period was found in a solution of pH 6–8, and then, the rate became almost the same as that at pH 4.75. It might be a surprising matter that the rate in a strongly acidic solution of pH 2 was a little faster than that in a solution of the higher pH. It appeared that the formation rate of the $[Co(edta)]^-$ ion by the mechanism of eq 1–8 was not greatly dependent on the acidity at least in the range pH 2–5.

Concluding Remarks. We demonstrated that the ligand-substitution reaction between $[CoCl(NH_3)_5]^{2+}$ and EDTA could be induced with irradiation by visible light of an aqueous solution containing a small amount of the $[Ru(bpy)_3]^{2+}$ ion as a photocatalyst. All the results obtained under various conditions were well accounted for by the proposed reaction mechanism. To our knowledge at least this time, this reaction is a new type of photosensitized ligand-substitution reaction for ligand-substitution-inert complexes such as those of cobalt(III). Analogous reaction systems may be successful in other reactions of $[CoX(NH_3)_5]^{2+}$ where X is a ligand other than Cl^- and where a substituting ligand other than EDTA is used.

Registry No. $[CoCl(NH_3)_5]^{2+}$, 14970-14-0; edta, 60-00-4; $[Ru(bpy)_3]^{2+}$, 15158-62-0; $[Co(edta)]^-$, 15136-66-0.

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Effects of Applied Pressure on the Emission Lifetimes and Spectroscopic Features of Some Chromium(III) Ammonia and Amine Complex Ions in Aqueous Media

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The emission lifetimes for $[Cr(NH_3)_6]^{3+}$, $[Cr(ND_3)_6]^{3+}$, $[Cr(NH_3)_5(CN)]^{2+}$, $[Cr(NH_3)_5(NCS)]^{2+}$, $[Cr(en)_3]^{3+}$, *trans*-$[Cr(en)_2(NCS)_2]^+$, *trans*-$[Cr(en)_2F_2]^+$, *trans*-$[Cr(cyclam)(CN)_2]^+$, and $[Ru(bpy)_3]^{2+}$, where en, cyclam, and bpy designate ethylenediamine, 1,4,8,11-tetraazacyclotetradecane, and 2,2′-bipyridine ligands, respectively, have been studied in aqueous media under applied pressures of up to 207 MPa. The apparent volumes of activation for the chromium complexes range from +0.1 mL mol^{-1} for *trans*-$[Cr(cyclam)(CN)_2]^+$ to +6.9 mL mol^{-1} for $[Cr(NH_3)_5(NCS)]^{2+}$, and that for $[Ru(bpy)_3]^{2+}$ is −0.65 mL mol^{-1}. For $[Cr(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$, the apparent volumes of activation are found to be independent of temperature (15.1–34.3 °C), and their apparent activation energies (43.5 and 46.0 kJ mol^{-1}, respectively) are independent of pressure. For certain of these complex ions, the effects of applied pressure on their ligand field absorption bands in the visible region and also on the doublet-state emission spectrum of $[Cr(NH_3)_6]^{3+}$ have been investigated. In general, the peak maxima of the spin-allowed quartet bands shift to higher wavenumbers on pressurization, and those for the spin-forbidden doublet bands move to lower wavenumbers although the rates of change are much less pronounced for the latter. The implications of the results for the photochemistries of these systems are discussed.

Introduction

The photochemistry and photophysics of octahedral type chromium(III) complex ions, containing ligands such as ammonia, amines, halogens, and pseudohalogens, have been under active investigation from both experimental and theoretical viewpoints for many years, and a number of reviews and commentaries have recently appeared that cover various facets of their electronic excited-state properties.[1-12] Studies of such complex ions are facilitated by the fact that while they are relatively inert to thermal substitutional processes, they do exhibit on irradiation with near-UV–visible light of their ligand field bands substantial levels of photosubstitution. This is frequently accompanied in room-temperature solutions by emission, generally from the spin-forbidden doublet state(s).

A facet of major and continuing attention has been the identification of the relative extent to which the lowest doublet and quartet levels participate in the photochemistry. For the systems of interest to this report, the results obtained from studies of partial quenching of photochemical reactions and of time-resolved measurements for formation of products indicate in general two stages or levels of reactivity.[13-22] The prompt and usually unquenchable component is attributable to reactions from short-lived quartet states. The longer term stage, the one subject to quenching, occurs with the same lifetime as that for emission from the doublet state(s), and it is this stage that is associated with the major percentage of photoreaction. For example, our results from time-resolved conductivity and emission studies indicate that for $[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_5(CN)]^{2+}$, $[Cr(NH_3)_5(NCS)]^{2+}$, and $[Cr(en)_3]^{3+}$ the percentage ranges between 67% and 80% and for *trans*-$[Cr(en)_2F_2]^+$ essentially 100%.[21,22] While it is clear in a

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general sense that the doublet states can play a major role in the photochemical events, different proposals have been put forward with regard to the specific details. One perspective is that the chemistry associated with the doublet state reflects primarily thermally activated back intersystem crossing from the doublet to a low-lying quartet state(s), followed by fast chemical reaction.[9,23-28] Our photoconductivity results for $[Cr(NH_3)_5(NCS)]^{2+}$ in combination with those for steady-state photolysis and photosensitization tended to support this viewpoint; however, as we have pointed out previously, this interpretation presumes that the sensitization process did not alter the chemistry, and the results given here are not supportive of this.[21,29-31] Others have placed the emphasis on direct chemical reaction from the doublet state(s),[32-35] and recently it has been proposed that such behavior may lead to formation of ground-state intermediates rather than directly to final products.[3,4,36]

The present work was undertaken in part to extend our earlier time-resolved conductivity and emission studies and so to further address the photobehavior of the doublet states of chromium(III) complex ions.[20,21] Since emission lifetimes provide a useful probe to study the activity of excited states, we have investigated the effects of applied pressure on the lifetimes for a number of chromium(III) systems. In the cases of $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5(NCS)]^{2+}$, the results complement and extend earlier ones directed at the effects of pressurization on the chemical quantum yields;[31,37] however, with regard to $[Cr(en)_3]^{3+}$, our pressure–lifetime measurements are at variance with those reported by others.[38] The second major facet of this report concerns investigations into the changes brought about by the application of pressure to the absorption bands, involving transitions to doublet and quartet states, for certain selected complexes, and in the case of $[Cr(NH_3)_6]^{3+}$, its emission spectrum has also been studied. The motivation for doing this derives partly from the fact that currently little information appears to be available on these aspects, but more importantly this spectroscopic information is also germane to consideration of excited-state processes.[39-41]

Experimental Section

Materials and Solutions. Hexaamminechromium(III) nitrate, $[Cr(NH_3)_6](NO_3)_3$, was prepared by the method reported by Oppegard and Bailar.[42] The corresponding perchlorate salt was obtained by addition of concentrated perchloric acid to an aqueous solution of the nitrate salt, followed by recrystallization of the perchlorate sample from water. The purities of the samples were found to be satisfactory as determined from their UV–visible absorption spectra and by analysis for chromium content. Perdeuteriohexaamminechromium(III) ion was prepared in situ from 0.02 M $[Cr(NH_3)_6](NO_3)_3$ in D_2O (99.7 atom %, Aldrich Chemical Co.). To induce H–D exchange, the pH of the solution was adjusted to 10 by addition of sodium hydroxide. This solution was allowed to stand for 5 min, and then it was acidified with nitric acid to pH 2. The completion of deuteration was confirmed by recording the ^1H NMR spectrum on a Varian T-60 (before and after exchange) and the emission spectrum of the doublet state on a Spex Fluorolog 222 spectrofluorometer: The latter spectrum was in good agreement with that reported for $[Cr(ND_3)_6]^{3+}$.[34] Limited amounts of the following compounds were used as received: cyanopentaamminechromium(III) perchlorate, $[Cr(NH_3)_5(CN)](ClO_4)_2$, from Dr. E. Zinato; *trans*-dicyano(1,4,8,11-tetraazacyclotetradecane)chromium(III) perchlorate, $[Cr(cyclam)(CN)_2]ClO_4$, from Dr. N. A. P. Kane-Maguire; (thiocyanato)pentaamminechromium(III) perchlorate, $[Cr(NH_3)_5(NCS)](ClO_4)_2$, from Dr. F. Wasgestian. A second sample of the last compound was prepared as described in the literature,[29] and its identity was confirmed by analysis for chromium content and by the good agreement between both samples for their absorption spectra and emission lifetimes.

Tris(ethylenediamine)chromium(III) perchlorate, $[Cr(en)_3](ClO_4)_3$, was prepared from the commercially available chloride salt (Alfa Products) by dropwise addition of concentrated perchloric acid to an aqueous solution of the chloride salt. The absorption spectrum of the perchlorate salt agreed with that reported.[43] The chloride salt also served as the starting material for the preparation of *trans*-bis(thiocyanato)bis(ethylenediamine)chromium(III) thiocyanate,[44] and *trans*-$[Cr(en)_2(NCS)_2]ClO_4$ was formed by addition of aqueous sodium perchlorate to a solution of the thiocyanate salt. The resulting perchlorate material was recrystallized from warm water, and its absorption spectrum agreed with that reported.[45] A sample of *trans*-difluorobis(ethylenediamine)chromium(III) perchlorate, $[Cr(en)_2F_2]ClO_4$, was prepared as described elsewhere, and its absorption spectrum matched that reported.[46,47] Tris(2,2′-bipyridine)ruthenium(II) perchlorate, $[Ru(bpy)_3](ClO_4)_2$, was made from $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (G. F. Smith Chemical Co.) by Ag_2SO_4 addition (BDH AnalaR) to an aqueous solution of the chloride complex. After removal of the silver chloride precipitate by filtration, saturated sodium perchlorate solution was added to the mother liquor. The resulting reddish orange material was twice recrystallized from water.

All solutions were prepared just prior to use from water purified through a Millipore Super-Q system, and this was done under red light conditions. Adjustments to pH were performed by adding either ultrapure perchloric acid or ultrapure nitric acid (Alfa Products) until the desired pH was achieved as determined through the use of a calibrated pH meter and with the choice of the acid being employed the same as the counteranion of the complex. As part of the procedure in filling the high-pressure vessels, the aqueous solutions were filtered through either a Corning F-porosity fritted filter or more generally a Millipore 0.22-μm Millex-GS filter to remove any possible suspended particles.

Measurements and Procedures. Absorption spectra were recorded for room-pressure conditions on a Cary 118C spectrophotometer and for high pressure (up to 210 MPa) on a specially designed Cary 17 spectrophotometer at 24.5 ± 1 °C.[41] With the latter, the monitoring light beam transverses the sample cell (and the reference cell) before it enters the monochromator. To minimize potential photodegradation of the samples with this arrangement, the spectra were recorded in segments, each covering one of the main spectral features of the visible region (300–750 nm) with a fresh sample being used for each segment. In addition, appropriate Corning glass filters cutting off at shorter wavelengths were placed in the sample and reference light beams before the optical cell: for the doublet region, CS3-68 ($T < 0.5\%$, 517 nm) and CS3-66 ($T < 0.5\%$, 550 nm); for the first quartet region, CS3-75 ($T < 0.5\%$, 365 nm); for the second quartet region, no filter. The high-pressure quartz optical cell was of the le Noble–Schlott design,[48] which allows for increases in concentration due to pressurization to be compensated by a corresponding decrease in light path from that at ambient pressure (1.33–1.36 cm), so that changes in absorbance with pressure indicate directly changes in the molar absorption coefficient.

For measurements of emission lifetimes and spectra, a high-pressure optical cell with the excitation and emission ports at right angles was used. This unit, constructed by Superpressure, Inc., has a pressure range of up to 410 MPa when it is used in conjunction with sapphire-disk windows ($^3/_8$-in. thickness, $^5/_8$-in. diameter) with a light entrance of

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Table I. Absorption Spectra and Effects of Pressurization[a]

		band				
syst	apparent isosbestic points, cm^{-1} [b]	type[c]	$\bar{\nu}_{max}$, cm^{-1} [d]	$\Delta\bar{\nu}_{max}/\Delta P$, cm^{-1} MPa^{-1}	$10^2(\Delta\epsilon/\epsilon)/\Delta P$, % MPa^{-1} [e]	10^3(rel fwhm change), % MPa^{-1} [f]
$[Cr(NH_3)_6](NO_3)_3$	20 900, 25 500, 27 700	Q_1	21 560	0.53 ± 0.03	1.9 ± 0.1	−4.3 ± 0.4
		Q_2	28 570	0.36 ± 0.02	2.1 ± 0.1	*g*
		D(0–0)	15 220	−0.055 ± 0.005	0 ± 2	0 ± 10
$[Cr(NH_3)_6](ClO_4)_3$	20 900, 25 500, 27 800	Q_1	21 560	0.53 ± 0.04	1.9 ± 0.1	−4.6 ± 0.7
		Q_2	28 550	0.38 ± 0.04	2.1 ± 0.2	−4.9 ± 0.9
$[Cr(en)_3](ClO_4)_3$	21 200, 25 900, 28 200	Q_1	21 870	0.66 ± 0.05	1.2 ± 0.1	−3.2 ± 0.4
		Q_2	28 620	0.43 ± 0.03	1.4 ± 0.1	−3.4 ± 0.6
		D(0–0)	14 935	−0.042 ± 0.005	0 ± 2	0 ± 10
trans-$[Cr(en)_2(NCS)_2]ClO_4$	19 600, 24 300, 26 300, 28 400	Q_1	20 560	0.33 ± 0.01	2.1 ± 0.1	−2.2 ± 0.5
		Q_2	27 440	0.71 ± 0.03	2.8 ± 0.1	*g*
trans-$[Cr(en)_2F_2]ClO_4$	18 200	Q_1'	19 000	0.9 ± 0.2	1.0 ± 0.5	...
		Q_1''	21 460	0.72 ± 0.05	2.3 ± 0.2	...
		Q_2'	25 000	1.5 ± 0.3	4.5 ± 0.5	...
		Q_2''	28 490	−0.80 ± 0.06	4.4 ± 0.1	...
		D	15 080	0.04 ± 0.01	−2.9 ± 0.8	...
		D	15 310	0 ± 0.05	−2.9 ± 0.8	...

[a] pH 3.0. [b] Estimated standard deviations range from ±80 to ±350 cm^{-1}. [c] Symbols: Q, quartet band; D, doublet band; 0–0, 0–0 transition. [d] Estimated standard deviations are ±20 and ±2 cm^{-1} for Q and D bands, respectively, whereas for *trans*-$[Cr(en)_2F_2]^+$ the values are about a factor of 2 larger. [e] Percentage change in the molar absorption coefficient of the peak maximum relative to that at ambient pressure per megapascal. [f] The relative percent change in the full-width half-maximum per megapascal is defined as Δ(fwhm)/(fwhm)$_0$ – MPa, where (fwhm)$_0$ is the value at ambient pressure. [g] Values were not measured owing to overlap of the Q_2 bands with other bands at higher energies.

$^1/_4$-in. diameter. Under laser irradiation, the sapphire windows were found to give intense emission, characteristic of the R lines of the Cr(III) dopant. Since the chromium(III) complex ions also emit in the same region, quartz windows (Suprasil I, Esco Products) were used in this study in place of the sapphire ones although this necessitated limiting the maximum pressure to 207 MPa to avoid cracking of the quartz windows. Conventional hand-operated hydraulic pumps coupled with pressure intensifiers were employed for pressurization along with separators to isolate the sample solution from the pressurizing fluid. The estimated error in pressure is ±0.7 MPa; however, error propagation analysis indicated temperature control to be the critical aspect. Water jackets mounted on the high-pressure-emission vessel provided control to ±0.1 °C for 25.0 °C and ±0.2 °C for 15.1 and 34.3 °C: A hole in the pressure cap allowed a calibrated thermometer to be placed in close proximity to the sample solution. Monitoring of pressure and temperature changes following pressurization indicated that equilibration was achieved within 10 min. For the absorption spectra and emission lifetime experiments, measurements were made at ambient pressure and at three other pressures unless otherwise indicated, and for emission spectra, readings were taken at room pressure and 207 MPa. Measurements were performed in a random sequence in going in the directions of pressurization and depressurization, and the results obtained gave no indication of any systematic trends due to pressurization or photolysis.[49]

The excitation source for the lifetime and emission spectral studies was a Spectra-Physics Model 171 argon ion laser, and the detection system employed a Jarrell-Ash Model 78-490 grating monochromator and time-correlated single phonon counting apparatus. This instrumentation and the procedures applied for data collection and analysis are described in detail elsewhere.[50,51] For the recording of emission spectra, the 488-nm line of the argon ion laser (CW mode) served as the excitation source, and the optical band-pass of the detection system was generally 0.4 nm. For the lifetime studies, irradiations of the first quartet ligand field bands of the complex ions were carried out with use of either the 488- or the 514-nm line of the argon ion laser with cavity dumping. The irradiation at 333 nm of the second quartet band of $[Cr(en)_3]^{3+}$ was performed by frequency doubling the output of a cavity-dumped DCM dye laser synchronously pumped by the mode-locked 514-nm line of the argon ion laser. Owing to the relatively long lifetime of *trans*-$[Cr(cyclam)(CN)_2]^+$, this system was studied with flash photolysis apparatus.[52] In this case, the detector was a Hamamatsu R928 PMT, and a Tektronix 5111 storage oscilloscope was used to record and compare the emission profiles at ambient pressure and at 207 MPa.

The emission lifetimes were generally investigated at the wavelengths corresponding to the apparent maxima in emission intensity with a typical optical band-pass of 1.4 nm. In some instances, broad-band conditions were employed where the monochromator was put in zero order and the emission isolated with Corning glass cutoff filters: for $[Cr(en)_3]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_5(CN)]^{2+}$, and *trans*-$[Cr(cyclam)(CN)_2]^+$, CS2-62 ($T < 0.5\%$, 585 nm); for *trans*-$[Cr(en)_2F_2]^+$, CS2-64 ($T < 0.5\%$, 640 nm) or CS7-69 ($T < 0.5\%$, 685). The use of broad-band conditions provided for improved signal to noise ratios and for changes in the laser intensity over a wider range than that with narrow-band conditions. Where comparisons could be made between narrow- and broad-band situations, the lifetimes were found to be the same within experimental error, and they did not change on altering the laser intensity.[53,54]

Emission lifetimes were determined by nonlinear least-squares regression analysis.[50] The fitting of the data was described in all cases by a single-exponential function as determined by comparison of the data points to the fitted curve and by consideration of plots for the weighted residuals and for the weighted autocorrelation function of the residuals vs. time. Plots of the absorption peak maxima in wavenumber units ($\bar{\nu}$) vs. pressure were found to be linear as determined by unweighted least-squares regression analysis. For the emission peak maxima, a linear change with pressure was presumed, and the cited ratio of $\Delta\bar{\nu}/\Delta P$ was calculated from the values of $\bar{\nu}$ at the two extremes of pressure. The wavelength calibrations of the optical detection systems were routinely checked with use of the lines from standard low-pressure neon lamps.

Apparent volumes of activation $\Delta V_{app}^*(\tau)$ were calculated from plots of ln (τ^{-1}) vs. pressure. Such plots were found to be linear on the basis of unweighted least-squares regression analysis, and $\Delta V_{app}^*(\tau)$ is defined as

$$\Delta V_{app}^*(\tau) = -RT\left(\frac{\partial \ln \tau^{-1}}{\partial P}\right)_T \qquad (1)$$

where R is the gas constant and T is temperature (K). In the cases where $\Delta V_{app}^*(\tau) \approx 1$ mL mol^{-1}, the changes in lifetime with pressure were too small to accurately measure points at pressures between the two extreme limits. For these situations, $\Delta V_{app}^*(\tau)$ was calculated by using the integrated form of eq 1 and presuming $\Delta V_{app}^*(\tau)$ to be independent of pressure. The numbers given in parentheses in Table III refer to the number of independent measurements made or to the number of data points used in the plotting routines.

Results

Absorption and Emission Spectra. The application of pressure up to 210 MPa caused changes in the ligand field absorption bands

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(49) Upon prolonged exposure of the samples to the laser beam, some decrease in emission intensity occurred; however, neither the shapes of the emission bands nor the lifetimes appeared to undergo change.

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Table II. Absorption and Emission Features for the Doublet Region of $[Cr(NH_3)_6]^{3+}$ [a]

absorption		emission		
rel pos, cm^{-1} [b]	$\Delta\bar{\nu}/\Delta P$, cm^{-1} MPa^{-1}	rel pos, cm^{-1} [b]	$\Delta\bar{\nu}/\Delta P$, cm^{-1} MPa^{-1}	rel intens change[c]
0	−0.055 ± 0.005	0	−0.04 ± 0.01	0
−160 ± 20	0 ± 0.1	256 ± 5	−0.05 ± 0.02	0
		196 ± 5	−0.05 ± 0.02	−0.04
220 ± 20 (sh)	0 ± 0.1	−200 ± 10 (sh)	−0.05 ± 0.02	0
250 ± 10	0 ± 0.06	−248 ± 5	−0.03 ± 0.02	−0.02
480 ± 20 (sh)	0 ± 0.1	−440 ± 10 (sh)	−0.03 ± 0.05	0
730 ± 10	0 ± 0.06	−719 ± 5	−0.03 ± 0.02	−0.03
780 ± 20 (sh)	0 ± 0.1	−790 ± 10 (sh)	−0.03 ± 0.05	0

[a] Conditions: absorption, 70 mM $[Cr(NH_3)_6](NO_3)_3$, pH 3.0, 24.5 ± 1 °C; emission, 20 mM, pH 1.9, 25.0 ± 0.1 °C. [b] Position taken relative to 0-0 line as being zero: 0–0 lines for absorption and emission are 15 217 ± 2 and 15 224 ± 2 cm^{-1}, respectively. [c] Percentage change per megapascal relative to the 0–0 line with an estimated error of ±0.05.

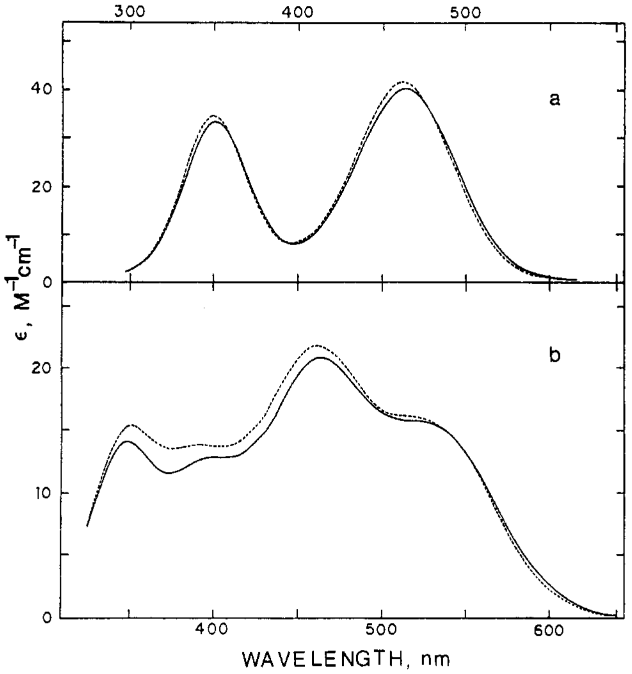

Figure 1. Absorption spectra of quartet ligand field bands at ambient pressure (—) and at 210 MPa (---) (pH 3.0, 24.5 ± 1 °C): (a) 12.8 mM $[Cr(NH_3)_6](ClO_4)_3$; (b) 20.9 mM *trans*-$[Cr(en)_2F_2]ClO_4$.

as exemplified in Figure 1 for the spin-allowed quartet transitions of $[Cr(NH_3)_6]^{3+}$ and *trans*-$[Cr(en)_2F_2]^+$. Table I provides a summary of the results for the systems studied, including both nitrate and perchlorate salts of $[Cr(NH_3)_6]^{3+}$. The former salt has been used in general in this study, owing to its greater solubility; however, the presence of an additional band with a peak near 304 nm associated with the nitrate anion complicates its spectrum relative to that of the perchlorate salt, where this band is absent (Figure 1). For the systems listed in Table I, their absorption characteristics at room pressure for the quartet bands and for the vibrationally structured doublet bands that lie to the red side of the Q_1 bands are in accord with earlier reports.[13,24,28,35,43,45,47,55–58]

On pressurization, the spectra of the quartet bands (Q_1 and Q_2) for the complexes of O_h microsymmetry and for *trans*-$[Cr(en)_2(NCS)_2]^+$ exhibit increases in wavenumber and molar absorption coefficient (given as a percentage increase per megapascal in Table I) for the peak maxima. This is coupled with the occurrence of apparent isosbestic points and slight decreases in the full-width half-maxima (fwhm) of the bands. While such changes in shape occur, the oscillator strengths for the quartet bands of $[Cr(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$ and for Q_1 of *trans*-$[Cr(en)_2(NCS)_2]^+$ remain constant within about ±1–2%.[59] Since these changes are reversed on depressurization, they are manifestations of pressure effects rather than those of chemical reaction. For *trans*-$[Cr(en)_2(NCS)_2]^+$ of D_{4h} microsymmetry, the splittings of the Q_1 and Q_2 bands that are anticipated on theoretical grounds are not discernible in room-temperature solution.[28,55] By contrast, this is observed for *trans*-$[Cr(en)_2F_2]^+$ as shown in Figure 1. For the three components of lower energy (Q_1', Q_1'', and Q_2'), they shift to the blue with increasing pressure whereas the component of highest energy (Q_2'') shifts to the red. Of further note is that the degrees of splitting between the components of Q_1 and Q_2 appear to decrease on pressurization. In addition, the weakly absorbing doublet region that lies on the red edge of Q_1' exhibits some structure to it, and one of the components (15 080 cm^{-1}) appears to undergo a slight blue shift. This stands in contrast to the slight red shifts encountered in the doublet regions for $[Cr(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$ (Table I). Perhaps the most notable aspect is that the values of $\Delta\bar{\nu}_{max}/\Delta P$ for the doublet regions are a factor of 10 or so less than those for the quartet bands. A general difficulty in examining in detail the doublet regions is not only their very low intensities ($\epsilon \lesssim 1$ M^{-1} cm^{-1}) but also the fact that they do fall on the tails of the much more intense Q_1 bands with the consequence that the former are not easily resolved from the latter, particularly for many non-O_h complexes.

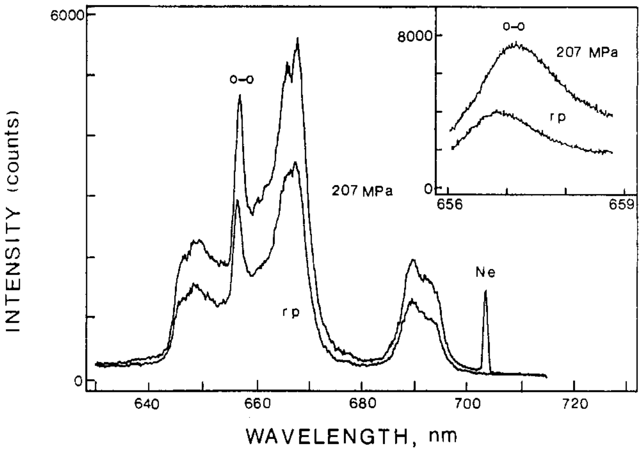

Figure 2. Emission spectra of doublet-state region (^2E_g) for 20 mM $[Cr(NH_3)_6](NO_3)_3$ at room pressure and at 207 MPa (488-nm excitation, pH 1.9, 25.0 ● 0.1 °C). The insert shows the expanded region around the 0–0 transition (656.85 nm at room pressure). The line at 703.24 nm is a calibration line from a standard neon lamp.

For $[Cr(NH_3)_6]^{3+}$, these complications seemed to be at a minimum for the systems studied here. For this reason, and because the doublet region of this complex ion is relatively rich in vibrational structure, both its absorption and emission spectra

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Table III. Summary of Lifetime Results[a]

complex ion	concn, mM	em wavelengths, nm excit	em wavelengths, nm obsd[b]	pH	temp, °C[c]	lifetime, μs[d]	$\Delta V_{app}^{\ddagger}(\tau)$, mL mol^{-1} [e]
$[Cr(NH_3)_6]^{3+}$	27-30	488	657.2	2.8	15.1	3.36 ± 0.01	3.8 ± 0.2 (7)
		514	657.2	2.8	15.1	3.37 ± 0.01	4.2 ± 0.1 (8)
		488	657.2	2.8	25.0	1.73 ± 0.03	4.0 ± 0.2 (6)
		514	657.2	1.8	25.0	1.80 ± 0.03	4.3 ± 0.4 (5)
		514	BB	1.8	25.0	1.80 ± 0.02	4.4 ± 0.3 (6)
		488	657.2	1.8	25.0	1.76 ± 0.02	4.2 ± 0.3 (5)
		514	657.2	1.8	25.0	1.78 ± 0.01	4.6 ± 0.3 (5)[f]
		488	BB	2.8	34.3	1.01 ± 0.04	4.2 ± 0 4 (8)
		514	BB	2.8	34.3	0.96 ± 0.02	4.4 ± 0.3 (7)
$[Cr(ND_3)_6]^{3+}$	20	488	656.7	2.0	23.0	3.76 ± 0.03	4.2 ± 0.2 (5)
$[Cr(NH_3)_5(CN)]^{2+}$	3.0	488	680.0	3.3	25.0	18.9 ± 0.1	3.4 ± 0.1 (4)[g]
$[Cr(NH_3)_5(NCS)]^{2+}$	3.0	488	686.0	2.0	25.0	0.223 ± 0.001	6.9 ± 0.1 (6)
		488	686.0	3.3	25.0	0.224 ± 0.001	7.0 ± 0.1 (5)
		488	686.0	3.3	25.0	0.224	6.9 ± 0.2 (5)[h]
		488	BB	3.3	25.0	0.223	6.7 ± 0.2 (4)
$[Cr(en)_3]^{3+}$	40	488	669.7	2.8	15.1	2.41 ± 0.02	3.4 ± 0.1 (7)
		488	669.7	2.8	25.0	1.30 ± 0.05	3.3 ± 0.1 (5)
		488	669.7	1.8	25.0	1.27	3.3 ± 0.5 (4)
		488	BB	2.8	34.3	0.78 ± 0.03	3.4 ± 0.4 (8)
		333	BB	1.9	25.0	1.30 ± 0.02	3.3 ± 0.2 (4)
trans-$[Cr(en)_2(NCS)_2]^+$	1.0	488	726.0	3.3	25.0	7.01 ± 0.07	0.4 ± 0.1 (5)[g]
trans-$[Cr(en)_2F_2]^+$	10	488	BB	1.8	25.0	1.34 ± 0.02	1.2 ± 0.2 (7)[i]
		514	BB	1.8	25.0	1.34 ± 0.03	1.2 ± 0.2 (7)
		514	BB	2.8	25.0	1.34	1.2 ± 0.1 (6)
trans-$[Cr(cyclam)(CN)_2]^+$	2.0	BB	BB	ca. 1	23.0	324.0 ± 6.0	0.1 ± 0.2 (4)[g,i]
$[Ru(bpy)_3]^{2+}$	0.045	488	601.9	ca. 7	25.0	0.526 ± 0.002	−0.65 ± 0.06 (16)

[a] Aerated conditions except for $[Ru(bpy)_3]^{2+}$. [b] BB signifies broad-band collection of emission. For narrow-band situations, the wavelength cited is that for maximum emission intensity but uncorrected for instrumentation response (see Experimental Section). [c] Temperature control was ±0.2 °C for 15.1 and 34.3 °C and ±0.1 °C for 23.0 and 25.0 °C. [d] Estimates of precision errors based on two to four separate measurements; all lifetimes at room pressure. [e] Numbers in parentheses refer to number of data points taken at four different pressures (ambient pressure to 207 MPa). [f] Perchlorate salt of $[Cr(NH_3)_6]^{3+}$; other measurements pertain to nitrate salt. [g] $\Delta V_{app}^{\ddagger}(\tau)$ calculated from τ values for ambient pressure and 207 MPa. [h] Sample provided by Dr. F. Wasgestian. [i] Emission maxima for *trans*-$[Cr(en)_2F_2]^+$ and *trans*-$[Cr(cyclam)(CN)_2]^+$ centered around 788 and 720 nm, respectively.

were investigated in some detail. Our findings are presented in Table II, and Figure 2 shows the effect of pressurization on the emission spectrum (uncorrected for instrument response): The line at 703.24 nm is that of the neon calibration lamp, and the insert in the figure is an expansion of the area around the 0–0 transition ($^4A_{2g} \leftarrow {}^2E_g$). The positions of the latter (emission and absorption) and the relative placements and intensities of the other lines are in general agreement with solution and solid-state measurements reported by others.[3,4,34,57,60-63] The emission and absorption spectra are nearly mirror images of each other, and the vibronic features are ascribed to NH_3 rocking motion in the region of 700–800 cm^{-1} and to NCrN deformations (t_{1u}, t_{2u}) for 100–500 cm^{-1} relative to the 0–0 lines (Table II).[3,4,60,62,63] From ambient pressure to 210 MPa, the percentage changes in the molar absorption coefficients are small (within ca. ±4%) whereas the emission intensity increases. After allowance is made for about a 7% decrease in bulk volume, the increase amounts to 40–50%. The data in column 5 of Table II indicate that this change is relatively uniform throughout the doublet region. In general, the effects of pressurization on the changes in positions and relative levels of absorption and emission appear to be minor, at least in comparison to the absorption changes observed for the quartet bands.

Emission Lifetimes from Doublet States. Given in Table III are the values of the lifetimes and the wavelengths of the apparent maxima in emission intensities for room-pressure conditions for a number of chromium complex ions, including the aforementioned ones and $[Ru(bpy)_3]^{2+}$, the latter being studied in deaerated medium. Our findings are generally in close accord with those reported previously for aerated and deaerated solutions.[7,17,19,21-23,26,28,32-34,64-67] Also given in the table are the apparent volumes of activation for the lifetimes, the determinations of which are described in the Experimental Section.

With the exception of the $[Ru(bpy)_3]^{2+}$ case, all of the values of $\Delta V_{app}^{\ddagger}(\tau)$ are positive, and they range from a low of ca. +0.1 mL mol^{-1} for *trans*-$[Cr(cyclam)(CN)_2]^+$ to a high of +6.9 mL mol^{-1} for $[Cr(NH_3)_5(NCS)]^{2+}$. In the case of $[Cr(en)]_3^{3+}$, we find for excitation at 488 nm and at 333 nm, corresponding to irradiation of the Q_1 and Q_2 bands, respectively, that the values of $\Delta V_{app}^{\ddagger}(\tau)$ are the same at +3.3 mL mol^{-1} with a maximum error of ±0.5 mL mol^{-1}, and for 488-nm excitation, the value is constant over the temperature range of 15.1–34.3 °C. Previously Kirk and Porter have measured the lifetimes of $[Cr(en)_3]^{3+}$ at ambient pressure and at 230 MPa (337-nm excitation, 16–18 °C), and from these measurements, they then calculated the value of $\Delta V_{app}^{\ddagger}(\tau)$ to be −1.6 ± 1.0 mL mol^{-1} using the integrated form of eq 1.[38] While we have no specific explanation for this disparity, several features may be noted. In contrast to our right-angle illumination–detection procedure, they used an in-line configuration for irradiation and collection of emission. Although nonfluorescent filters were employed to exclude laser light from their detection system, the excitation wavelength of 337 nm is nearly half that of phosphorescence (670 nm) for $[Cr(en)_3]^{3+}$, and thus they reported encountering a severe scattered light problem. This was not a difficulty in the present study, and we suspect, on the basis of our experience, that their use of sapphire windows, which emit around 700 nm, might have also contributed to the scattered light situation. For $[Ru(bpy)_3]^{2+}$, where the emission quantum yield is considerably larger than that of $[Cr(en)_3]^{3+}$ and the

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emission region is at shorter wavelengths (Table III), our value of $\Delta V_{app}^*(\tau) = -0.65 \pm 0.06$ mL mol^{-1} is in good agreement with their value of -0.7 ± 0.2 mL mol^{-1}.[38] To our knowledge, the only other reported study of the effect of pressurization on the doublet-state lifetimes of Cr(III) systems is that of Cr(III) in a MgO host lattice.[68] In this case, the lifetime increases with pressure, implying a positive value for $\Delta V_{app}^*(\tau)$.

The effects of temperature changes over the range of 15.1–34.3 °C have been studied for $[Cr(en)_3]^{3+}$ and $[Cr(NH_3)_6]^{3+}$, and within experimental error the values of $\Delta V_{app}^*(\tau)$ are not altered over this temperature interval. Concurrently the apparent activation energies for the lifetimes have been determined at four different pressures from ambient to 207 MPa. The values of $E_a(\tau)$ for $[Cr(en)_3]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ are found to be constant over this pressure range, and the respective values are 43.5 ± 0.8 and 46.0 ± 1.3 kJ mol^{-1}. These numbers are in reasonable agreement with those previously reported for room-pressure conditions.[23,25,32,34,36,66] With the notable exception of *trans*-$[Cr(cyclam)(CN)_2]^+$, where the estimated $E_a(\tau)$ is quite low at 5 kJ mol^{-1},[69] the values for the other complexes studied here are similar to those given above.[9,32,34,70] In the present context, the mechanical work applied to the solutions is small ($P\Delta\bar{V} \lesssim 0.26$ kJ mol^{-1}) relative to the apparent activation energies, and furthermore, the transition state for any particular process is defined by the maximum in the energy profile rather than by the volume profile, which may or may not exhibit an extremum.[71] These aspects in conjunction with the constancy of $E_a(\tau)$ and $\Delta V_{app}^*(\tau)$ over our range of pressure (and temperature) implies that the values of ΔV_i^* for the individual mechanistic steps as discussed below remain essentially constant under our conditions.

Discussion

Spectral Features. For $[Cr(NH_3)_6]^{3+}$ of O_h microsymmetry and for the lower symmetry complexes $[Cr(en)_3]^{3+}$ and *trans*-$[Cr(en)_2(NCS)_2]^+$ that are spectrally similar to the ammonia complex, the peak maxima for both quartet bands (Q_1 and Q_2 of Table I) shift to shorter wavelength with increasing pressure although the oscillator strengths remain relatively constant. The values of $\Delta\bar{\nu}_{max}/\Delta P$ for the Q_1 bands (${}^4T_{2g} \leftarrow {}^4A_{2g}(O_h)$) provide a direct measure of the changes in $10Dq$.[40,72] The observed blue shifts indicate that the Dq values increase, and this is commensurate with pressurization leading to a general compression of the complex ion. Parsons and Drickamer[40] have reported similar blue shifts of the Q_1 and Q_2 bands for $[Cr(NH_3)_6]Cl_3$ in the solid state although the values of $\Delta\bar{\nu}_{max}/\Delta P$ decrease somewhat with pressure over their much larger range (up to ca. 13.2 GPa). From their limiting slopes ($P \Rightarrow 0$), we calculate that the values of $\Delta\bar{\nu}_{max}/\Delta P$ for the solid state to be about half of our values for the aqueous solution measurements, and this comparison suggests that $[Cr(NH_3)_6]^{3+}$ may be more compressible in solution relative to the solid phase.

The energy maximum of the Q_2 band, representing the ${}^4T_{1g} \leftarrow {}^4A_{2g}$ transition (O_h), is a function of both Dq and the Racah interelectronic repulsion parameter B,[40,72,73] and thus the energetic differences between the maxima for the Q_1 and Q_2 bands can be used to calculate B. The latter was done in the strong-field formalism; however, the use of this formalism rather than a weak-field one will not affect the feature of interest here, namely the change in B values with pressure since we find plots of B vs. pressure to be linear.[73] The slopes of the plots are negative with the B values decreasing by ca. 4×10^{-3} % MPa^{-1} and 2×10^{-3} % MPa^{-1} for $[Cr(en)_3]^{3+}$ and $[Cr(NH_3)_6]^{3+}$, respectively, and the decreases implicate a trend of increasing degree of covalency on pressurization.[74]

For these two complex ions, the energies of the spin-forbidden ${}^2E_g \leftrightarrow {}^4A_{2g}$ transitions depend upon the Racah B and C parameters if configurational interaction is neglected.[72,73] On this presumption and that of the ratio of C/B remaining relatively constant, then a decrease in B with increased pressure will lead to some decrease in the $\bar{\nu}(0\text{–}0)$ line of the ${}^2E_g \leftarrow {}^4A_{2g}$ transition. This expectation is qualitatively in agreement with our small observed red shifts. Such is also found for the R_1 line of ruby material.[75]

In the case of *trans*-$[Cr(en)_2(NCS)_2]^+$, the anticipated splittings of the ${}^4T_{2g}$ and ${}^4T_{1g}$ bands in D_{4h} microsymmetry are not readily apparent under our conditions whereas these are clearly observed (Figure 1a) for *trans*-$[Cr(en)_2F_2]^+$. The low-energy Q_1' and high-energy Q_1'' components of the ${}^4T_{2g}(O_h)$ band are assigned to ${}^4E_g' \leftarrow {}^4B_{1g}$ and ${}^4B_{2g} \leftarrow {}^4B_{1g}$ transitions, respectively.[55,76-78] The peak wavenumber of the latter transition (Table I) provides a direct measure of $10Dq$(en).[55,79,80] As one might expect, the value of $Dq(\text{en}) = 2146$ cm^{-1} and that of $\Delta\bar{\nu}_{max}/\Delta P$ are relatively close to the corresponding values for the first quartet band of $[Cr(en)_3]^{3+}$ (Table I). The difference $\Delta\bar{\nu}_{max}({}^4E_g'-{}^4B_{2g})$ of -2460 cm^{-1} equals $(35/4)Dt$ so that the tetragonal parameter Dt is -280 cm^{-1}, which is similar to those of previous studies.[55,76-78] In the context of Perumareddi's sign convention, Dt equates to $-{}^4/{}_7[Dq(\text{en}) - Dq(\text{F})]$ and leads to $Dq(\text{F}) = 1650$ cm^{-1}.[55,79,81]

The effect of pressurization on the components Q_1' and Q_1'' suggests that the energy gap between ${}^4E_g'$ and ${}^4B_{2g}$ decreases, although this is not unequivocal when the errors for $\Delta\bar{\nu}_{max}/\Delta P(Q_1'$ and $Q_1'')$ are considered (Table I). On the presumption that $\Delta\bar{\nu}_{max}/\Delta P(Q_1') > \Delta\bar{\nu}_{max}/\Delta P(Q_1'')$, then Dt decreases by ca. 1.5% as the pressure is increased from ambient to 210 MPa. Since the ${}^4B_{2g} \leftarrow {}^4B_{1g}$ transition (Q_1'') also shifts to the blue, the implication is that $\Delta[Dq(\text{F})]/\Delta P$ and $\Delta[Dq(\text{en})]/\Delta P$ are both positive values but with the former being somewhat larger than the latter. The larger effect on Dq(F) suggests that the Cr–F bond may be longer than that of Cr–N, and consequently it may experience a greater degree of contraction.[82,83] This effect and the positive values for $\Delta[Dq]/\Delta P$ seem reasonable from the physical viewpoint that not only does the application of hydrostatic pressure cause an overall compression but also the direction of change may be toward a more spherical-like environment around the metal center. On this basis also, one anticipates the other tetragonal parameter Ds to decrease with increasing pressure (see below).

This parameter reflects the degree of splitting of the second quartet level ${}^4T_{1g}(O_h)$ under D_{4h} microsymmetry; i.e., the difference in energies between the components ${}^4A_{2g}$ and ${}^4E_g''$ is given by $6Ds - {}^5/{}_4Dt$.[72] Low-temperature spectroscopic studies, including a single-crystal polarized spectral one, have led to the assignment of the low-energy Q_2' and the high-energy Q_2'' bands as ones involving the transitions ${}^4E_g'' \leftarrow {}^4B_{1g}$ and ${}^4A_{2g} \leftarrow {}^4B_{1g}$, respectively, with positive values for Ds and negative values for Ds/Dt (-2.18 to -2.5).[76-78] Perumareddi's earlier interpretation has these signs reversed so that the ${}^4E_g''$ state was placed energetically above that of the ${}^4A_{2g}$ level, although he recognized that this order might be inverted.[55] This original assignment predicts that the higher energy component (${}^4E_g'' \leftarrow {}^4B_{1g}$) will shift to the red with a decrease in Dt along with a blue shift of the lower energy band (${}^4A_{2g} \leftarrow {}^4B_{1g}$) (see Figure 1 of ref 81) whereas in the situation of the ${}^4E_g''$ level being below the ${}^4A_{2g}$ state, the prediction seems to be that both will move in the blue direction (see Figure 3 of ref 78). Our observation of a red shift for Q_2'' and a blue

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(70) At room pressure, we measured $E_a(\tau)$ for *trans*-$[Cr(en)_2F_2]^+$ to be 45.6 ± 0.4 kJ mol^{-1}.

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movement for Q_2' (Table I and Figure 1a) with increasing pressure appears to be more readily explainable in terms of Perumareddi's interpretation. In the context of both assignments, the effects of pressurization indicate that the numerical values of *Ds* and of the *Ds*/*Dt* ratio decrease by about 10–15% on going from ambient pressure to 210 MPa.

Photochemical and Photophysical Features. For the complex ions of interest here, the photobehavior is one of aquation, generally involving the ammonia or the amine ligand; however, *trans*-$[\mathrm{Cr(cyclam)(CN)_2}]^+$ appears to be unreactive.[9,65] The chemical quantum yields are substantial (0.2–0.5), and they are nearly independent of wavelength, although for $[\mathrm{Cr(NH_3)_5(NCS)}]^{2+}$ and *trans*-$[\mathrm{Cr(en)_2(NCS)_2}]^+$, the values of the minor photoreactions show more variation.[13,15,17,18,22–24,27–31,35,37,45,66,84–89] As discussed in the Introduction, there are generally two stages of reaction. The major and longer term one indicates that passage through the doublet states plays a salient role in the photochemistries. Since the doublet levels are generally perceived to be in thermal equilibrium with their surroundings, we have used below the formalism of the activated complex theory although it is not certain if such an approach is suitable for describing the short-lived events at the quartet levels. The occurrence of two stages does emphasize the point that phenomenological descriptors such as apparent volumes and energies of activation are composite quantities, reflecting the effects of pressure and temperature on all of the excited-state processes,[90] and thus their interpretations are strongly dependent on the mechanistic model that one adopts.

In this context, we consider three mechanistic cases that are currently under active discussion. The differences arise in part from the proposition that either thermally activated back intersystem crossing from the doublet to the lowest quartet state (bisc) or chemical reaction tends to dominate the deactivation of the doublet state. Because of the complexities of the schemes, particularly when more than one type of photoproduct occurs, our analysis focuses in the main on $[\mathrm{Cr(NH_3)_6}]^{3+}$. In addition, pressure studies on the photochemistry of this ion and of $[\mathrm{Cr(NH_3)_5(NCS)}]^{2+}$ have been reported.[31,37] Figure 3 portrays schematically the excited-state processes of interest.

Case a: **Direct Reaction from the Doublet State to Final Product(s) without bisc.** For $[\mathrm{Cr(NH_3)_6}]^{3+}$, the apparent volumes of activation for the lifetime and the total chemical quantum yield (Φ_{rx}) are +4.3 mL mol^{-1} (Table III) and −6.7 mL mol^{-1}, respectively,[31] and they can be expressed by the eq 2 and 3, where

$$\Delta V_{\mathrm{app}}^{\ddagger}(\tau) = \eta_{\mathrm{D}}\Delta V_{\mathrm{D}}^{\ddagger} + \eta_{\mathrm{em}}\Delta V_{\mathrm{em}}^{\ddagger} + \eta_{\mathrm{nr}}\Delta V_{\mathrm{nr}}^{\ddagger} \qquad (2)$$

$$\Delta V_{\mathrm{app}}^{\ddagger}(\Phi_{\mathrm{rx}}) = f_{\mathrm{Q}}(1 - \Phi_{\mathrm{rx}})\Delta V_{\mathrm{Q}}^{\ddagger} + f_{\mathrm{D}}(1 - \eta_{\mathrm{D}})\Delta V_{\mathrm{D}}^{\ddagger} + (\eta_{\mathrm{isc}}/\Phi_{\mathrm{rx}})(\eta_{\mathrm{D}} - \Phi_{\mathrm{rx}})\Delta V_{\mathrm{isc}}^{\ddagger} - \eta_{\mathrm{ic}}\Delta V_{\mathrm{ic}}^{\ddagger} - f_{\mathrm{D}}\eta_{\mathrm{em}}\Delta V_{\mathrm{em}}^{\ddagger} - f_{\mathrm{D}}\eta_{\mathrm{nr}}\Delta V_{\mathrm{nr}}^{\ddagger} \qquad (3)$$

$\Delta V_{\mathrm{app}}^{\ddagger}(\tau)$ is defined by eq 1 with $\tau^{-1} = k_{\mathrm{D}} + k_{\mathrm{em}} + k_{\mathrm{nr}}$ and η_i and $\Delta V_i^{\ddagger}$ refer to the efficiency and volume of activation of the *i*th process. The definitions of $\Delta \mathrm{V}_i^{\ddagger}$ and $\Delta \mathrm{V}_{\mathrm{app}}^{\ddagger}(\Phi_{\mathrm{rx}})$ are analogous to eq 1 but with τ^{-1} being replaced by k_i or by Φ_{rx}, respectively.[90] The latter is a sum of chemical contributions from the lowest quartet and doublet states of Figure 3; i.e. $\Phi_{\mathrm{rx}} = \eta_{\mathrm{Q}} + \eta_{\mathrm{isc}}\eta_{\mathrm{D}}$. The value of Φ_{rx} is 0.45, and that for $\Phi_{\mathrm{em}}(=\eta_{\mathrm{isc}}\eta_{\mathrm{em}})$ is 5.5×10^{-5}.[17,64] The fractional chemical yields as determined by time-resolved measurements[21] are $f_{\mathrm{D}} = 0.80$ and $f_{\mathrm{Q}} = 0.20$, and these in turn lead to $\eta_{\mathrm{Q}} = f_{\mathrm{Q}}\Phi_{\mathrm{rx}} = 0.09$ and $f_{\mathrm{D}}\Phi_{\mathrm{rx}} = \eta_{\mathrm{isc}}\eta_{\mathrm{D}} = 0.36$. This information indicates that η_{isc} can range from 0.36 to 0.91 as η_{D} varies from 1.0 to 0.40. The terms in eq 2 and 3 involving emission can be neglected as $\eta_{\mathrm{em}} \lesssim 6.0 \times 10^{-5}$. In addition, the vibronic features that promote emission and absorption ($^2\mathrm{E_g} \leftrightarrow {}^4\mathrm{A_{2g}}$)[3,4,62,63] are found to be affected very little over our pressure range (Table II), indicating that the radiative processes are not notably sensitive to pressure.

The foregoing information, while being insufficient to solve for specific $\Delta V_i^{\ddagger}$ values, does define two general situations. If $\Delta V_{\mathrm{D}}^{\ddagger}$ is a negative quantity (or zero), as would be expected of an associative reaction,[91,92] then $\Delta V_{\mathrm{nr}}^{\ddagger}({}^4\mathrm{A_{2g}} \leftarrow\!\rightsquigarrow {}^2\mathrm{E_g})$ is greater than or equal to +7 mL mol^{-1}, and a similar analysis for $[\mathrm{Cr(NH_3)_5(NCS)}]^{2+}$, where $\Phi_{\mathrm{rx}} \simeq 0.45$,[29,31,37] $\Delta V_{\mathrm{app}}^{\ddagger}(\Phi_{\mathrm{rx}}) = -6.4$ mL mol^{-1},[31] and $f_{\mathrm{D}} = 0.80$,[21] indicates $\Delta V_{\mathrm{nr}}^{\ddagger} \gtrsim +11$ mL mol^{-1}.[93] Several features strongly militate against such large values for $\Delta V_{\mathrm{nr}}^{\ddagger}$. For $[\mathrm{Cr(NH_3)_6}]^{3+}$ and related amine complexes, Kühn and co-workers find at low temperatures a good correlation between the radiationless transition rates and the number of active hydrogen atoms attached to the nitrogen atoms.[94] While this may be less important at room temperatures, our lifetime results for $[\mathrm{Cr(NH_3)_6}]^{3+}$ and $[\mathrm{Cr(ND_3)_6}]^{3+}$ (Table III) do nevertheless suggest a normal type of isotope effect on the nonradiative transition. The major point to note is that, within experimental error, the values of $\Delta V_{\mathrm{app}}^{\ddagger}(\tau)$ are the same. This implies that while the nonradiative process is significant, it is not markedly sensitive to pressure changes. The complex ion *trans*-$[\mathrm{Cr(cyclam)(CN)_2}]^+$ is photochemically unreactive, and it exhibits a low value of $E_{\mathrm{a}}(\tau)$ coupled with an apparently large doublet–quartet energy gap that most likely precludes any significant back intersystem crossing.[6,65,70,95–97] While the cyclic nature of the cyclam ligand may be a notable factor, nevertheless the $\Delta V_{\mathrm{app}}^{\ddagger}(\tau)$ value of +0.1 mL mol^{-1} is probably a close approximation to $\Delta V_{\mathrm{nr}}^{\ddagger}$. To our knowledge, the only specific values of $\Delta V_{\mathrm{nr}}^{\ddagger}$ so far reported are those for the excited triplet states of $[\mathrm{Rh(ND_3)_5Cl}]^{2+}$ and $[\mathrm{Rh(ND_3)_5Br}]^{2+}$, and they are small, −2.6 and +2.5 mL mol^{-1}, respectively.[98] On the basis of the foregoing features, we conclude that the numerical value of $\Delta V_{\mathrm{nr}}^{\ddagger}$ for $[\mathrm{Cr(NH_3)_6}]^{3+}$ (and related systems) is probably less than 7 mL mol^{-1}, with the consequence that, within the framework of this mechanism, $\Delta V_{\mathrm{D}}^{\ddagger}$ has a positive value. The implications of a positive value are considered below; however, we next address the scheme where the bisc process is included.

Case b: **Doublet-State Deactivation via a Thermally Activated bisc Process.** For $[\mathrm{Cr(NH_3)_6}]^{3+}$ and several of the other systems studied here, time-resolved measurements indicate that the rate of formation of the doublet state is much faster than the decay rate,[14,21,99] and in this circumstance,[100,101] k_{app} $(=1/\tau)$ and $\Delta V_{\mathrm{app}}^{\ddagger}(\tau)$ are approximated by eq 4 and 5. For the reasons given

$$k_{\mathrm{app}} \simeq k_{\mathrm{D}} + k_{\mathrm{nr}} + k_{\mathrm{em}} + (1 - \eta_{\mathrm{isc}})k_{\mathrm{bisc}} \qquad (4)$$

$$\Delta V_{\mathrm{app}}^{\ddagger}(\tau) \simeq (k_{\mathrm{D}}/k_{\mathrm{app}})\Delta V_{\mathrm{D}}^{\ddagger} + (k_{\mathrm{bisc}}/k_{\mathrm{app}})\{(1 - \eta_{\mathrm{isc}})\Delta V_{\mathrm{bisc}}^{\ddagger} - \eta_{\mathrm{isc}}[(1 - \eta_{\mathrm{isc}})\Delta V_{\mathrm{isc}}^{\ddagger} - \eta_{\mathrm{Q}}\Delta V_{\mathrm{Q}}^{\ddagger} - \eta_{\mathrm{ic}}\Delta V_{\mathrm{ic}}^{\ddagger}]\} \qquad (5)$$

above under case a, the additive terms $(k_{\mathrm{nr}}/k_{\mathrm{app}})\Delta V_{\mathrm{nr}}^{\ddagger}$ and $(k_{\mathrm{em}}/k_{\mathrm{app}})\Delta V_{\mathrm{em}}^{\ddagger}$ have not been included in eq 5. The values of

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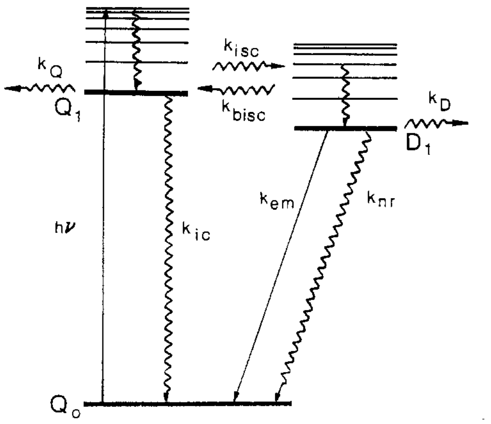

Figure 3. Schematic diagram of the ground state (Q_0) and of the lowest quartet (Q_1) and doublet (D) states and associated processes.

ΔV_{isc}^*, ΔV_{bisc}^*, and ΔV_{ic}^* are not known, but their signs and magnitudes might be surmised from the differences in the partial molar volumes of the ground state and of the thexi doublet and quartet states. Wilson and Solomon[60] have deduced the bond length changes associated with the tetragonal distortion for the lowest quartet state. This information plus the modeling of the ground state and the excited thexi quartet state as a sphere and an ellipsoid, respectively, suggest a difference ($\bar{V}(Q_1)_0 - \bar{V}(Q_0)$) of +3–4 mL mol^{-1}. Since there is a reasonably good mirror image relationship between the ground-state–doublet-state absorption and emission spectra, this indicates that these two states have quite similar geometries, and thus $\bar{V}(Q_1)_0 - \bar{V}(D)_0$ could also be in the +3–4 mL mol^{-1} range.[102,103] Less can be surmised about ΔV_Q^*, although if reaction from the quartet state is associative,[5,31] it may be a negative value; however, the fact that 80% of the chemical reaction occurs with the lifetime of the doublet state suggests that η_Q is relative small (ca. 0.1).[21] These features imply that the term $(k_{bisc}/k_{app})\{\}$ of eq 5 may be a positive value, but we have serious reservations that this contribution is in fact significant when one considers the foregoing in conjunction with the following features.

An important factor to a thermally activated bisc process is the energy difference between the thexi doublet and quartet levels. While these are not known precisely for $[Cr(NH_3)_6]^{3+}$ and related complexes, the energy gaps ($E(Q_1)_0 - E(D)_0$) appear to be about 4000 cm^{-1} (vs. $RT \simeq 200$ cm^{-1}).[4,25,36,104] Endicott and co-workers have used such differences and calculated rate constants for intersystem crossing to obtain approximate values of the bisc rate constants for $[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_5(NCS)]^{2+}$, and *trans*-$[Cr(en)_2(NCS)_2]^+$ of about 5×10^3, 10^4, and 5×10^4 s^{-1} (or less), respectively.[4] These values in combination with measured lifetimes (Table III) predict the corresponding k_{bisc}/k_{app} values to be about 0.01, 0.002, and $\lesssim$0.35. Even if these values are too low (perhaps 1 order of magnitude or more for the ammonia complexes), it is doubtful if the contribution by the second term of eq 5 is at all substantial. Further to this point is that if the η_{isc} values for $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5(NCS)]^{2+}$ approach the experimentally determined upper limit of 0.91 such as a value of 0.7 as reported for $[Cr(en)_3]^{3+}$,[27,105] then the specific contribution of ΔV_{bisc}^* is considerably reduced, owing to its multiplication by the factor $1 - \eta_{isc}$ (eq 5). These features also apply to the consideration of apparent activation energies because the form of eq 5 is the same except for the replacement of ΔV^* by the corresponding E_a value. Noteworthy also are the findings by Kane-Maguire and co-workers[33] on the lifetimes at 297 K for solution and solid phases: $[Cr(NH_3)_6]^{3+}$, 2.2 μs (solution) and 27 μs (solid); $[Cr(ND_3)_6]^{3+}$, 3.1 μs (solution) and 538 μs (solid). While one expects changes between different phases, it is difficult to perceive how such large effects at *room temperature* can reflect the predominance of a bisc process of intramolecular character.

Case c: Reaction from Doublet State to Ground-State Intermediate. Endicott and co-workers[3,4,36] have proposed recently an alternative model, involving reaction of the doublet state to yield a ground-state intermediate that subsequently reacts to form the final product(s). The intermediate is considered to be seven-coordinate although coordination of the solvent may be quite weak. Within the framework of this scheme, formation of final product(s) is at least one step removed from deactivation of the doublet state in contrast to the implied interchange mechanism of case a. Consequently, $\Delta V_{app}^*(\Phi_{rx})$ as given by eq 3 becomes even more complex owing to the inclusion of additional terms for the ground-state intermediate; however, eq 2 for $\Delta V_{app}^*(\tau)$ remains the same except that ΔV_D^* pertains to the formation of the inteimeidate(s) rather than the final product(s).

The positive values of $\Delta V_{app}^*(\tau)$ for $[Cr(NH_3)_6]^{3+}$ and related complexes (Table III) suggest that the reactivity of the doublet level has a greater degree of dissociative character than associative, although this should not be interpreted to mean necessarily an absence of solvent participation (see below). A dissociative viewpoint is consistent with the results of photoanation of $[Cr(NH_3)_6]^{3+}$ by Cl^- (and Br^-), where the sum of the quantum yields for anation and aquation remains essentially constant as does the emission lifetime up to very high chloride ion concentrations ($\gtrsim$8 M Cl^-).[17] The initial slopes for plots of Φ(anation) vs. halide concentration are also the same for Cl^- and Br^-, suggesting a low degree of selectivity for the intermediate, due perhaps to a very short lifetime. Our conductivity results point to such short lifetimes ($\tau << 1$ μs).[21]

For *trans*-$[Cr(en)_2F_2]^+$ and *trans*-$[Cr(en)_2(NCS)_2]^+$, the values of $\Delta V_{app}^*(\tau)$ are close to zero although the $E_a(\tau)$ values are similar to those of the ammonia complexes and $[Cr(en)_3]^{3+}$.[22,32,34,36,70] Any direct correspondence between the low $\Delta V_{app}^*(\tau)$ values and a trans configuration seems doubtful since the predominant reaction of the difluoro complex involves release of amine with retention of configuration, whereas for *trans*-$[Cr(en)_2(NCS)_2]^+$, the major process is substitution for NCS^- to yield *cis*-$[Cr(en)_2(NCS)(H_2O)]^{2+}$.[28,87] A possible explanation in the latter case is that the development of charge separation will be accompanied by an increase in solvent electrostriction,[91,92] and this negative contribution to ΔV_D^* may tend to counteract a positive contribution from bond-lengthening action.

The foregoing analysis, while being of a semiquantitative nature, does on balance favor some degree of chemical reaction from the doublet state(s), and it is less supportive of a major contribution arising from bisc processes for the complexes studied here. These results and those obtained by others recently indicate that high-pressure photochemical and photophysical investigations can provide important insight into the excited-state behavior of metal complex ions.

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Registry No. $[Cr(NH_3)_6]^{3+}$, 14695-96-6; $[Cr(ND_3)_6]^{3+}$, 31504-63-9; $[Cr(NH_3)_5(CN)]^{2+}$, 42213-67-2; $[Cr(NH_3)_5(NCS)]^{2+}$, 16884-60-9; $[Cr(en)_3]^{3+}$, 15276-13-8; *trans*-$[Cr(en)_2(NCS)_2]^+$, 29845-02-1; *trans*-$[Cr(en)_2F_2]^+$, 24407-74-7; *trans*-$[Cr(cyclam)(CN)_2]^+$, 84277-86-1; $[Ru(bpy)_3]^{2+}$, 15158-62-0.

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(102) For the bulkier complexes $[Fe(acac_2trien)]^+$ and $[Fe(Sal_2trien)]^+$ the measured ΔV° values for the spin equilibrium ($^2T \leftrightarrow {}^6A$) range between ca. +10 and +14 mL mol^{-1},[103] and this suggests that although our estimate for the smaller chromium complex may be low, the sign (+) is probably correct.

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