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Effects of Solvent, Pressure, and Temperature on the Spectroscopy, Photophysics, and Photochemistry of the Hexaamminechromium(III) Ion, $[Cr(NH_3)_6]^{3+}$

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The solvent sensitivity of the spectroscopy, emission lifetime, and photosubstitution quantum yield of the hexaamminechromium(III) ion, $[Cr(NH_3)_6]^{3+}$, has been investigated in water, dimethylformamide, dimethyl sulfoxide, and hexamethylphosphoramide. The vibronic features in the emission and absorption spectra show solvent-induced trends with the Gutmann donor number scale which are consistent with a specific electron-donor interaction between the solvent and complex. Emission lifetimes are also seen to vary with solvent, and a strong correlation is observed at 315 K between $\ln(k_{obs})$, where k_{obs} is the reciprocal of the observed doublet-state lifetime, and donor number. The corresponding activation energies $E_a(k_{obs})$ and volumes of activation $\Delta V^{\ddagger}(k_{obs})$ range 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, respectively. Quantum yields for photosolvolysis are much less solvent-dependent at 296 K; these are the same in H_2O and DMF (0.44 ± 0.01) and are only slightly decreased in DMSO (0.40 ± 0.01). The values of Φ_{rx} at 298 K in H_2O are the same for both quartet and doublet band irradiation (0.43 and 0.44, respectively), as are the associated activation volumes $\Delta V^{\ddagger}(\Phi_{rx})$, which are about −6 cm^3 mol^{-1} for irradiation of either band. The differences in solvent and pressure dependencies for the measured photophysical and photosubstitutional parameters give evidence of a dominant decay route proposed to be a nonradiative thermally-activated back-intersystem crossing from the ^2E_g state to the $^4T_{2g}$ state.

Introduction

The behaviors of electronically excited states of transition metal complexes have been a source of considerable interest to inorganic chemistry. Much of this attention has centered on chromium(III) systems, due in part to the presence in room-temperature liquid media of both emission (phosphorescence) and substantial photosubstitutional quantum yields. The photobehaviors of chromium(III) complexes have been reviewed extensively; however a number of facets continue to be open to discussion.[1−11] These features include identification of the state(s) responsible for photoreactivity, the identity of excited-state decay processes, and the possible participation of ground-state intermediates. In general, excited states decay by competitive pathways, both emissive and nonradiative in nature. While the environment is recognized to play key roles in mediating these processes for chromium complexes, the specific details are as yet not clearly understood.

Recently, we have reported the effects of solvent, temperature, and pressure on the doublet-state decay of *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$, where cyclam is the saturated macrocyclic tetraamine ligand 1,4,8,11-tetraazacyclotetradecane.[12,13] This species displays a *photochemically inert character*. Thus this situation allowed for the investigation of solvent, temperature, and pressure effects on the nonradiative decay pathways of the doublet state unencumbered by competitive photochemistry. A strong correlation is observed between the rate constant for thermally-activated doublet decay and Gutmann donor number for the solvent, the latter being an empirical measure of the electron-donating ability or donicity of the solvent.[14] This correlation represents an unusual occurrence because in general the competitive decay pathways would be expected to possess very different solvent dependencies, leading to an absence of a strong correlation with a *single* solvent scale. Consequently, the presence of such a strong correlation indicates a dominant decay pathway. From the associated temperature and pressure dependencies, this pathway is proposed to be thermally activated back-intersystem crossing to the lowest excited quartet state. These studies have underlined the importance of specific solvent−solute interactions in mediating or "tuning" the nonradiative excited-state decay of this system.

The present study represents the extension of this work to the *photochemically reactive* hexaamminechromium(III) ion, $[Cr(NH_3)_6]^{3+}$. The aqueous photochemistry of this system has been well-established to be one of photoaquation with a quantum yield of ca. 0.45 upon irradiation with visible light.[8,15−21] This

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complex displays vibrationally-structured phosphorescence from the lowest excited doublet state with a 2 μs lifetime in aqueous solution at room temperature.[22-24] Its structural simplicity and well-established spectroscopy have led to many studies of this system: assignment of vibrational modes in the ground and excited states;[25-27] structural investigations of the excited states;[28] rationalizations of the photochemical and photophysical pathways.[1,8,11,17,18,23,29-33] Notwithstanding these extensive studies, the excited-state events and the role(s) of the medium in these processes remain unresolved. This situation provides a propitious opportunity to compare effects of solvent, pressure, and temperature on the photochemically reactive $[Cr(NH_3)_6]^{3+}$ to those for a system possessing a very similar octahedral microstructure (CrN_6), namely *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$, but which is photochemically unreactive. By comparison of the environmental dependencies of the two systems insight can be gained into the relative importance of the doublet and quartet excited states with respect to photosubstitution for $[Cr(NH_3)_6]^{3+}$. Furthermore, the identification of solvent-scale correlations as reported here can assist in identifying situations where a dominant decay channel exists. This combined approach provides a potentially powerful tool to further our understanding of the photobehaviors of chromium(III) systems as demonstrated here for $[Cr(NH_3)_6]^{3+}$.

Experimental Section

Materials and Solutions. Hexaamminechromium(III) nitrate, $[Cr(NH_3)_6](NO_3)_3$, and perchlorate, $[Cr(NH_3)_6](ClO_4)_3$, were synthesized according to literature methods.[22,34] The *p*-toluenesulfonate salt, $[Cr(NH_3)_6](C_7H_7SO_3)_3$, was prepared by adding a saturated aqueous solution of recrystallized *p*-toluenesulfonic acid (BDH) to an aqueous solution of the nitrate salt. The product was twice recrystallized from water and washed with cold 95% ethanol, absolute ethanol, and diethyl ether. The absorption and emission spectra agreed with those of the nitrate salt. Anal. Found (calcd) for $[Cr(NH_3)_6](C_7H_7SO_3)_3$: N, 12.47 (12.59); C, 37.97 (37.77); H, 5.93 (5.89).

Caution: Perchlorate salts of Cr(III) complexes are potentially explosive.[35] Only very small amounts should be prepared.

Pentaammineaquachromium(III) perchlorate, $[Cr(NH_3)_5(H_2O)](ClO_4)_3$, and pentaammine(dimethylformamide)chromium(III) perchlorate, $[Cr(NH_3)_5(DMF)](ClO_4)_3$, were made as described in the literature.[36,37] Attempts to prepare pentaammine(dimethyl sulfoxide)chromium(III) perchlorate, $[Cr(NH_3)_5(DMSO)](ClO_4)_3$, using a published method led to complexes with low % C analyses.[36] Therefore, this complex was prepared by reacting $[Cr(NH_3)_5Cl](ClO_4)_2$ with $AgClO_4$ in warm DMSO, followed by precipitation using saturated $LiClO_4$ in methanol. The crude product was reprecipitated from ice-cold 0.01 M aqueous $HClO_4$ using an acidified saturated aqueous solution of $NaClO_4$, washed with absolute ethanol and diethyl ether, and dried over P_2O_5. Anal. Found (calcd) for $[Cr(NH_3)_5(DMSO)](ClO_4)_3$: N, 13.54 (13.64); C, 4.42 (4.68); H, 4.08 (4.12). UV–visible absorption spectra for all the hexaammine- and pentaamminechromium(III) species were in agreement with reported literature values.[22,36,37] Attempts to prepare the corresponding pentaammine hexamethylphosphoramide complex by analogous thermal reactions or by extensive photochemical irradiation of $[Cr(NH_3)_6]^{3+}$ in HMPA were not successful as they gave rise to a mixture of unstable products.

All solutions were prepared just before use under dim red light. Water was purified by a Millipore Super-Q system. Acidification of the aqueous solvents was performed using ultrapure or reagent grade perchloric or nitric acid (BDH or Alfa). Dimethylformamide and dimethyl sulfoxide (BDH, Omnisolv) and hexamethylphosphoramide (Aldrich, 99%) were used as received or distilled under vacuum; the phosphorescence lifetime of $[Cr(NH_3)_6]^{3+}$ was independent of distillation of the solvent. Deuterium oxide (99.9 atom %) and deuterium chloride (99.5 atom %) were obtained from Aldrich. Syringe filters (Millex-GS 0.22 μm for aqueous solutions and Millex-SR 0.50 μm for nonaqueous solutions) were used to filter solutions prior to use.

Apparatus and Methods. The high-pressure equipment using quartz windows and the time-resolved apparatus employing an argon-ion laser with cavity dumping (488 and 514 nm output) or an Excimer-pumped dye laser (436 nm output) with visible emission detection have been described elsewhere.[13,22,38-40] Emission spectra were recorded with a Spex Fluorolog 222 spectrofluorometer. Emission quantum yields were calculated using the method of Demas and Crosby;[41] the value for $[Cr(NH_3)_6]^{3+}$ in aqueous solution ($\Phi_{em} = 5.5 \times 10^{-5}$) was used as the reference.[42] UV–visible absorption spectra were obtained on a Cary 2315 spectrophotometer. Infrared spectra of the complexes in solution were taken using a Bio-Rad FTS-40 FTIR and a Buck Scientific ATR cell with ZnSe crystal, with solvent subtraction being performed using a 3240-SPC data station.

Light sources for determinations of photochemical quantum yields were the CW mode of an argon-ion laser (Spectra-Physics Model 171 for 458 nm), an argon-ion pumped DCM dye laser (Spectra-Physics Model 375 for 646 nm) or a 1000 W Xe(Hg) high-pressure lamp (Oriel) in conjunction with a Corning CS 3-75 cutoff filter and a Bausch & Lomb H9-436 interference filter (437 nm). Reineckate actinometry was performed to determine the number of photons absorbed by the solutions.[43] Concentrations of photolysis products were determined by changes in pH (for aqueous solutions) or by calculation from the difference spectra of irradiated and unirradiated solutions (for H_2O, DMF, and DMSO). The latter method involved least-squares fitting of the experimental difference spectra to those calculated using the differences in molar absorptivities of the reactant ($[Cr(NH_3)_6]^{3+}$) and product ($[Cr(NH_3)_5X]^{3+}$, where X = H_2O, DMF, or DMSO) over the range 350–600 nm at 1 nm intervals. Detailed descriptions of this method have been given elsewhere.[44,45] To minimize secondary photolysis effects, the percentage of photolysis was kept below 11% for all solvents. As a further precaution, solutions were irradiated for longer periods to ascertain the presence of isosbestic points; these were present up to 47% photolysis in DMF, 28% photolysis in 0.01 M $HClO_4$,

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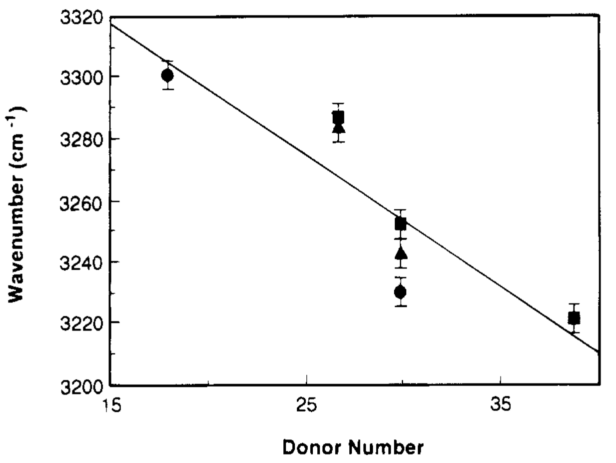

Figure 1. Wavenumber of the N–H stretch of $[Cr(NH_3)_6]^{3+}$ (concentration = 0.02–0.2 M) versus donor number of solvent at room temperature: ●, NO_3^- salt; ▲, ClO_4^- salt; ■, $C_7H_7SO_3^-$ salt.

and over 20% photolysis in DMSO. Procedures for the calculation of volumes of activation from the emission lifetimes and reaction quantum yields have been given elsewhere.[12,13,22,38] Variable-pressure studies were performed in the range 0–207 MPa.

Results and Discussion

Spectroscopic Features. The absorption spectrum of $[Cr(NH_3)_6]^{3+}$ in the visible region is dominated by two ligand field absorption bands, which are spin-allowed transitions from the ground $^4A_{2g}$ state to the $^4T_{2g}$ state (lower energy) and the $^4T_{1g}(F)$ state (higher energy).[46] The former transition gives directly the value of the ligand-field parameter $10Dq$. The changes in peak wavelength of this transition with solvent are relatively small (from 465 nm in H_2O, DN = 18.0, to 463 nm in HMPA, DN = 38.8) (DN = donor number) and shift to higher energy with increasing Gutmann donor number. Molar absorptivities also vary with solvent to some degree (from 40 M^{-1} cm^{-1} in H_2O to 49 M^{-1} cm^{-1} in DMF).

The vibrationally-structured nature of the low-intensity $^2E_g \leftrightarrow {}^4A_{2g}$ absorption and emission is well-known.[26-28] The solvent dependence of the Cr–N deformation modes at 200–300 cm^{-1} and Cr–N–H modes at 700–800 cm^{-1} from the 0–0 position follows that for *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$: they show small increases in frequency in the higher donor number solvents.[12] The energy of the 0–0 band itself is decreased in higher donor number solvents (15 215 cm^{-1} in H_2O to 15 180 cm^{-1} in HMPA). High-frequency N–H stretching vibrations were accessible in the ground-state IR region using FTIR spectroscopy. Figure 1 shows that the N–H stretch frequency decreases with increasing donor number although there also appears to be some variation with anion, suggesting the occurrence of ion-pair interactions.

These trends parallel those for *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ and clearly indicate the presence of specific solute–solvent interactions. According to the Gutmann bond-length variation model, donor-type interactions at the N–H sites would be expected to decrease the force constant and stretching frequency of the N–H bond and increase those of the Cr–N bond.[14] These qualitative predictions are consistent with the experimentally observed vibrational features. Small increases in the ligand-field splitting parameter $10Dq$ also indicate some contraction of the Cr–N inner sphere with increased donor strength as anticipated from the above model.[22] The energy of the 0–0 transition between the $^4A_{2g}$ and ^2E_g states is dependent on the Racah electron-repulsion parameters.[47] Decreases in this energy with increasing donor number implicate increasing electron delocalization and lowered interelectronic repulsion over the Cr–N framework, which also point toward compression of the inner framework.

Photophysical Features. The quantum yields of phosphorescence Φ_{em} from the doublet state measured upon quartet irradiation are listed in Table 1. The value of Φ_{em} is related to the observed lifetime of the double state τ_{obs} $(=1/k_{obs})$ by eq 1,

$$\Phi_{em} = k_{em}\eta_{isc,obs}\tau_{obs} \qquad (1)$$

where k is the actual radiative rate constant and $\eta_{isc,obs}$ is the apparent efficiency of intersystem crossing from the excited quartet state to the doublet state.[2,10] Values for $k_{em}\eta_{isc,obs}$ in all solvents studied here at room temperature are in the range 20–40 s^{-1}. These values, coupled with an estimate of 0.69 for η_{isc} (*vide infra*), indicate that k_{em} is a very minor deactivation route at room temperature where k_{obs} values exceed 10^5 s^{-1}. One can conclude that the major exiting channels from the doublet state are nonradiative processes of either a physical or chemical nature.

The observed emission lifetimes are independent of irradiation wavelength ($^4T_{2g}$ irradiation at 488 nm, ^2E_g irradiation at 646 nm), the presence or absence of oxygen, concentration of complex (3–30 mM), and counterion (NO_3^-, ClO_4^-, and $C_7H_7SO_3^-$). The values of k_{obs} are, however, highly dependent on both temperature and solvent as shown in Figure 2. An Arrhenius-type of behavior is observed at or above room temperature in all of the solvents studied, and the apparent activation energies and pre-exponential factors are given in Table 1. Some deviation from linearity in liquid HMPA is observed below 30 °C, and such has also been found for other solvents but at temperatures below 0 °C.[5,24] It has been previously shown that the low temperature behavior is dominated by weakly-coupled nonradiative decay involving the ^2E_g and $^4A_{2g}$ states.[2,3,10,48]

In the high-temperature region a strongly-coupled transition dominates, where the displacement between states along a

Table 1. Photophysical and Photochemical Properties of $[Cr(NH_3)_6]^{3+}$ in Various Solvents

solvent	donor no.	$10^5\Phi_{em}$[a]	$E_a(k_{obs})$[b] (kJ mol^{-1})	ln A[b]	$\Delta V^{\ddagger}(k_{obs})$[b,c] (cm^3 mol^{-1})	Φ_{rx}	$\Delta V^{\ddagger}(\Phi_{rx})$ (cm^3 mol^{-1})
H_2O	18.0	5.5	46.0 ± 1.3	31.9 ± 0.5	+4.3 ± 0.3	0.44 ± 0.01[d]	
						0.47 ± 0.01[e]	−6.7 ± 0.5[e]
						0.43 ± 0.02[f]	−6.0 ± 1.0[f]
						0.44 ± 0.02[g]	−5.6 ± 0.7[g]
DMF	26.6	9 ± 1	50.6 ± 0.4	33.4 ± 0.2	+3.8 ± 0.2	0.44 ± 0.01[d]	
DMSO	29.8	12 ± 1	50.6 ± 0.4	33.1 ± 0.1	+3.5 ± 0.2	0.40 ± 0.01[d]	
HMPA	38.8	24 ± 2	51.5 ± 0.8	32.8 ± 0.3	+3.4 ± 0.2		

[a] Value for H_2O from ref 43. Conditions for DMF, DMSO, and HMPA: $T = 22.0 \pm 0.2$ °C; [Cr] = 1.3–1.5 mM; excitation wavelength = 464 nm; $C_7H_7SO_3^-$ salt. [b] [Cr] = 3–30 mM; excitation wavelengths = 488 nm and 646 nm; observed emission wavelength = 657 nm or broad-band collection (HMPA). [c] Pressure range 0–207 MPa. $T = 25$ °C for all solvents except HMPA (30 °C). [d] Irradiation wavelength = 437 nm; $T = 23.0$ °C; light intensity = 1.2×10^{-7} einstein s^{-1}; [Cr] = 12–15 mM; spectrophotometric product analysis. [e] From ref 18. [f] Irradiation wavelength = 458 nm, $T = 25.0$ °C; light intensity = 2.5×10^{-9} einstein s^{-1}; [Cr] = 17 mM; pH 3.2. [g] Irradiation wavelength = 646 nm; $T = 25.0$ °C; light intensity = 2.2×10^{-9} einstein s^{-1}; [Cr] = 20 mM; pH 3.2.

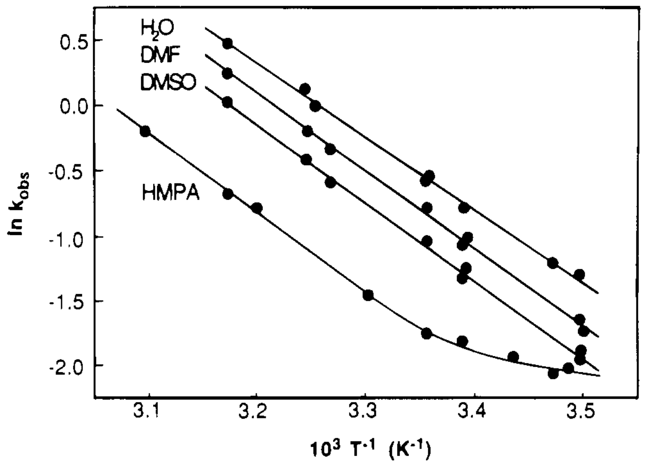

Figure 2. Plot of ln(k_{obs}) versus reciprocal temperature in different solvents. Conditions: [Cr] = 3–30 mM; excitation wavelengths = 488 nm and 646.4 nm; observed emission wavelength = 657.2 nm or broad band collection (HMPA); aerated solutions.

nuclear coordinate is substantial.[3,48] One anticipates a nonzero volume of activation associated with the crossing, and for $[Cr(NH_3)_6]^{3+}$ the values for the different solvents (Table 1) range between +3.4 and +4.3 cm^3 mol^{-1}. Notably, for the photochemically unreactive *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$, the increase in $\Delta V^{\ddagger}(k_{obs})$ values to about +7 cm^3 mol^{-1} from near zero at low temperatures coincides with the onset of the Arrhenius-like high-temperature region.[12,13] The origin of the strongly-coupled high-temperature decay can potentially be ascribed to one or more processes: a direct doublet-state chemical reaction, a thermally-activated back-intersystem crossing from the doublet to a low-lying excited quartet state, or a surface crossing to a ground-state intermediate which may in turn re-form the starting species or react to form the photochemical product.[1–3,5,8,10,11,23,49] Doublet-state reaction directly to product via an interchange mechanism appears unlikely because there is the strong similarity of doublet-state behaviors between $[Cr(NH_3)_6]^{3+}$ and the photoinert *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ and because it is difficult to reconcile the positive values of $\Delta V^{\ddagger}(k_{obs})$ for the lifetimes in the various solvents with the considerable negative values for the observed volumes of activation of the chemical quantum yields (Table 1).[12,35]

A scheme incorporating the remaining possible pathways is shown in Figure 3, where Q_0 and GSI represent the ground state of $[Cr(NH_3)_6]^{3+}$ and a ground-state intermediate, respectively. The symbols Q_1 and D_1 designate the lowest quartet ($^4T_{2g}$) and doublet (^2E_g) excited state, respectively. The thermally relaxed Q_1 level has been shown in low-temperature solids to be tetragonally distorted relative to Q_0 (and D_1),[28] and the results of theoretical calculations suggest the energy gap ΔE between the relaxed Q_1 and D_1 states of $[Cr(NH_3)_6]^{3+}$ in aqueous solution to be ca. 50 kJ mol^{-1}.[50] This value is very close to the values for $E(k_{obs})$ listed in Table 1. Although the observed activation energy is itself a composite function of the individual E_a-values for the competing pathways of Figure 3, the close correspondence between the observed E_a values and the calculated gap ΔE can be rationalized if thermally activated back-intersystem occurs and is the dominant process. It is noteworthy that this type of close correspondence also occurs in comparing the estimated molar volume difference $\Delta \bar{V}$ between Q_1 and D_1 of +3 to +4 cm^3 mol^{-1} with the experimental values of $\Delta V^{\ddagger}(k_{obs})$ for the different solvents listed in Table 1.[22]

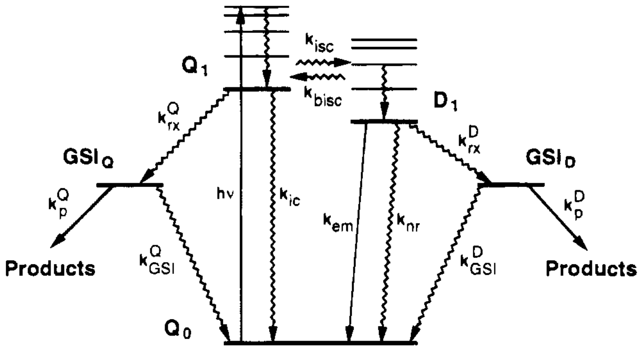

Figure 3. Diagram illustrating processes between ground $^4A_{2g}$ and excited $^4T_{2g}$ quartet states (Q_0 and Q_1, respectively), doublet ^2E_g state (D_1), and possible ground-state intermediates (GSI_Q and GSI_D).

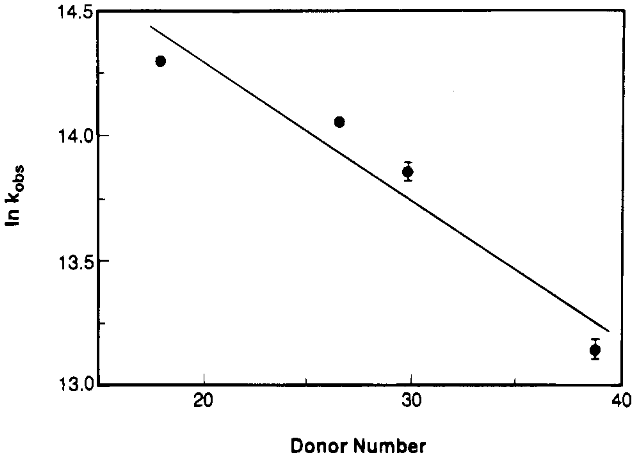

Figure 4. Plot of ln(k_{obs}) versus solvent Gutmann donor number at 42.2 °C (slope = −0.0559, r^2 = 0.933). Conditions are as for Figure 5.

As shown in Figure 2, the nature of the solvent influences substantially the values of k_{obs} describing the behavior of the doublet excited state at a given temperature.l Correlations were sought between k_{obs} values at 42.2 °C and 11 single-parameter solvent scales in the manner described previously for the case of *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ in these same solvents.[12] The strongest correlation is found to be a semilogarithmic fit of k_{obs} versus Gutmann donor number as shown in Figure 4. As for *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$, the ln($k_{obs}$) values decrease with increasing donor number, and this result is notable on several accounts.[12] As portrayed in Figure 3, exiting from the doublet state involves competing processes where the solvent can exert a differing influence over each of these decay channels. As a result, the correlation of a composite quantity such as ln(k_{obs}) with a single-parameter solvent scale is generally not to be expected unless one process were to dominate.

Others have interpreted the negative activation volumes for the chemical quantum yields to indicate that the photosubstitution is of an associative character.[4,18] If exiting from the doublet state were to reflect strongly an associative chemical path involving the solvent, an increase in ln(k_{obs}) with increasing solvent donicity would be anticipated. By contrast, the negative slope of Figure 4 suggests that at the stage of the doublet-state decay, the dominant role of the solvent is a physical one involving N–H–solvent interaction rather than a chemical role. The strong solvent-based similarities for the doublet-state behaviors of $[Cr(NH_3)_6]^{3+}$ and the photochemically *unreactive*

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trans-$[Cr(cyclam)(NH_3)_2]^{3+}$ are now brought into focus because both cases reflect a parallel effect of solvent as a physical "tuning agent" in the manner described above for a dominant nonchemical pathway, i.e. a thermally activated back-intersystem crossing (BISC) between the D_1 and Q_1 states.[51]

Photochemical Features. The quantum yields for chemical reaction (Table 1) as determined both from release of ammonia (Δph method) and from spectrophotometric analysis are in good agreement and are in concordance with other recent determinations of Φ_{rx} and of $\Delta V^{\ddagger}(\Phi_{rx})$ for irradiation of the quartet bands.[16,18,21,44] The results from this work also show that *both* the chemical quantum yields and their associated activation volumes are the same within experimental error for irradiation of the lower energy quartet band and of the doublet band.

A key point that emerges is the different responses of the lifetime of the lowest doublet state and of the chemical quantum yield to variations in the environmental parameters (pressure, temperature, and solvent). Specifically, the chemical yields for photosolvolysis are only marginally affected on changing the solvent, unlike the substantial solvent dependence of the lifetimes. In the higher temperature region, the activation energy of the chemical quantum yield for quartet irradiation is very small ($E_a(\Phi_{rx})$ ca. 4 kJ mol^{-1}) in contrast to the much larger values ($E_a(k_{obs})$ ca. 50 kJ mol^{-1}) for the lifetime.[8,44] Applied pressures lead to a decrease in the rate of decay of the doublet state ($\Delta V^{\ddagger}(k_{obs})$ ca. +4 cm^3 mol^{-1}; Table 1) whereas the opposite effect occurs for the chemical yield ($\Delta V^{\ddagger}(\Phi_{rx})$ ca. −6 cm^3 mol^{-1}; Table 1). Any mechanistic interpretation needs to incorporate within its framework a rationale for these markedly contrasting behaviors, and we begin to address these and related facets in the context of the schematic representation shown in Figure 3.

The scheme of Figure 3 explicitly introduces the possible occurrences of thermally-activated back-intersystem crossing (BISC) and of the formation of the solvated product proceeding through ground-state intermediates (GSI) derived from a surface crossing at the doublet and quartet levels.[3-5,31,49] In the case of $[Cr(NH_3)_6]^{3+}$, time-resolved measurements have not let to direct detection of a ground-state intermediate so such an occurrence may be problematical; however, a chemically reactive GSI has been found for *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$.[13,15] Laser flash photolysis measurements for $[Cr(NH_3)_6]^{3+}$ using conductivity detection have shown that for irradiation of the quartet bands, the release of ammonia occurs in two stages. There is a prompt, initial phase that is ascribed to reaction from the quartet level, and this is followed by a slower phase, the latter occurring with the same lifetime as the decay of the doublet state.[15] The fraction of chemical reaction f_D occurring with the lifetime of doublet state is 0.74 ± 0.04 (347 nm, irradiation of second-quartet band) and 0.80 ± 0.04 (530 nm, irradiation of first-quartet band). Krause and Wasgestian have measured using steady-state techniques the chemical yield for quartet irradiation in the presence of the doublet-quenching agents, hydroxide anion and aqueous cobalt(II) cation, and the respective chemical yields are $\Phi_{rx} = 0.45 \pm 0.04$ (unquenched) and $\Phi_{rx,nq} = 0.14 \pm 0.01$ (with quenching).[17] The fraction of unquenched reaction $f_Q = 0.31 \pm 0.04$, and thus f_D $(=1 - f_Q) = 0.69 \pm 0.04$. The f_D values obtained by these different approaches are in reasonable agreement, and they demonstrate that passage through the doublet state is the major pathway to chemical reaction. Because the value of $\Phi_{rx,nq}$ is required for the calculations, we have used the results of Krause and Wasgestian in the calculations of numerical values cited below.

On the assumption that multiple passes may occur through the doublet state prior to chemical reaction, eqs 2−4 are

$$\Phi_{rx}^{Q} = \frac{\eta_{p}^{Q}\eta_{rx}^{Q} + \eta_{p}^{D}\eta_{rx}^{D}\eta_{isc}}{1 - \eta_{isc}\eta_{bisc}} \tag{2}$$

$$\Phi_{rx}^{D} = \frac{\eta_{p}^{D}\eta_{rx}^{D} + \eta_{p}^{Q}\eta_{rx}^{Q}\eta_{bisc}}{1 - \eta_{isc}\eta_{bisc}} \tag{3}$$

$$\Phi_{rx,nq}^{Q} = \eta_{p}^{Q}\eta_{rx}^{Q} = f_{Q}\Phi_{rx}^{Q} \tag{4}$$

applicable to the model and their derivations are available as supplementary material. The symbol η_j^i designates the efficiency of the *j*th step occurring from the *i*th electronic state (D_1 or Q_1). The efficiency of reaction from the GSI derived from the *i*th state is designated as η_p^i and this parameter allows for the possibility that, in competition with product formation, the intermediate(s) may revert to $[Cr(NH_3)_6]^{3+}$ in its ground state. The foregoing relationships lead to the intersystem crossing efficiency η_{isc}, where $\eta_{isc} = f_D(\Phi_{rx}^Q/\Phi_{rx}^D)$ and the value of η_{isc} is 0.69 ± 0.06. Even with the considerable amount of experimental data available, there are in the absence of direct information on the values of η_p^i for the ground-state intermediate too many unknowns to be able to determine all of the other η_j^i values. However, the fact that Φ_{rx}^D equals Φ_{rx}^Q within experimental error ($\Phi_{rx}^Q/\Phi_{rx}^D = (1.0 \pm 0.1)/1$), along with the solvent and pressure dependencies of k_{obs} noted above, indicate that a more limiting set of boundary conditions may apply which still allows for retention of the general features of the model.

As noted above, the emissive and weakly-coupled nonradiative processes are minor contributors at room temperature. Thus we can assume initially that $\eta_{rx}^D + \eta_{bisc} \cong 1$, and this assumption leads to η_{bisc} being expressed by the ratio $(\eta_p^D - \Phi_{rx}^D)/(\eta_p^D - \Phi_{rx}^Q)$. If Φ_{rx}^D were *exactly* equal to Φ_{rx}^Q, then η_{bisc} would be unity and η_{rx}^D would now be zero. Clearly the "if" condition need not be precisely so; however within experimental error, the numerical values of Φ_{rx}^D and Φ_{rx}^Q are the same, and this strongly supports the situation where η_{bisc} approaches unity. To the extent that η_{bisc} begins to closely approach one, the remarkable contrasts in the effects of the environmental parameters on the lifetime and chemical quantum yield as cited above become more understandable because while changes in solvent, pressure, and temperature can significantly affect the rate of passage through the double state, the outcome remains essentially unchanged. This perspective has the attendant implication that any ground-state intermediate derived from the quartet level is nonselective as inferred from the fact that the chemical quantum yield does not depend markedly on the solvent and that the putative intermediate does not discriminate readily between chloride and bromide ion in photoanation.[17] Furthermore, since $\eta_p^i \leq 1$ and as no fluorescence is observed, this means that $\eta_{rx}^Q + \eta_{ic} + \eta_{isc} = 1$, and thus $\eta_{rx}^Q \geq 0.14$ and $\eta_{ic} \leq 0.18$.

Other specific features can be accounted for within this context because as $\eta_{bisc} \rightarrow 1$, then both Φ_{rx}^D and Φ_{rx}^Q approach the expression given in eq 5. In turn the effect of pressure on

$$\Phi_{rx} = \eta_p^Q\eta_{rx}^Q/(1 - \eta_{isc}) \tag{5}$$

the quantum yields for irradiation of the doublet and quartet states are predicted to approach the same value, as found experimentally (Table 1). Although the risetime for population of the doublet state upon irradiation of the lowest quartet levels is not known precisely, time-resolved measurements on [Cr-

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(51) Further support for a physical N−H−solvent interaction centered on the solvent lone pairs is given by the lack of a solvent isotope effect in acidic H_2O and D_2O: τ_{obs} is 2.1 ± 0.1 μs at 22 °C in both solvents.

$(NH_3)_6]^{3+}$ and on related chromium(III) amine complex ions clearly indicate that the growth is much shorter than the measured decay lifetime, and therefore the reciprocal of the latter can be approximately expressed by eq 6.[1,10,22] With the

$$k_{obs} = k_{em} + k_{nr} + k_{rx}^{D} + (1 - \eta_{isc})k_{bisc} \qquad (6)$$

presumption of back-intersystem crossing predominating and with $\eta_{isc} = 0.69$, then k_{obs} is effectively determined by the last term of eq 6. In conjunction with the definitions of activation volume and energy (eqs 7 and 8), the experimentally measured

$$\Delta V^{\ddagger}(k) = -RT\left(\frac{\partial \ln k}{\partial P}\right)_T \qquad (7)$$

$$E_a(k) = RT^2\left(\frac{\partial \ln k}{\partial T}\right)_P \qquad (8)$$

activation energy and volume of activation for the lifetime can be related to the effects of temperature and pressure on η_{isc} and k_{bisc} by eqs 9 and 10, Estimates of the values of $E_a(\eta_{isc})$ and

$$E_a(k_{obs}) = E_{a,bisc} - \left(\frac{\eta_{isc}}{1 - \eta_{isc}}\right)E_a(\eta_{isc}) \qquad (9)$$

$$\Delta V^{\ddagger}(k_{obs}) = \Delta V^{\ddagger}_{bisc} - \left(\frac{\eta_{isc}}{1 - \eta_{isc}}\right)\Delta V^{\ddagger}(\eta_{isc}) \qquad (10)$$

$\Delta V^{\ddagger}(\eta_{isc})$ can be obtained from the effects of temperature and pressure on the emission quantum yield upon quartet-band irradiation through the relation

$$\Phi^{Q}_{em} \cong \left(\frac{\eta_{isc}}{1 - \eta_{isc}}\right)\left(\frac{k_{em}}{k_{bisc}}\right) \qquad (11)$$

which in conjunction with eqs 7 and 8 lead to eqs 12 and 13.

$$E_a(k_{obs}) - E_a({\Phi_{em}}^{-1}) = E_a(\eta_{isc}) + E_{a,em} \qquad (12)$$

$$\Delta V^{\ddagger}(k_{obs}) - \Delta V^{\ddagger}({\Phi_{em}}^{-1}) = \Delta V^{\ddagger}(\eta_{isc}) + \Delta V^{\ddagger}_{em} \qquad (13)$$

The left-hand sides of eqs 12 and 13 are experimentally measurable quantities. Using the value of $E_a(k_{obs})$ for aqueous media as given in Table 1 and that for $E_a(\Phi_{em}^{-1})$ measured by Kane-Maguire and Langford (44 kJ mol^{-1}), one obtains $E_a(\eta_{isc}) + E_{a,em} = 2 \pm 2$ kJ mol^{-1}.[52] Since the dependence of k_{em} on temperature is very small, $E_a(\eta_{isc}) \leq 2$ kJ mol^{-1}.[2] The effect of pressure changes on the emission intensity from the doublet state in aqueous solution indicates that $\Delta V^{\ddagger}(\Phi_{em}^{-1}) = +5 \pm 1$ cm^3 mol^{-1}, and in conjunction with $\Delta V^{\ddagger}(k_{obs})$ being $+4.3 \pm 0.3$ cm^3 mol^{-1}, from eq 13 one obtains $\Delta V^{\ddagger}(\eta_{isc}) + \Delta V^{\ddagger}_{em} = -1 \pm 1$ cm^3 mol^{-1}.[22] Although these latter quantities could be either positive or negative in sign, one anticipates $\Delta V^{\ddagger}_{em} \cong 0$ on the basis of its being a radiative transition between the doublet and ground state so that $\Delta V^{\ddagger}(\eta_{isc})$ is then ca. -1 cm^3 mol^{-1}. These values of $E_a(\eta_{isc})$ and $\Delta V^{\ddagger}(\eta_{isc})$ in conjunction with eqs 9 and 10 lead to estimates of $E_{a,bisc}$ and $\Delta V^{\ddagger}_{bisc}$ of 50 ± 5 kJ mol^{-1} and $+2.1 \pm 2.3$ cm^3 mol^{-1}, respectively. The value of $E_{a,bisc}$ corresponds closely to the theoretically calculated $Q_1 - D_1$ energy gap, and that for $\Delta V^{\ddagger}_{bisc}$, although small and possessing a large relative error, suggests an expansion consistent with a crossing from the D_1 level to the Q_1 state (see above).

A dominant BISC pathway ($\eta_{bisc} \cong 1$) leads to the conclusion that both Φ^{D}_{rx} and Φ^{Q}_{rx} are given by eq 5 and thus the corresponding activation-volume expression is

$$\Delta V^{\ddagger}(\Phi_{rx}) - \left(\frac{\eta_{isc}}{1 - \eta_{isc}}\right)\Delta V^{\ddagger}(\eta_{isc}) = (1 - \eta^{Q}_{p})(\Delta V^{\ddagger Q}_{P} - \Delta V^{\ddagger Q}_{GSI}) + (1 - \eta^{Q}_{rx})\Delta V^{\ddagger Q}_{rx} - \eta_{ic}\Delta V^{\ddagger}_{ic} - \eta_{isc}\Delta V^{\ddagger}_{isc} \qquad (14)$$

Substituting the appropriate experimental values into the left side of the equation yields a value of -4 ± 2 cm^3 mol^{-1}. Several unknowns on the right-hand side preclude a numerical solution for the individual components; however, inferences can be made as to the signs (positive or negative) of the $\Delta V^{\ddagger}$ values. Time-resolved conductivity and emission experiments show that delayed ammonia release occurs with the same rate constant within experimental error as doublet decay,[15] i.e. no direct evidence for a ground-state intermediate has been obtained, and the model provided here agrees equally well with a reaction proceeding directly from the excited quartet state. This shows that GSI formation is not a requirement, although the photochemical results for the macrocyclic complex *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$ suggest that the occurrence of a GSI should not necessarily be excluded.[13] An intersystem-crossing process from the distorted quartet state to the doublet state (which has a smaller molar volume) may be expected to have a negative $\Delta V^{\ddagger}_{isc}$ – value; the same argument may be applied to the internal conversion pathway, since the ground $^4A_{2g}$ state and the excited ^2E_g state possess similar geometries. Furthermore, the contribution of the latter process must be small (≤ 0.17) since $\eta_{isc} = 0.69$ and Φ^{Q}_{rx} must be between 0.14 (i.e. $\eta^{Q}_{p} = 1$ in eq 14 assuming reaction occurs directly from the quartet) and 0.31. These values suggest that $\Delta V^{\ddagger Q}_{rx}$ is likely to be negative, implying associative character for the chemical reaction step.

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Supporting Information Available: Text describing the derivation of eqs 2 and 3 (2 pages). Ordering information is given on any current masthead page.

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