogous results which fit this general picture are to be found[22,24] for a number of other complexes. These results demonstrate that in the photoactive complexes, the decay of the doublet state is dominated under solution photochemical conditions by a strong-coupled process. In contrast, for the photoinert trans isomers, this high-temperature decay pathway is inhibited, allowing the low-temperature weak-coupled decay process to remain dominant up to and above room temperature. Also note that for many photoreactive complexes in room-temperature solid state, there remains a deuterium effect signaling weak-coupled decay. This demonstrates that for these complexes different processes are controlling the decay in the solid state and solution. The process in solution has the characteristics expected for BISC.

There are three arguments commonly used to argue against the viability of BISC in these complexes: (i) the calculated energy barrier to BISC based on the estimated quartet position exceeds the experimental values from temperature-dependent phosphorescence studies, (ii) there is a lack of correlation between the doublet lifetime and the ligand-field stabilization energy, and (iii) fluorescence has been searched for carefully and not found. The first two points are often one and the same as the 5%-absorption procedure[32] is usually used to estimate the doublet/quartet energy gaps used as input. A second procedure used[22] has subtracted an arbitrary, constant 2500 cm^{-1} from the energy of the first quartet absorption band maximum. Theoretical work on $Cr(NH_3)_6^{3+}$ suggests[152] these methods may seriously overestimate the true energy gap at the relaxed geometry, which also likely varies with solvent and other medium effects. BISC involves an expansion of the molecule, so it would be expected to be sensitive to environmental factors, particularly those involving compressive strains. This is nicely demonstrated in a recent spectroscopic study[194] of $Cr(urea)_6^{3+}$ in low-temperature solid state, where an increase in pressure causes a change in the nature of the luminescence from delayed fluorescence to phosphorescence. It seems clear from the ongoing debate on the doublet/BISC/GSI issue that it is unlikely to be resolved by arguments based on lifetime correlations, especially when there is so much uncertainty about the input parameters used. In addition, solvent interactions, steric perturbations/distortions, and ligand flexibility seem to play an important role in the doublet-state deactivation processes. A recent study[195] of the solvent dependence of the lifetime of *trans*-$Cr(cyclam)(CN)_2^{+}$ has claimed that the solvent dependence is a multiparameter phenomenon and that attempts to fit a range of data with a single-parameter approach are doomed to failure. The specific studies of particular complexes that are central to the debate and evidence from stereochemical and reaction mode data, which will be discussed next, have been more helpful in resolving the issues.

C. Specific Mechanistic Studies

Photolysis yields and emission lifetimes for *trans*-$Cr(NH_3)_2(NCS)_4^{-}$ in acetone were recorded[196] over the range from −93 to 10 °C. Quenching by oxygen permitted exploration of the temperature dependence of the quenchable and unquenchable reactions. Prompt photoreaction had a temperature-independent quantum yield of 0.02, while the slow photolysis correlated with depopulation of the ^2E_g state. The results were consistent with back-intersystem crossing as the pathway for this reaction. A later study of the dependence of photoreaction and ^2E_g relaxation rate as a function of solvent showed[197] that at low temperatures the fast process did not depend on solvent fluidity while the slow process began only when solvent motions were fast on the timescale of doublet decay. The influence of these solvent motions on doublet-state relaxation is further studied in recent work[174] on a group of complexes with different quartet/doublet energy spacings. The author concluded that doublet decay occurred by BISC in most of the complexes studied and that solvent interactions functioned to alter the barrier to BISC.

The debate regarding the mechanism of reaction via the doublet in $Cr(en)_3^{3+}$ typifies the problems that arise for the important group of $Cr(N)_6^{3+}$ complexes for which the spectroscopic estimates of the doublet/quartet barrier are large and seem to many to preclude BISC and quartet reaction. Direct product monitoring experiments were interpreted[155] as supporting a direct reaction from the doublet state. The kinetic modeling used required an intersystem crossing yield of 0.3, however, and therefore predicted at least a 2-fold increase in the photochemical quantum yield on direct doublet irradiation. Experiment shows that despite a conflict between the two reported values, Table 1, doublet irradiation does not give anything close to the predicted quantum yield of 0.8. Furthermore, as described earlier, measurement of the intersystem crossing yield by several methods gives values near 0.7. It was argued[38,172] that all the data could be fit by the BISC/quartet model. Such an intepretation is supported by the important finding[64] that the stereochemistry of the photoproducts is the same for the reaction via quartet and doublet states. It is the opinion of this reviewer that to get a completely self-consistent picture of this photochemistry and photophysics, it is only necessary to reject the spectroscopic estimate of the barrier to BISC.

The analogous $Cr(tn)_3^{3+}$ shows the same quantum yield of photoaquation on doublet- and quartet-state irradiation,[198] 0.16 ± 0.01 and 0.15 ± 0.02, respectively. Here 78% of the photoreaction occurs[82] with the doublet lifetime. Using hydroxide ion as a quencher, it was found that the quenchable and unquenchable reactions gave different proportions of the *trans*- and *cis*-$Cr(tn)_2(tn\text{-}H)(H_2O)^{4+}$ photoproducts. Also for the unquenchable fraction of reaction there was a wavelength dependence in the red edge of the first quartet absorption band which was not reproduced in a later reinvestigation.[199] The discrepancy was attributed to unrecognized thermal reactions of photoproducts in the earlier work. The differences in photoproduct isomer ratios, 35% cis via the doublet and 47% cis via the quartet, were interpreted as indicating that the unquenchable (quartet) reaction occurred in competition with vibrational relaxation at least in part.

cis- and *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ differ markedly in their photochemical and photophysical properties.[192,200−203] The trans isomer is photoinert, although a photoredox process[200] with $\phi = 0.01$ occurs in the presence of nitrate ion. In contrast, the cis isomer photoaquates ammonia with a quantum yield of 0.15 ± 0.05 independent of irradiation wavelength, including directly into the doublet state.[200] On quartet irradiation, a high percentage of this photoreaction, >90%, occurs via the doublet state. The small deuterium isotope effect[192] on the doublet decay in room-temperature solution shows it is a strong-coupled process, in contrast to the weak-coupled process implied for the trans isomer, Table 5. Of the greatest importance, conductivity monitoring of direct photoproduct formation shows[200,203] that *cis*-$Cr(cyclam)(NH_3)_2^{3+}$ reacts via an aquated intermediate, $Cr(cyclam)(NH_3)_2(H_2O)^{3+}$, which has a lifetime of about 4 μs, is in its ground electronic state, participates in acid−base reactions with an estimated pK_a of 4.4, and reacts to give the final products *cis*-$Cr(cyclam)(NH_3)(H_2O)^{3+}$ and NH_3. The original authors were unable from their evidence to be specific about the nature of this intermediate. However, it has been suggested[182] that it is a seven-coordinate species and its existence has been considered as evidence in support of the GSI model for the reaction via the doublet state. Pressure- and temperature-dependence studies[200] of the doublet decay lifetime gave a $\Delta V^{\ddagger}$ value of 2.9 ± 0.4 cm^3 mol^{-1} and an apparent activation energy of 36 ± 1 kJ mol^{-1}. The trans isomer gave 6.7 cm^3 mol^{-1} and 59 ± 2 kJ mol^{-1} for the high-temperature regime. The volume expansion and greater energy barrier than the 50 kJ mol^{-1} estimated by the 5%-absorption rule were considered consistent with BISC as the doublet decay process for the trans isomer, while the cis doublet was thought to decay by a strong-coupled pathway that could generate the photochemical intermediate.

A spectroscopic study[204] of the two isomers of $Cr(cyclam)(NH_3)_2^{3+}$ in solid state at low temperature estimated the zero−zero energies of the lowest quartet states as similar at about 18 800 cm^{-1}, which leads to an estimated minimum barrier (low temperature, solid state) to BISC of about 47 kJ mol^{-1} for both. To account for the different observed solution values, it was proposed that interaction of the Lewis base solvent with the vacant t_{2g} orbital in a photoreactive quartet state serves to lower the crossing-point energy between the doublet- and quartet-state potential energy surfaces, reducing the barrier to BISC in the photoactive cis isomer but not in the photoinert trans. More recently this suggestion has been extended[16] to include the possibility that BISC may be assisted by such a solvent interaction.

The putative seven-coordinate intermediate is of obvious importance. A recent search for such intermediates[205] by laser flash photolysis with conductivity detection using a series of complexes including $Cr(NH_3)_6^{3+}$, $Cr(en)_3^{3+}$, $Cr(tn)_3^{3+}$, *trans*- and *cis*-$Cr(tn)_2(NH_3)_2^{3+}$, $Cr(sen)^{3+}$, and $Cr([18]aneN_6)^{3+}$ confirms that *cis*-$Cr(cyclam)(NH_3)_2^{3+}$ is truly unique in forming an intermediate with a microsecond lifetime longer than that of the doublet state of the complex.

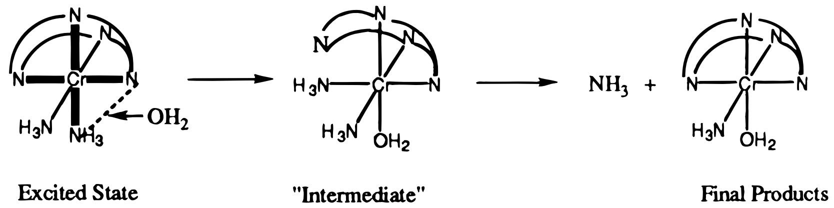

Figure 7. Proposal regarding the intermediate formed in *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ photoaquation. H-atoms of the cyclam ring have been omitted for clarity. The heavy bonds in the starting molecule indicate the plane of labilization. Loss of a ring N by labilization-plane edge displacement with ammonia migration leads to the unstable photochemical product shown, the intermediate. On recoordination of the ring N, ammonia is ejected, leading to the same products as those obtained from direct ammonia aquation.

Were there to be seven-coordinate intermediates, as suggested, we would have expected to find evidence for similar species among the variety of macrocyclic and pendant arm ligand complexes studied, some of which aquate ammonia and some of which form products with pendant primary amine ligands. We conclude that the weight of evidence suggests that the *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ intermediate is most likely a six-coordinate product, corresponding to the species shown in Figure 7, with one coordination site on the cyclam ring displaced from Cr. This is not original, such species having been considered possible before.[88,203,206] Molecular modeling shows that loss of ring-N ligands is quite possible, particularly the V-groove nitrogens, and the resulting three-coordinate cyclam complex does not have an excessively high steric energy. Moreover, applying the labilization-plane edge-displacement model of photostereochemistry to the photoaquation, Figure 7, predicts that if such ring-N loss does occur, an ammonia ligand should occupy the position vacated by the ring-nitrogen atom. When thermal recoordination then occurs, ammonia will be displaced to give the *cis*-Cr(cyclam)$(NH_3)(H_2O)^{3+}$ final product, exactly the kinetic behavior required of the intermediate by the experimental data. If these arguments turn out to be correct, this intermediate is merely a photoproduct but one that happens to be thermally unstable with respect to recoordination of the cyclam ring nitrogen. The term intermediate is obviously not incorrect, but it does not carry the mechanistic significance that has been attributed to it in the GSI context. Unfortunately our efforts to find complexes for which a ring-N-deligated product can be isolated and structurally characterized have not succeeded so far.

The effects of solvent and temperature on the spectroscopic properies of *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ have been carefully documented.[202] In DMF, DMSO, hexamethylphosphoramide (HMPA), and aqueous media, the phosphorescence yields are small ($1-4 \times 10^{-3}$) and vary linearly with changes in decay lifetime. The doublet lifetime temperature dependence is best fit by a double-exponential function. The low-temperature contribution has a small activation energy and A factor (≤ 6 kJ mol^{-1} and $\leq 6 \times 10^4$ s^{-1}), while at high temperatures the activation energy is in the range 64−78 kJ mol^{-1} with A factors in the range 2×10^{15} to 2×10^{16} s^{-1}. In water or DMF, the volumes of activation are nearly zero for the low-temperature contribution and increase to ~7 cm^3 mol^{-1} in the high-temperature region. The data nicely document the participation of a low-temperature radiationless transition to the ground state and a high-temperature strong-coupled process, attributed to BISC, although the suggestion was made that the distinction between this and crossing to a GSI may be more semantic than real. The solvent study showed that the log of the doublet decay rate constant decreases linearly with increasing Gutmann donor number. This was associated with a lengthening of the N−H bonds and a shortening of the Cr−N bonds, confirmed by the infrared spectral frequency changes. In turn, this will increase the ligand-field strength of the ligands and increase the BISC barrier.

To this reviewer, the photoinert nature of these *trans*-Cr(cyclam)$(L)_2^{n+}$ complexes, where L = NH_3, CN, F, Cl, is difficult to understand on the GSI model. Accepting that the reaction mode associated with stereochemical change is prevented by the steric constraints imposed by the ligand, what then prevents tunneling to the transition state for the stereoretentive ground-state photoaquation? In *trans*-Cr(cyclam)$(Cl)_2^{+}$, a small quantum yield, $\sim 3 \times 10^{-4}$, of the *trans*-Cr(cyclam)$(H_2O)Cl^{2+}$ product was reported[43] but this inefficient process is clearly different from the efficient photoreaction with stereochemical change usually seen for *trans*-$Cr(N)_4(Cl)_2^{+}$ complexes.

$Cr(NH_3)_6^{3+}$ has been extensively studied.[9,27,44,45,76−78,81,82,153,157,207,208] The molecule photoaquates ammonia with a wavelength-independent quantum yield of 0.44, and about 75% of the reaction occurs via the doublet state and is quenchable by hydroxide ion. Two independent studies have shown that the photoreaction has a negative volume of activation; the values reported were −7.0 and −6.0 cm^3 mol^{-1}, respectively. The quantum yield of reaction is the same on quartet and doublet irradiation.[39] In the presence of either chloride ion or thiocyanate ion, photoanation competes[76,78] with photoaquation and the ratio of the resulting products is the same for the quenchable and unquenchable pathways.

Temperature studies[153] gave pressure-independent apparent activation energies for the high-temperature regime doublet lifetime decay rate constant of 43.6 kJ mol^{-1} for $Cr(NH_3)_6^{3+}$ and 46.0 kJ mol^{-1} for $Cr(en)_3^{3+}$. Accompanying studies of the pressure dependence of the room-temperature emission lifetime for a series of complexes gave the values (complex, $\Delta V^{\ddagger}(\tau^{-1})$ cm^3 mol^{-1}): $Cr(NH_3)_6^{3+}$, 4.4; $Cr(ND_3)_6^{3+}$, 4.2; $Cr(NH_3)_5(NCS)^{2+}$, 6.9; $Cr(en)_3^{3+}$, 3.3; *trans*-$Cr(en)_2(NCS)_2^{+}$, 0.4; *trans*-$Cr(en)_2(F)_2^{+}$, 1.2; $Cr(NH_3)_5(CN)^{2+}$, 3.4; and *trans*-Cr(cyclam)$(CN)_2^{+}$, 0.1 ± 0.2. The first two results show that deuteration has no effect on $\Delta V^{\ddagger}(\tau^{-1})$. With increasing pressure,

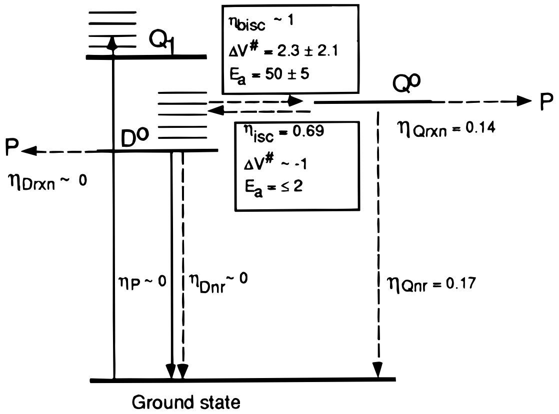

Figure 8. Kinetic scheme for $Cr(NH_3)_6^{3+}$ photoaquation. Units of $\Delta V^{\ddagger}$ are $cm^3\ mol^{-1}$ and of E_a $kJ\ mol^{-1}$. The published scheme[39] showed the quartet-state reaction occurring via a ground-state intermediate and is kinetically equivalent to this simpler version.

the first five (excluding $Cr(ND_3)_6^{3+}$) complexes showed shifts to higher energy of their first ligand-field absorption band maxima while the doublet absorption showed only small shifts to lower energy. These effects were consistent with compression causing an increase in the ligand-field strength and covalency of the complex. The positive volumes of activation for doublet decay were analyzed kinetically and shown to favor a positive volume of activation $\Delta V^{\ddagger}$(Drxn) for the fraction of the doublet decay that leads to reaction. Since the photochemistry has a negative overall $\Delta V^{\ddagger}$, this argued against direct doublet reaction and left open the choice between BISC and crossing to a GSI.

In a follow up study[39] of $Cr(NH_3)_6^{3+}$, the solvent sensitivity of the spectroscopy, emission lifetime, and photosubstitution quantum yield was investigated in water, DMF, DMSO, and hexamethylphosphoramide (HMPA). The vibronic features in the emission and absorption spectra showed solvent-induced trends with the Gutmann donor number which paralleled the specific electron-donor interaction between the solvent and complex described above for *trans*-Cr(cyclam)$(NH_3)_2^{3+}$. Emission decay rate constants also correlated with solvent donor number; at 42 °C, $\ln(\tau^{-1})$ decreases linearly with increasing donor number. The activation energies $E_a(\tau^{-1})$ increased and activation volumes $\Delta V^{\ddagger}(\tau^{-1})$ decreased with increasing donor number ranging from 46.0 ± 1.3 kJ mol^{-1} and +4.3 ± 0.3 $cm^3\ mol^{-1}$ in H_2O to 51.5 ± 0.8 kJ mol^{-1} and +3.4 ± 0.2 $cm^3\ mol^{-1}$ in HMPA. The quantum yields at 296 K for photosolvolysis were much less solvent-dependent; they were the same in H_2O and DMF (0.44 ± 0.01) and decreased slightly in DMSO (0.40 ± 0.01). Also, as mentioned earlier, the photoaquation quantum yield was the same for irradiation in the quartet and doublet bands; moreover, the associated activation volumes $\Delta V^{\ddagger}$(rxn) were the same at −6.0 ± 1.0 and −5.6 ± 0.7 $cm^3\ mol^{-1}$, respectively.

These results were subjected to a detailed analysis, which the interested reader is urged to study, and led to a mechanistic scheme equivalent to that shown in Figure 8. This rationalizes the known experimental behavior in terms of prompt quartet reaction accompanied by slow doublet reaction via BISC and further quartet reaction. The quartet state reaction was shown occurring through a ground-state intermediate, not included in Figure 8, which allows the recognition that the conventional quartet nonradiative decay process, Qnr, may occur all or in part by collapse of the intermediate to the starting complex in its ground state. However, the summary of Figure 8 is kinetically indistinguishable from the scheme in the original paper if one assumes the same GSI is formed by doublet and quartet routes. In support of the BISC/quartet mechanism is the parallel between the solvent effects on $Cr(NH_3)_6^{3+}$ and *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ which strongly suggests that BISC dominates for both. Also, the analysis indicated that $\Delta V^{\ddagger}$(Qrxn) was negative, showing that the photoreaction step was associative rather than dissociative. The value implied was small and in the range expected[209] for an I_a process.

A few studies have found differences in photochemical quantum yields on doublet and quartet irradiation. Table 1 lists the data for $Cr(sen)^{3+}$, which appears to be unusual in giving[210,211] a smaller quantum yield on doublet, $\phi = 0.074 \pm 0.002$, than on quartet irradiation, $\phi = 0.099 \pm 0.006$. The complex has an unusually short doublet lifetime, and this has been attributed to efficient doublet deactivation by a mechanism involving a trigonal twist to relieve ligand steric strain.[12,184] Because of the very short lifetime, it was not possible to determine the fraction of the reaction that occurred via the doublet either by quenching experiments or by direct monitoring of photoproduct. However, assuming for simplicity that η_{PISC} and η_P are zero and that reaction occurs only via the thermally equilibrated quartet state, the effficiency of BISC can be calculated from eqs 1−4. When these assumptions are substituted into the full equations, eqs 1−4, one obtains the simple expression

$$\phi_{Dirrad}/\phi_{Qirrad} = \eta_{BISC} = 0.074/0.099 = 0.76 \quad (8)$$

The quantum yields can then be modeled[211] by the BISC/quartet reaction model with the parameter values shown in Figure 9, where the efficiency of ISC has been arbitrarily assumed to be 0.7, the same as that for $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$. Obviously this modeling is not unique but, as shown in Figure 9, the correct quantum yields for doublet and quartet irradiation are predicted. Furthermore, the observed phosphorescence lifetime in solution in the high-temperature regime was well-described by a double-exponential Arrhenius equation with *A* factors/activation energies of $(1.2 \pm 1.0) \times 10^{15}\ s^{-1}/(45 \pm 1)$ kJ mol^{-1} and $(5.4 \pm 1.2) \times 10^{11}\ s^{-1}/(29 \pm 1)$ kJ mol^{-1} for the two rate constants involved. The first set of parameters is consistent with expectations for BISC (compare $Cr(NH_3)_6^{3+}$ above), while the second set have a temperature coefficient of the order expected for doublet nonradiative decay (compare[212] $Cr(CN)_6^{3-}$). These expressions lead to an independent calculated value of $\eta_{BISC} = k_{BISC}/(k_{BISC} + k_{Dnr}) = 0.76$ at 295 K, concordant with the value obtained from the modeling of the photochemical quantum yields. The results confirm that there is a rapid nonradiative decay

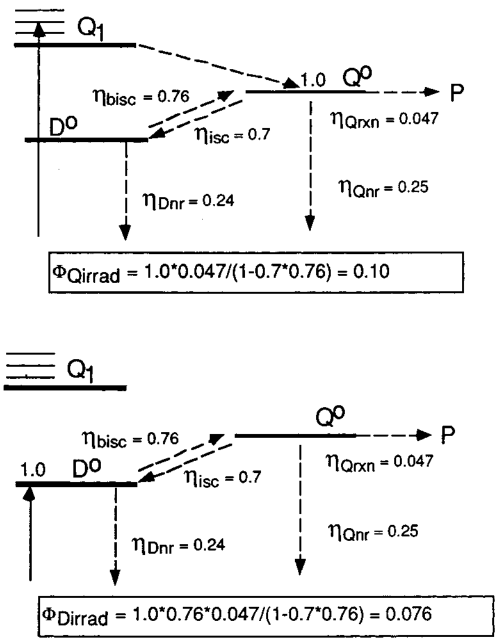

Figure 9. Kinetic scheme for $Cr(sen)^{3+}$ photoaquation. The upper half shows how the scheme leads to the observed 0.099 quantum yield for quartet irradiation, while the lower half shows it also gives the 0.075 quantum yield for doublet irradiation.

process influencing the doublet lifetime in $Cr(sen)^{3+}$; it is not direct reaction, and it competes with BISC.

Another system that shows[102] differences in the photochemistry for the reaction via the doublet and quartet is $Cr(NH_3)_5(py)^{3+}$, although here the distinction was between the quenched and the unquenched photochemistry using $Cr(ox)_3^{3-}$ as the quencher. It was found that the unquenchable photoreaction, which was about 20% of the total, gave a ratio of py/NH_3 aquation of about unity. In contrast, the quenchable fraction showed a py/NH_3 ratio closer to 2. Two possible explanations were offered for this result. The first proposed a direct reaction via the doublet state, a reaction that favored loss of pyridine ligand. The second was in terms of reaction from the two lowest quartet states, ^4E_g and $^4B_{2g}$, which have AOM-predicted photoaquation modes of py and NH_3, respectively. If the Franck–Condon quartet state and BISC from the doublet state give rise to different populations of these two states, then the different product ratio can be accounted for. The explanation of this photochemistry remains to be finalized.

A strong case has been made[213,214] for direct doublet-state reaction in Cr(III) polypyridyl complexes. In these complexes, the doublet state is particularly long-lived, with room-temperature solution lifetimes approaching 0.5 ms for some substituted phenanthroline complexes. Quantum yields of photoaquation of a polypyridyl ligand are small and show a pH dependence attributed to the "titration" of a seven-coordinate aqua intermediate. The same pH dependence is seen for the thermal reaction and the photochemistry. As a means to explore the mechanism of the doublet reaction, the temperature dependence of the quenchable and unquenchable reaction in $Cr(bpy)_3^{3+}$ has been investigated[215] using iodide as a quencher. The unquenchable quantum yield, about 2% of the total quantum yield, was found to show a pH dependence with a "titration curve" centered at pH 7 that was parallel to the behavior of the quenchable photochemistry. Apparent activation energies were obtained from Arrhenius plots of $\ln(\phi)$ vs $1/T$ for the two components of the reaction, and the values 40 and 8.0 kJ mol^{-1} were obtained for the unquenchable and quenchable fractions, respectively. These were then analyzed in terms of the possible mechanisms of doublet reaction, not including the GSI model which was not then current. First it was noted that the 40 kJ mol^{-1} value for the activation energy of the reaction via the quartet state was higher than would be expected. The reviewer agrees and notes it is much higher than for other Cr(III) photochemical apparent activation energies, including the 9.2 kJ mol^{-1} reported for the analogous $Cr(phen)_3^{3+}$. No explanation for the high value was given. There are precedents[216] for reactive quenching, and if this contributed in a temperature-dependent fashion, it could account for this unusually high activation energy.

More important and relevant, when the quenchable reaction was modeled as a direct doublet reaction, the activation energy for this process was found to be 41 kJ mol^{-1}. In contrast, an effort to model the reaction in terms of BISC and quartet reaction was not acceptable as it implied that the thermally equilibrated quartet state had an energy equal to or less than the doublet state. The authors concluded that the reactions from the doublet and quartet states to form the $Cr(bpy)_3(H_2O)^{3+}$ intermediate had essentially the same 41 kJ mol^{-1} activation enthalpy, and this was attributed to a large degree of disruption of the ion structure and solvation shell to form a seven-coordinate configuration. If correct, this would make the behavior of this complex quite unusual, given the differences in electronic configurations of the states involved in the quenchable and unquenchable photochemistry. It would be of interest to explore a fit of the data on these Cr(III) polypyridyl complexes to the full kinetic scheme[23] of Figure 2.

The extreme sensitivity of the doublet state of these complexes to environment is illustrated in a study[217] of the effects of electrolyte and solvent on the doublet-state lifetime and its susceptibility to ground-state quenching. At low temperature in aqueous solution, the doublet lifetime and emission intensity show a decrease of about 20% at higher pH with a pH functionality showing an inflection point at pH 6–7. For $Cr(phen)_3^{3+}$, the activation energies for the doublet lifetime are 37 kJ mol^{-1} at pH 3–4 and 31 kJ mol^{-1} at pH 9–10. In the presence of 1 M NaCl, these pH effects are greatly diminished and the lifetime in acidic solution becomes a function of [Cl^-]. These results were interpreted in terms of the existence of water, hydroxide, or chloride in the intraligand pockets where they influence the metal center. It was suggested that the relatively minor photochemical pathway involved incorporation of intraligand water or hydroxide to form a seven-coordinate intermediate. The incorporation of species into intraligand pockets would be consistent with observations[218] of the volume of activation for the doublet lifetime and the formation of photoproduct in $Cr(bpy)_3^{3+}$ of −1.6 and 2.9 $cm^3\ mol^{-1}$, respectively. The latter positive value was recognized as consistent with incorporation of a water molecule already located in the intraligand pockets, although a dissociative step was also considered possible.

The laser flash photolysis studies with conductivity detection[124,125] allowed comparison of the kinetic behavior of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$. These authors found that for $Cr(bpy)_3^{3+}$, about 93% of the reaction occurred via the doublet state. There was clear evidence for an aqua intermediate that released protons with a pK_a value of about 2; the authors considered that it was likely that this was an excited-state pK_a value for the intermediate $^*Cr(bpy)_3(H_2O)^{3+}$ rather than for the equivalent ground-state intermediate for which they anticipated a pK_a value closer to 5−6. The behavior of $Cr(phen)_3^{3+}$ was similar in outline but showed a significant difference in that no intermediate with an excited-state pK_a value was evident. The authors concluded that with $Cr(phen)_3^{3+}$, an intermediate only formed on direct attack by hydroxide ion. On the basis of the kinetic differences between the two complexes, it was decided that it was likely that the intermediate was six-coordinate, having a monodentate polypyridyl ligand, rather than a seven-coordinate species. One important result was that for $Cr(bpy)_3^{3+}$ but not for $Cr(phen)_3^{3+}$ transient bleaching was seen in acid solution, indicating the presence of a long-lived intermediate. Also, the hydroxide ion dependence of the observed rate constants for the conductivity decay for the two complexes was of the form $k_{obs} = k_i + k_s[OH^-]$, where the k_i term includes ring closure to form the starting complex. It was found that $k_i(phen)/k_i(bpy)$ was about 3×10^3, consistent with the fact that the less-flexible monodentate phen is more restricted than bpy in the number of conformations available to it in solution, favoring more rapid ring closure.

D. Evidence from Photochemical Reaction Modes and Stereochemistry

Wavelength dependence studies of photoreaction modes have shown that many complexes show the same ratio of two different photoreaction modes for the quenchable and unquenchable reactions. As an example involving intermolecular competition, the photoaquation and photoanation of $Cr(NH_3)_6^{3+}$ by chloride, bromide,[76] and thiocyanate[78] ions has already been mentioned. Examples involving aquation of more than one ligand are the ethanediamine and thiocyanate ion photoaquation ratios from *trans*-$Cr(en)_2(NCS)Cl^+$,[158] *trans*-$Cr(en)_2(NCS)_2^+$,[135] and *trans*-$Cr(en)_2(NCS)F^+$ (with a superimposed wavelength dependence from the unquenchable reaction mode)[219] and most striking of all the NH_3:NCS^-:CN^- ratios for *trans*-$Cr(NH_3)_4(NCS)(CN)^+$ which are the same[97] for the quenchable (75%) and unquenchable (25%) reactions.

Some complexes show the same stereochemistry for the reactions via quartet and doublet. Examples are Δ-$Cr(en)_3^{3+}$, which gives 28% Δ-*cis*-, 7% Λ-*cis*-, and 65% *trans*-$Cr(en)_2(enH)(H_2O)^{4+}$, and $Cr(NH_3)_5(CN)^{2+}$, which gives 67% *cis*- and 33% *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$. These results suggest[16] a common pathway for the doublet and quartet reactions. Complexities are again encountered, however. A small difference in the product isomeric ratios was reported[198,199] for the quenchable and unquenchable reactions in $Cr(tn)_3^{3+}$ and ascribed to prompt reaction in the quartet state.

E. Wavelength Dependences

As described in the previous sections, the wavelength dependence of ISC yields has been found for several complexes, and also irradiation into the charge-transfer bands of many Cr(III) complexes promotes redox reaction. It is the possibility of an additional wavelength dependence on irradiation in the ligand-field bands that is considered here. It has been observed that although most homoleptic complexes photoreact with wavelength-independent quantum yields (wavelength dependence of the quenchable yield in $Cr(NH_3)_6^{3+}$ has been reported,[7] however), a number of tetragonal complexes of the type $Cr(N)_4XY^+$ show a wavelength variation of quantum yields and reaction mode ratios. Relevant data are given in other reviews.[1,2,16,24] The effect was recognized in the first Cr(III) photochemical rules.[220] Rules 1 and 2 proposed preferential photosubstitution of the strong-field ligand on the weak-field axis, but rule 3, which is not usually mentioned, referred to a less discriminating reaction pattern on irradiation into the next higher LF quartet band. On the basis of the early MO appproaches,[67,221,222] it was recognized that this wavelength dependence of reaction modes could be interpreted[158] in terms of reaction from both the lowest ^4E and the higher $^4B_2$ state. This represents a departure from the common assumption that photoreaction occurs only from the lowest excited state of a given multiplicity in parallel with Kasha's rule[223] for emission. Thus, in *trans*-$Cr(en)_2(NCS)Cl^+$, the ratio of en:NCS^- aquation increases to higher energy.[158] The lowest quartet state is ^4E for which mainly thiocyanate photoaquation is expected by the AOM bond indices of 8.7 and 12.1 × 10^3 cm^{-1} for Cr−NCS and Cr−N, respectively. However, the next highest $^4B_2$ state has labilization only in the *xy* plane, favoring photoaquation of ethylenediamine. Evidence to support such a reaction from the higher quartet state was obtained in a study of differential quenching[219] of photoreaction in *trans*-$Cr(en)_2(NCS)F^+$. The lowest quartet and doublet states reacted to give a 4:1 ratio of NCS^-:en, but on irradiation to higher energy, a wavelength-dependent unquenchable ethylenediamine mode occurred in addition. This can be interpreted in terms of a variable branching of the Franck−Condon (FC) state to populate the reactive $^4B_2$ and ^4E states. To interpret it as a prompt reaction from the FC states (a DOSENCO process[5]) raises the question of why it would be so specific to ethylenediamine loss. Reaction via $^4B_2$ and ^4E states has similarly been used to rationalize[24,224,225] the wavelength dependence of the am(m)ine and cyanide photoaquation modes in several cyanoam(m)ine complexes. There is further support for this two-quartet-state photochemical model from wavelength- and temperature-dependence studies[226,227] of the reaction modes in *trans*-$Cr(en)_2(NCS)F^+$ and *trans*-$Cr(en)_2(NH_3)F^+$.

An interesting feature of that part of the photoreaction that proceeds via the doublet is that its reaction mode ratio and stereochemistry is the same as that for the quartet-state reaction seen for long-wavelength irradiation. If the above two-quartet-state model is truly viable and if the doublet fraction of the reactivity goes via BISC and quartet reaction, this requires the doublet state to thermally populate both $^4B_2$ and ^4E in a non-Boltzmann ratio. To resolve this dilemma, it has been proposed[16] that in solutions at ordinary temperatures, BISC may be a solvent-promoted process that is controlled by the kinetics of solvent interaction with the complex. The recent findings of decreasing doublet lifetime with increasing solvent donor number[39] are consistent with such a picture. Solvent- and temperature-dependence studies involving complexes with more than one reaction mode would be very useful.

F. Photostereochemistry

Stereochemical change associated with photosubstitution is well-established for acidoam(m)ine complexes, and a simple pictorial representation of the AOM that explains the phenomenon was presented in Figure 3 and its caption. For fluoro and cyano complexes, however, stereochemical change has proven to be less complete. This, as well as the observation that the same putative five-coordinate intermediates generated from *trans*- and *cis*-$Cr(NH_3)_4F_2^+$ lead to different product ratios, stimulated further development of the theory. One interpretation recognized that the five-coordinate tbp intermediates can be generated in an excited state which reacts with an opposite stereochemical requirement than its ground state. Different extents of reaction from the excited- and ground-state tbp intemediates then rationalized the observed differences in product ratios. The other interpretation is in terms of the Jahn−Teller behavior of the tbp intermediates, described in the theoretical section and in Figure 5.

These two models do rationalize[150] the photoproducts found[148,226] for the fluoroammine complexes. In the photochemistry of $Cr(NH_3)_5F^{2+}$, which loses mainly axial ammonia, 15% of *trans*-$Cr(NH_3)_5(H_2O)F^{2+}$ product was observed. This was unusual for an acidopentammine and, by comparison with the photochemistry of the model compound *trans*-$Cr(en)_2(NH_3)F^{2+}$, was likely to arise from photoaquation of equatorial ammonia from the ^4E excited state of the complex. Correction for the leaving-group ability of en relative to ammonia then indicated a 20% *trans*/80% *cis* ratio for the $Cr(NH_3)_5(H_2O)F^{2+}$ product of this reaction mode. The explanation offered for this was that the tbp intermediate with an equatorial fluoride ligand is generated in its excited state. If it reacts before decay, it leads to the trans isomer, while after decay to its ground state it reacts to give the cis isomer.

For the difluorotetrammine complexes, the results can again be explained with either model; we discuss only the JT version and refer the reader to the original paper[148] for the other. Table 2 gives information on the photoproduct ratios found as a result of photoaquation of ammonia from these geometric isomers. Ammonia loss from *cis*-$Cr(NH_3)_4F_2^+$ leads to an sp_{cis} fragment with one axial and one equatorial fluoride as shown on the right-hand side of part (c) of Figure 5. The crossing that occurs close to the decay pathway to tbp_{ee} will then favor transverse decay, leading to fragments sp_{bas} and sp_{cis} in roughly equal amounts, consistent with the experimental findings of 45% *trans-mer*- and 55% *cis-mer*-$Cr(NH_3)_3(H_2O)F_2^+$. In contrast, ammonia loss from *trans*-$Cr(NH_3)_4F_2^+$ gives sp_{bas}, left, which decays via the same tbp_{ee} intermediate. However, the crossing point is now displaced away from the entry point, leading to a more random decay pattern. The product ratio found is 29% *trans-mer*- and 71% *cis-mer*-$Cr(NH_3)_3(H_2O)F_2^+$, close to the statistical ratio. Note that these models predict the absence of significant amounts of the facial photoproduct for both isomers, as does the simple model of edge displacement in the plane of labilization encapsulated in Figure 3.

The photostereochemistry of $Cr(NH_3)_5(py)^{3+}$ is unusual. The pyridine loss mode cannot easily be studied because of the indistinguishability of the ammonia ligands, but the ammonia loss mode gives both *cis*- and *trans*-$Cr(NH_3)_4(py)(H_2O)^{3+}$. For reaction by loss of axial ammonia ligand from the lowest ^4E state, the stereochemical prediction (Figure 3) is exclusive formation of cis isomer, whereas experiment showed an estimated 20−30% of trans isomer was present. This trans isomer could of course arise from a stereoretentive photoaquation of axial ammonia, but the authors[102] preferred to consider it as a concerted substitution with stereochemical change and attributed the reaction to loss of equatorial ammonia from the ^4E state. This generates, in its excited state, the tbp intermediate with an equatorial pyridine ligand for which the allowed entry of water trans to pyridine leads to the observed trans product. This parallels the findings and explanations presented above for the fluoro analogues. The authors were careful to emphasize that although they presented these arguments in terms of dissociative intermediates, they considered that the processes involved were likely to be associative and concerted.

More complex mixtures of photoproducts have also been observed for the cyanoammine complexes, $Cr(NH_3)_5(CN)^{2+}$ and *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$. For the first two complexes, the lowest excited quartet state is $^4B_2$ for which photoaquation of equatorial ammonia is predicted to be the exclusive reaction mode. For the cis isomer, the lowest excited quartet state is ^4E, which offers the possibility of photoaquation of an equatorial or axial ammonia ligand. The product ratios found for irradiation into the lowest quartet states of the complexes are listed in Table 2. These results have been discussed[4,24] in terms of the model of reaction via excited- and ground-state tbp intermediates. They are consistent with expectations only if one allows for reaction via both $^4B_2$ and ^4E states. However, the observed changes in the products for irradiation at higher energies implied[24] reaction via two states for the cis isomer but only one for the trans.

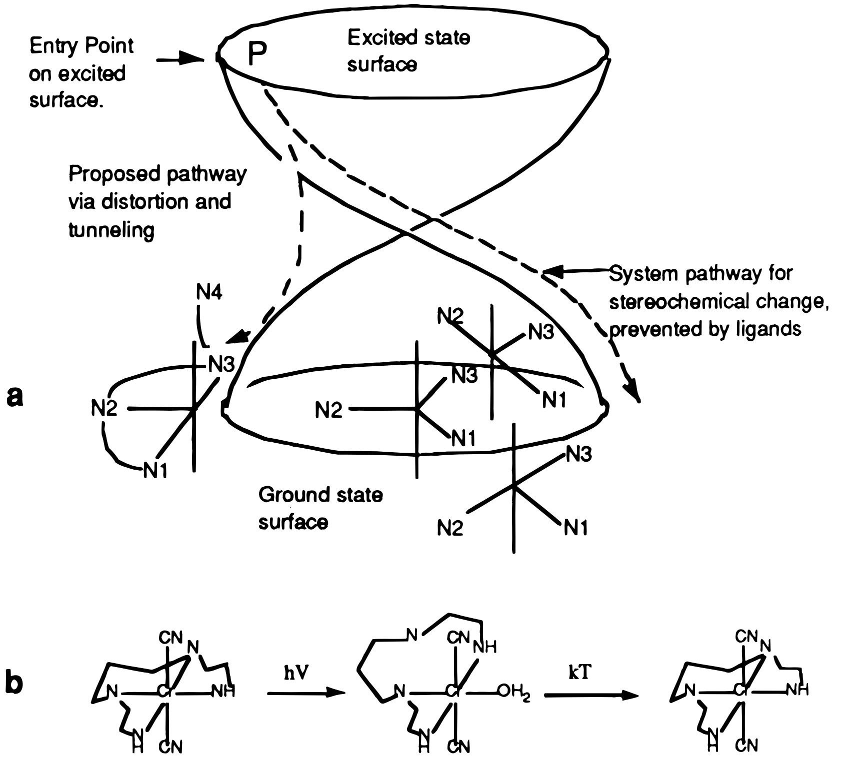

Figure 10. Possible mechanisms for *trans*-Cr(2,3,2-tet)(CN)$^{2+}$ photochemistry. (a) In the JT model, decay from the entry point, P, on the excited-state surface leads to the conical intersection at tbp geometry and the nuclear momentum carries the system to the sp intermediates that lead to stereochemical change. The macrocylic ligand prevents this but may be sufficiently flexible to allow ligand dissociation, followed by coordination of solvent to the resulting ground-state sp species at the left of the figure. (b) Hypothetically, loss of a secondary nitrogen ligand may occur with stereochemical change to give the product shown in the center. Recoordination of the ligand will eventually lead back to the starting material with trans cyano ligands, as observed experimentally.

The complexity of the products obtained[225] from photoaquation of 1,3-propanediamine in *trans*-Cr(tn)$_2$(CN)$_2$$^+$ prevented detailed application of these stereochemical models. The product Cr(tn)(tnH)(H$_2$O)(CN)$_2$$^+$ was formed with trans and cis cyano ligands in a ratio of ~7 at 488 nm and ~5 at 458 nm, however. This implicates reaction of both excited- and ground-state tbp intermediates along with participation of ^{4}E and ^{4}B$_2$ states in a wavelength-dependent manner.

Unfortunately no analysis of the results for these cyanoam(m)ine systems in terms of the JT model has been published to date. Consider Cr(N)$_5$(CN)$^{2+}$ and *trans*-Cr(N)$_4$(CN)$_2$$^+$ as examples. For photodissociation of an in-plane nitrogen ligand from the lowest ^{4}B$_{2g}$ state, the resulting five-coordinate intermediates have three identical nitrogen ligands in the equatorial plane (with one or two cyano ligands on the orthogonal axis), so the excited- and ground-state potential surfaces for the five-coordinate species are degenerate at the tbp configuration, as in Figure 5. This provides a rationale only for formation of the single product with an equatorially substituted aqua ligand, *cis*-Cr(N)$_4$(H$_2$O)(CN)$^{2+}$ or *trans-mer*-Cr(N)$_3$(H$_2$O)(CN)$_2$$^+$ for these two starting materials, respectively. The same products are formed whether or not the substitution occurs with mechanistic stereochemical change. This analysis makes clear that no *trans*-Cr(N)$_4$(H$_2$O)(CN)$^{2+}$ or *cis-mer*-Cr(N)$_3$(H$_2$O)(CN)$_2$$^+$ can arise from these reactions of the ^{4}B$_{2g}$ state; to account for these products, reaction from the ^{4}E$_g$ state must be invoked. The only alternative is to abandon these photochemical models.

In an attempt to test the proposition that stereochemical change was a requirement of the above reaction via the ^{4}B$_2$ state, the molecule *trans*-Cr(2,3,2-tet)(CN)$_2$$^+$ was synthesized.[109,110] In the equatorial plane of this molecule, the ligand constraints prevent stereochemical change, so that were it to be a requirement of photoreaction, the molecule should be photoinert. In contrast, on photolysis the compound gave a proton uptake quantum yield of 0.09 ± 0.01 with no cyanide release. The isolated photoproduct, on standing at 25 °C, recoordinated in a pH-sensitive manner (half-life of 8 min at pH 6, 30 min at pH 9, and 30 h at pH 3)[206] to the *trans*-Cr(2,3,2-tet)(CN)$_2$$^+$ starting material, showing that the photoproduct had trans cyano ligands. These results preclude reaction via the ^{4}E$_g$ state with stereochemical change and lead to the conclusion that the reaction occurred from the ^{4}B$_{2g}$ state but in a stereoretentive manner. Shown in part a of Figure 10 is one explanation offered for this behavior in terms of the JT model and the expected loss of primary amine ligand. As the system decays from the entry point P toward the tbp configuration, the ligand constraints come into play and prevent the transverse crossing normally expected. However, there is probably sufficient ligand flexibilty to allow approach to the crossing point with full dissociation of the primary amine ligand and channeling to the ground state of the starting sp intermediate leading to stereoretentive reaction.

Our recent exploration of intermediate formation in photoreactions of Cr(III) complexes with macrocyclic ligands implies the viability of dechelation of a ring-N atom from *cis*-$Cr(cyclam)(NH_3)_2^{3+}$, Figure 7. This now suggests an alternative explanation for the data on *trans*-$Cr(2,3,2\text{-tet})(CN)_2^{+}$. Loss of a secondary nitrogen of the 2,3,2-tet ligand could give the ring-dechelated aquaproduct, as shown in the mechanism of part b of Figure 10, and on thermal recoordination this would reform the starting material as observed. The reactions shown, if they occur, maintain the integrity of edge displacement in the plane of excitation. Unfortunately our efforts to isolate and confirm the structure of intermediates of this type have not yet succeeded, so the correct explanation of this photochemistry remains an open question. More important, it leaves the field still open for a definitive experiment that would prove whether $^4B_{2g}$ excited-state reaction occurs with required stereochemical change. There appears to be no theoretical reason to expect a difference in photostereochemistry from the ^4E_g and $^4B_{2g}$ lowest quartet excited states.

Finally, it is appropriate to finish this discussion by recalling that the preponderance of evidence indicates that these photoreactions proceed by associative pathways. It appears, nevertheless, that the JT model of five-coordinate intermediates rationalizes a great deal of the observed photostereochemistry. A theory involving equivalent seven-coordinate intermediates is not currently available but is a desirable objective. The reviewer considers that the same electronic driving forces could be determining the stereochemical course of reactions via seven-coordinate intermediates as in the simple pictorialization of Figure 3. This leaves us currently in a situation that has been seen before in chemistry; a fairly workable model that conflicts with reality.

VI. Applications

The potential of Cr(III) polypyridyl complexes for use in solar energy conversion schemes has been considered.[6] The absorption spectra are reasonably favorable, as the compounds have moderate absoption up to 500 nm and there is an expectation that chromophoric ligands can be used to extend this range. Phenyl- and halo-substitution on phenanthroline rings can be used to achieve a spectral red shift. Absorption leads to the doublet excited states with essentially unit efficiency in aqueous media, although ISC yields are reduced[167,228] in D_2O, in mixed organic/aqueous solvents, or in the presence of electrolytes.[6] The doublet excited state has a fairly low E_{00}, about 1.7 eV, which helps move the absorption to the red, but means the enhancement of the excited-state redox potentials is less than that seen for $Ru(bpy)_3^{2+}$. When combined with the ground-state potentials, however, the result is that $^*Cr(bpy)_3^{3+}$ is a particularly poor reducing agent but a better oxidizing agent than $^*Ru(bpy)_3^{2+}$. This Cr(III) complex undergoes redox quenching reactions with $Fe^{2+}(aq)$, I^-, $Ru(NN)_3^{2+}$, and organic amines which have quenching rate constants in the range from 10^7 to 10^{10} M^{-1} s^{-1}. Unfortunately, as with other systems, the back-electron-transfer processes are fast, requiring the use of sacrificial reagents to try to increase net yields of photoredox products. It is hoped that the sensitivity of the doublet properties to medium effects might provide avenues to improve the performance of photoredox systems based on Cr(III) polypyridyls.

Phenol photooxidation in aqueous solution was recently shown to be sensitized[229,230] by $^*Cr(bpy)_3^{3+}$. The products found were 1,4-benzoquinone with some $Cr(bpy)_2(H_2O)_2^{3+}$, but there was no evidence of redox products. In the absence of oxygen, no benzoquinone was produced and flash photolysis experiments failed to detect any $Cr(bpy)_3^{2+}$. Consequently, the photosensitized reaction was attributed to energy transfer from $^*Cr(bpy)_3^{3+}$ to generate singlet oxygen, which then oxidizes phenol to benzoquinone. This paralleled the process that is seen using Rose Bengal as a singlet-oxygen generator. Acetylacetonato complexes of Cr(III) are similarly effective photocatalysts[231] for the oxygenation of α-pinene. The quantum yield of singlet oxygen generated in quenching of $Cr(bpy)_3^{3+}$ by molecular oxygen has recently been measured[232] as 0.86, a greater efficiency than that for the popular oxygen-sensitizer Rose Bengal ($\phi = 0.80$). The authors concluded that in the other 14% of quenching events, spin-catalyzed conversion to the ground states of $Cr(bpy)_3^{3+}$ and oxygen occurred. $Cr([9]aneN_3)(NCS)_3$ has also been reported[107] to be an efficient generator of singlet oxygen with a quantum yield of about 0.5 in oxygen-saturated acetone. This property of Cr(III) complexes has other potential applications, for example, as in photodynamic therapy.

Photoinitiated polymerization has also been studied. In one approach that has been the subject of two patents,[233,234] $K[Cr(NH_3)_2(NCS)_4]$ has been used[235] as a photochemical source of the thiocyanate anion, which then catalyzes the polymerization of ethyl α-cyanoacrylate (CA). The mechanism involves thiocyanate addition to the double bond of the acrylate monomer, which initiates the chain polymerization process. The patents cover the application of this technique using metal complexes that photolyze to produce various anions, which will react with a variety of substrate species.

In the other approach, based on an observation[236] that $Cr(H_2O)_6^{3+}$ appeared to be an efficient photoinitiator of vinyl monomer polymerizations, the aqueous solution polymerization of acrylamide (AA) by $^*Cr(bpy)_3^{3+}$ has been studied.[237] The phosphorescence intensity from $^*Cr(bpy)_3^{3+}$ showed Stern–Volmer quenching with $k_q = 3 \times 10^3$ M^{-1} s^{-1}. Irradiation at 365 nm in the presence of 1 M AA indicated formation of $Cr(bpy)_2(H_2O)_2^{3+}$ with the same yield in the presence or absence of AA. Polymerization of AA was observed only in the absence of oxygen. The initiation step leading to polymerization was considered to be electron transfer from AA to $^*Cr(bpy)_3^{3+}$ to produce a radical chain carrier. Termination was attributed to reduction of ground-state $Cr(bpy)_3^{3+}$ by the polymer radical species, leading to a dependence of polymerization rate constant on light intensity, $[AA]^2$ and $1/[Cr(bpy)_3^{3+}]$, consistent with the kinetic observations. Unfortunately the polymerization process was quite inefficient owing to the low quenching rate constant coupled with the inefficiency of the initiating redox step resulting from rapid back electron transfer.

Intermolecular interactions have been probed via variations in Cr(III) photochemical quantum yields and emission intensities. Photoaquation of $Cr(NH_3)_6^{3+}$ in the presence of aminopolycarboxylate anions in alkaline medium showed[208] an increase in the photoaquation quantum yield at low concentrations, where solvent-separated ion pairs were present, followed by an overall reduction in yield at higher concentrations. Concurrent increases in emission yield were attributed to inhibition by the aminopolycarboxylate of quenching of the doublet state by hydroxide ion. The photoaquation yield reduction was attributed to steric blocking which prevents loss of five of the ammonia ligands in the contact ion pair formed[208] between the EDTA and $Cr(NH_3)_6^{3+}$ at higher concentrations. Analogously, $Cr(CN)_6^{3-}$ showed[238] a 3-fold reduction in the photoaquation quantum yield on formation of a supramolecular structure with [32]aneN_8. This was explained in terms of the formation of a “belt” structure in which the protonated form of the macrocycle encircled four equatorial cyano ligands, preventing their photodissociation. The immobilization in this way of two-thirds of the cyano ligands accords well with the observed 3-fold reduction in photoaquation quantum yield.

Cr(III) complexes have a long history[15,239] as useful quenchers for excited states of other molecules, organic and inorganic. Recent work[240−245] testifies to their continued utility both as energy-transfer and electron-transfer quenchers. There is also continued interest in developing the Cr(III) doublet state as a light-emitting center both in polynuclear complexes[246] and for optical applications.[247,248] Related to this is the utility of the Cr(III) phosphorescence as a probe of environment in solids such as alums,[249,250] zirconia catalysts,[251] and proteins.[252]

Finally, Cr(III) complexes have found application[253] as precursors to the formation of films of metallic chromium, and the observation of Cr(III) in terrestrial fog[254] implies the relevance of Cr(III) photochemistry to the environmental chemistry area.

VII. Summary

Much of Cr(III) photochemistry is now well-understood, despite outstanding questions. First, reaction from the excited quartet state, a central assumption of the angular overlap model, is established experimentally for a large number of complexes. This model correctly determines the plane of labilization in a complex, and the ligand rearrangements that accompany photosubstitution are confined to that plane of labilization. Indeed, the latter prediction may be the strongest feature of the model. The predictions of the leaving ligand based on the calculated bond indices are reasonably good, but here there do seem to be some problem cases. Since the calculations of the excited-state bond strengths are based on a very simple model and the bond strength is only one of several factors influencing ligand loss, this is perhaps not too surprising. One approach to overcoming this problem is to establish a sequence of leaving-group abilities for different ligands, and given these, reasonable estimations of photolabilization modes can be made. Other factors to consider in making such predictions are that ligand-field parameters are not truly independent of the other ligands present and that ligand loss from the plane of labilization appears to be a competitive process.

To explain the photosubstitution modes in some tetragonal complexes and, in particular, to rationalize the wavelength dependences of quantum yields for substitution of the individual ligands, it is also necessary to conceive of reaction from both of the lowest quartet excited states, ^4E_g and $^4B_{2g}$. The actual quartet state energies are very uncertain and present an important unsolved problem. The AOM estimates their values for the complex (often based on parameters from crystal absorption spectra) at ground-state geometry, and there is no information available on the energies of the photochemically relevant tetragonally distorted relaxed excited states. The empirical 5%-absorption rule often used as a substitute for this information correlates low-temperature solid-state spectroscopic estimates of the zero−zero quartet energy to room-temperature solution absorption spectra. It, therefore, does not resolve the problem. For complexes in which BISC is the main process depleting the doublet, the best estimate[255] of the maximum quartet energy can be obtained via the apparent activation energy for the phosphorescence decay lifetime.

That the excited quartet states are extremely short-lived is suggested by the fast rise time for the doublet-state population and the general failure to observe fluorescence; they may have subpicosecond lifetimes consistent with reaction on the time scale of vibrational motion. It is also very probable that in solution the quartet states strongly interact with Lewis donor solvents via the vacant t_{2g} orbital, an interaction that is likely to have a profound effect on their energy and configuration. In many instances, this solvent interaction will lead to photosubstitution but not invariably so. In regard to the photochemical outcome, it has been argued that a fast quartet-state reaction should be recognizable via its effects on the room-temperature solution absorption spectrum. This is an issue that should be carefully investigated. Experimental studies of small molecules in the gas phase[256,257] indicate that dissociation on the time scale of a few femtoseconds causes vibrational band broadening of just over 1000 cm^{-1}, consistent with the estimate based on the Heisenberg principle. Given the breadth of the Cr(III) quartet absorption bands, this might easily go unnoticed. For many hexam(m)ine complexes, the quartet absorption band in room-temperature solution tails out to underlie the doublet absorption, 5000 cm^{-1} lower in energy than the spectroscopic estimate of the quartet-state energy. It is reasonable to hypothesize that the cause of this may be spectral broadening arising from a rapidly reactive quartet state in solution. One would not expect such broadening to be limited to photoactive complexes. The presence of the vacant t_{2g} orbital invites strong interaction with a nucleophilic solvent in the excited state, even if it results in no net reaction. The coordination of solvent to give a seven-coordinate species, followed by return to the starting material, could be an important mechanism for fast radiationless decay to the ground state under photochemical conditions. There is evidence for an influence of solvent rigidity on the intersystem crossing yield in the red edge of the first ligand-field band[166] that may arise because of such strong solvent interactions.

Also to be considered is the significance of the stereochemical change commonly, and uniquely, observed for Cr(III) photoreactions. Like the Walden inversion in nucleophilic substitution at carbon, this has strong mechanistic significance. The AO theory provides a plausible explanation in terms of quartet reaction, as shown in Figure 3. There are a few complexes that do not show this complete stereochemical change, and some, but not all, of these can be rationalized nicely by a new model of the Jahn–Teller behavior of five-coordinate intermediates. Furthermore, the assumption that reaction can occur from both of the lowest quartet ^4E_g and $^4B_{2g}$ states allows a rationalization of the observed wavelength dependencies of photoproduct stereochemistry.

The published stereochemical models involve five-coordinate species, in conflict with the volume of activation evidence that indicates the photochemistry is associative, if only marginally so. For some complexes, small negative apparent activation volumes have been obtained, while for others, small positive values have been seen. Also, it must be remembered that these are composite quantities, not easily converted into the true activation volume for the reaction step itself. In terms of the mechanisms of Figure 3, the distinction is the degree to which breaking of the Cr–A bond precedes the formation of the Cr–W bond. It would be nice to have an equally successful theory that derives parallel results for the asymmetric pentagonal bipyramidal intermediates[14,16] that are more realistically the true intermediates in all this photochemistry. However, it should not be considered mandatory and given the subtleties of the I_d and I_a distinction, this deficiency is not a very good argument against the model. Because of literature discussions centering on the importance of ground-state intermediates, it is worth emphasizing that in the associative AOM pathway shown in Figure 3, the molecule begins at an excited quartet state and evolves via a seven-coordinate ground-state species to the ground state of the photoproduct. It is not clear whether the seven-coordinate entity should be called an intermediate or a transition state.

Looked at from the other direction, the success of the model supports the assumption of quartet reaction and, by extension, the BISC pathway of doublet reaction for those complexes which show the same stereochemistry for the quenchable and unquenchable photochemistry, such as[64] $Cr(en)_3^{3+}$ and $Cr(NH_3)_5CN^{2+}$.[95] There is no reason to attribute analogous stereochemical features to the proposed alternatives of a direct reaction from the doublet state or via a GSI formed by tunneling to the ground state. For the direct doublet reaction, the expectation is that the substitution reactions would mimic those of the ground state, which are strongly stereoretentive. Most of the unequivocal doublet-state reactivity that has been reported consists of bimolecular redox chemistry. For the GSI the expectations are obscure, but it is hard to see why what should be considered a “hot” species with the ground-state electronic configuration should in so many complexes show a stereochemical outcome that is so specific and so different from that of the ground state. Also, why then should complexes such as *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ be photoinert?

The recent support for a reaction pathway via BISC and quartet reaction in hexam(m)ine complexes leaves but a few complexes where these other mechanisms of reaction seem to be required. The Cr(III) polypyridyls are the best documented examples supporting direct doublet reactivity. The complexes have very long solution doublet lifetimes, up to milliseconds, so if bimolecular reaction involving the doublet state is going to occur, such as with the strong nucleophile hydroxide ion, these molecules have the best opportunity. It should be noted, however, that the photochemical behavior of these complexes parallels the hexammine systems in showing quenchable and unquenchable reaction modes having the same pH dependence, etc. In light of the possibility that the energy barrier to BISC may be very uncertain and may not be quite so dominant as hitherto thought, the time may be ripe for another look at these systems.

How far can one go with this argument? Surveying the higher ligand-field strength complexes suggests that the energy barrier to BISC truly is prohibitive in hexacyanochromate(III), $Cr(NH_3)(CN)_5^{2-}$, and in $Cr(py)(CN)_5^{2-}$. These complexes show two important characteristics that set them apart from the weaker field systems; there is no slow, quenchable component to the reaction (i.e., notably, the doublet does not react directly or by tunneling to a GSI) and, second, the quantum yield is small and of comparable magnitude to that found for the unquenchable fast reaction in hexammine complexes.

Now consider the application to complexes that react via both ^4E_g and $^4B_{2g}$ states. The same product distributions are often observed for the quenchable and unquenchable reactions. It follows that either the doublet state happens to react in the same proportions as the quartet state or that back-intersystem crossing occurs to these states in much the same ratio as is obtained by direct excitation. Moreover, this ratio is different from that expected for a Boltzmann distribution based on the spectroscopic quartet state energies. To accommodate this requirement, it has been proposed[16] that BISC may be kinetically controlled in room-temperature solutions. If true, the distinction between direct doublet reaction and BISC/quartet reaction becomes semantically subtle, but the positive volume of activation for doublet decay and the negative volume of activation for reaction in $Cr(NH_3)_6^{3+}$ clarify[39] the distinction between the one-step and two-step processes.

The occurrence of stereochemical change has important implications for photoracemization via bond-rupture mechanisms that, with one exception,[258] have not so far been taken into account. Certainly the outcome would not be statistical as usually assumed. Photoracemization via a twist mechanism is an interesting problem. It may be a minor process and therefore dangerous to speculate about, but the AOM stereochemical model does not provide an obvious driving force for the process. As mentioned, it may be a DOSENCO process, but then it should be manifest as a prompt unquenchable reaction. The excited-state participation should be explored, particularly in systems where a twist mechanism appears to be operative.

Changes in the photochemical and photophysical properties arising from asymmetries and constraints imposed by the ligands are still poorly understood. The main model proposed to explain effects on doublet lifetime is couched in terms of dynamic effects, in particular a trigonal twist[12,13] that serves to relieve ligand strain. However, there are large effects on doublet lifetimes in cage compounds and on absorption spectral intensities which are not explicable[190] in these terms. Other factors such as different kinds of static distortions, ligand flexibility, and coupling to solvent motions could be just as important as steric strain imposed on the coordinated ligand. A beginning has been made, but further studies are required before we can claim any adequate understanding of these aspects. The subject is important as it is central to any efforts to tune the photophysical properties of Cr(III) complexes. The development of complexes with very long-lived doublet states has considerable potential in various applications.

VIII. Ligand Abbreviations

2,3,2-tet = 1,9-diamino-3,7-diazanonane
[32]aneN$_8$ = 1,5,9,13,17,21,25,29-octaazacyclodotriacontane
[9]aneN$_3$ = 1,4,7-triazacyclononane
acac = acetylacetonato
atc = 3-acetylcamphorato
bpy = 2,2′-bipyridine
cyclam = 1,4,8,11-tetraazacyclotetradecane
diamsar = 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo-[6.6.6]eicosane
ditn = 1,5,9-triazanonane
dmf = *N*,*N*-dimethylformamide
dmso = dimethyl sulfoxide
en = 1,2-ethanediamine
Me$_5$-tricosaneN$_6$ = 1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane
Me$_6$-tetracosaneN$_6$ = 1,5,9,13,20,23-hexamethyl-3,7,11,15,18,22-hexaazatricyclo[10.4.4.4$^{4-9}$]tetracosane
meam = methylamine
ox = oxalato
phen = 1,10-phenanthroline
py = pyridine
sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
sen = 4,4′,4″-ethylidynetris(3-azabutan-1-amine)
sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane
TAE[9]aneN$_3$ = 1,4,7-tris(aminoethyl)-1,4,7-triazacyclononane
TAP[9]aneN$_3$ = 1,4,7-tris(aminopropyl)-1,4,7-triazacyclononane
trans-chxn = *trans*-1,2-diaminocyclohexane
tet-a = C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
tfa = 1,1,1-trifluoro-2,4-pentanedionato
tn = 1,3-propanediamine
tren = β,β',β''-triaminotriethylamine
tryp = tryptophanato

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X. References

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