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Effects of Solvent, Temperature, and Pressure on the Photophysical and Visible-Spectroscopic Behavior of the *trans*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) Ion

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The visible absorption and emission spectra of the *trans*-diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) ion, $[Cr(cyclam)(NH_3)_2]^{3+}$, have been studied along with the emission lifetimes and quantum yields in the liquid phase for dimethylformamide, dimethyl sulfoxide, hexamethylphosphoramide, and aqueous solvents. The measured quantum yields for emission from the photochemically unreactive doublet excited state are small ($1–4 \times 10^{-3}$), and they vary in an approximately linearly manner with changes in the observed lifetimes. The reciprocal lifetimes τ^{-1} in the different media are a function of temperature, and this dependence is described by a sum of two exponential terms. The term expressing the lifetime behavior at lower temperatures is characterized by low apparent activation energies (≤ 6 kJ mol^{-1}) and relatively small preexponential factors ($\leq 6 \times 10^4$ s^{-1}) whereas in the high-temperature region the activation energies and preexponential factors are much larger, ranging from 64 to 78 kJ mol^{-1} and from 2.2×10^{15} to 1.7×10^{16} s^{-1}, respectively. For aqueous solution and dimethylformamide, the volumes of activation for τ^{-1} in the low-temperature region are nearly zero; by contrast, those describing the effects of pressure in the high-temperature region are near +7 cm^3 mol^{-1}. The nature of the solvent has notable effects on the visible electronic spectra and on the vibrational bands observed in the emission and infrared spectra, and the calculated rate constants describing the decay of the doublet excited state in the high-temperature region exhibit a semilogarithmic relationship to Gutmann donor numbers (and solvent scales that are proportional to the donor number scale). The natures of the nonradiative processes and the influence of solvent as a mediating agent are discussed.

Introduction

For over a quarter of a century, the understanding of the photochemical, photophysical, and spectroscopic features and behaviors of chromium(III) octahedral-type complex ions in fluid and solid media has continued to challenge both the experimentalist and theoretician.[1-23] This sustained interest arises in part from a number of outstanding issues, including the relative chemical importance of the lowest electronically excited states (spin-forbidden doublet and spin-allowed quartet states), the types and roles of nonradiative processes, particularly the possible involvement of thermally activated back-intersystem crossing (bisc) from the lowest doublet to a low-lying quartet state(s) versus direct chemical reaction from the doublet excited state, and the occurrence of chemically reactive ground-state intermediates. Underlying all of these issues is the discernment of the roles of the surrounding media or environment, where interest here derives partly from the recognition that the photochemistry is frequently one of photosolvolysis.

The results from a great many studies have clearly established that all facets of the photobehaviors of chromium(III) complex ions are influenced by their environments albeit the extent of this depends upon the nature and composition of the media; however much of this information has been obtained from investigations on glassy or crystalline environments at low temperatures where the photochemical reactions are eliminated or greatly suppressed.[2,4,6-8,11,13,15-20,24-26] In the liquid phase where photochemical reactions are manifested, there have been found only a few cases where photobehavior, such as excited-state lifetimes (generally phosphorescence emission from the lowest doublet states) and quantum yields, correlates to solvent scales or bulk solvent properties although the occurrence of isokinetic relationships (Barclay–Butler type of plots) in regards to lifetime measurements are more commonly encountered and the potential importance of hydrogen bonding between chromium(III) amine complex ions and the neighboring solvent molecules has been commented upon.[19,27,28,33-35,38,40,42] The general absence of simple

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and widely occurring relationships is partly understandable in that measured lifetimes and quantum yields are in themselves composite quantities reflecting competing chemical, emissive, and nonradiative processes, which will be influenced to different degrees and manners by the surrounding solvent. While chromium(III) complex ions are generally perceived to be photochemically reactive, the chemical quantum yields seldom exceed 0.5 and the emission yields are in general below 10^{-3}. Consequently in the overall sense, nonradiative–nonchemical processes predominate in the energy dissipation scheme, and this situation will inevitably complicate attempts to understand the solvent role(s) as a chemical reactant.

In this context, we have sought to investigate under photochemical like-conditions the effects of variations in solvent, temperature, and pressure on the photophysical and spectroscopic features of *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$, where cyclam is 1,4,8,11-tetraazacyclotetradecane. This complex ion, which has six nitrogen atoms bonded to the chromium center, exhibits a number of attributes (absorption–emission spectra, lifetime and emission quantum yields) similar to those of many photochemically reactive homoligated systems such as $[Cr(NH_3)_6]^{3+}$. It and the analogous *trans*-dichloro and -dicyano complexes are atypical in that they appear to show little if any photochemical reactivity in aqueous media.[29,47–49] Kutal and Adamson have proposed that the greatly reduced quantum yield for chloride release ($\phi_{Cl^-} = 8.0 \times 10^{-3}$) from *trans*-$[Cr(cyclam)(Cl)_2]^+$ relative to those for other *trans*-dichloro complexes may reflect the nature of the macrocyclic ligand through its inhibiting solvent attack and stereochemical rearrangement.[49] For many trans complexes, photosolvation is accompanied by trans to cis rearrangement, and it is perhaps notable that *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$ undergoes photoaquation with retention of configuration and via a chemically reactive ground-state intermediate.[17,47] Our study of *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ has also provided the propitious opportunity to study the effects of different solvents and pressures under liquid-phase conditions on the lifetime of the emitting doublet state, where a biphasic dependence on temperature is encountered. Although the insolubility of the trans complex in solvents of low polarity has restricted our investigations to more polar media, the absences of significant amounts of photochemical reaction have offered a highly advantageous situation to address the contentious issue of whether or not a thermally activated bisc pathway between the doublet excited state and a low-lying quartet state(s) can represent a competitive channel to decay of the doublet excited state.

Experimental Section

Apparatus and Methods. The high-pressure equipment employing quartz windows and the time-resolved emission apparatus using pulsed lasers (347- and 530-nm output) and conventional flash photolysis are described elsewhere.[47,50,51] For excitation at 308 nm, a Lumonics Hyper EX-400 laser with Xe/HCl gas mixture (ca. 130 mJ/pulse; 20-ns pulse duration) was used, and this output was also employed to pump the dye Stilbene420 (Exciton; 0.2 mM dye in BDH OmniSolv methanol) having emission centered around 430 nm (fwhm ca. 8 nm; 30 mJ/pulse). Emission near 680 nm from the chromium complex was detected (right angle configuration) with a Bausch & Lomb monochromator (Model 33-86-77; band-pass ca. 50 nm) in combination with a Corning colored filter (CS 2-64) eliminating wavelengths below about 600 nm. The photomultiplier tube was a Hamamatsu R928, and its output was recorded on a Tektronix 7D20 digitizer with the resulting waveform being transferred to an AT&T PC6300 microcomputer for storage and analysis. For a given set of temperature, pressure, and solvent conditions, the decay of emission from the doublet state of *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ was found to be well characterized over three lifetime periods by a single exponential (unweighted least-squares regression analysis) or single exponential plus a constant function (unweighted Newton–Raphson method);[52] however because at higher temperatures in the nonaqueous solvents thermal decomposition occurred and because of the presence of a low-level background emission encountered with the hexamethylphosphoramide solvent, the waveforms were routinely analyzed for multicomponent decay (up to three exponentials plus as a constant). As an additional precaution, the reproducibilities of the emission lifetimes were measured for varying periods of exposure time for a given set of conditions, and each lifetime used in the data sets is an average of four to five measurements with the precision error being within ±6%.

The observed volumes of activation $\Delta V^{*}_{obs}(\tau^{-1})$ as defined by eq 1, where R is the gas constant and T is temperature (K), were calculated

$$\Delta V^{*}_{obs}(\tau^{-1}) = -RT[(\partial \ln (\tau^{-1}))/\partial P]_{T,solvent} \qquad (1)$$

from plots of ln (τ^{-1}) versus pressure (room pressure to 207 MPa), and these plots were found to be linear on the basis of unweighted least-squares regression analysis. The effects of varying temperature on the emission lifetime were studied using a double-wall quartz cell with emission being detected at right angles to the laser excitation. The outer jacket contained the thermostating liquid (water, ethylene glycol, glycerol, or water–alcohol mixtures). Although the laser beam penetrated the thermostating liquid, no emission was observed from water or ethylene glycol and the small amount of emission from glycerol was determined to have no effect within experimental error on the measured lifetime for the chromium complex. Temperatures were measured using a Fluke 2175A digital system with the thermistor inserted directly into the solution containing the chromium compound but outside of the laser beam path. Temperature reproducibility was within ±0.2°; however a slight systematic bias occurred relative to the readings of a mercury thermometer calibrated against ice–water (0.00 °C) and boiling distilled water (98.56 °C, 721.6 Torr). Below ca. 12 °C, the recorded temperatures were too low by 0.5°, but above 12 °C, they were too high by 0.4°; however in view of the very extended temperature ranges employed in this work (80–160 °C), no temperature correction has been made for this small bias. The limits to the temperature ranges covered were set by the freezing or boiling points of the solutions or for the nonaqueous solutions by the thermal decomposition of the chromium complex at higher temperatures.

Emission spectra were recorded with a Spex Fluorolog 222 spectrofluorometer, and the emission quantum yields were determined relative to that for $[Cr(NH_3)_6]^{3+}$ ($\phi_{em} = 5.5 \times 10^{-5}$) using the procedure described by Demas and Crosby: only in the case of the HMPA was it necessary to correct the emission yield for emission from the solvent matrix.[53,54] UV–visible absorption spectra were taken on a Cary 2315 spectrophotometer, and the gaussian analysis of the spectra was performed using Microsoft Excel 3.0 and Solver software. Infrared measurements were performed with a Bio-Rad FTS-40 FTIR and 3240-SPC data station. Spectra were taken using potassium bromide pellets, or in the case of liquids, the difference spectra (solution minus solvent absorption) were recorded using a Bio-Rad diffuse reflectance assembly and a Buck Scientific attenuated reflectance cell with ZnSe crystal.

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Materials and Solutions. The compound *trans*-[Cr(cyclam)$(NH_3)_2](PF_6)(NO_3)_2 \cdot {}^1/_2H_2O$ and *trans*-[Cr(cyclam)$(NH_3)_2](OTS)_3 \cdot H_2O$, where OTS is the tosylate anion, were prepared in a manner similar to those described in the literature;[29,47,55] however we found that recrystallization from acidified water of the intermediate chromium compounds improved both the uniformity of the bright yellow color of the *trans*-diammonia complex and its emission lifetime (increase of 5% over previous reports). Anal. Found (calcd) for [Cr(cyclam)$(NH_3)_2](OTS)_3 \cdot H_2O$: C, 45.60 (45.50); H, 6.53 (6.53); N, 10.32 (10.28); Cr, 6.34 (6.36); 1.04 ± 0.15 mol of hydrated water as determined by loss of weight on heating (200 °C, ca. 12 h). The measured UV-visible absorption peaks for the OTS salt were sh 445 nm, 422 nm (32.6 M^{-1} cm^{-1}), and 336 nm (42.6 M^{-1} cm^{-1}). For the infrared studies, small amounts of the corresponding trinitrate and triperchlorate salts were prepared by precipitation of the complex ion by addition of aqueous $HNO_3/NaNO_3$ or $HClO_4$. *Caution! The perchlorate salt is known to be explosive.*[29] Previously we have shown that the presence of nitrate anion can lead to photoinduced decomposition, and thus the use of the tosylate salt has been preferred in our studies because of its better photostability and solubility in the nonaqueous media.[47]

Water purified by a Millipore Super-Q system was used to prepare the aqueous solutions. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were BDH OmniSolv grade and hexamethylphosphoramide (HMPA) was obtained from Aldrich (99% grade): further purification of these materials by vacuum distillation did not change the lifetimes of the trans complex in these solvents, and thus both distilled and undistilled materials have been used. In the pure solvents, the trans-chromium complex was found in general to be thermally unstable; however the addition of one to two drops of concentrated aqueous perchloric acid (ultrapure, Johnson Matthey) or concentrated nitric acid (BDH Assured grade) to 25 mL of the organic solvent significantly retarded the rate of decomposition. For the emission studies, the concentration of the trans-chromium complex ranged in general from 1 to 10 mM, and the lifetime was found to be independent of the complex concentration and of the nature and concentration of added acid ($HClO_4$, 1–33 mM; HNO_3, 1–37 mM). Addition of known amounts of water to the nonaqueous solvents showed that the lifetimes were independent of the mole fraction of water up to about 0.1, a level well in excess of those (mole fraction < 0.002) introduced into the nonaqueous solvents by the additions of the aqueous acids. Deaeration of the media by bubbling with molecular nitrogen or by saturation with dioxygen did not affect the measured lifetimes, and thus the experiments were carried out under aerated conditions. The solutions were generally filtered through micropore filters prior to their use: Millex-GS 0.22 μm and Millex-SR 0.5 μm for aqueous and nonaqueous solutions, respectively. Deuterium oxide (99.9 atom % D) and deuterium chloride (99.5 atom % D) were obtained from Aldrich.

Results and Discussion

Visible Absorption and Emission Spectra. The trans-complex ion exhibits two main ligand field absorption bands, which correspond within the context of O_h microsymmetry to the quartet spin-allowed transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (lower energy) and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (higher energy). Theory predicts that, under the reduced symmetry of D_{4h}, the bands will each be split into two components;[56-58] however in both low-temperature solids and in liquid phases, only the lower energy band is detectably split with a shoulder appearing to the red side of the peak maximum, and by comparison with related ethylenediamine and ammonia complexes, the lower energy quadrate component can be assigned to the ${}^4B_{1g} \rightarrow {}^4E_g{}^Q$ transition and the higher energy peak corresponds to the ${}^4B_{1g} \rightarrow {}^4B_{2g}$ transition.[29,56-59] The energy of the latter transition provides a direct measure of the ligand field of the in-plane cyclam ligand (10*Dq*(cyclam)) whereas the corresponding parameter for the ammonia ligand (10*Dq*(NH_3)) can be derived from the splitting between the two components: the splitting equates to ${}^{35}/_4(Dt)$, where $Dt = {}^4/_7(Dq(\text{cyclam}) - Dq(NH_3))$.[57] Resolution of the split band into two gaussian components indicates a small decrease to *Dq*(cyclam) as the Gutmann donor number (DN) of the solvent increases: 2462 cm^{-1} (H_2O; DN 18.0), 2455 cm^{-1} (DMF; DN 26.6), 2450 cm^{-1} (DMSO; DN 29.8), and 2437 cm^{-1} (HMPA; DN 38.8) with an estimated precision of ±6 cm^{-1}.[60] The values for *Dq*(NH_3) are smaller at 1950 cm^{-1} (H_2O), 1975 cm^{-1} (DMF), 1965 cm^{-1} (DMSO), and 1960 cm^{-1} (HMPA), and although these values are within experimental error (±20 cm^{-1}) the same, the suggested difference in pattern of change with solvent between *Dq*(cyclam) and *Dq*(NH_3) may be one indication of different degrees of interaction between the ligands of the complex ion and the molecules of the surrounding solvent (see below). Of parenthetical note is that in the solid state the bond length Cr–NH_3 (209.8 pm) is longer than those for the Cr–amine distances (205.9, 207.4 pm) and for Cr–N in $[Cr(NH_3)_6]^{3+}$ (206 pm) and that correspondingly *Dq*(NH_3) for the hexaammine complex in aqueous media is somewhat higher (2156 cm^{-1}) than those for the trans complex in the different solvents.[51,61,62]

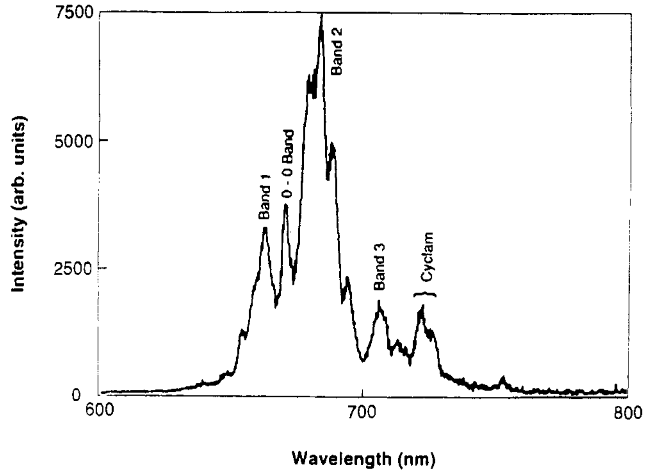

Figure 1. Spectrum for phosphorescence emission from the doublet state of 1.94 mM *trans*-[Cr(cyclam)$(NH_3)_2](OTS)_3$ in aerated, aqueous 1 mM $HClO_4$ solution at 20.0 ± 0.2 °C with excitation at 440 nm.

No fluorescence from the quartet levels has so far been identified; however near-670-nm emission is observed in the liquid phase as shown in Figure 1 and also in low-temperature crystalline powders, and correspondingly a weak absorption band system (ϵ < 1 mol^{-1} cm^{-1}) is found in close juxtaposition.[47,59] These features are assigned to an intraconfigurational ($t_{2g}{}^3$) spin-forbidden transition, which in O_h microsymmetry is ${}^4A_{2g} \leftrightarrow {}^2E_g$. Although the doublet level will be split in D_{4h} microsymmetry (${}^2A_{1g}$, ${}^2B_{1g}$), such splitting is small and only apparent under high resolution at low temperatures. Within the angular overlap model, the tetragonal splitting of the t_{2g} shell depends upon the difference in the π-bonding capabilities of the ligands, which is presumed to be zero for the saturated nitrogen ligators.[9,60] We have shown previously for the trans complex in aqueous media the existence of an extensive mirror image relationship between absorption and phosphorescence emission.[47] This feature permits clear identification of the 0–0 transition although its location in the *liquid* phase seems dependent on the counterion. For the tosylate salt, both emission and absorption occur at 14 930 cm^{-1}, but for the NO_3^-/PF_6^- salt, the absorption and emission occur at 14 940 and 14 920 cm^{-1}, respectively. In low-temperature solids (5–6 K), the mirror image relationship is readily apparent (14 921 cm^{-1} for absorption and emission),[59] and we find in room-

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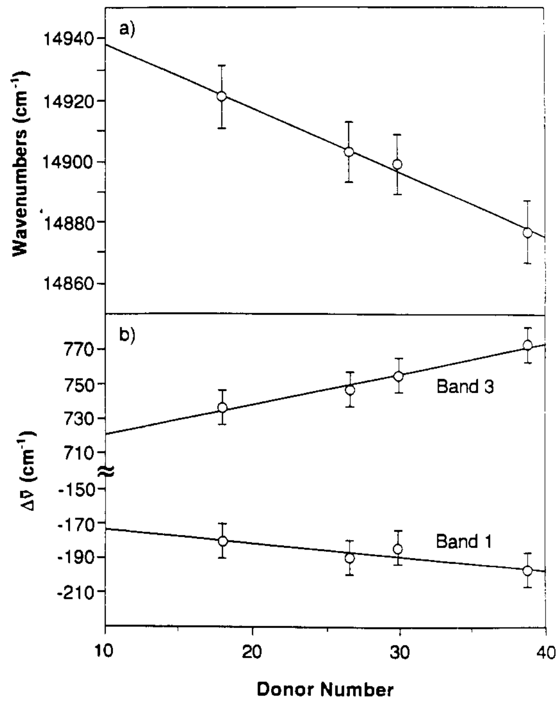

Figure 2. Effects of solvent on the 0–0 transition and vibronic features of the emission spectra of 1.32–1.94 mM *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ at 20.0 ± 0.2 °C with excitation at 440 nm: (a) Plot of wavenumber of 0–0 transition versus Gutmann donor number of solvent (slope = 2.097 cm^{-1}; index of fit (r^2) = 0.994); (b) plot of $\Delta\bar{\nu}$ ($=\bar{\nu}(0\text{–}0) - \bar{\nu}(\text{vibr bd})$) versus donor number (band 1, slope = 0.764 cm^{-1}, r^2 = 0.803; band 3, slope = 1.75, r^2 = 0.977).

temperature DMSO media a similar relationship with absorption at 14 925 cm^{-1} (NO_3^-/PF_6^- salt) and emission at 14 900 cm^{-1} (OTS salt).

The comparison of the spacings of the bands shown in Figure 1 and the very similar ones observed for low-temperature crystals–powders with the infrared spectra for the trans-complex indicates that these emission bands are vibronic in origin.[59] The vibronic features shown in Figure 1 for higher wavelengths than the 0–0 transition are not observed at low temperatures (5–6 K), and this finding along with the comparison of the spacings of the high- and low-energy components implies that the higher energy components are anti-Stokes lines (hot bands): for example both band 1 and the first shoulder of the most intense band (band 2 of Figure 1) lie at ±180 cm^{-1} with respect to the 0–0 point. The spectral features (relative intensity, spacing) for the trans complex strongly resemble those for $[Cr(NH_3)_6]^{3+}$, and by analogy to the latter, the major features (bands 1–3) can be ascribed to odd-parity deformation modes (N–Cr–N; Cr–N–H) even though, for the trans case, the nitrogen atoms pertain both to the cyclam amine and to the ammonia ligands.[59,63,64]

The emission spectra for the doublet state in nonaqueous media exhibit the same general features as shown in Figure 1 for the case of aqueous media; however the position of a particular band does depend upon the nature of the solvent as shown in Figure 2. The 0–0 transition is found to decrease linearly with increasing Gutmann donor number of the solvent. If off-diagonal matrix elements in D_{4h} microsymmetry are neglected, the energy of this transition can be approximated as $9B + 3C$, where B and C are the Racah interelectronic repulsion parameters.[58] The Gutmann donor number provides a measure of the electron donicity of the solvent toward the positively charged complex ion, and thus the implication is that as this interaction increases, there is a progressive increase in delocalization of electronic charge that is

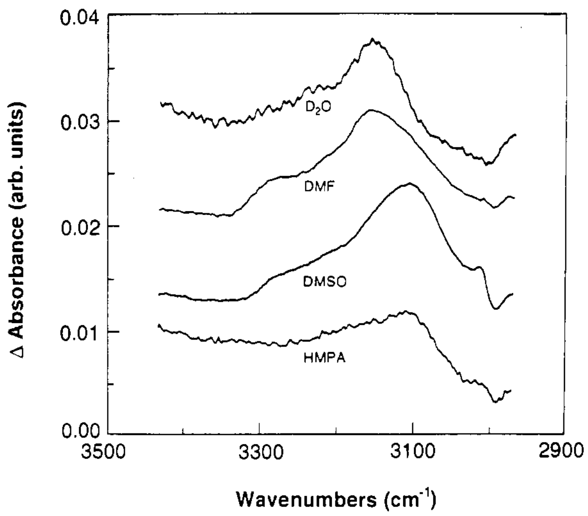

Figure 3. Plot of the difference in infrared absorbance between the solution of the trans complex and the pure solvent versus wavenumber in the N–H stretch region.

manifested in a lowering of interelectronic repulsion in the proximity of the metal center. The most intense emission feature, designated as band 2 in Figure 1, consists of several closely spaced vibronic bands, and the lack of resolution here makes it difficult to identify precisely the effect of the change in solvent on the individual components; however at the qualitative level, the central peak may shift slightly to the red but the three side bands move toward the blue with respect to the 0–0 transition as the donor number of the solvent increases. The situation is more clearly discernible as shown in Figure 2b for band 1 (a hot band) and band 3 where their spacings relative to the 0–0 transition increase with increasing donor number of the solvent. The general tendency for these deformation modes to increase in wavenumber suggests that the chromium–nitrogen bond strengths increase on progressing to solvents with higher Gutmann donor numbers.

The high-frequency N–H stretch modes are not observed in the optical absorption–emission spectra under our conditions; however changes with solvent to the corresponding infrared bands are observed as shown in Figure 3. Although several overlapping bands occur, due to the presence of both amine and ammonia N–H stretches, the shifts appear to be to lower wavenumber with increasing donor number, and this observation implies some weakening of the N–H bonds. While the foregoing vibronic features apply in the main to the ground-state condition, we presume in our discussion below that corresponding effects occur in the doublet excited state and this presumption is based on the existence of a strong mirror image relationship between absorption and emission for the ground state–doublet transition, which indicates very similar potential energy surfaces for the two states.

The nature of the solvent also affects the quantum yields and lifetimes of emission, and a plot of these quantities is shown in Figure 4. For the HMPA case, some background emission attributable to impurities in the solvent was present, and in Figure 4 both the corrected and uncorrected values of ϕ_{em} are shown; however the fitted straight line has been based upon the background-corrected value. The emission yield is seen to increase approximately linearly with increase in emission lifetime, and thus the product of the radiative rate constant and the intersystem crossing yield ($k_{em}\phi_{isc}$ = slope) is nearly constant. Although the radiative lifetime τ^0 ($= 1/k_{em}$) will vary slightly with solvent owing in part to its dependence on the index of refraction, an estimate of its value based upon the integrated absorption coefficient of the doublet state in aqueous media is 14 ms.[4,65] This value is close to radiative lifetimes reported for related chromium complex ions;[65,66] however it is about a factor of 10 greater than

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(64) Urushiyama, A.; Schönherr, T.; Schmidtke H.-H. *Ber. Bunsen-Ges. Phys. Chem.* **1986**, *90*, 1188.
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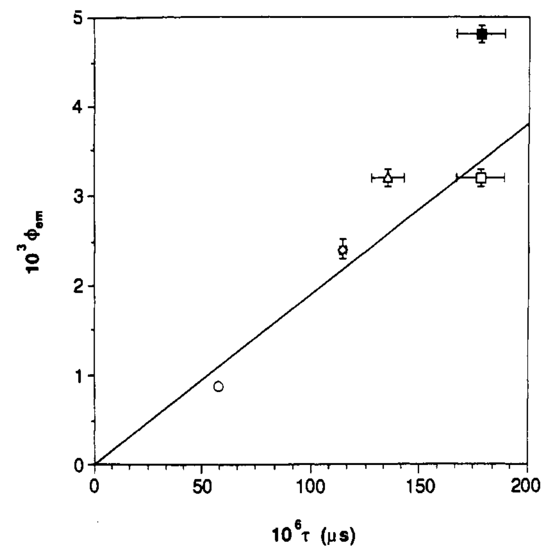

Figure 4. Plot of emission quantum yield (excitation 440 nm) versus measured lifetime at 20.0 ± 0.2 °C for 1.4–1.9 mM *trans*-[Cr(cyclam)$(NH_3)_2]^{3+}$ in acidified media: (○) aqueous solution, (◇) DMF, (△) DMSO, (□) HMPA (solid square, uncorrected for background emission). Slope of line = 19 s^{-1} (r^2 = 0.873).

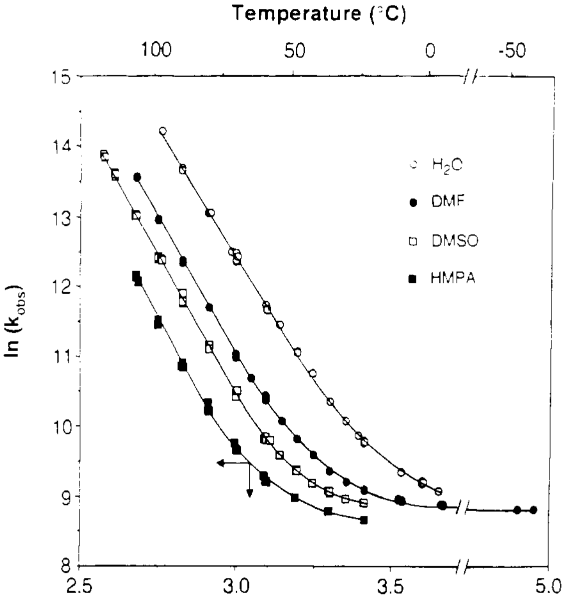

Figure 5. Plot of the observed first-order rate constant for the decay of the doublet excited state with changes in temperature and solvent.

observed lifetimes in different media at 77 K. This latter aspect is consistent with the proposal by Fucaloro and Forster based upon comparative lifetimes of the protiated and deuterated forms of the trans complex that even at low temperatures for the protiated form, the nonradiative process(es) prevails over the radiative one.[26,29,67,68]

Effects of Temperature and Pressure on Emission Liftimes for Decay of the Doublet Excited State. The value of the observed first-order rate constant k_{obs} (=τ_{obs}^{-1}) that describes the decay of the doublet excited state varies significantly with changes in temperature as shown in Figure 5. This nonlinear behavior has also been observed for other chromium(III) complexes in different media (mixed solvents, glassy matrices, polymeric films), and it is characterized by two regions.[2,4,11,13,24,26,31,33,37,46,69–71] At higher temperatures, there is a strong Arrhenius-like temperature dependence whereas, at lower temperatures, the rate of change is far less with temperature; however the *trans*-diammonia complex and its congeneric *trans*-dicyano complex are unusual in that the onset of the high-temperature region occurs at or above room temperature whereas for other chromium(III) systems this onset occurs generally well below 0 °C. To model this nonlinear type of behavior, three mathematical expressions as presented in eqs 2–4 have been considered, and although these form of equations

$$k_{obs}\,(=\tau_{obs}{}^{-1}) = A_1e^{-E_{a1}/RT} + B_1 \qquad (2)$$

$$k_{obs} = A_2e^{-E_{a2}/RT} + B_2e^{-E_b/RT} \qquad (3)$$

$$k_{obs} = [C/(x\coth(x/T))^{1/2}]e^{-E_{a3}/(x\coth(x/T))} + B_3 \qquad (4)$$

$$x = \hbar\langle\omega\rangle/2k_BT \qquad \langle\omega\rangle = 2\pi(2.9979\times10^{10})\langle\bar{\nu}\rangle$$

have proven useful in describing the temperature response of other chromium(III) systems studied, little attention has been given by others as to which form may be the most appropriate phenomenological description. Each equation consists of two terms with the first term representing the strong temperature-dependent contribution (high-temperature region) and the second term pertaining to the low-temperature region. In eq 3, each term is expressed in an Arrhenius exponential form with R and T being the gas constant and temperature, respectively, whereas, in eq 2, the low-temperature contribution is treated as a constant (B_1), which is independent of temperature. Similarly in eq 4, the low-temperature region is characterized by a constant (B_3) and the term indicative of the high-temperature region has the functional form proposed by Englman and Jortner to express a strongly coupled nonradiative process.[72] Within the Englman–Jortner model, the parameter C includes the electronic coupling matrix elements, constants, and the molecular nuclear relaxation energy, and the parameter $\langle\bar{\nu}\rangle$ stands for the mean vibrational wavenumber.

In the present study, each data set for the different solvent systems has been considered in the context of eqs 2–4, using as criteria the randomness in the scatter of the residuals (difference between observed and calculated rate constants) and the nonlinear minimization of the sum of the squares of the residuals. The fitting programs followed the procedure given by Bevington and employed statistical weighting (1/emission intensity) with extended arithmetical precision (19–20 decimal places), the latter being used to minimize possible effects of round-off error.[73] All three functions (eqs 2–4) provided reasonable bases to describe the variation of ln (k_{obs}) with temperature; however on the basis of the aforementioned criteria, the double-exponential function was found to be the most satisfactory descriptor even though as discussed below this led in the case of the DMSO solvent to a small negative activation energy (E_b) for the low-temperature region. In Figure 6, the fit to the data using the double-exponential function (eq 3) is shown for the case of DMF solvent, and the maximum relative deviation (|residual/k_{obs}|) is less than 1% over the temperature interval of −59.5 to 100.0 °C.

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(66) Ryu, C. K.; Lessard, R. B.; Lynch, D.; Endicott, J. F. *J. Phys. Chem.* **1989**, *93*, 1752.

(67) On the basis of the estimated τ^0 of 14 ms and the slope of the plot in Figure 4, the intersystem yield is ca. 0.3. For the closely related complex *trans*-[Cr(cyclam)$(CN)_2]^+$, the experimentally measured ϕ_{isc} is 1.11 ± 0.10,[68] and this may imply that our estimated ϕ_{isc} of 0.3 for the ammonia congener would be too low; if so, then the value of τ^0 would be larger than 14 ms.

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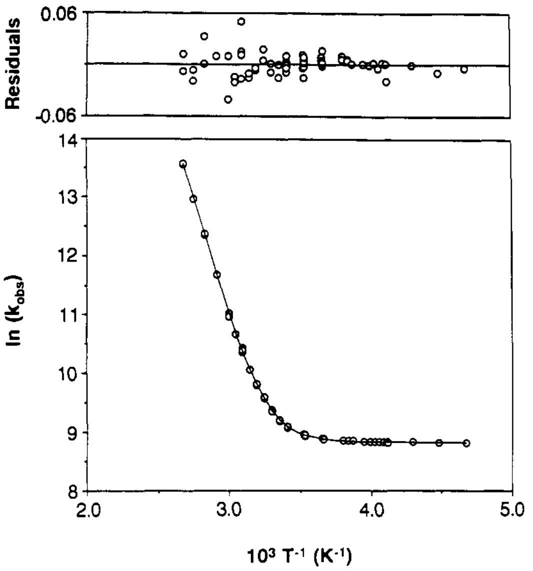

Figure 6. Plot of ln (k_{obs}) versus reciprocal temperature where the solid line is the calculated fit using a double-exponential function (eq 3 in text) and the open circles are experimentally measured points for the case of DMF solvent.

Table I. Parameters for the Reciprocal Lifetime for *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ Expressed as a Function of Temperature (K) in the Form of the Sum of Two Exponential Terms[a–c]

		first term		second term	
solvent	no. of data pts	$10^{-15}A_2$, s^{-1}	E_{a2}, kJ mol^{-1}	$10^{-3}B_2$, s^{-1}	E_b, kJ mol^{-1}
H_2O	35	2.7	64	40	4
DMF	70	3.3	69	7.7	0.2
DMSO	52	2.2	69	0.18	-8.7
		2.8	70	5.8	0.02[d]
HMPA	23	17	78	61	6

[a] $\tau^{-1} = A_2e^{-E_{a2}/RT} + B_2e^{-E_b/RT}$. [b] Estimated uncertainties: A_2, $\leq\pm5\%$; E_{a2}, $\leq\pm1\%$; B_2, $\leq\pm17\%$; E_b, $\leq\pm23\%$. [c] Temperature ranges: H_2O, 1.0–88.8 °C; DMF, -59.5 to 100.0 °C; DMSO, 20.0–115.2 °C; HMPA, 20.0–100.0 °C. [d] Data set includes the lifetime at 77 K from ref 29.

Table II. Parameters for the Reciprocal Lifetime of *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ Expressed as a Function of Temperature (K) in the Form of a Sum of a coth Function and a Constant Term[a–c]

		first term		second term
solvent	$\langle\bar{\nu}\rangle$, cm^{-1}	$10^{-6}C$, $J^{1/2}$ s^{-1}	E_{a3}, kJ mol^{-1}	$10^{-3}B_3$, s^{-1}
H_2O	240	16	83	6.4
DMF	210	8.3	84	6.8
DMSO	195	3.2	82	5.3
HMPA	190	11	89	5.9

[a] $\tau^{-1} = (C/(x \coth (x/T)^{1/2}e^{-E_{a3}/(x\coth(x/T))} + B_3$, where $x = \hbar\langle\omega\rangle/2k_BT$ and $\langle\omega\rangle = 2\pi(2.9979 \times 10^{10})\langle\bar{\nu}\rangle$. [b] Estimated uncertainties: $\langle\bar{\nu}\rangle$, $\leq\pm1\%$; C, $\leq\pm5\%$; E_{a3}, $\leq\pm1\%$; B_3, $\leq\pm1\%$. [c] Temperature ranges and number of data points are the same as those given in Table I.

The fitting parameters associated with the double-exponential expression (eq 3) and with the coth function (eq 4) are summarized in Tables I and II, respectively. The corresponding results for eq 2 are available as supplementary information. By comparison, the values of the activation energies E_{a1} (eq 2) and E_{a2} (eq 3) differ by 3% or less and the preexponentials (A_1 and A_2) change by less than 25% except for the case of HMPA solvent where A_2 (Table I) is about twice as large as A_1. The values of E_{a1} and E_{a2} for aqueous media (both 64 kJ mol^{-1}; 1–88.8 °C) are comparable to two previous reported values for E_{a1} (80 and 59 kJ mol^{-1}) although the latter were determined over a smaller temperature range (0–61 °C).[29,47] The activation energy of 67 kJ mol^{-1} determined for DMF over the range of 41–63 °C is in accord with our determinations of E_{a2} and E_{a1} (both 69 kJ mol^{-1}).[29] The values of B_1 and B_3, which represent the low-temperature region as being temperature independent, differ by less than 20% although B_3 is systematically higher than B_1. For the three functions considered, the most notable difference is that the apparent activation energies E_{a3} as determined from eq 4 are 15–30% larger than those for E_{a2} (and E_{a1}).

Endicott and co-workers have also noted this aspect for several other chromium(III) complexes and they consider the inferred activation barriers to be extremely large,[11] and we also have reservations about the computed values of the mean vibrational numbers $\langle\bar{\nu}\rangle$, which seem too low. Partly this situation may arise as an artifact of our treatment because we have treated the C-parameter as a single entity whereas in fact in the Englman–Jortner model it is a composite quantity, including matrix elements and nuclear relaxation energy. Of perhaps more fundamental concern is the extent to which theoretical models of nonradiative transitions can be applied to electrostatically charged complex ions because the models assume that the surrounding medium is inert (a heat bath); i.e., it does not change considerably the energy levels or the intramolecular coupling terms.[18,21,72] While the longevity of the doublet excited state (microsecond scale) indicates near vibrational equilibration with the surroundings (or a thexi-state situation), the results shown in Figures 2 and 3 clearly demonstrate measurable effects of coupling to the solvent on the internal modes of the complex ion. The interfacial forces between the complex and nearest solvent molecules are anticipated to be quite large; for example, it is estimated the effective hydrostatic pressure to be 3.2 GPa, which is more than a factor of 10 higher than the applied pressures used in this work (see below).[74]

For the DMSO case, the apparent activation energy E_b (Table I) is of negative sign, and this is improbable on a physical basis. This situation led us to consider the possibility that even though the data were collected over wide intervals of temperature (80–160 °C) and the fittings achieved using eqs 2–4 are satisfactory, the data sets may be sensitive to the points at the temperature extremes. Examination of the data for all of our liquid phase results did not give clear evidence of this; however we believe that this may be the explanation for the negative value of E_b in DMSO for two reasons. The inclusion into the data set of the reported value of k_{obs} at 77 K (DMSO) yielded a good fit using the double-exponential function (eq 3) with the value of E_b now being *positive* but with little or no change to the parameters A_2 and E_{a2}, which describe the high-temperature behavior (Table I).[75] Second, Fucaloro and Forster find for the trans complex in the mixed solvent DMSO/H_2O that the lifetime data over the range 77–325 K can be reasonably well fitted using a double-exponential function, provided that the small inflection point near 150 K (due to "solvent" melting) is ignored, and their parameters and ours where the value of k_{obs} at 77 K is included (Table I) are in reasonable agreement.[4,76]

In an earlier study of the effect of change in pressure on the lifetime, we have found that the observed volume of activation $\Delta V^{*}_{obs}(\tau^{-1})$ in aqueous media changes in a concerted manner with temperature from a value of +1.5 ± 0.3 cm^3 mol^{-1} at 4.0 °C to +6.6 ± 0.6 cm^3 mol^{-1} at 57.8 °C (see Figure 1 of ref 47) and similarly for DMF solvent, $\Delta V^{*}_{obs}(\tau^{-1})$ is determined in the

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(75) Using the data presented in Table I leads to a calculated lifetime of 180 μs at 77 K for DMF, which is in close accord with the observed value of 169 μs.[29]

(76) Data cited in ref 4: $A_2 = 1.3 \times 10^{15}$ s^{-1}, $E_{a2} = 63.6$ kJ mol^{-1}; $B_2 = 6 \times 10^3$ s^{-1}, $E_b = 2.5$ kJ mol^{-1} for mixed solvent DMSO/H_2O. It should be noted that these parameters are based upon lifetimes which have been corrected for contributions which the authors consider to be independent of temperature whereas we have not attempted to make such corrections even though such are expected to be small over our range of temperatures. Second, we observe that the lifetimes vary with the composition of the DMSO–H_2O mixture (pure DMSO, $\tau = 135$ μs; 0.5 mol fractions of DMSO and of water, $\tau = 116$ μs at 20.0 °C) so that the foregoing parameters and ours (Table I) may differ slightly due to different solvent composition.

present study to be +7.0 ± 0.2 $cm^3\ mol^{-1}$ at 61.7 °C and +0.3 ± 0.1 $cm^3\ mol^{-1}$ at 1.9 °C. To model this behavior, the definition of the volume of activation (eq 1) has been applied to the form of k_{obs} given by eq 3 to yield eq 5. The assumption made in this

$$\Delta V^{\ddagger}{}_{obs}(\tau^{-1}) = [(\Delta V^{\ddagger}{}_{h})(A_2 e^{-E_{a2}/RT}) + (\Delta V^{\ddagger}{}_{l})(B_2 e^{-E_b/RT})]/k_{obs} \quad (5)$$

derivation is that the parameters $\Delta V^{\ddagger}{}_{l}$ and $\Delta V^{\ddagger}{}_{h}$, which represent the intrinsic volumes of activation for the lower and higher temperature regions, respectively, are themselves independent of pressure, and the linearity found in the plots of ln (k_{obs}) versus pressure indicates that this assumption is a reasonable approximation over our range of pressures (room pressure to 207 MPa). The values of $\Delta V^{\ddagger}{}_{h}$ are determined to be +7 ± 1 $cm^3\ mol^{-1}$ (H_2O) and +7.4 ± 0.2 $cm^3\ mol^{-1}$ (DMF) whereas for the low-temperature region the values of $\Delta V^{\ddagger}{}_{l}$ are essentially zero (+0.4 ± 0.7 $cm^3\ mol^{-1}$ (H_2O) and −0.4 ± 0.1 $cm^3\ mol^{-1}$ (DMF)).

Because of the substantial changes in lifetimes with temperature, it is essential to discern if this behavior arises from the presence of either permanent or transitory chemical reactions associated directly with the doublet excited state. In aqueous media under prolonged steady-state laser irradiation, small absorption changes in the visible region do occur; however these changes do not appear to be of direct consequence to the doublet-state behavior because the absorption changes depend upon the nature of the counteranion whereas the lifetime is unaffected by the anion's nature and concentration.[47] The release of ammonia or the partial loss of the cyclam ligand and their subsequent protonation in acidic media would lead to change in proton concentration, but we find little or no change either in time-resolved conductivity measurements ($\phi(\Delta[H^+]) \leq 0.007$; ca. 25 °C)[47] or in steady-state experiments ($\phi(\Delta[H^+]) \leq 0.006$; 54 °C). On the presumption that chemical reaction from the doublet excited state would lead to change in proton concentration, an upper limit to the associated rate constant k_{rx} can be calculated from the relationship $k_{rx} = k_{em}(\phi(\Delta[H^+])/\phi_{em})$, and this leads to the estimate that k_{rx} will be less than 5% of k_{obs} at room temperature and at 54 °C. The foregoing results indicate that, in aqueous media, chemical reaction from the doublet state is not significant and that the variations in lifetime with temperature are predominantly due to changes in nonradiative processes. For the nonaqueous media, the situation is more problematical because thermal decomposition is a notable factor, particularly in the high-temperature region as discussed in the Experimental Section. Two features suggest however that significant photochemical reaction from the doublet state is improbable: Figure 5 shows that k_{obs} for aqueous media is always larger than those values for the nonaqueous solutions at a given temperature, and in the high-temperature region there is an approximate linear correlation between ln (A) and E_a, which implies a similarity in mechanisms between the various solvent systems. Our general conclusion is that the changes with temperature (and solvent) as shown in Figure 5 reflect predominantly alterations to the nonradiative events.

The values of $\Delta V^{\ddagger}{}_{l}$ for DMF and aqueous media, which characterize the low-temperature section, are nearly zero and correspondingly the activation energies are small (Table I). Kane-Maguire and co-workers find for this region strong deuterium–hydrogen isotope effects: τ(N–D)/τ(N–H) for aqueous media being 5.3/1 at 10 °C, for DMF 7.5/1 (20 °C) and 21.7/1 (77 K), and for DMSO 11.9/1 (20 °C) and 20.7/1 (77 K).[29] These features in association with the mirror image relationship found for the absorption–emission spectra of the doublet-ground-state transition indicate that the decay of the doublet excited state in the low-temperature region is primarily a manifestation of a weak coupling scheme involving tunneling between the doublet excited level and the ground state.

By contrast, the behavior of the doublet excited state in the high-temperature region is markedly different where the values of $\Delta V^{\ddagger}{}_{h}$ in both DMF and aqueous solutions of ca. +7 $cm^3\ mol^{-1}$ indicate a process(es) associated with considerable volume expansion. Similarly the activation energies are substantial (Table I) and in aqueous media only a moderate deuterium–hydrogen isotope effect of 1.3/1 at 61 °C is encountered.[29] These experimental results point toward a strong coupling mechanism entailing considerable configurational change although for the trans complex this does not lead to chemical reaction.[72] Two possible mechanisms are a surface crossing from the doublet excited state to a ground-state intermediate, which subsequently reverts to the ground-state form of *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$, or the occurrence of back-intersystem crossing from the doublet excited level to an excited quartet state(s) followed by radiationless transition to the ground state. Time-resolved measurements have given no evidence for a ground-state intermediate although such does occur for *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$ in aqueous solutions.[47]

Low-lying, equilibrated quartet levels are generally perceived to be distorted relative to the ground and lowest excited-doublet states; for example with the homoligated system $[Cr(NH_3)_6]^{3+}$, the $^4T_{2g}$ excited state is found spectroscopically in low-temperature single crystals to undergo tetragonal distortion, and the molar volume of the relaxed-quartet state is estimated to be 3–4 $cm^3\ mol^{-1}$ greater than that for the doublet level.[51,77] In this context also, recent results from theoretical calculations for the hexaamminechromium(III) complex lend considerable credence to the possible involvement of a bisc pathway.[3] For the *trans*-diammonia complex, the 0–0 energy gap ΔE between the doublet and lowest quartet excited states has been estimated by the procedure of Fleischauer and co-workers to be in the range 50–60 kJ mol^{-1} and a second approach based upon the onset at 5 K of the first-quartet ligand-field absorption band yields an estimate of ca. 47 kJ mol^{-1}.[22,24,47,59] The values of activation energies given in Tables I and II for the four different solvents exceed the estimates of the ΔE gap. This facet in conjunction with positive values of $\Delta V^{\ddagger}{}_{h}$ support the possibility of a significant contribution from a bisc type of pathway in the high-temperature region.[78]

Solvent Effects on the Emission Lifetime for Decay of the Doublet Excited State. As shown in Figure 5, the value of the observed rate constant for the decay of the doublet state at a given temperature depends markedly upon the specific solvent; however perusal of Tables I and II shows also that the solvent effects are multifarious. In the high-temperature region, increases in the activation energies as defined by eqs 2 and 3 tend to be compensated for by increases in the preexponential factors with approximate linearity between ln (A) and E_a, and such isokinetic behavior is encountered with a number of related chromium(III) complexes.[19,33,41] With the exception of the DMSO case, increasing values of the activation energies (eq 4) are accompanied by decreasing values of the mean vibrational wavenumber $\langle \bar{\nu} \rangle$ although there are also changes to the C-parameter (Table II). In view of these trends, we have looked for possible empirical correlations between the values of the rate constants determined from the fits to eqs 2–4 (for both the high- and low-temperature regions) and approximately two dozen solvent scales and bulk properties.[79-82] This exercise was carried out using a least-squares regression analysis program (Curfit.bas program; Hewlett-Packard) employing common mathematical functions and taking as a general criteria that the index of fit (r^2) should exceed 0.98.[83]

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(77) Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1978**, *17*, 1729.

(78) Under the assumption that the radiative rate constant and intersystem crossing efficiency η_{isc} are temperature independent, the contribution of back-intersystem crossing to τ^{-1} of the doublet excited state is given approximately by $(1 - \eta_{isc})k_{bisc}$,[4] and thus the temperature dependence will reflect k_{bisc}.

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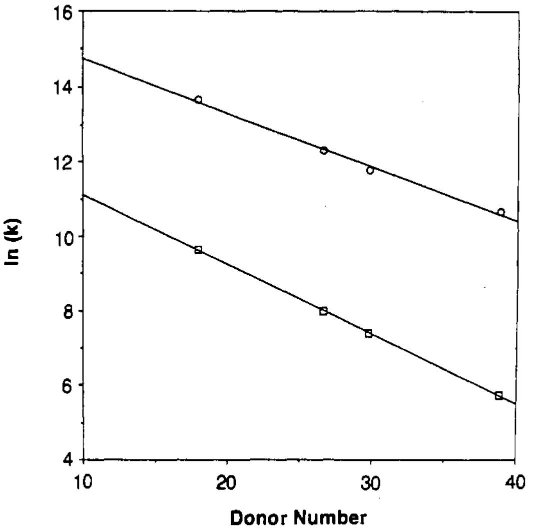

Figure 7. Plot of ln (k) versus Gutmann donor number of the solvent where k is the calculated value of the first term of eq 3: (○) 80 °C, slope of line = −0.14 ($r^2 = 0.993$); (□) 25 °C, slope of line = −0.19 ($r^2 = 1.000$).

The search for possible correlations in the low-temperature region did not yield any clearly discernible trends even though, for many related chromium(III) amine complexes, the radiationless transition rates are found to increase with the number of active N–H bonds.[4,18,65,69] For the high-temperature region, decreasing values of the calculated rate constants (eqs 2–4) are associated with increasing boiling point (an exponential relationship) and with increasing molar polarizability, molecular weight, and volume of the solvent, and these trends may be an *indirect* indication of increasing interaction between the positively charged complex ion and the surrounding solvent molecules (see below). Strong correlations are found between the values of the rate constant and the Gutmann donor numbers and the solvent scales D(II,I), $\Delta\nu_D$, and $\Delta\nu_{PFP}$ that bear a linear relationship to the donor number scale, and the plot of ln (k) versus donor number (Figure 7) shows that the rate constant describing the high-temperature pathway decreases with increasing donor number of the solvent.[79,82,84] A comparative situation arises in the photobehavior of a ligand-field triplet state of $[Rh(NH_3)_5Cl]^{2+}$ in water, formamide, dimethyl sulfoxide, and dimethylformamide.[85,86] As shown in Figure 8, the semilogarithmic plot of the nonradiative rate constant for the decay of the triplet excited state shows the same type of downward movement with increasing donor number; however, it is also notable that the rate constants for ammonia release and chloride loss do not correlate with donor number and that in fact chloride loss relates strongly to Gutmann acceptor number.

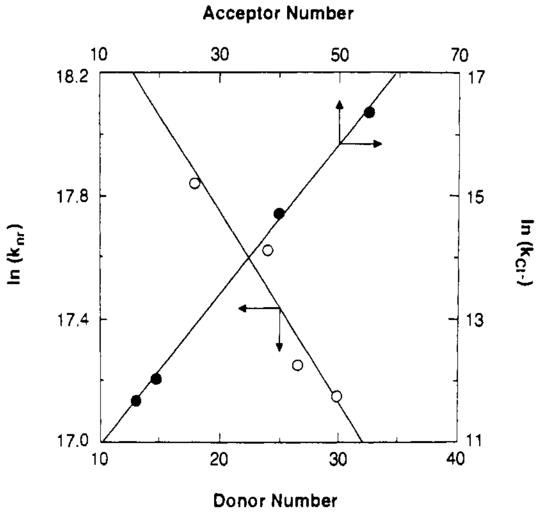

Figure 8. Plots of ln (k_{nr}) versus donor number and of ln (k_{Cl^-}) versus acceptor number for the reactive triplet ligand-field state of $[Rh(NH_3)_5Cl]^{2+}$ in the solvents water, formamide, dimethyl sulfoxide, and dimethylformamide with data taken from ref 86: (○) Plot of ln (k_{nr}) versus donor number, slope of line = −0.062 ($r^2 = 0.923$); (●) plot of ln (k_{Cl^-}) versus acceptor number, slope of line = 0.12 ($r^2 = 0.998$).

The use of the donor number scale has found little employment in describing the photobehavior of chromium(III) complex ions; however its application either alone or in conjunction with multiparameter scales has proven useful to the consideration of redox and charge-transfer phenomena and of linkage isomerization processes involving cobalt and ruthenium amine complexes where solvent–H–N interactions are considered to play a prominent role(s).[40,87–91] In this context, the $\Delta\nu_D$ and $\Delta\nu_{PFP}$ scales can be more insightful as both pertain to the effect of solvent on the O–H stretch frequencies in the respective reference compounds methanol and p-fluorophenol. Increasing values of $\Delta\nu_D$ and $\Delta\nu_{PFP}$, which relate to increasing values of donor number, signify decreasing stretch frequencies.[79,92] Arnett and co-workers have observed that enthalpies of hydrogen-bond formation do correlate reasonably well with donor numbers and with $\Delta\nu_{PFP}$ for closely related compounds such as our solvents, which presumably interact at the oxygen–solvent sites.[92] A heuristic picture of the effects of hydrogen bonding between the solvent and complex ion can be derived from the application of Gutmann's bond-length variation rules.[60] The predictions are that as the strength of interaction between the solvent and amine hydrogens increases (as reflected in increasing donor number), the N–H bonds will lengthen and those of Cr–N will shorten. The presumed corollary is that the vibrational frequencies associated with the N–H bonds will decrease and those of the Cr–N bonds will increase with the magnitudes of these changes depending upon the particular type of vibrational motion being observed. Qualitatively the predictions are in accord with the observed vibrational spectral changes shown in Figures 2 and 3. This simple model also underscores or reminds one that the solvent–complex interactions affect more than one thing even though the trend toward lower mean vibrational number $\langle\bar{\nu}\rangle$ with increasing donor number of the solvent (Table II) may indicate that changes to the high-frequency N–H modes are on balance more influential to the proposed back-intersystem crossing process. At the same time, however, changes to the activation energies with solvent also occur (Tables I and II). This aspect in conjunction with the moderately large values of ΔV^{*}_{h} suggest the possibility of significant differences in solvation between the

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(82) The following solvent scales were considered, and material presented by Griffiths and Pugh provides a discussion of the scales and their interrelationships: Dimroth–E_T; Gutmann's acceptor and donor numbers; Kagiya–$\Delta\nu_D$; Kosower-Z; Selbin–D(II,I); Winstein–log (k_{ion}), $\delta(^{23}Na)$; ΔPPM; $\Delta\nu_{FPF}$.[79] Several multiparameter solvent scales were also investigated.[80,81] Bulk properties of solvents considered were boiling and melting point, density, dielectric constant (including Kirkwood equation), dipole moment, molar polarizability, molecular volume and weight, refractive index, specific conductance, viscosity, and fluidity ($1/\eta$).

(83) Mathematical functions examined: $k = D + D'(P)$; $k = De^{D'(P)}$; $k = D(P)^{D'}$; $k = D + D'/P$; $k = P/(D + D'(P))$; $k = D + D'\log(P)$. D and D' are fitted parameters and P and k are a solvent property or scale and the rate constant, respectively.[82]

(84) The semilogarithmic plot of Figure 7 has analogy to a linear free-energy relationship because donor number as originally defined is the absolute value of the enthalpy of the reaction in dichlorethane between a donor molecule and $SbCl_5$ to form the donor–$SbCl_5$ adduct.[60]

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doublet excited state and the transition state, and theoretical calculations for the $[Cr(NH_3)_6]^{3+}$ ion suggest that changes in solvation effects may contribute about 25% to the apparent activation energy.[3]

Concluding Remarks

The results of the current study carried out in the liquid phase show the occurrence of different types of competing nonradiative processes, which are more often discernible in low-temperature glasses or solids. The volumes of activation in conjunction with the earlier reported N–H/N–D isotope effects demonstrate that the process(es) in the low-temperature region involves a weakly coupled event (tunneling) between the doublet excited state and the ground state whereas the predominant process in the high-temperature domain is of the strong coupling type. We propose that the latter involves back-intersystem crossing; however in the absence of direct detection of the quartet level by emission and of a ground-state intermediate, the distinction between a bisc pathway and a strongly coupled crossing to a ground-state species may be more semantic than factual. Nevertheless, the solvent does play a major role in this event where, for example, the values of the rate constants at 80 °C differ by a factor of 20, but at the same time the effects are composite ones involving changes to both the preexponential factors and the activation energies.

The Gutmann donor number scale has proven useful here in describing the overall effects; however there is a general cautionary note, namely, that even though different processes may originate from a given excited state, they will not necessarily exhibit a similar or parallel dependence on the solvent, and this is well illustrated by Figure 8. Furthermore, because the measured lifetimes are composite functions of individual processes, one does not anticipate in general that the lifetimes will bear a direct relationship to any one solvent scale; however the potential usefulness of such an occurrence is in assisting to identify situations where one type of process may predominate and be highly sensitive to the nature of the solvent. Absences of strong correlations between lifetimes and one-parameter solvent scales are in general borne out for many chromium(III) complexes in fluid media, but there are notable exceptions such as for $[Cr(NH_3)_6]^{3+}$, where the situation is analogous to that of Figure 7, and for *trans*-$[Cr(NH_3)_2(NCS)_4]^-$, where the logarithm of τ^{-1} for a dozen different solvents correlates well with Brownstein's *S*-scale.[19,29,30,33,34,36,38]

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Supplementary Material Available: A table listing the parameters fitted to eq 2 of the text (1 page). Ordering information is given on any current masthead page.