The photochemistry and photophysics of Cr(III) complexes has had a long and noble history (1, 2). In the preceding paper, Kirk (3) has described the behavior of Cr(III)-ammine complexes under UV-visible irradiation. Here, we examine the photochemical and photophysical behavior of chromium(II1)-polypyridyl complexes, \( \text{Cr}^{2+} \text{NN} \), in which \( \text{NN} \) is 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen), or one of their substituted derivatives; a comprehensive review was published recently (4).

Properties of Ground State \( \text{Cr}^{2+} \text{NN} \) Complexes

Geometric and Electronic Structure

Although \( \text{Cr}^{2+} \text{NN} \) possesses dihedral (\( D_d \)) symmetry (bidentate NN ligands define the blades of a propeller), it is common to discuss such complexes in terms of octahedral symmetry, \( O_h \), where the ground electronic state is a quartet, \( ^4A_2 \). Cr(III) species possess a \( d^3 \) electronic configuration (\( t_{2g} e_g^0 \) in octahedral microsymmetry); under the influence of a very strong crystal field environment, two electronic transitions are possible: \( t_{2g} e_g^0 \rightarrow t_{2g} e_g^1 \) and \( t_{2g} e_g^0 \rightarrow t_{2g} e_g^2 \). At intermediate fields, however, more than two transitions may occur. A typical absorption spectrum of a Cr(III) complex consists of three weak absorption bands (quartet-quartet) in the UV-visible spectral region, and two very weak, spin-forbidden bands (quartet-doublet) in the red range of the visible region. The quartet-quartet bands correspond to the spin-allowed transitions from the \( ^4A_2 \) ground state to the three excited quartet stages \( ^4T_2, ^4T_1, \) and \( ^4T_1 \); the two spin-forbidden transitions correspond to \( ^4A_2 \rightarrow ^4E \) and \( ^4A_2 \rightarrow ^2E \). To the extent that these electronic transitions occur between \( t_{2g} \) and \( e_g \) levels which have predominantly metal character, these states are denoted as metal-centered states and transitions between such states are referred to as metal-centered transitions. These transitions are illustrated in the energy level diagram of Figure 1 for \( d^3 \) complexes of octahedral symmetry. In Figure 2 we present the absorption spectra of four typical \( \text{Cr}^{2+} \text{NN} \) complexes [\( \text{NN} = \text{bpy}, \text{phen}, 4,4'-\text{Ph}_2\text{bpy}, 4,7-\text{Ph}_2\text{phen} \)].

Electronic Absorption Spectra

König and Herzog (5) have made a thorough analysis of the ground state absorption spectrum of \( \text{Cr}^{2+} \text{bpy} \). In octahedral microsymmetry, the three spin-allowed bands at 23.4, 28.9, and 35.6 \( \times 10^3 \) cm\(^{-1} \) arise from the transitions \( ^4A_2 \rightarrow ^4T_2, ^4A_2 \rightarrow ^4T_1, \) and \( ^4A_2 \rightarrow ^2T_1 \), respectively. The three unresolved shoulders centered at \( \sim 23.4 \times 10^3 \) cm\(^{-1} \) originate from vi-
brational co-excitation involving coupling of electronic $d-d$
transitions and vibrational transitions within the bpy ligand.
Such coupling implies some electron delocalization within the
excited states (i.e., some degree of $\pi$ bonding). The bands at
32.7 and 42.1 $\times 10^2$ cm$^{-1}$ are due to bpy ligand-centered
transitions, $^{4}A_2 \rightarrow ^{4}B_1$ and $^{4}A_1 \rightarrow ^{1}A_1$, respectively (5). The
lowest-energy multicomponent band arises from the $^{4}A_2 \rightarrow
^{4}T_2$ transition and this band yields the ligand field parameter
$\Delta$. For substituted Cr(NN)$^{4+}$, the spectral profile is dependent
on the nature of the ligand substituents (6). Both methyl and
phenyl substitution at the 4,4'-positions of the bpy ligand
cause a slight blue shift in the bands corresponding to the
$^{4}A_2 \rightarrow ^{4}T_2$ transition. By contrast, methyl substitution on the
phen ligand framework blue-shifts this low-energy transition,
while phenyl- and halo-substitution cause a red shift. In addi-
tion, phenyl substitution on both bpy and phen ligands
significantly increase the molar absorptivity.

Redox Potentials

Formal redox potentials for the couples Cr(NN)$^{2+}$/Cr(NN)$^{3+}$ are summarized in Table 1. In all cases, the
Cr(NN)$^{3+}$ species are moderately good reducing agents
with substituents dramatically affecting their reducing
character. For both bpy and phen complexes, electron-donat-
ing methyl substituents increase the reducing ability of
Cr(NN)$^{3+}$, whereas electron-withdrawing halo and phenyl
substituents decrease the reducing ability. Also noteworthy
are the positions of the substituents in this regard. Methyl
substitution at the 5,6-positions of the phen framework hardly
affects $E^0[Cr(NN)^{2+}/Cr(NN)^{3+}]$ compared to the parent phen
complex, but substitution at the 4,7-positions significantly
decreases $E^0[Cr(NN)^{2+}/Cr(NN)^{3+}]$ by $\sim$0.2 V. This suggests that
in the latter case, electron density is shifted to the Cr$-$N
bond.

Thermal Reactivity

Knowledge of structure-reactivity relationships of ground
state $^{4}A_2$Cr(NN)$^{3+}$ complexes is important in the under-
standing and elucidation of the photoreactivity of these
complexes. Cr(bpy)$^{3+}$ thermally aquates (reaction (1)) in the
pH range 0–10.7 via pH-dependent (see Fig. 3), first order
kinetics with $k_{th} < 10^{-8}s^{-1}$ at pH $\leq 6$, and $4.7 \times 10^{-5}s^{-1}$ at pH
9–10.7 and 11°C (7).

$$
\text{Cr(NN)}^{3+} + \text{H}_2\text{O} \rightarrow \text{Cr(NN)}_2\text{(H}_2\text{O})^{3+} + \text{NH}_3
$$

(1)

Aquation appears to proceed via an interchange mechanism
involving, as the rate determining step, formation of a

Cr(NN)$_2$(H$_2$O)$_3^{3+}$ intermediate by nucleophilic attack of a
water molecule at the Cr(III) center. The very small and
pH-independent $k_{th}$ at pH $\leq 6$ can be rationalized in terms
of relaxation of the initially-formed intermediates back to
Cr(NN)$_2^{3+}$ via acid-dependent and -independent pathways
(reaction (2)) (8).

$$
\text{Cr(NN)}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Cr(NN)}_2\text{(H}_2\text{O})^{3+}
$$

(2)

Subsequently, Cr(NN)$_2$(H$_2$O)$_3^{3+}$ can undergo deprotonation
to form the short-lived Cr(NN)$_2$(OH)$_2^{3+}$ species as shown by
the inflection point at pH 6–8 in the plot of $k_{th}$ versus pH il-
ustrated in Figure 3. This hydroxy intermediate can then
undergo irreversible loss of monodentate NN.

$$
\text{Cr(NN)}_2\text{(OH)}^{2+} \rightarrow \text{Cr(NN)}_2\text{(OH)}^{3+} + \text{NN}
$$

(3)

The plateau region at pH 9–10.7 reflects the complete titration
of Cr(NN)$_2$(H$_2$O)$_3^{3+}$ so that $k_{th}$ represents the rate constant
for the rate-determining attack of H$_2$O on Cr(NN)$_2^{3+}$. The
thermal substitution reaction has been extended to include
the pH range 10.7–14 for Cr(bpy)$^{3+}$ (9) and the pH range 0–14
for Cr(phen)$^{3+}$ (10). The thermal behavior of the latter complex
parallels identically that of Cr(bpy)$^{3+}$. Above pH 10.7, $k_{th}$ is
linearly dependent on [OH$^{-}$] in the range 10.7 $\leq$ pH $\leq
12.2$, indicating possible OH$^{-}$ attack of the chromium(III)
core. Where [OH$^{-}$] = 0.1–1.0 M, $k_{th}$ varies as [OH$^{-}$]$^2$.
Table 2. Thermal Activation Parameters for Cr(bpy)$_2^{3+}$ and Cr(phen)$_2^{3+}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>bpy</th>
<th>phen</th>
<th>bpy</th>
<th>phen</th>
<th>0.50 M OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{\text{bio}}$, kcal/mol</td>
<td>22.3</td>
<td>23.3</td>
<td>20.7</td>
<td>21.6</td>
<td>18.9</td>
</tr>
<tr>
<td>$\Delta S_{\text{bio}}$, eu</td>
<td>$-8.6$</td>
<td>$-8.4$</td>
<td>$-12.6$</td>
<td>$-11$</td>
<td>$-11$</td>
</tr>
<tr>
<td>$k_{\text{bio}}$, $s^{-1}$</td>
<td>$3.3 \times 10^{-8}$</td>
<td>$7.9 \times 10^{-7}$</td>
<td>$6.9 \times 10^{-6}$</td>
<td>$4.3 \times 10^{-6}$</td>
<td>$2.9 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

* From references (7, 9, 14) in 0.008 M Britton-Robinson buffer; ionic strength = 1.0 M with NaCl.

Properties of Excited $(2T_1/2E)\text{Cr(NN)}^{3+}$ Complexes

Energetics and Structure

Absorption of light into the lowest energy quartet ligand field band of a Cr(III) complex populates a vibrationally excited Franck-Condon quartet state (isogemetric with the ground state) which subsequently relaxes to the thermally-equilibrated (thexi) (II) quartet state $(2T_1)$. This thexi state must be severely distorted with respect to the $A_2$ ground state inasmuch as the promotion of an electron from a predominantly nonbonding $d\pi$ orbital ($d_{x^2}$, $d_{y^2}$, and $d_{z^2}$) to a formally $\sigma^*$ antibonding orbital ($d_{x^2-y^2}$ or $d_{z^2-x^2}$) must result in increased Cr-N bond lengths. Any fluorescence $(2T_1 \rightarrow 2^1E_2)$ is expected to be broad and red-shifted with respect to the corresponding absorption band $(4^1A_2 \rightarrow 4^1T_2)$. However, no such fluorescence emission has been observed in Cr(phen)$_2^{3+}$ complexes in fluid solutions at room temperature or in low temperature glasses and so decay of the quartet state via this path is inconsequential. The energy of $(2^1T_2)$ is unknown but has been estimated to be at $\approx 59-62$ kcal above the ground state (8).

As depicted in Figure 1, the quartet state can dissipate its excess energy via nonradiative decay to $1A_2(h_{\text{nr}})$, via nonradiative decay (intersystem crossing) to the spin-forbidden states $2^1T_1/2^3E(h_{\text{inc}})$, and via reactive decay ($h_{\text{qs}}$) to give products. These lowest energy doublet states are not expected to be distorted with respect to $A_2$ inasmuch as the $A_2 \rightarrow 2^1T_1/2^3E$ transition involves no electron promotion to $\sigma^*$ antibonding orbitals; rather, electron spin-pairing or spin-flip occurs within the $t_{2g}$ level, i.e., the transition is intraconfigurational. Cr-N bond lengths are, therefore, expected to be nearly identical for $A_2$ and $2^1T_1/2^3E$. Indeed, the nuclear equilibrium geometries of $A_2$ and $2^1T_1/2^3E$ are essentially identical inasmuch as absorption $(4^1A_2 \rightarrow 2^1T_1/2^3E)$ and emission $(2^1T_1/2^3E \rightarrow 4^1A_2)$ maxima are coincident, there being no Stokes shift (12) (see Fig. 2). The 0-0 doublet levels occur at $\approx 39$ kcal above the ground state (Table 1).
Emission and Absorption Spectra

The emission spectra bands, which represent the 0-0 transitions of the $^2T_1, ^2E \rightarrow ^4A_2$ electronic transitions, are only slightly sensitive to the nature of the ligand substituents. Table 1 reveals that substitution varies the energy of the low energy transitions in the order: bpy > 4,4'-Me-bpy > 4,4'-Ph-bpy. Ligand substitution on the phen complexes decreases the energy of the $^2E$ state in the order: phen ~ 5-Cl-phen > 5-Br-phen > 5-Ph-phen ~ 5-Me-phen > 4,7-Me-phen > 4,7,8-Me-phen > 4,7,8,9-Me-phen. The doublet state absorption spectra of Cr(NN)$_3^+$ complexes have been obtained by conventional microsecond flash photolysis techniques (6); those for which NN = bpy, 4,4'-Ph-bpy, phen, and 4,7-Ph-phen are illustrated in Figure 4. Where NN = bpy, the spectrum shows bands at 590, 445, and 390 nm with shoulders at ~650 and 475 nm (8). The entire spectrum decays via first-order kinetics in acidic, neutral, and alkaline media with $k = 1.6 \times 10^{4} \text{ s}^{-1}$ at 22°C. The transient absorption is quenched by oxygen ($1.7 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$) (8), I$^-$ ($1.2 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$) and Fe$_{\text{III}}^{3+}$ ($1 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$) (13). Coincidence of the decay of the phosphorescence emission ($^2E \rightarrow ^4A_2$) and decay of the transient absorption identified this transient as the $^2E$ state; this was further substantiated by similar temperature dependencies exhibited by the transient and phosphorescence decays, as well as by the similarities evident in the oxygen and iodide quenching results (Table 1). Phenyl substitution at the 4,4'-positions of Cr(bpy)$_3^+$ red-shifts both the 390- and 445-nm bands of (Cr(bpy)$_3^+$) to 480 and 525 nm, respectively. The band at 500 nm is not sensitive to ligand substituents. This indicates that the doublet manifold reached by absorption is predominantly metal-centered. The remaining two higher energy bands, red-shifted by the presence of substituents, must correspond to electronic transitions to doublet states containing some ligand character and are probably $^2E$ + $^2$LMCT transitions. The doublet absorption spectrum of *Cr(phen)$_3^+$ is characterized by a broad band centered at ~515 nm and appears sensitive to phenyl substitution.

Excited State Lifetimes

The lifetimes of the $^2T_1$ and $^2E$ states (14) responsible for the two emission bands from excited Cr(bpy)$_3^+$ are identical indicating that these two states are in thermal equilibrium and are often denoted simply as $^2E$. The observed lifetime of $2\tau_{\text{obs}} = 1/(2h \nu) = 1/(2h)\gamma$ $^2E$, where $\gamma$ represents the rate constant of the individual decay modes. In the absence of quenchers and other environmental perturbations, $2\tau_{\text{obs}} = 1/(2h \nu) = 1/(2h)\gamma$ $^2E$, the $^2E$ states of Cr(NN)$_3^+$ react with water ($e_w$) in competition with radiative ($h\nu_{\text{rad}}$) and nonradiative ($h\nu_{\text{nr}}$) decay back to $^4A_2$ species; back intersystem crossing ($h\nu_{\text{isc}}$) to $^2T_1$ appears to be unimportant (15). For Cr(bpy)$_3^+$, radiative decay is insignificant ($h\nu_{\text{rad}} \sim 10^{-9}$) (6, 16) in comparison with nonradiative ($h\nu_{\text{nr}}$ $\sim 10^{-9}$) and reactive ($h\nu_{\text{nr}}$ $\sim 0.9$) decay modes. Thus, $2\tau_{\text{obs}} \sim 1/(2h \nu) + r_{\text{rel}}$, with the nonradiative decay mode being the predominant decay channel of $^2E$ (17). By contrast, chemical reaction is the important decay mode of the $^2E$ state of trans-Cr(NH$_3$)$_2$SCN complexes (18). Under high laser power, $^2E$ (Cr(phen)$_3^+$ and $^2E$ (Cr(4,7-Me-phen)$_3^+$) decay via a second-order, doublet-doublet annihilation process (19).

Interaction with Solution Medium

The value of $2\tau_{\text{obs}}$ is strongly dependent on solution medium. The lifetime of $^2E$ is prolonged by the presence of anions. At [ClO$_4$]$^-$ > 1 M in aqueous solution, $2\tau_{\text{obs}}$ and $4\tau_{\text{rad}}$ are markedly increased and the quantum yield of photoaquation ($4\tau_{\text{rad}}$) is decreased for both Cr(bpy)$_3^+$ and Cr(phen)$_3^+$ (20). This anion effect is the result of changes in the nonradiative and reactive rate constants with the latter exhibiting a greater decrease (17). Such $^2E$-lifetime prolongation effects by high concentrations of anions appears to be a general phenomenon in Cr(NN)$_3^+$ complexes (6, 21, 22). In the case of CrO$_4^{2-}$, the presence of the Cr(III) core and the anions in the interligand pockets as well as in the solvation sphere, thereby curbing access to the core by solvent water molecules resulting in a decrease of $\tau_{\text{obs}}$; also, the "wedged" anions in the pockets can reduce the motion of the critical vibrational modes in the ligand. These effects are more pronounced in the Cr(bpy)$_3^+$ complex with the more rigid phen analogue being less prone to such anion perturbations; in 11.7 M HClO$_4$, $\tau_{\text{obs}}$ for Cr(bpy)$_3^+$ has been increased by a factor of >10, but only by a factor of ~2 for (Cr(phen)$_3^+$) relative to $\tau_{\text{obs}}$ in 1 M Cl$_2$ (20).

Figure 5. Lifetime of ($^2E$(Cr(phen)$_3^+$) as a function of [substrate] in deaerated aqueous solutions at 22°C (4). Insert represents a plot of $1/2\tau_{\text{obs}}$ for Cr(phen)$_3^+$ as a function of [substrate] in deaerated 1.0 M HCl solution at 22°C. (From reference (3).)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Lifetime (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.038</td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>0.33</td>
</tr>
<tr>
<td>HC$_2$O$_4$</td>
<td>1.0</td>
</tr>
<tr>
<td>HC$_3$N$_2$O$_7$</td>
<td>10</td>
</tr>
</tbody>
</table>

Thus, for Cr(phen)$_3^+$ in 1 M HCl media at 22°C, $\kappa_0 = 3.0 \times 10^3$ s$^{-1}$ and $\kappa_2 = 2.9 \times 10^6$ s$^{-1}$, while $\kappa_0 = 1.0 \times 10^3$ s$^{-1}$ and $\kappa_2 = 1.3 \times 10^6$ s$^{-1}$ for Cr(bpy)$_3^+$ in 5 M HCl media at 22°C (22). The other Cr(NN)$_3^+$ complexes show similar behavior (21) with the data demonstrating that, in addition to the solution medium, both the size of the Cr(III) cation and the nature of the ligand substituents have an effect on $\tau_{\text{obs}}$. This second-order rate constant reflects the encounter of ion-paired ground state ($^4A_2$)Cr(NN)$_3^+$ and excited state ($^2E$Cr(NN)$_3^+$) species which can be viewed as forming an "ion-bridged excimer", [Cr(NN)$_3^+$$^−$:Cl$^−$⋅⋅⋅Cr(NN)$_3^+$$^+$. This rapidly decays nonradiatively via coupling of the vibrational modes in the aggregate. Ground state quenching of Cr(III) excited states in solid matrices has previously been attributed to formation of such aggregates (23). The generality of ground state quenching for Cr(phen)$_3^+$ in other anionic media has recently been demonstrated (24). Clearly $2\tau_{\text{obs}}$ must be established for the specific experimental conditions; $\tau_{\text{obs}}$ reflects the nonradiative and reactive
decay modes. As evident in Table 1, subtle modification of the poly(pyridyl) ligand by the variation of substituents alters $2\tau_{0}$. We see that 4,4'-substitution on the bpy framework and 4,7-dimethyl, 4,7-diphenyl, 5-methyl, 5,6-dimethyl, and 3,4,7,8-tetramethyl substitution on the phen ligand increases $2\tau_{0}$, while 5-bromo, 5-chloro, and 5-phenyl substitution on phen decreases $2\tau_{0}$; it appears that the greater vibrational rigidity of the phenanthroline complexes decreases the non-radiative decay mode relative to the analogous bipyrindine complexes, with consequentially larger values of $2\tau_{0}$. These variations in the doublet lifetimes are understood in terms of the ligand acting as both an oscillating perturbation dipole and as an energy acceptor. Halo substituents could provide an increased dipole perturbation that would increase $2\tau_{0}$; by comparison, methyl and phenyl substitution on the poly(pyridyl) could decrease the perturbation dipole, probably through their effect on the critical ligand vibrational modes. Moreover, the large interligand pockets in the dihedral Cr(NN)$_2$ structure could allow solvent molecules to penetrate close to the Cr(III) core and provide an additional decay channel; substituents on the ligands that can isolate the metal core from solvent molecules should lead to increased $2\tau_{0}$ (6). This structural effect is most evident at the 4,7-positions in the phen ligand framework. Variations of solvent medium also affects $2\tau_{0}$; Van Houten and Porter (25) found $2\tau_{0}$ decreased 3 ps in dimethylformamide.

Redox Potentials
Transition metal poly(pyridyl) complexes have proven of value in electron- and energy-transfer studies inasmuch as they provide a wide range of excited state properties that can be “fine tuned” by alteration of the metal center, by alteration of the type of ligand, or simply by variation of the substituents on the poly(pyridyl) framework. One property of excited states that is dependent on ligand substituents is the redox potential; the changes are expected to parallel those noted earlier for the ground state species.

Where the Stokes shift between ground state absorption and excited state emission is small, and the differences in shape, size, and solvation between the two states are also small, the entropy differences between ground and excited states are negligible. The redox potentials for the $^{2E}$Cr(NN)$_2$ complex can be estimated from eqn. (5), where $E_{00}$($^{2E}$Cr($^{1+}$)/Cr($^{3+}$)) is the one electron potential corresponding to the 0-0 spectroscopic energy of the excited state (less 1.7 eV).

$$E_{00}(^{2E}Cr(NN)_2) = E^0(0/Cr^{3+}/Cr^{1+}) + E_{00}(Cr^{1+}/Cr^{3+})$$  \hspace{1cm} (5)

The redox potentials evaluated in this manner are given in Table 1 (6, 26-28). The validity of this procedure for Cr(NN)$_2$ complexes has been verified by Balzani and co-workers (29). The $^{2E}$Cr complexes are moderately strong oxidizing agents compared to the $^{4A_2}$ species; this effect is a consequence of the excitation of an electron from a low energy orbital to a higher energy orbital leading to a reduction of the ionization potential and to an increase of the electron affinity. The 5-halo phen complexes are the strongest oxidants while the poorest oxidizing agents are those containing methyl-substituted phen ligands.

Electron and Energy Transfer Reactions

Of the various decay pathways available to excited states, the principal quenching modes are electron transfer and energy transfer. It is often difficult to discriminate between these two quenching modes inasmuch as energy-transfer reactions can lead to the same oxidized or reduced products expected from electron-transfer reactions, and electron-transfer reactions may yield, in the end, nonreduced or nonoxidized products (30). Knowledge of the energy of the $^{2E}$ excited state, the energy of the lowest excited state of the quencher, and the ground state redox potentials of Cr(NN)$_2$ has been useful in assigning the operative quenching mode. Correlations between the quenching rate constants, $k_{q}$, and the thermodynamic quantities involved have also been critical, in some cases, in defining the nature of the quenching mechanism.

Experiments have been carried out (13) to show that the emission of $^{2E}$Cr(bpy)$_3$$^+$ is quenched by Ru(bpy)$_3$$^+$ via reductive electron transfer. Energy transfer is not possible inasmuch as the energies of the lowest excited states of Cr(bpy)$_3$$^+$ and Ru(bpy)$_3$$^+$ are 13.7 x 10$^{-3}$ and 17.1 x 10$^{-3}$ cm$^{-1}$, respectively. For electron transfer, the redox potentials for the *Cr(bpy)$_3$$^+$/Cr(bpy)$_3$ and Ru(bpy)$_3$$^+$/Ru(bpy)$_3$ couples are 1.44 V and 1.30 V versus NHE (31), respectively. Flash photolysis experiments demonstrate that $^{2E}$Cr(bpy)$_3$$^+$ is quenched by $^{1-}$ and Ru(bpy)$_3$$^+$ via electron transfer reactions (6)-(8); reaction (9) constitutes back electron transfer of the charge-separated species.

$$Cr(bpy)_3^{2+} \rightarrow (T_{1}Cr(bpy)_3)^{+} \rightarrow (^{2E}Cr(bpy)_3)^{2+}$$ \hspace{1cm} (6)

$$^{2E}Cr(bpy)_3^{2+} + l^{-} \rightarrow Cr(bpy)_3^{3+} + l^{-}$$ \hspace{1cm} (7)

$^{2E}Cr(bpy)_3^{2+} + Ru(bpy)_3^{2+} \rightarrow Cr(bpy)_3^{3+} + Ru(bpy)_3^{2+}$ \hspace{1cm} (8)

$Ru(bpy)_3^{2+} + Cr(bpy)_3^{2+} \rightarrow Cr(bpy)_3^{2+} + Ru(bpy)_3^{2+}$ \hspace{1cm} (9)

The rate constants of reactions (7)-(9) are 1.4 x 10$^{4}$ (6), 4.0 x 10$^{3}$ (32) and 2.6 x 10$^{3}$ (13) M$^{-1}$s$^{-1}$, respectively. The product of reaction (7) is not observed because the reaction products undergo prompt back electron transfer within the solvent cage; however, in the absence of $^{1-}$, the electron transfer products of reaction (8) are observed. Because Cr(bpy)$_3^{2+}$ can quench the lowest excited state of Ru(bpy)$_3$$^{2+}$, reactions (10) and (11) also occur

$$Ru(bpy)_3^{2+} \rightarrow (MLCT)Ru(bpy)_3^{2+} \rightarrow (MLCT)Ru(bpy)_3^{2+}$$ \hspace{1cm} (10)

$$^{3MLCT}Ru(bpy)_3^{2+} + Cr(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + Cr(bpy)_3^{2+}$$ \hspace{1cm} (11)

$k_{11} = 3.3 \times 10^9$ M$^{-1}$s$^{-1}$ (32). $^{2E}$Cr(bpy)$_3$$^+$ is quenched by aliphatic and aromatic amines and methoxybenzenes via reductive electron transfer leading to one-electron oxidized products of the quenchers (29). Luminescence quenching of $^{2E}$Cr(bpy)$_3$$^+$ by various transition metal cyano complexes has shown that reductive electron transfer occurs with Mo(CN)$_6$$^{3-}$, Fe(CN)$_6$$^{3-}$, Ru(CN)$_6$$^{3-}$, and Ni(CN)$_6$$^{3-}$ and oxidative electron transfer with Fe(CN)$_6$$^{3-}$ and Cr(CN)$_6$$^{3-}$; with Cr(CN)$_6$$^{3-}$ quenching occurs via energy transfer (33). The relationship between $k_{q}$ and the redox potentials of the excited states and quencher species is consistent with reductive or oxidative electron transfer. Plots of log $k_{q}$ versus the driving force for electron transfer, $\Delta G^*$, show no inverted region as predicted by the Marcus theory of electron transfer (34). There is no decrease in $k_{q}$ at the larger negative values of $\Delta G^*$ (29, 33); rather, the trend in $k_{q}$ follows the modified theory of Rehm and Weller (35).

As Table 1 shows, $^{1-}$ quenches the $^{2E}$ states of all 12 Cr(NN)$_2$ complexes and the values of $k_{q}$ range over two orders of magnitude. To the extent that the lowest excited states of $^{1-}$ have energies greater than 37.0 x 10$^{-3}$ cm$^{-1}$, an energy transfer pathway is ruled out. The $k_{q}$ values decrease as the oxidizing ability of the $\{^{2E}Cr(NN)$_2$\}$ species decreases; the strongest oxidant, $^{2E}$Cr(5-Clphen)$_3$$^+$, has the highest $k_{q}$ while the weakest oxidant, $^{2E}$Cr(3,4,7,8-Me$_4$phen)$_3$$^+$, has the lowest value of $k_{q}$. For quenching of $^{2E}$Cr(NN)$_2$$^+$ by Fe$_{25}$, the formation of Cr(NN)$_2$$^+$ and its subsequent second order reaction with Fe$_{25}$ is observed (6). The availability of low-lying states of Fe$_{25}$ at 10.4 x 10$^{-3}$ cm$^{-1}$ ($^{2T_{2g}}$) and at ~14.4 x 10$^{-3}$ cm$^{-1}$ (probably $^{2T_{2g}}$) (36) above the $^{2A_g}$ ground state renders direct energy transfer energetically feasible. A scheme for $^{2E}$Cr(NN)$_2$$^+$-Fe$_{25}$ quenching involving both electron- and energy-transfer modes is depicted by reactions (12)-(17), where [I] denotes an encounter pair in a solvent cage with reaction (14) thermodynamically allowed.
equivalent via formation of an intermediate. Recovery of photosolvolytic release.

thermally aquated solutions (7) are identical, with isosbestic points at 306, 270, 262, and 254 nm (8). The overall action appears consequential.

Quantum Photoaquation of aqueous solutions leads to substitution of one polypyridyl ligand by two water (or hydroxyl) molecules (8, 10, 17). The spectral changes and formation of free polypyridine mimic those observed for the corresponding thermal reactions (7, 10). For Cr(bpy)$^{3+}$ at pH 9.6, the absorption spectral changes of continuously photolyzed (8), repeatedly flashed (8), and thermally aquated solutions (7) are identical, with isosbestic points at 306, 270, 262, and 254 nm (8). The overall stoichiometry of the photoaquation (reaction 20) is similar to reaction 1, where $\Phi_{\text{rx}}$ is the observed quantum yield for NN release.

$\text{(2E)Cr(NN)\text{H}_2} \rightarrow \text{Cr(NN)}^{3+} + \text{HOO}^-$ (20)

The complexes are relatively inert toward thermal- (7, 10) and photoaquolysis (8, 21) in acidic media. This observation, together with the observation that $k_{\text{irb}}$ of reaction 1 and $\Phi_{\text{rx}}$ of the photoreaction 20 show very similar pH dependences, (Fig. 3) suggests that the two reactions proceed through a common ground state intermediate. The interchange mechanism alluded to before applies equally to reaction 20, where the intermediate species is formed by attack of H$_2$O on the $^3\text{Cr(NN)H}_2$ metal core (8, 17).Flash photolysis experiments on Cr(bpy)$^{3+}$ in acidic media reveal transient bleaching of the ground state following decay of the $^2T_1/2E$ states implying formation of a nonabsorbing (at the monitoring wavelength) intermediate. Recovery of ground state absorption proceeds via acid-dependent and -independent paths believed to be the equivalent of reaction (2) with rate constants of $4 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and $< 10 \text{ s}^{-1}$ (8), respectively. The H$^+$-dependent path is believed (38) to be the primary reaction leading to the relative photochemical and thermal stability of Cr(bpy)$^{3+}$ in acid solution. However, because of the ground state quenching phenomenon, measurements of $\Phi_{\text{rx}}$ and $^{2}T_{1/2E}$ must be made in well defined solution media. These data are summarized in Table 3 for 12 Cr(NN)$^{3+}$ complexes.

The population of $^{2}T_{1/2E}$ depends on the efficiency of intersystem crossing ($^{*}\text{Cr} \rightarrow^{2}T_{1/2E}$ where $^{*}\text{Cr} = ^{4}A_1\text{Cr(ppy)}^{3+}$ and $^{2}T_{1/2E}$ is the efficiency of reaction out of $^{2}T_{1/2E}$ species that pass to Cr(ppy)$\text{OH}^{2+}$ in alkaline solution leads rapidly, irreversibly, and quantitatively to Cr(ppy)$\text{OH}^{4+}$, then $\Phi_{\text{py}} = \frac{^{*}\text{Cr}^{2}T_{1/2E} + \eta_{\text{py}}}{^{*}\text{Cr}^{2}T_{1/2E} + \eta_{\text{py}}}$ where $\eta_{\text{py}}$ is the efficiency of reaction out of $^{2}T_{1/2E}$ ($=^{2}k_{\text{obs}}$ and $^{*}\text{Cr}$) is the efficiency of reaction out of $^{*}\text{Cr}$. Inasmuch as the portion of the observed value of $\Phi_{\text{py}}$ that cannot be quenched by $\cdot$, a very efficient doublet state quencher, is $< 10\%$ of $\Phi_{\text{py}}$ (15), $\eta_{\text{py}}$ may be neglected. Therefore, $\Phi_{\text{py}} \approx \frac{^{*}\text{Cr}^{2}k_{\text{obs}}}{^{*}\text{Cr}^{2}k_{\text{obs}}}$ Taking $^{*}\text{Cr} \approx 1$ (39), $\Phi_{\text{py}} = ^{*}\text{Cr}^{2}k_{\text{obs}}$. Calculated values of $^{*}\text{Cr}$ are collected also in Table 3.

Ligand Substituent Effect

According to our model, $^{2}k_{\text{obs}}$ reflects the ease with which the Cr(ppy)$_2$(H$_2$O)$_2$ intermediate forms upon interaction of the solvent with $^{2}T_{1/2E}$Cr(ppy)$^{3+}$. It is possible to visualize the distortion and loosening of the ligand structure in order to accommodate the incoming water molecule; the intermediate may be seven-coordinate in nature with some capped octahedral or pentagonal bipyramidal structure (40). Thus, the flexibility of the ligand structure and the extent of hydrophlicity in the vicinity of the interligand pockets will dictate the value of $^{2}k_{\text{obs}}$. Examination of the data of Table 3 shows that the more flexible bpy framework is more amenable to distortion than is the more rigid phen framework; in all cases, $^{2}k_{\text{obs}}$ for bpy complexes is larger than for phen. The highly

<table>
<thead>
<tr>
<th>NN</th>
<th>$[\text{Cr(DI)}]$ (mM)</th>
<th>$\Phi_{\text{py}}$ (py)</th>
<th>$^{2}k_{\text{obs}}$ (py) s$^{-1}$</th>
<th>$^{2}k_{\text{obs}}$ (py) s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>1.0</td>
<td>0.139 (3)</td>
<td>0.071</td>
<td>1.6 X 10$^3$</td>
</tr>
<tr>
<td>4,4'-Me$_2$bpy</td>
<td>0.12</td>
<td>0.0025 (1)</td>
<td>0.18</td>
<td>3.5 X 10$^2$</td>
</tr>
<tr>
<td>4,4'-Phbpy</td>
<td>0.048</td>
<td>0.012 (2)</td>
<td>0.050</td>
<td>4.2 X 10$^2$</td>
</tr>
<tr>
<td>5-Cphen</td>
<td>0.14</td>
<td>0.0025 (1)</td>
<td>0.640</td>
<td>1.3 X 10$^3$</td>
</tr>
<tr>
<td>5-Brphen</td>
<td>0.12</td>
<td>0.0065 (2)</td>
<td>0.063</td>
<td>1.3 X 10$^3$</td>
</tr>
<tr>
<td>phen</td>
<td>1.5</td>
<td>0.005 (5)</td>
<td>0.074</td>
<td>7.5 X 10$^1$</td>
</tr>
<tr>
<td>5-Mephen</td>
<td>0.12</td>
<td>0.04 (4)</td>
<td>0.16</td>
<td>6.7 X 10$^1$</td>
</tr>
<tr>
<td>5,6-Mephen</td>
<td>0.11</td>
<td>0.09 (5)</td>
<td>0.19</td>
<td>3.4 X 10$^1$</td>
</tr>
<tr>
<td>4,7-Mephen</td>
<td>0.11</td>
<td>0.0505 (2)</td>
<td>0.25</td>
<td>1.4 X 10$^1$</td>
</tr>
<tr>
<td>3,4,7,8-Mephen</td>
<td>0.084</td>
<td>0.0002 (5)</td>
<td>0.21</td>
<td>7.6</td>
</tr>
<tr>
<td>5-Phphen</td>
<td>0.072</td>
<td>0.036 (3)</td>
<td>0.061</td>
<td>7.4 X 10$^1$</td>
</tr>
<tr>
<td>4,7-Phphen</td>
<td>0.034</td>
<td>0.012 (5)</td>
<td>0.074</td>
<td>1.9 X 10$^1$</td>
</tr>
</tbody>
</table>

* See reference (21) for experimental conditions.

2 It is worth noting that seven-coordinate geometry for the first row transition metals is no longer an unusual geometry. See, for example, the extensive review by Drew (41).
especially multiply substituted, exhibit lower values of $k_{obs}$ due to decreased hydrophilic environment. The values of $k_{obs}$, therefore, reflect the competition between the hydrophilic and hydrophobic environments. Methyl and phenyl derivatives, especially those with electronegative chlorine and bromine atoms in the 5-position of phen, clearly facilitate water entry (compared to unsubstituted phen) into the pockets thereby providing an increased hydrophilic environment. Doublet state quenchers such as $I^-$ and $O_2$ act to decrease the population of $^2E$ and the value of $\Phi_{rx}$. Thus, with increasing concentration of $I^-$, $\Phi_{rx}$ diminishes to a plateau at $[I^-] \approx 0.1-0.4 M$ in deaerated alkaline solution for both Cr(bpy)$_3^+$ and Cr(phen)$_3^+$; at that $[I^-]$, $\sim 99.99\%$ of the reaction from $^2T_1/2E$ is quenched. The observed value of $\Phi_{rx}$ is $2 \times 10^{-8}$ and $7 \times 10^{-5}$ for Cr(bpy)$_3^+$ and Cr(phen)$_3^+$, respectively, at pH 9.3 (15). The lower value of $\Phi_{rx}$ for the phen complex is attributed to the $^4T_2$ state of this complex accommodating less distortion than the bpy complex owing to the greater rigidity of the phen framework. The effect of the presence of air is to reduce $\Phi_{rx}$ from a value of 0.13 for Cr(bpy)$_3^+$ in alkaline solution (absence of $I^-$) to a value of 0.10 in air-saturated solution.  

The value of $\Phi_{rx}$ for the photoaquation of Cr(bpy)$_3^+$ in O$_2$-free alkaline solution increases from 0.089 at 279.5 K to 0.13 at 309.5 K (15). Activation parameters are $\Delta H_{rx} = 9.7$ kcal mol$^{-1}$ and $\Delta S_{rx} = -11$ cal deg$^{-1}$ mol$^{-1}$. Thus, the enthalpy of activation for reaction from $^2T_1/2E$ is considerably less, by $\sim 13$ kcal mol$^{-1}$, than the comparable reaction from the $^4A_2$ ground state, but the entropy of activation is about the same; the photoreaction is faster by about ten orders of magnitude. Inasmuch as $^2T_1/2E$ and $^4A_2$ have the same geometry, the greater excited state photoreaction is attributed to the $^4T_2$ state which we suggest possesses some degree of reduced electron density in theta levels compared to the $^4A_2$ ground state.  

### Solution Medium Effects

One of the most interesting aspects of the photochemical studies of Cr(NN)$_3^+$ complexes is the alteration of the solution medium and its effect on the properties of the excited state complexes. One such effect, pH changes on $\Phi_{rx}$, has already been noted.  

Ground state quenching of $^2T_1/2E$ results in a diminution in the population of the states and must consequently result in a decrease of the quantum yields of the various processes that arise from doublet states. $\Phi_{rx}$, for example, is expected to decrease with increased [substrate] in 1.0 M NaCl inasmuch as $\Phi_{rx} = 2k_{obs}^2 + k_{obs}^2$. Although $\Phi_{rx}$ has been determined for most of the Cr(NN)$_3^+$ complexes over a concentration in substrate of greater than one order of magnitude (21), only three complexes (NN = 5-Brphen, 5-Phphen, and 4,7-Ph$_2$phen) show the effect outside of experimental error. This limitation arises from the very low values of $\Phi_{rx}$ (Table 3). This notwithstanding, the resulting $2k_{obs}^2$ values obtained from $\Phi_{rx}$ studies agree reasonably well with $2k_{obs}$ values obtained from $\tau_{obs}$ studies in 1.0 M media (21).  

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4A_2$Cr(NN)$_3^+$ $\rightarrow$ $^4T_2$Cr(NN)$_3^+$</td>
<td>Light absorption</td>
</tr>
<tr>
<td>$^4T_2$Cr(NN)$_3^+$ $\rightarrow$ $^4A_2$Cr(NN)$_3^+$</td>
<td>Internal conversion</td>
</tr>
<tr>
<td>$^4A_2$Cr(NN)$_3$ $\rightarrow$ $^4T_2$Cr(NN)$_3$</td>
<td>Nonradiative decay</td>
</tr>
<tr>
<td>$^4T_2$Cr(NN)$_3$ $\rightarrow$ $^4A_2$Cr(NN)$_3$</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>$^4A_2$Cr(NN)$_3$ $\rightarrow$ $^4T_2$Cr(NN)$_3$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>$^4A_2$Cr(NN)$_3$ $\rightarrow$ $^4T_2$Cr(NN)$_3$</td>
<td>Nonradiative decay</td>
</tr>
<tr>
<td>$^4A_2$Cr(NN)$_3$ $\rightarrow$ $^4T_2$Cr(NN)$_3$</td>
<td>Phosphorescence</td>
</tr>
<tr>
<td>$^4T_2$Cr(NN)$_3$ $\rightarrow$ $^4A_2$Cr(NN)$_3$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>$^4T_2$Cr(NN)$_3$ $\rightarrow$ $^4A_2$Cr(NN)$_3$</td>
<td>Chemical reaction</td>
</tr>
</tbody>
</table>

Table 4. Summary of the General Mechanism for the Photochemistry and Photophysics of Cr(NN)$_3^+$ Complexes in Aqueous Solution

In air-saturated solution, the value of $\Phi_{rx}$ for the Cr(bpy)$_3^+$ complex is 0.015, as determined for Cr(bpy)$_3^+$ in alkaline solution (absence of $I^-$) to a value of 0.10 in air-saturated solution.  

Activation parameters are $\Delta H_{rx} = 9.7$ kcal mol$^{-1}$ and $\Delta S_{rx} = -11$ cal deg$^{-1}$ mol$^{-1}$. Thus, the enthalpy of activation for reaction from $^2T_1/2E$ is considerably less, by $\sim 13$ kcal mol$^{-1}$, than the comparable reaction from the $^4A_2$ ground state, but the entropy of activation is about the same; the photoreaction is faster by about ten orders of magnitude.  

Inasmuch as $^2T_1/2E$ and $^4A_2$ have the same geometry, the greater excited state photoreaction is attributed to the $^4T_2$ state which we suggest possesses some degree of reduced electron density in theta levels compared to the $^4A_2$ ground state; this aspect would result in less reorganizational energy being required to form the activated complex (42).
Summary

From the various studies, a general mechanism has evolved for the photochemistry and photophysics of Cr(NN)₃⁺ complexes in aqueous solutions which is summarized in Table 4.

Unanswered Questions and Future Directions

As in all areas of research, the more one knows, the more questions are raised. Despite the enormous body of knowledge on the photochemistry and photophysics of Cr(III) complexes in general, and Cr(NN)₃⁺ in particular, there remain many unanswered questions that will serve as the basis for future research.

1) What is the energy of the \( \text{the}x \text{i} T_{1g} \text{ state, its geometry, and its lifetime? Without any detectable fluorescence from that state, it will remain an enigma. Perhaps it can be detected by its absorption spectrum using picosecond pulsed laser excitation.}

2) What is the origin of the wavelength dependence of the quenchable and unquenchable photoaquation quantum yields and the phosphorescence quantum yield (43, 44) which shows a sharp decrease between 470 and 510 nm? It is clear that \( \Phi_{\text{ph}} \) is wavelength-dependent in that region (45) suggesting that prompt intersystem crossing and photoreaction occur at an energy higher than that of the \( \text{the}x \text{i} T_{1g} \text{ state.}

3) What is the mechanism by which solution medium affects the value of \( \Phi_{\text{ph}} \)? We know that the addition of ClO₄⁻ to aqueous solutions of Cr(bpy)₃⁺ prolongs the lifetime but decreases the quantum yield of photoaquation (47). We also know that DMF (29), CH₃CN and mixed CH₃CN-H₂O (48) decrease both \( \Phi_{\text{ph}} \) (25, 48) and \( \Phi_{\text{ph}} \) (17, 48). Details for other nonaqueous solvents and mixed solvents are not available.

4) To what extent can Cr(NN)₃⁺ complexes be used in solar energy conversion and storage schemes? We have addressed the question of the potentiality of these complexes (49) and find that their photochemical and thermal stabilities in acidic solution, their long-lived excited states, and their excited state retool potentials are positive aspects; their absorption spectra and lability of their corresponding Cr(II) species are negative aspects.

Acknowledgment

We are particularly grateful to our associates, Drs. Marian S. Henry, R. Sriram, and Mary Jamieson, without whose efforts much of our work would not have been realized. We are grateful also for the support we have obtained through the years from the Natural Sciences and Engineering Research Council of Canada, the Fonds F.C.A.C. du Quebec, the National Science Foundation, and the North Atlantic Treaty Organization.

Literature Cited