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# Photophysics of Chromium(III)-Polypyridyl Complexes. Effect of pH and [Cl⁻] on the Lifetimes of the $^2T_1/^2E$ Excited States[1]

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The lifetimes of the lowest doublet excited states ($^2T_1/^2E$) of tris(polypyridyl) complexes of Cr(III) ($Cr(NN)_3^{3+}$) have been measured in deoxygenated dilute aqueous solution as a function of pH at 5 °C. At pH 3–4, $\tau_{obsd}$, is significantly longer than at pH 9–10; $\tau_{obsd}$ and the intensity of luminescence from $^2T_1/^2E$ exhibit parallel pH functionality with an inflection point at pH ~6–7. For example, for $Cr(phen)_3^{3+}$, $\tau_{obsd}$ = 1.1 ms at pH 2 and 0.65 ms at pH 10; the activation energies of $\tau_{obsd}$, measured at 5–35 °C, are 37 kJ mol$^{-1}$ at pH 3–4 and 31 kJ mol$^{-1}$ at pH 9–10. The results are interpreted in terms of the existence of $H_2O$ or $OH^-$ within the intraligand pockets of $^2T_1/^2E$ due to the deep hydration of the long-lived, highly charged cation, with the rate of the nonradiative decay of $^2T_1/^2E$ reflecting the environment in the vicinity of the metal center. Because $\tau_{obsd}$ and the quantum yields of photoaquation exhibit a parallel pH dependence, we suggest that the relatively minor photochemical decay path involves the incorporation of intraligand $H_2O$ or $OH^-$ in a seven-coordinate intermediate. Inasmuch as $^2T_1/^2E$ and the ground state ($^4A_2$) have the same charge and geometry, and the rate constants of thermal aquation of the ground states, as well as the quantum yields of photoaquation from the very short lived $^4T_2$ manifolds, exhibit a pH dependence identical with that of $\tau_{obsd}$ of $^2T_1/^2E$, consideration is given to the possibility that the ground states of $Cr(NN)_3^{3+}$ are deeply hydrated in aqueous solution. In the presence of 1 M NaCl, the magnitude of the pH effect is greatly diminished; for example for $Cr(phen)_3^{3+}$, $\tau_{obsd}$ = 0.62 and 0.61 ms at pH 3.3 and 9.5, respectively. In acidic solution, $\tau_{obsd}$ is a function of [Cl⁻]; for example, for $Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$ at pH 3.3, $\tau_{obsd}$ ranges between 1.7 and 0.64 ms in 0.001 and 1 M Cl⁻, respectively. The existence of Cl⁻ within the intraligand pockets of $^2T_1/^2E$ and, by extension, $^4A_2$, is also suggested.

## Introduction

The photophysics of Cr(III) complexes in general,[3] and tris(polypyridyl) complexes ($Cr(NN)_3^{3+}$) in particular,[4] have been very well studied. $Cr(NN)_3^{3+}$ complexes luminesce in fluid solution at room temperature, showing two bands at ~695 and ~725 nm corresponding to emission from the thermally equilibrated lowest doublet excited states designated, with use of term symbols appropriate to octahedral microsymmetry, $^2T_1$ and $^2E$, respectively.[5] The observed lifetimes of these states ($\tau_{obsd}$) are very long, ranging from 0.070 ms for $Cr(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) to 0.64 ms for $Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$ (Me = methyl; phen = 1,10-phenanthroline) in aqueous solution at room temperature.[6,7] The long lifetimes of $^2T_1/^2E$, the high ionic charges of the complexes, and the hydrophobic nature of the environment around the ligands make $\tau_{obsd}$ extremely sensitive to the nature of the solvent[8,9] and the solution medium, such as the presence of anions[10-12] and the concentration of the substrate.[11,12]

Ground-state ($^4A_2$) $Cr(NN)_3^{3+}$ quenches $^2T_1/^2E$ in solutions containing a high concentration (~1 M) of anionic species, according to the relationship $(1/\tau_{obsd}) = (1/\tau_0) + k_g[Cr(III)]$, where $\tau_0$ is the intrinsic lifetime of $^2T_1/^2E$ in the solution medium and $k_g$ is the rate constant for the bimolecular interaction of ion-paired excited- and ground-state species.[7,11,12] For example, in 1 M NaCl at room temperature, values of $k_g$ are in the range $10^6$–$10^8$ M$^{-1}$ s$^{-1}$, with the more highly substituted Me- and Phphen (Ph = phenyl) complexes exhibiting the larger values. This ground-state quenching phenomenon predicts that, at constant $[Cr(NN)_3^{3+}]$, $\tau_{obsd}$ should be a function of [Cl⁻], reflecting the ion pairing of the ground- and excited-state species. To date, this specific functionality has not been demonstrated.

Apparent conflicts exist regarding the pH dependence of the luminescence from $^2T_1/^2E$. Our previous measurements of $\tau_{obsd}$ for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, performed on aerated solutions containing 1 M NaCl at 15 °C, did not reveal any dependence on pH except in highly alkaline solution (pH >12) where OH⁻ quenches $^2T_1/^2E$ directly.[13,14] Similar measurements by Lilie and Waltz[15] on $Cr(bpy)_3^{3+}$ in deaerated solutions at room temperature in the absence of added solutes (beyond those necessary to control the pH) showed no variation of $\tau_{obsd}$ with pH (2.3–11.0). For $Cr(phen)_3^{3+}$ under the same conditions,[16] however, $\tau_{obsd}$ was ~25% shorter at pH ~9 than in acidic medium; no explanation of this observation was offered. Kane-Maguire and Langford[17] reported that the intensity of luminescence (*I*) from aerated solutions of $Cr(phen)_3^{3+}$ at pH 13 was about half that in acidic solution, with the pH profile resembling a "titration curve" centered about pH 9; at the same time, the shape of the emission spectrum was not altered. These latter authors explained their observation in terms of the addition of OH⁻ to the aromatic rings of the ligands in the ground- or excited-state complex.

In this paper, we report the results of our measurement of $\tau_{obsd}$ and *I* for $Cr(NN)_3^{3+}$ as a function of pH and [Cl⁻] at 5 °C, a temperature chosen to optimize the experimental conditions so that variations in the measured quantities would be sufficiently outside experimental error for ambiguity to be absent.

## Experimental Section

**Materials.** The $Cr(NN)_3^{3+}$ complexes, as their $ClO_4^-$ salts, were available from our laboratory stock.[7,11-14,18] All other chemicals were reagent grade. Doubly distilled water was further purified by passage through a Millipore train. For the 4,4′-$Me_2$bpy complex, a small quantity of $CH_3CN$ (4% v/v) was present in the aqueous solution in order to effect dissolution.

**Apparatus.** A Perkin-Elmer MPF-2A spectrofluorimeter equipped with a red-sensitive R-446 (Hamamatsu) photomultiplier tube was used to determine the intensity of luminescence from Ar-purged solutions thermostated to ±0.5 °C; $\lambda_{ex}$ = 370 nm, $\lambda_{em}$ = 720 nm. No alteration of emission (or ground-state absorption) spectra was observed upon

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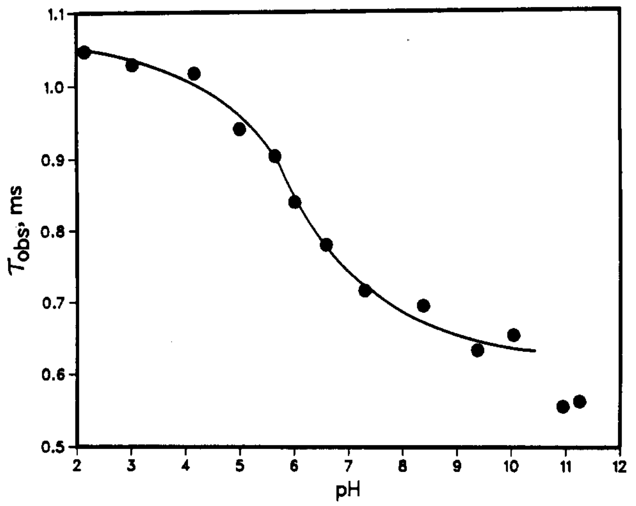

**Figure 1.** Dependence of $\tau_{obsd}$ on pH for Ar-purged solutions containing 10–15 $\mu$M $Cr(phen)_3^{3+}$ at 5 °C. Each point represents the average of 2–5 duplicate experiments from all the techniques available.

variation of pH or [$Cl^-$]. Values of $\tau_{obsd}$ (reproducible to ±5%) were determined from the first-order decay of the $^2T_1/^2E$ absorption monitored at an appropriate wavelength[16] (excitation with conventional flash lamps and a frequency-tripled Nd:YAG pulsed laser at 355 nm)[19,20] and the decay of $^2T_1/^2E$ emission monitored at 690–730 nm (excitation with a frequency-doubled pulsed ruby laser at 347 nm)[21] from thermostated Ar-purged solutions; the decay profiles were always represented by single exponentials.

A Radiometer Model 82 pH meter was used; the correction for $Na^+$ was employed where appropriate.

**Procedures.** All operations were performed under dim incandescent or red-filtered light; stock solutions were refrigerated, and samples were freshly prepared prior to each set of experiments. Solutions for laser excitation and spectrofluorimetry were contained in a 1-cm cuvette provided with a Teflon stopcock. Conventional flash photolysis was performed with a 22-cm cell surrounded by a Pyrex filter; the analyzing light was filtered though 5 cm of neat acetone or a saturated solution of naphthalene in cyclohexane.

## Results

**Effect of pH on $\tau_{obsd}$.** In a preliminary experiment, Ar-purged, solutions containing 10 $\mu$M $Cr(bpy)_3^{3+}$ at 5 °C were excited at 347 nm; $\tau_{obsd}$ for $^2T_1/^2E$ was systematically 20% lower in alkaline than in acidic solution (~0.23 ms), a difference that is outside experimental error. However, because of the small magnitude of the effect, further studies on this complex were not carried out. Rather, $\tau_{obsd}$ was measured for other $Cr(NN)_3^{3+}$ complexes that exhibited larger pH effects. The values of $\tau_{obsd}$ obtained for any given complex upon use of both the excited-state absorption and emission techniques were identical.

Figure 1 shows the dependence of $\tau_{obsd}$ on pH for Ar-purged solutions containing 10–15 $\mu$M $Cr(phen)_3^{3+}$ at 5 °C each point represents the average of 2–5 duplicate experiments from all the techniques available. Fresh solutions were always used for each flash in alkaline solution; in acidic solution, no more than two flashes were employed. The pH was controlled with HCl, $H_2SO_4$, $HClO_4$, and NaOH and $<10^{-4}$ M $Na_2HPO_4$, $NaH_2PO_4$, $Na_3PO_4$, and $Na_2B_4O_7$; $\tau_{obsd}$ was not a function of the nature of the buffer used nor of the concentration of the substrate in the range studied. The reversibility of the effect of pH on $\tau_{obsd}$ was demonstrated with a solution at pH 9.2 made acidic to pH 3.1 and returned to the original pH.

The dependence of $\tau_{obsd}$ on pH at 5 °C in the absence of added NaCl (Table I) was a general phenomenon for those $Cr(NN)_3^{3+}$ complexes examined; the magnitude of the effect is a function of the nature of the ligand and substituents.

**Table I.** Values of $\tau_{obsd}$ and $\tau_0$ for $(^2T_1/^2E)Cr(NN)_3^{3+}$ at 5.0 °C

| NN | pH | $\tau_{obsd}$, ms (absence of added NaCl) | $\tau_{obsd}$, ms (presence of 1.0 M NaCl) | $\tau_0$, ms (presence of 1.0 M NaCl) |
|---|---|---|---|---|
| phen | 3.3 | 1.0 | 0.62 (0.30)[a] | 0.68 |
| | 9.5 | 0.65 | 0.61 (0.27)[a] | |
| 5-Clphen | 3.3 | 0.46 | 0.31 | 0.36 |
| | 9.5 | 0.40 | 0.32 | |
| 5-Mephen | 3.2 | 0.95 (0.37)[b] | | |
| | 3.3 | | 0.46 | 0.63 |
| | 9.2 | 0.67 (0.30)[b] | | |
| | 9.5 | | 0.52 | |
| 5-Phphen | 3.3 | 0.77 | 0.33 | |
| | 9.5 | 0.52 | | |
| 4,7-$Me_2$phen | 3.3 | 1.3 | 0.75[c] | 0.83[c] |
| | 9.5 | 0.55 | 0.65[c] | |
| 3,4,7,8-$Me_4$phen | 3.4 | 1.7 | 0.75 | 1.1[d] |
| | 9.0 | 0.64 | 0.64 | |
| 4,4'-$Me_2$bpy[e] | 3.3 | 0.46 | 0.46 | |
| | 8.9 | | 0.41 | |
| | 9.1 | 0.34 | | |
| | 9.6 | | 0.43 | |

[a] $T$ = 22 °C. [b] $T$ = 20 °C. [c] 0.93 M NaCl. [d] 0.86 M NaCl. [e] In 4% v/v $CH_3CN/H_2O$.

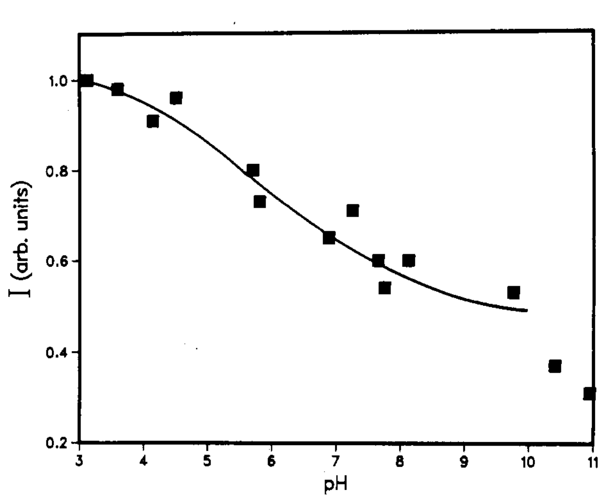

**Figure 2.** Relative values of $I$ as a function of pH at 5 °C in Ar-purged solutions ([$Cr(phen)_3^{3+}$] = 60 $\mu$M). The line has been drawn to reflect the superimposition of this plot and Figure 1.

The relative emission intensity from Ar-purged solutions containing 60 $\mu$M $Cr(phen)_3^{3+}$ was determined as a function of pH at 5 °C. Great care was taken to ensure that the absorbance of the solutions was always the same; $I$ in acidic solution was taken as the actinometric standard. Figure 2 shows the relative value of $I$ as a function of pH; when plotted together on a relative scale, the data of Figures 1 and 2 superimpose quite well.

The activation energies for the decay of $(^2T_1/^2E)Cr(phen)_3^{3+}$ at pH 3–4 and 9–10 were determined from values of $\tau_{obsd}$ obtained from 5 to 35 °C. A fit of the data in Figure 3 with a correlation coefficient of 0.99 yields the following results: $E_a$(pH 3–4) = 37 kJ mol$^{-1}$ and $E_a$(pH 9–10) = 31 kJ mol$^{-1}$. Analogous experiments performed with 15 $\mu$M $Cr(5\text{-Mephen})_3^{3+}$ yielded values of 41 and 30 kJ mol$^{-1}$ for acidic and alkaline media, respectively.

**Effect of [$Cl^-$] on $\tau_{obsd}$.** In general, the presence of 1 M NaCl reduces $\tau_{obsd}$ in acidic solution at 5 °C by a significant factor while not affecting the value in alkaline medium to any great extent (if at all), resulting in a great diminution of the pH effect (Table I). Values of $\tau_{obsd}$ at 5 °C for $Cr(phen)_3^{3+}$, $Cr(5\text{-Mephen})_3^{3+}$, $Cr(5\text{-Phphen})_3^{3+}$, $Cr(4,7\text{-Me}_2\text{phen})_3^{3+}$, and $Cr(3,4,7,8\text{-Me}_4\text{phen})_3^{3+}$ were determined at pH 3.3 (controlled by HCl) as a function of the total concentration of $Cl^-$ (with the addition of NaCl); the results are shown in Figure 4. Interestingly, no effect of [$Cl^-$] on $\tau_{obsd}$ was observed for $Cr(4,4'\text{-Me}_2\text{bpy})_3^{3+}$ (in 4% v/v $CH_3CN/H_2O$).

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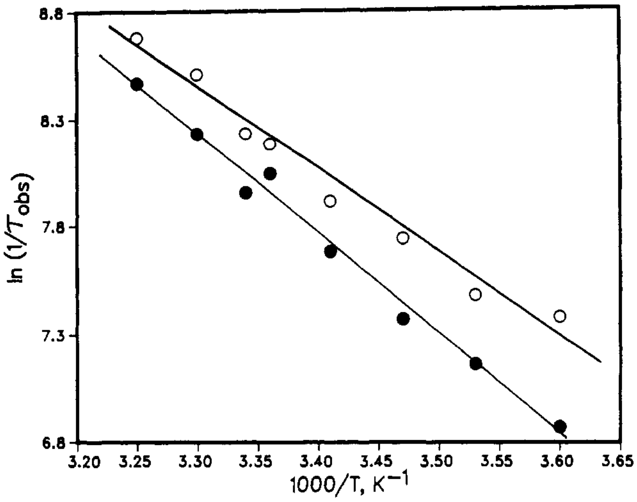

**Figure 3.** Arrhenius plots for the decay of $^2T_1/^2E$ at pH 3–4 (●) and 9–10 (○) in Ar-purged solutions ([$Cr(phen)_3^{3+}$] = 10–15 $\mu$M).

The value of $\tau_{obsd}$ at 5 °C is a function of the concentration of the complex at high [$Cl^-$] (~1 M NaCl) due to the quenching of $^2T_1/^2E$ by the ground state. Plots of $1/\tau_{obsd}$ vs. [Cr(III)] (5.0–50 $\mu$M) at pH 3.3 (HCl) are linear for NN = phen, 5-Clphen, 5-Mephen, 4,7-$Me_2$phen, and 3,4,7,8-$Me_4$phen, yielding slopes ($k_q$) in the range of (1–2) × $10^7$ $M^{-1}$ $s^{-1}$; extrapolation of these plots to infinite substrate dilution yields the values of $\tau_0$ given in Table I.

## Discussion

**Overview.** The dependences of $\tau_{obsd}$ and *I* on pH, which track each other almost perfectly (Figures 1 and 2), are supportive of other observations[16,17] but would appear, at first glance, to be in conflict with previous reports made by us.[13,14] However, as we have noted continually,[4] the details of the photophysics and photochemistry of $Cr(NN)_3^{3+}$ complexes are strongly affected by the specific nature of the solution medium. Thus, whereas other authors[16,17] examined the luminescence from $Cr(phen)_3^{3+}$ in the absence of a high concentration of anions, our previous measurements[13,14] were conducted in 1 M NaCl, a medium chosen to provide a high and constant ionic strength for reactions, such as electron transfer, between ionic species. Our observation here, that the presence of 1 M NaCl minimizes the pH effect, serves to reconcile these apparently conflicting reports. We conclude, in the first instance, that *the dependence of $\tau_{obsd}$ on pH is a real phenomenon in the absence of high concentrations of anions.*

Inasmuch as $^2T_1/^2E$ is quenched by $OH^-$ in highly alkaline solution,[14] the falloff in the values of $\tau_{obsd}$ and *I* at pH >11 in Figures 1 and 2 can be attributed to that process. The remaining points describe a "titration curve" with an inflection at pH ~6–7, considerably lower than the one obtained by Kane-Maguire and Langford[17] under experimental conditions (25 °C, aerated solutions) where $\tau_{obsd}$ and *I* are low and, perhaps, less precise. Because of the difference in $E_a$ in acidic and alkaline solutions, the pH dependence of $\tau_{obsd}$ is emphasized at low temperatures; at room temperature, the values of $\tau_{obsd}$ in acidic and alkaline solutions approach each other. As a result, *the dependence of $\tau_{obsd}$ on pH for some complexes, even in the absence of high concentrations of anions, may be obscured at room temperature.*

The value of $\tau_{obsd}$ for the decay of $^2T_1/^2E$ reflects the nonradiative deactivation of the states almost exclusively; radiative[22] and reactive[4] modes of decay are of low efficiency. The lack of a solvent isotope effect on $\tau_{obsd}$ of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ in aqueous solution,[10,23,24] unlike the behavior exhibited by the MLCT states of $Ru(NN)_3^{2+}$,[25,26] has been taken as evidence for the lack of direct vibrational coupling (e.g. through hydrogen bonding) between $^2T_1/^2E$ and the bulk solvent. The ligand serves as both the oscillating dipole and the energy acceptor, thereby providing a pathway for electronic-to-vibrational energy transfer in the excited state. Any factor that affects the vibrational modes of the ligands, alters the frequency of the low-energy vibration of the metal–nitrogen bond, and/or changes the dipolar nature of the ligands would be expected to change the rate of nonradiative decay and, hence, $\tau_{obsd}$. Thus, *the dependence of $\tau_{obsd}$ on pH cannot be attributed to a weak interaction.*

For this reason, and because the acid–base effect on $\tau_{obsd}$ occurs across the neutral pH range, simple outer-sphere ion pairing of $OH^-$ with $^2T_1/^2E$ as the source of the effect can be ruled out immediately. Similarly, since a dependency proportional to [$OH^-$] (as is the case of the quenching in highly alkaline solution) is not observed, any direct attack of $OH^-$ on $^2T_1/^2E$ can be also ruled out. Other possible mechanisms involving $^2T_1/^2E$ can also be eliminated. Deprotonation of an acidic ring carbon, suggested as a means whereby ground-state $M(bpy)_3^{3+}$ complexes are reduced in highly alkaline solution,[27] does not appear to be appropriate under the mild solution medium conditions involved here. The nucleophilic addition of $H_2O$ (or $OH^-$) to a ring carbon adjacent to the coordinating nitrogen of a polypyridine ligand would yield a covalent hydrate (pseudobase); there is precedence for the formation of covalent hydrates in coordinated[28] and free[29] heterocycles. Although the rate of formation of a pseudobase from $OH^-$ is considerably greater than from $H_2O$,[30] $K_{eq}$ for the interaction of $OH^-$ and ground-state $M(NN)_3^{3+}$ complexes, where M = Rh and Ru, is believed to be <1 $M^{-1}$;[31] this interaction cannot be important except in highly alkaline solution. For ($^2T_1/^2E$)-$Cr(NN)_3^{3+}$, which exhibits no discernible change in the emission spectrum as a function of pH, the extent of pseudobase formation in the pH range studied must be negligible.

Therefore, the dependence of $\tau_{obsd}$ on pH must be attributed to a strong interaction, with an inflection point at pH ~6–7, that does not result in any apparent change in the energies of the metal-centered emitting states. This interaction must be of a nature to cause a change in the rate of nonradiative decay and the corresponding $E_a$ as a function of pH, and be reversible. At the same time, one cannot help noticing the striking similarity of the "titration curves" for $\tau_{obsd}$ and $\Phi_{obsd}$, the observed quantum yield of photoaquation.[7,13,14,32] In the latter case, $\Phi_{obsd}$ is very low in acidic solution, exhibits an inflection point at pH ~6–7, and reaches a plateau value at pH 9–10; in highly alkaline solution, $\Phi_{obsd}$ rises again due to the direct quenching of $^2T_1/^2E$ by $OH^-$.

**Background.** Several years ago, having observed that $\tau_{obsd}$ is independent of pH (due to the presence of 1 M NaCl) and $\Phi_{obsd}$ is pH-dependent (in the presence or absence of NaCl), we proposed[4] that $^2T_1/^2E$ species, which, like their ground-state antecedents, do not possess moieties that have acid–base properties, react with $H_2O$ in competition with their nonradiative decay to form a seven-coordinate aqua intermediate; in acidic solution, the [$H^+$]-dependent and -independent loss of the coordinate water was viewed as leading to the re-formation of the ground-state complex. We attributed the pH dependence of $\Phi_{obsd}$ to the deprotonation of the coordinated $H_2O$ and the subsequent fast and irreversible reactions of the resulting seven-coordinate hydroxy intermediate.

However, as the results reported here show, $\tau_{obsd}$ *is* a function of pH in the absence of NaCl, which requires a reevaluation of the photophysical and photochemical mechanisms. Indeed, the parallel functionality of $\tau_{obsd}$ and $\Phi_{obsd}$ toward pH indicates, with

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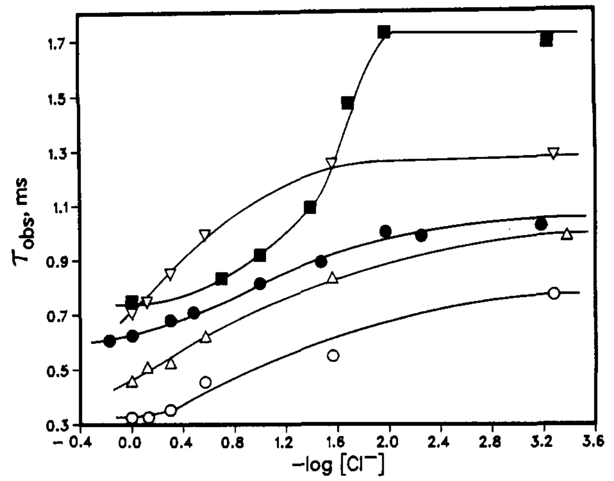

**Figure 4.** Values of $\tau_{obsd}$ in Ar-purged solutions at 5 °C and pH 3.32 (controlled with HCl) as a function of the total concentration of $Cl^-$ (addition of NaCl): (●) 15 μM $Cr(phen)_3^{3+}$; (△) 10 μM $Cr(5\text{-}Me\text{-}phen)_3^{3+}$; (○) 10 μM $Cr(5\text{-}Phphen)_3^{3+}$; (▽) 10 μM $Cr(4,7\text{-}Me_2phen)_3^{3+}$; (■) 10 μM $Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$.

great surety, that the two processes are coupled and have common origins.

**Deep Hydration Model.** We wish to propose that $^2T_1/^2E$, during its long lifetime, exists in aqueous solution in a more highly hydrated condition than would result from the usual solvation of a 3+ ion. An examination of space-filling models of $Cr(NN)_3^{3+}$ reveals the existence of pockets between the hydrophobic ligands in which $H_2O$ can reside with the electronegative oxygen atom oriented toward the highly electropositive metal center. However, in the absence of pertinent data, the existence of a covalent hydrate interaction between the penetrating $H_2O$ and the aromatic heterocyclic ligands is not precluded. This deeply hydrated $^2T_1/^2E$ species, designated as $*[H_2O\cdots Cr(NN)_3^{3+}]$, would decay primarily via nonradiative return to the ground state, with a rate constant and activation parameters dictated by the facility of electronic–vibrational energy transfer between the metal-centered excited states and the ligands in the presence of the interacting $H_2O$. The fact that $\tau_{obsd}$ for $^2T_1/^2E$ of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ is the same in $H_2O$ and $D_2O$ suggests, in terms of the model proposed here, that the interacting $H_2O$ molecule is effectively isolated from the bulk solvent and may reside in the interligand pocket for a period of time longer than that which one usually associates with solvent exchange.

The unique $H_2O$ molecule, held within the positively charged field of the cation, would be a stronger acid than is a bulk solvent molecule and could exhibit $pK_a \approx 6–7$. Thus, we propose that deprotonation of $*[H_2O\cdots Cr(NN)_3^{3+}]$ occurs across the neutral pH region (reaction 1), yielding the hydroxo analogue

$$*[H_2O\cdots Cr(NN)_3^{3+}] \rightleftarrows *[^-HO\cdots Cr(NN)_3^{3+}] + H^+ \quad (1)$$

$*[^-HO\cdots Cr(NN)_3^{3+}]$. Because the decay of $^2T_1/^2E$ occurs via a single exponential, the equilibrium must occur in a time frame shorter than that of the decay. Inasmuch as the interacting species has been changed as a function of pH, the kinetics of nonradiative decay would be expected to be different to some extent; the fact that $\tau_{obsd}$ is shorter in alkaline solution indicates that $OH^-$ facilitates the metal-to-ligand energy transfer due to its charged nature and greater basicity compared to that of $H_2O$.

The values of $\tau_{obsd}$ for the complexes studied, and the extent to which they are changed upon the variation of pH, become a measure of the complex interplay of electronic–vibrational coupling, ligand dipole moment, and $H_2O/OH^-$-induced perturbations. Examination of Table I reveals that the ratio of the decay rates of $^2T_1/^2E$ in acidic and alkaline solutions at 5 °C in the absence of added NaCl ranges from 1.1 for 5-Clphen to 2.6 for the highly substituted $Me_4phen$. This ratio correlates very well with $\tau_{obsd}$ in acidic solution for the phen complexes, with the longest lived states yielding the fractionally greatest effect of the conversion of intraligand $H_2O$ to $OH^-$. We suggested earlier[7] that the shorter lifetimes of halo-substituted phen complexes could be the result of the effect of the dipole moment created by the electronegative halogen atoms on the rate of nonradiative decay; the long lifetimes of the highly substituted phen complexes appear to be due to their high degree of hydrophobicity and increased isolation from solution perturbations. Thus, the conversion of $H_2O$ to $OH^-$ within the intraligand pockets does not increase the rate of nonradiative decay to any great extent in systems in which the dipole perturbation already exists; however, when the ligand vibrations and the metal-localized states are isolated, any dipole perturbation is highly effective.

The pathways leading to net photochemistry can be viewed as relatively minor decay modes of $*[H_2O\cdots Cr(NN)_3^{3+}]$ and $*[^-HO\cdots Cr(NN)_3^{3+}]$ in competition with the nonradiative and radiative processes. One can visualize the bonding of the $H_2O$ and $OH^-$ units to the metal center through Lewis acid–base reactions to form ephemeral excited seven-coordinate species ($*[H_2O–Cr(NN)_3^{3+}]$ and $*[^-HO–Cr(NN)_3^{3+}]$), which, because of the symmetry and geometry changes necessitated by the coordination of the new ligand, deactivate very rapidly to their respective ground states.[33] Reactions 2 and 3 represent composites

$$*[H_2O\cdots Cr(NN)_3^{3+}] \rightarrow [H_2O–Cr(NN)_3^{3+}] \quad (2)$$

$$*[^-HO\cdots Cr(NN)_3^{3+}] \rightarrow [^-HO–Cr(NN)_3^{3+}] \quad (3)$$

of these processes. The subsequent reactions of the seven-coordinate species, as previously proposed and discussed above, would lead to the final products with values of $\Phi_{obsd}$ that are functions of pH, reflecting the population of the acid–base forms of $^2T_1/^2E$ as well as the dependencies of the secondary reactions. It should be noted that the fractional change in $\tau_{obsd}$ between acidic and alkaline solution is much smaller than that of $\Phi_{obsd}$, especially in the presence of 1 M NaCl at room temperature, indicating that the variation of photochemical behavior cannot be attributed simply to the change in the rate of nonradiative decay of $^2T_1/^2E$.

**Implications for the Ground State.** Because $^2T_1/^2E$ and $^4A_2$ have the same charge and geometry, there being no Stokes shift in the absorption and emission between those states,[34] it is intriguing to consider that the properties of both the ground and excited states, regarding the penetration of the solvent into the intraligand pockets, are the same. If this were so, the ground states would exist as $[H_2O\cdots Cr(NN)_3^{3+}]$ and $[^-HO\cdots Cr(NN)_3^{3+}]$ in acidic and alkaline solution, respectively, and would exhibit approximately the same acid–base behavior as their $^2T_1/^2E$ counterparts (reaction 4). We have reported[14,35,36] that the rate constants of the thermal

$$[H_2O\cdots Cr(NN)_3^{3+}] \rightleftarrows [^-HO\cdots Cr(NN)_3^{3+}] + H^+ \quad (4)$$

$$[H_2O\cdots Cr(NN)_3^{3+}] \rightarrow [H_2O–Cr(NN)_3^{3+}] \quad (5)$$

$$[^-HO\cdots Cr(NN)_3^{3+}] \rightarrow [^-HO–Cr(NN)_3^{3+}] \quad (6)$$

aquation ($k_{th}$) of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ follow pH profiles identical with those of $\Phi_{obsd}$ and have attributed the phenomenon to the reaction of $H_2O$ with the ground-state complexes to form the seven-coordinate intermediate; the same secondary reactions would render the complexes essentially inert in acidic solutions and labile in alkaline solutions. In terms of the model proposed here, the slow coordination of $OH^-$ and, even much more slowly, $H_2O$ would yield the same seven-coordinate intermediates (reactions 5 and 6) and subsequent reactions.

Further support for the hypothesis that $^4A_2$ exists as $[H_2O\cdots Cr(NN)_3^{3+}]$ and $[^-HO\cdots Cr(NN)_3^{3+}]$ comes from the pH dependence of $\Phi_{obsd}$ in the presence of sufficient $I^-$ such that $^2T_1/^2E$ is virtually completely quenched.[37] This quantum yield for the

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unquenchable photoaquation reaction, $\Phi_{un}$, which exhibits a profile identical with that of $k_{th}$ and $\Phi_{obsd}$ in the absence of $I^-$, is attributed to a minor reactive pathway that competes with efficient excited-quartet → doublet intersystem crossing from the lowest energy metal-centered quartet manifold ($^4T_2$). Picosecond pulsed-laser flash photolysis experiments have indicated that $^2T_1/^2E$ is populated, by monophotonic excitation, in the subnanosecond time frame;[38,39] our recent studies of multiphoton-induced processes have shown that $^4T_2$ has a lifetime of ~50 ps.[40] Excitation would populate a Franck–Condon state that has the same solvation configuration as the ground state. During the short lifetime of $^4T_2$, that configuration would be maintained; the pH dependence of $\Phi_{un}$ would reflect the difference in the reactivities of the acid–base forms toward formation of the seven-coordinate intermediate.

It follows then, if the ground state exists as $[H_2O\cdots Cr(NN)_3{}^{3+}]$ and $[^-HO\cdots Cr(NN)_3{}^{3+}]$, excitation to, and radiative and nonradiative decay from, $^2T_1/^2E$ could be expressed by reactions 7 and 8. Although no direct proof of the existence of the deeply hydrated ground state is given in this paper, the indirect evidence based on the pH dependence of $\tau_{obsd}$ suggests that $^4A_2$ possesses acid–base properties due to reaction 4.

$$[H_2O\cdots Cr(NN)_3{}^{3+}] \overset{h\nu}{\rightleftharpoons} {}^*[H_2O\cdots Cr(NN)_3{}^{3+}] \qquad (7)$$

$$[^-OH\cdots Cr(NN)_3{}^{3+}] \overset{h\nu}{\rightleftharpoons} {}^*[^-OH\cdots Cr(NN)_3{}^{3+}] \qquad (8)$$

**Effect of $Cl^-$.** The presence of 1 M NaCl causes $\tau_{obsd}$ to diminish markedly in acidic solution but negligibly in alkaline solution (Table I), thereby virtually eliminating the pH effect for all the complexes except those with methyl-substituted phen ligands, for which the effect is still minimally seen. The equilibrium constant for the ion pairing of Cr(III) complexes by $Cl^-$ is ~4 $M^{-1}$;[41] the complexes are, doubtlessly, ion-paired in 1 M NaCl across the pH range of this study.

The results indicate that the effect of the presence of NaCl on $\tau_{obsd}$ in acidic solution is essentially the same as that caused by a pH change across the neutral region in the absence of NaCl. If, as was argued above, a weak interaction, such as ion pairing, cannot be responsible for significant changes in $\tau_{obsd}$, a perturbation by $Cl^-$ within the intraligand pockets of $^2T_1/^2E$ and, by extension, $^4A_2$ must be invoked here as well. The ground-state species can be represented as $[^-Cl\cdots Cr(NN)_3{}^{3+}]$; one can visualize a competition between $H_2O$ and $Cl^-$ in acidic solution for entry into the intraligand pockets. The excitation to and decay from $^2T_1/^2E$, via radiative and nonradiative modes, is represented by reaction 9. Inasmuch as there is no evidence for the incorporation of $Cl^-$, thermally or photochemically, into the inner coordination sphere of the complexes, reactions analogous to (5) and (6) cannot be written.

$$[^-Cl\cdots Cr(NN)_3{}^{3+}] \overset{h\nu}{\rightleftharpoons} {}^*[^-Cl\cdots Cr(NN)_3{}^{3+}] \qquad (9)$$

In alkaline solution in the presence of 1 M NaCl, $OH^-$ and $Cl^-$ will compete for inclusion into the intraligand pockets. However, because of its greater basicity, $OH^-$ will be preferentially incorporated even in mildly alkaline solution, and $^2T_1/^2E$, and $^4A_2$ by extension, will exist as $[^-OH\cdots Cr(NN)_3{}^{3+}]$. As a result, $\tau_{obsd}$ is, in general, virtually the same in alkaline solution in the presence or absence of 1 M NaCl, and $\Phi_{obsd}$ is independent of the presence of $Cl^-$.

The general dependence of $\tau_{obsd}$ on $[Cl^-]$ at pH 3.3 (Figure 4) exhibits an inflection point at ~0.1 M $Cl^-$ for $[Cr(III)] \approx 10$ $\mu M$. This result is consistent with a value of the ion-pairing constant of ~4 $M^{-1}$ and suggests that the incorporation of $Cl^-$ into the intraligand pockets occurs via transfer from the outer coordination sphere. The shapes of the curves in Figure 4 for the specific complexes will reflect, to some extent, the increased quenching of $^2T_1/^2E$ by $^4A_2$ as $[Cl^-]$ is increased and $Cl^-$ is incorporated into the pockets, resulting in a decrease in the effective positive charge of the complex; $\tau_0$ at infinite substrate dilution at a particular $[Cl^-]$ is greater than $\tau_{obsd}$, with the magnitude of the difference being a function of the value of $k_g$. The small extent of ground-state quenching at 1 M $Cl^-$ may be the cause of the differences in the values of $\tau_{obsd}$ for some complexes in alkaline solution in the presence and absence of NaCl. In general, however, at the concentrations of Cr(III) used in this study, the effect of ground-state quenching is small so that $\tau_{obsd} \approx \tau_0$; the dependence of $\tau_{obsd}$ on $[Cl^-]$ reflects, in the main, the dependence of $\tau_0$, the intrinsic lifetime of $^2T_1/^2E$ in the particular solution medium.

For all the complexes studied here, except when NN = 4,4′-$Me_2$bpy, $\tau_0$ is higher in the absence of NaCl and lower in its presence at 5 °C in acidic solution. For $Cr(phen)_3{}^{3+}$, $\tau_0$ is 1.1 ms in the absence of NaCl and 0.68 ms in the presence of 1 M NaCl at 5 °C; in comparison, $\tau_0$ is 0.25 ms in neat $H_2O$ and 0.33 ms in 1 M HCl at 22 °C.[7] This change in functionality with temperature suggests that $E_a$ for nonradiative decay is different for ${}^*[H_2O\cdots Cr(NN)_3{}^{3+}]$ and ${}^*[^-Cl\cdots Cr(NN)_3{}^{3+}]$. The prolongation of $\tau_0$ at room temperature in the presence of high concentrations of anions is a general phenomenon,[12] although the activation parameters are not yet known. The effect of 1 M $ClO_4{}^-$ is the most dramatic, yielding $\tau_0 = 0.49$ ms for $Cr(phen)_3{}^{3+}$;[12] the details of the dependence of $\tau_0$ on $[ClO_4{}^-]$ for $Cr(bpy)_3{}^{3+}$ and $Cr(phen)_3{}^{3+}$ will be presented in a separate paper.[42] It would appear that the behavior of $^2T_1/^2E$ and, by extension, $^4A_2$ and $^4T_2$ is dictated by the nature of the species within the intraligand pockets and its interaction with the metal center and the ligands.

## Summary

We have observed that the lifetimes of the $^2T_1/^2E$ excited states of $Cr(NN)_3{}^{3+}$ complexes at 5 °C are a function of pH and $[Cl^-]$ in aqueous solution. The magnitude of the pH effect is diminished greatly in the presence of NaCl and is also diminished upon the raising of the temperature due to a small, but real, difference in the activation energies of the nonradiative decays of the states. Because simple outer-sphere ion pairing does not appear to be a sufficiently strong interaction to cause a variation in the rate of nonradiative decay of $^2T_1/^2E$, we are led to a model that involves the existence of $H_2O$, $OH^-$, or $Cl^-$ in the intraligand pockets to account for the experimental effects.

The pH dependences of the observed lifetimes of $^2T_1/^2E$ ($\tau_{obsd}$) and quantum yields of photoaquation ($\Phi_{obsd}$) exhibit the same profile with an inflection point at pH ~6–7; we propose that the reactive decay of $^2T_1/^2E$ involves the incorporation of intraligand $H_2O$ and $OH^-$ into a seven-coordinate intermediate, followed by the same secondary reactions that have been proposed before. Inasmuch as the $^2T_1/^2E$ and $^4A_2$ states have the same charge and geometry, we suggest that the ground-state complexes have the same intraligand configuration; this hypothesis is supported by the fact that the rate constants of thermal aquation ($k_{th}$) and the quantum yields of unquenchable photoaquation ($\Phi_{un}$) in the presence of $I^-$, an efficient quencher of $^2T_1/^2E$, exhibit identical pH dependences.

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**Registry No.** $Cr(phen)_3{}^{3+}$, 15276-16-1; $Cr(5\text{-}Cl\text{-}phen)_3{}^{3+}$, 51194-62-8; $Cr(5\text{-}Mephen)_3{}^{3+}$, 51194-70-8; $Cr(5\text{-}Phphen)_3{}^{3+}$, 51194-60-6; $Cr(4,7\text{-}Me_2phen)_3{}^{3+}$, 51194-72-0; $Cr(3,4,7,8\text{-}Me_4phen)_3{}^{3+}$, 51194-74-2; $Cr(4,4'\text{-}Me_2bpy)_3{}^{3+}$, 58220-56-7; $Cl^-$, 16887-00-6.

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