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Inorganic Chemistry Article

Solvent Effects on the Spectroscopic and Photophysical Properties of the *trans*-(1,4,8,11-Tetraazacyclotetradecane)diisothiocyanatochromium(III) Ion, *trans*-$[Cr(cyclam)(NCS)_2]^+$

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The spectroscopy and photophysics of *trans*-$[Cr(cyclam)(NCS)_2]^+$ (where cyclam is 1,4,8,11-tetraazacyclotetradecane) were studied in a range of solvents. The cyclam NH stretching vibration [ν(NH)] wavenumber correlates with the Gutmann donor number, whereas the thiocyanate CN stretching vibration [ν(CN)] wavenumber correlates with the Snyder solvent strength (P') scale. These results signify that there is a difference in the solvent interactions with the two types of ligands. The energy of the ligand-to-metal charge transfer absorption maximum between 310 and 320 nm and the energy of the spin-forbidden (doublet–quartet) absorption and emission bands above 700 nm correlate with the ν(CN) wavenumber. This establishes the dominant role of solvent effects at the NCS^- ligand in "tuning" the energy of these spectroscopic features. Quantum yields ϕ_{rx} for photosubstitution are <0.02 at 54 °C and <0.002 at 22 °C, demonstrating that photochemical reaction is a very minor pathway. The effects of solvent and temperature on the nonradiative decay of the doublet excited-state were investigated by observing the time-resolved phosphorescence between 700 and 750 nm. Below 30 °C, the lifetimes are relatively temperature-independent, whereas at higher temperatures, a strong Arrhenius-type dependence is observed. Values for the preexponential factor (A) and the activation energy (E_a) are solvent-dependent and follow a Barclay–Butler-type correlation. These observations are consistent with a dominant back-intersystem crossing pathway for nonradiative decay in the higher-temperature region. From trends observed between ln(A) and the ν(CN) frequency, it appears that solvent effects at the thiocyanate ligand play a dominant role in influencing the rate of nonradiative decay in the high-temperature region.

Introduction

The photochemical and photophysical behavior of Cr(III) complexes have intrigued researchers for several decades.[1−17] These systems show several characteristics that make them particularly attractive for investigating photochemical and photophysical kinetics. They are thermally inert in solution but possess appreciable quantum yields for photosubstitution upon visible irradiation. Significantly, many Cr(III) systems show measurable phosphorescence corresponding to a radia-

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(1) Forster, L. S. *Coord. Chem. Rev.* **2006**, *250*, 2023.
(2) Forster, L. S. *Coord. Chem. Rev.* **2004**, *248*, 261.
(3) Forster, L. S. *Adv. Photochem.* **1991**, *16*, 215.
(4) Forster, L. S. *Chem. Rev.* **1990**, *90*, 331.
(5) Sykora, J.; Sima, J. *Coord. Chem. Rev.* **1990**, *107*, 1.
(6) Endicott, J. F.; Ramasami, T.; Tamilarasan, R.; Lessard, R. B.; Ryu, C. K.; Brubaker, G. R. *Coord. Chem. Rev.* **1987**, *77*, 1.
(7) Endicott, J. F.; Lessard, R. B.; Lei, Y.; Ryu, C. K.; Tamilarasan, R. *ACS Symp. Ser.* **1986**, *307*, 85.
(8) Kirk, A. D. *Coord. Chem. Rev.* **1981**, *39*, 225.
(9) Hollebone, B. R.; Langford, C. H.; Serpone, N. *Coord. Chem. Rev.* **1981**, *39*, 181.
(10) Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 301.
(11) Adamson, A. W. *Pure Appl. Chem.* **1979**, *51*, 313.
(12) Zinato, E. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 4.
(13) Vagnini, M. T.; Kane-Maguire, N. A. P.; Wagenknecht, P. S. *Inorg. Chem.* **2006**, *45*, 3789.
(14) Wagenknecht, P. S.; Hu, C.; Ferguson, D.; Nathan, L. C.; Hancock, R. D.; Whitehead, J. R.; Wright-Garcia, K.; Vagnini, M. T. *Inorg. Chem.* **2005**, *44*, 9518.
(15) Wright-Garcia, K.; Basinger, J.; Williams, S.; Hu, C.; Wagenknecht, P. S.; Nathan, L. C. *Inorg. Chem.* **2003**, *42*, 4885.
(16) Irwin, G.; Kirk, A. D.; Mackay, I.; Nera, J. *Inorg. Chem.* **2002**, *41*, 874.
(17) Kirk, A. D. *Chem. Rev.* **1999**, *99*, 1607.

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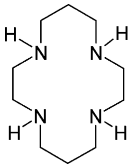
Scheme 1



tive transition between the lowest excited doublet state and the ground quartet state. This emission allows the experimentalist to probe the time-resolved behavior of the doublet state, which, in many cases, has a lifetime of a microsecond or more at room temperature in solution. Yet, despite the widespread interest in these systems, several key issues continue to be controversial. These include the relative importance of the various excited states and the possible occurrence of intermediates in the photochemical act and the role that the surrounding medium and environment play in influencing the rates of the photochemical and photophysical pathways that constitute the decay of the excited state.

Macrocyclic amine ligands such as cyclam (1,4,8,11-tetraazacyclotetradecane; Scheme 1) place steric constraints on Cr(III) complexes that effectively "shut off" the photochemical pathway.[16,18] This has allowed the investigation of temperature, pressure, and solvent effects on nonradiative excited-state decay pathways of complexes such as *trans*-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$.[19,20] For this complex, the solvent influences the photophysical behavior through donor-type interactions at the ammonia and cyclam N−H sites, thus affecting the frequency of vibrational modes that are coupled to the nonradiative decay.[19] These observations illustrate that the solvent molecules surrounding the complex cannot be considered a simple "heat bath" for the dissipation of energy. Rather, individual molecules of solvent can influence nonradiative decay events by specific interactions between the solvent and complex.

In this paper, we have extended these studies to *trans*-[Cr(cyclam)(NCS)$_2$]$^+$ in order to determine whether the solvent donor model is applicable to Cr^{III}(cyclam) complexes that also possess non-amine ligands. This complex is soluble in a wider range of solvents than the diammine complex, thus providing an opportunity to study how the replacement of NH$_3$ ligands by unsaturated NCS$^-$ ligands affects the solvent dependence of the spectroscopic and photophysical features of the complex.

Experimental Section

Synthesis of *trans*-[Cr(cyclam)(NCS)$_2$]ClO$_4$. The synthesis of this complex was modified from previous procedures.[21,22] A total of 8.2 g of *trans*-[Cr(cyclam)(NO$_3$)$_2$]NO$_3$·2H$_2$O (synthesized according to literature procedures[18]) was dissolved in 550 mL of H$_2$O and heated at 90 °C for 3.5 h. After this, 80 g of NaSCN was added with stirring and the solution was evaporated to a small volume and then cooled. Crude orange *trans*-[Cr(cyclam)(NCS)$_2$](SCN) precipitated out along with NaSCN. Room-temperature H$_2$O was then added in small amounts with stirring until NaSCN just dissolved. The orange precipitate was filtered and washed with 40 mL of cold absolute ethanol and diethyl ether. The yield of crude *trans*-[Cr(cyclam)(NCS)$_2$](SCN) was 5.0 g. This was reprecipitated as the perchlorate salt by dissolving it in warm (35−40 °C) H$_2$O (approximately 2 g of crude product per 350 mL of H$_2$O), filtering, and adding a saturated aqueous NaClO$_4$ solution dropwise to the filtrate until a precipitate appeared. The mixture was cooled, and the precipitate was filtered and washed with 100 mL of a cold 4:1 diethyl ether/absolute ethanol mixture, followed by 150 mL of diethyl ether. The yield of *trans*-[Cr(cyclam)(NCS)$_2$]ClO$_4$ was 4.7 g (58%). ***Warning!*** *Perchlorate salts of Cr(III) complexes are potentially explosive. In the future, it is strongly recommended that this complex be precipitated with a different anion such as* PF_6^- *or* $C_7H_7SO_3^-$.

To purify, the ClO$_4^-$ salt was dissolved in a minimum volume of acetone (approximately 0.5 g of complex per 50 mL of BDH Omnisolv acetone) and purified on a column (60 cm × 4 cm i.d.) packed with silica gel (230−400 mesh ASTM), with acetone elution. The solution separated into an orange-yellow band, which passed through the column, and an almost stationary pink band (later determined to be the cis isomer by comparison of its UV−visible absorption spectrum with an authentic sample of *cis*-[Cr(cyclam)(NCS)$_2$]ClO$_4$). After elution, the yellow solution was evaporated to dryness and the residual solid was dissolved in 0.001 M HClO$_4$ and filtered with a 0.22 μm syringe filter. Several milliliters of concentrated HClO$_4$ were added to the filtrate, and the resulting mixture was cooled in an ice bath. The resulting precipitate was collected, washed with a 4:1 diethyl ether/absolute ethanol mixture and diethyl ether, and air-suction dried. The percent recovery was 45% (2.1 g of purified *trans*-[Cr(cyclam)(NCS)$_2$]ClO$_4$ from 4.7 g of original perchlorate salt). Analysis for [Cr(C$_{10}$H$_{24}$N$_4$)(NCS)$_2$](ClO$_4$). Found (calcd): N, 17.89 (17.96); C, 30.82 (30.80); H, 4.90 (5.17). UV−visible absorption spectrum in H$_2$O: λ_{max} (ϵ_{max}) = 482 nm (87 M^{-1} cm^{-1}), 310 nm (9810 M^{-1} cm^{-1}). The wavelength of the first absorption band noted above agrees with the literature value; however, our molar absorptivity of 87 M^{-1} cm^{-1} is nearly 40% less than the value previously reported.[21] Before chromatographic purification, our samples had slightly higher ϵ_{max} values at 482 nm of 96−98 M^{-1} cm^{-1}. Because the cis isomer (which has an ϵ of nearly 200 M^{-1} cm^{-1} at similar wavelengths) was present in our product before column chromatography, there is a strong possibility that the previously published values for ϵ_{max} were actually derived from an isomeric mixture.

Solvents and Solutions. H$_2$O purified by a Millipore Super-Q system was used for aqueous solutions in this study. All solvents were used as received from BDH or Aldrich; *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), and nitromethane were also distilled after drying with CaH$_2$ or molecular sieves. These solutions were acidified by the dropwise addition of concentrated HClO$_4$ (BDH Aristar) to the solvents to make solutions that were 0.015 M in acid. ***Warning!*** *Considerable care must be exercised when adding perchloric acid to organic solvents! The addition of concentrated* $HClO_4$ *to DMSO resulted in small explosions and a subsequent darkening of the solution; therefore, concentrated* HNO_3 *(BDH ACS grade) was added to DMSO.* All solutions for photophysical measurements were deoxygenated by argon bubbling in a 1 cm cell. Bubbling times varied from 30 min (acetone and acetonitrile) to 25 h (HMPA and

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(18) Kane-Maguire, N. A. P.; Wallace, K. C.; Miller, D. B. *Inorg. Chem.* **1985**, *24*, 597.
(19) Vincze, L.; Friesen, D. A.; Mezyk, S. P.; Waltz, W. L. *Inorg. Chem.* **1992**, *31*, 4950.
(20) Friesen, D. A.; Lee, S. H.; Lilie, J.; Waltz, W. L.; Vincze, L. *Inorg. Chem.* **1991**, *30*, 1975.
(21) Poon, C. K.; Pun, K. C. *Inorg. Chem.* **1980**, *19*, 568.
(22) Kane-Maguire, N. A. P.; Bennett, J. A.; Miller, P. K. *Inorg. Chim. Acta* **1983**, *76*, L123.

propylene carbonate). The degree of deoxygenation was checked by measuring the emission lifetimes at various bubbling times; constancy in lifetimes signaled efficient deoxygenation. As a further check, an aqueous solution of the trans complex was deaerated with several freeze−pump−thaw cycles under vacuum. In this case, lifetimes at room temperature achieved with 30−40 min of argon bubbling were the same as those obtained by eight freeze−pump−thaw cycles.

Spectroscopic and Time-Resolved Methods. IR absorbance spectra were obtained using a Bio-Rad FTS-40 FTIR with a TGS detector. For diffuse-reflectance IR spectra of the powder, a diffuse-reflectance assembly was used, with the sample being mixed with finely ground KBr powder before taking the spectrum. Solution IR absorbance spectra were obtained using a Buck Scientific attenuated-reflectance assembly with a ZnSe crystal and were solvent-subtracted. UV−visible absorption spectra were recorded with a Cary 2315 spectrophotometer. Steady-state emission spectra were obtained with a Spex Fluorolog 222 spectrofluorometer in photon-counting mode with RCA C31034 PMT detection. Emission quantum yields were determined using the method of Demas and Crosby for optically dilute solutions.[23] The reference was a dilute acidic aqueous solution of $[Cr(NH_3)_6]^{3+}$, for which $\phi_{em} = 5.5 \times 10^{-5}$ at 22 °C.[24]

Excitation at 484 nm for the time-resolved emission measurements was obtained by pumping a methanol solution of LD 490 dye (Exciton) by the output from a XeCl excimer laser (Lumonics HyperEX-400, $\lambda_{lase} = 308$ nm, 20 ns width). Sample emission between 730 and 740 nm was collected at right angles to the excitation pulse and was detected by a Hamamatsu R928 PMT after passing through a Corning CS 2-64 glass filter (to cut off stray light below 600 nm) and a Bausch & Lomb monochromator (model 33-86-77). Emission decays were recorded with a Tektronix 7D20 digitizer, which was interfaced to a PC. All emission decays showed satisfactory fits to a single-exponential function. Sample temperatures were controlled with a Polyscience 9000 constant-temperature circulator (±0.2 °C) and were monitored with a Fluka 51 K/J digital thermometer.

Irradiation at 436 nm for the photochemical experiments was provided by a 1000 W Hg (Xe) lamp (Oriel) in combination with a 0.1 M $CuSO_4$ solution filter, CS 0-52 and CS 3-75 cutoff filters, and a Bausch & Lomb H9-436 interference filter. Irradiation was also provided in some cases by the XeCl excimer−LD 490 dye laser combination noted above. Actinometry was performed using the reineckate procedure.[25,26] For photochemical quantum yield determinations, the released thiocyanate ions were detected spectrophotometrically using literature procedures.[26−29] Aliquots of irradiated solutions (5 mL) were diluted to 50 mL with acidic (0.5 M $HClO_4$) aqueous solutions of ferric nitrate (0.1 M). The absorbance at 450 nm was measured and subtracted from that of a parallel solution kept in the dark. The concentration of photoreleased NCS^- was calculated using a value of 4260 M^{-1} cm^{-1} for the molar absorptivity of $FeSCN^{2+}$ in an aqueous solution at 450 nm.[30] Changes in the solution pH were monitored with a Fisher AccupHast combination electrode connected to an Orion 801A pH meter.

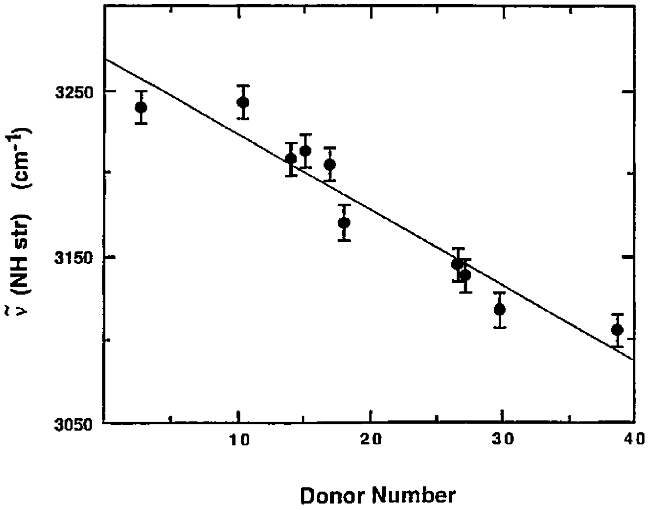

Figure 1. Wavenumber of ν(NH) vs solvent donor number for *trans*-$[Cr(cyclam)(NCS)_2]^+$ at room temperature. Slope of line = 4.52 cm^{-1} ($r^2 = 0.916$).

Results

The solid-state diffuse-reflectance IR spectrum of *trans*-$[Cr(cyclam)(NCS)_2]^+$ is similar to those previously reported for thiocyanatochromium(III) complexes.[31−33] Absorptions corresponding to the cyclam NH stretching vibrations [ν(NH)] occur at 3211 and 3155 cm^{-1}, while the intense thiocyanate CN stretch [ν(CN)] appears at 2069 cm^{-1}. In solution, the ν(NH) absorptions are broadened (full width at half-maximum >100 cm^{-1}) so that only one peak is observed. The wavenumber of the ν(NH) absorption maximum correlates strongly with the Gutmann donor number (an empirical measure of the solvent electron-donating ability[34−36]), as shown in Figure 1 and Table 1.[37] Correlations of the NH stretching frequency with the donor number, which are due to solvent−donor interactions with ammine ligands, have also been noted for $[Cr(NH_3)_6]^{3+}$ and for *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$.[19,38]

The energy of the prominent ν(CN) absorption of the thiocyanato ligand is also solvent-dependent. We attempted

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(23) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.
(24) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887.
(25) Demas, J. N. In *Creation and Detection of the Excited State*; Ware, W. R., Ed.; Marcel Dekker: New York, 1976; Vol. 4, Chapter 1.
(26) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.
(27) Forster, L. S.; Vandermark, J.; Rund, J. V. *Inorg. Chim. Acta* **1992**, *202*, 141.
(28) Cusumano, M.; Langford, C. H. *Inorg. Chem.* **1978**, *17*, 2222.
(29) Sastri, V. S.; Henwood, R. W.; Behrendt, S.; Langford, C. H. *J. Am. Chem. Soc.* **1972**, *94*, 753.
(30) Lee, S. H. Ph.D. Dissertation, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, 1985.
(31) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.
(32) Bailey, R. A.; Kozak, S. L.; Michelsen, T. W.; Mills, W. N. *Coord. Chem. Rev.* **1971**, *6*, 407.
(33) Hughes, M. N.; McWhinnie, W. R. *J. Chem. Soc. A* **1967**, 592.
(34) This scale has been proposed on the basis of adduct formation between the molecule of interest and $SbCl_5$ in an inert medium (1,2-dichloroethane). The donor number is defined as the enthalpy of this reaction multiplied by −1.
(35) Gutmann, V. *Electrochim. Acta* **1976**, *21*, 661.
(36) Gutmann, V.; Wychera, E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 257.
(37) The energy of the absorption maximum for the complex in D_2O is plotted assuming a donor number of 18.0 (the value for H_2O) because the strong OH band of H_2O obscures the cyclam NH stretching peaks in this solvent. It is assumed that the donor numbers of H_2O and D_2O should be similar because replacement of H by D should not affect greatly the electron-donating ability of the O lone pairs.
(38) Friesen, D. A.; Lee, S. H.; Nashiem, R. E.; Mezyk, S. P.; Waltz, W. L. *Inorg. Chem.* **1995**, *34*, 4026.
(39) Snyder, L. R. *J. Chromatogr. Sci.* **1978**, *16*, 223.
(40) Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum: New York, 1978.

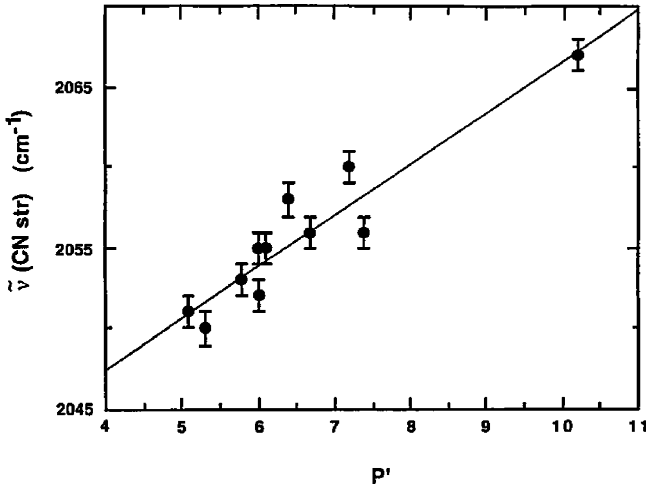

Figure 2. Wavenumber of ν(CN) vs P' at room temperature. Slope of line = 3.21 cm^{-1} (r^2 = 0.891).

Table 1. IR Absorption Data for *trans*-[Cr(cyclam)(NCS)$_2$]$^+$ at 23 °C[a]

	solvent scales[39,40]		wavenumber of the absorption maximum	
	donor number	P'	ν(NH) (±10 cm^{-1})	ν(CN) (±1 cm^{-1})
nitromethane	2.7	6.0	3239	2052
ACAN	10.5		3243	2053
acetonitrile	14.1	5.8	3208	2053
PC	15.1	6.1	3213	2055
acetone	17.0	5.1	3205	2051
H_2O	18.0	10.2	3170	2067
methanol	19.0	5.1		2051
NMF		6.0		2055
DMF	26.6	6.4	3145	2058
NMP	27.3	6.7	3138	2056
DMSO	29.8	7.2	3118	2060
pyridine	33.1	5.3		2050
HMPA	38.8	7.4	3105	2056

[a] Solvent abbreviations: ACAN, acetic anhydride; PC, propylene carbonate; NMF, *N*-methylformamide; DMF, *N*,*N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethyl sulfoxide; HMPA, hexamethylphosphoramide.

to correlate the wavenumber of the CN stretch with more than 30 solvent scales (including the donor number),[41,42] but the best correlation was an increase in the wavenumber of ν(CN) with increases in Snyder's solvent strength scale (P'), a measure of the solvent polarity (Figure 2 and Table 1).[39,43,44] Thus, the cyclam ligand and the thiocyanate ligands respond differently to the presence of solvent molecules.

This complex displays absorption bands in the UV−visible region typical of Cr(III) complexes (Figure 3). A ligand-field d−d absorption is observed at 482 nm in an aqueous solution (ϵ = 87 M^{-1} cm^{-1}), corresponding in O_h microsymmetry to the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition. Under the reduced symmetry of these complexes, this transition splits into two components;[45] however, this splitting is barely apparent because the higher energy $^4B_{2g} \leftarrow {}^4B_{1g}$ band is swamped by the more intense $^4E_g \leftarrow {}^4B_{1g}$ peak. More intense absorptions in the near-UV region are assigned to ligand-to-metal charge-transfer (LMCT) transitions that have been observed for chromium(III) isothiocyanates.[46−48] The lower-energy peak for *trans*-[Cr(cyclam)(NCS)$_2$]$^+$ (at 310 nm in H_2O) represents electron transfer from a ligand-based orbital of mainly π character to a metal-based t_{2g} orbital.[45,48,49] Table 2 shows that the energy of this absorption is solvent-dependent. Notably, the wavenumber of the absorption maximum is well-correlated with the ν(CN) wavenumber, as shown in Figure 4.

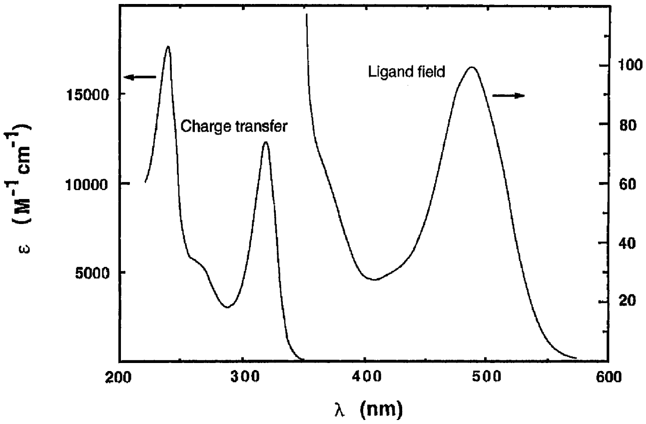

Figure 3. UV−visible absorption spectrum for *trans*-[Cr(cyclam)(NCS)$_2$]$^+$ in methanol.

Absorption and emission, representing spin-forbidden transitions between the ground quartet state and the lowest-energy excited doublet state, are observed above 700 nm (Figure 5). These show some vibrational structure, although the features are much less distinct than those for the amine analogue *trans*-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$.[19] The emission is relatively weak in deaerated H_2O (ϕ_{em} = 0.0045), as is observed for many other Cr(III) complexes.[24] The vibrational structure shows a modest mirror-image relationship, and the 0−0 transition was assigned based on the coincidence of a resolved band in the emission and absorption spectra (13 650 ± 10 cm^{-1} for absorption and 13 610 ± 10 cm^{-1} for emission in acidified H_2O). In contrast to *trans*-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$, the 0−0 band is the most intense emission peak. The shoulder in the region 200−260 cm^{-1} from the 0−0 band represents CrN skeletal vibrations, as has been noted for the diammine analogue.[19,50] The peak at 460−520 cm^{-1} from the 0−0 band corresponds to the δ(NCS) vibration of the thiocyanato ligand. Other features (between 700 and 2100 cm^{-1} from the 0−0 position) are less resolved. The energies of the 0−0 bands for emission and absorbance both show a positive correlation with the ν(CN) wavenumber of the NCS$^-$ ligand, as shown in Figure 6 for emission.

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(41) Griffiths, T. R.; Pugh, D. C. *Coord. Chem. Rev.* **1979**, *29*, 129.
(42) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.
(43) Snyder, L. R. *J. Chromatogr.* **1974**, *92*, 223.
(44) This scale is based on the sum of the logarithms of corrected gas−liquid partition coefficients of ethanol, dioxane, and nitromethane in the solvent of interest.
(45) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 1984.
(46) Nakano, M.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3563.
(47) Sandrini, D.; Gandolfi, M. T.; Moggi, L.; Balani, V. *J. Am. Chem. Soc.* **1978**, *100*, 1463.
(48) Schmidtke, H.-H. *Ber. Bunsen-Ges.* **1967**, *71*, 1138.
(49) Jørgensen, C. K. *Prog. Inorg. Chem.* **1970**, *12*, 101.
(50) Kirk, A. D.; Güdel, H. U. *Inorg. Chem.* **1992**, *31*, 4564.

Table 2. UV−Visible Absorption and Emission Data for *trans*-$[Cr(cyclam)(NCS)_2]^+$ at 23 °C[a]

	wavenumber of the absorption maximum			
	LMCT ($\pm$40 cm^{-1})	d−d ($\pm$30 cm^{-1})	spin-forbidden ($\pm$10 cm^{-1})	wavenumber of the emission maximum ($\pm$10 cm^{-1})
nitromethane		20 590 (107)	13 534	13 501
ACAN	31 370 (14 060)	20 540 (105)		13 515
acetonitrile	31 510 (13 690)[b]	20 640 (101)	13 557	13 530
PC		20 630 (104)	13 565	13 530
acetone		20 580 (101)	13 563	13 526
H_2O	32 300 (9 810)[c]	20 760 (87)	13 654	13 611
methanol	31 410 (12 300)[d]	20 530 (100)	13 569	13 528
NMF	31 570 (12 990)	20 550 (98)	13 576	13 559
DMF	31 730 (12 330)	20 580 (93)	13 609	13 561
NMP	31 690 (12 590)	20 580 (94)	13 594	13 583
DMSO	31 870 (12 280)	20 570 (89)	13 624	13 589
pyridine		20 500 (91)		13 492
HMPA		20 510 (87)	13 613	13 574

[a] Values for molar absorptivity (ϵ_{max}) are given in parentheses. [b] Bands at higher energy: 41 980 cm^{-1} (ϵ = 18 860 M^{-1} cm^{-1}) and shoulder 38 260 cm^{-1} (ϵ = 5610 M^{-1} cm^{-1}). [c] Band at higher energy: 43 100 cm^{-1} (ϵ = 18 890 M^{-1} cm^{-1}). [d] Bands at higher energy: 41 910 cm^{-1} (ϵ = 17 740 M^{-1} cm^{-1}) and shoulder 37 910 cm^{-1} (ϵ = 5620 M^{-1} cm^{-1}).

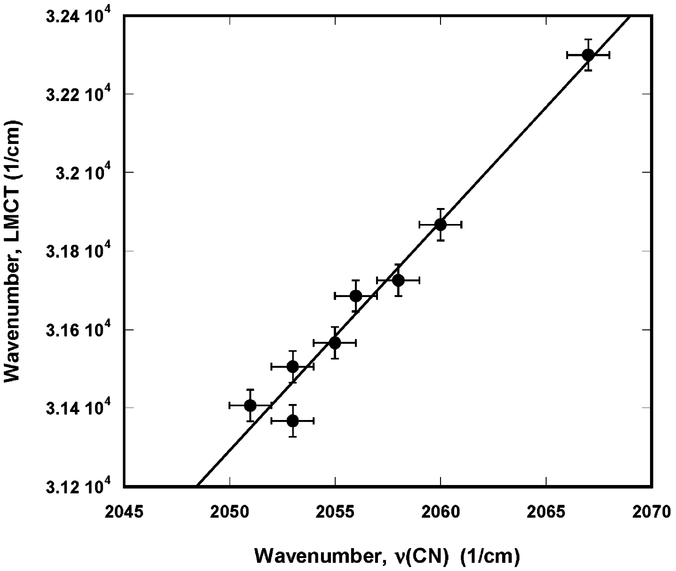

Figure 4. Plot of the wavenumber of the LMCT absorption maximum vs wavenumber of the CN stretch at 23 °C. Slope of line = 58.3 (r^2 = 0.971).

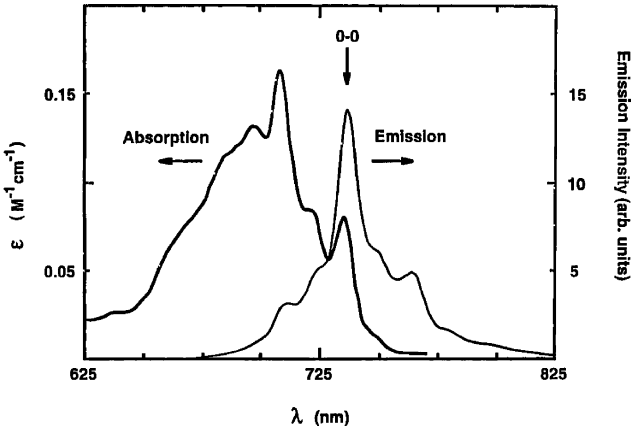

Figure 5. Emission and absorption spectra in the doublet region for *trans*-$[Cr(cyclam)(NCS)_2]^+$ in an aqueous solution at room temperature. Conditions for emission: [Cr] = 2.5 mM; solvent = 0.001 M aqueous $HClO_4$; Ar(g)-saturated solution; excitation wavelength = 482 nm. Conditions for absorption: [Cr] = 4.16 mM; 10 cm path length cell; solvent = 0.01 M aqueous $HClO_4$; aerated solution.

The decay of the emission, corresponding to the doublet state → ground quartet state transition, displays single-exponential behavior in time-resolved emission studies with an observed lifetime (τ_{obs}) of 182 μs in a 25 °C Ar-saturated aqueous solution. The emission lifetime is sensitive to the presence of dissolved O_2; for example, τ_{obs} is 3.7 and 220 μs in O_2- and Ar-saturated CH_3CN solutions of the complex, respectively. The oxygen sensitivity is in contrast to *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ but is consistent with observations for other Cr(III) complexes possessing unsaturated ligands such as bipyridine.[28,51−58] Time-resolved emission studies of O_2-saturated acetonitrile solutions of *trans*-$[Cr(cyclam)(NCS)_2]^+$ have indicated that singlet oxygen $[^1\Delta_g(O_2)]$ forms as a result of the quenching process.[59] It has been shown that Cr(III) species with π-electron density on the coordinated ligand ("conducting ligands" such as NCS^-) may allow interactions with O_2, leading to energy transfer.[56]

The temperature dependence of the doublet-state lifetime displays two main regions, which are typical of Cr(III) complexes. As shown in Figure 7, the observed doublet decay rate constant k_{obs} ($=\tau_{obs}^{-1}$) consists of a nearly temperature-independent region at lower temperatures and a strongly temperature-dependent region at higher temperatures. In the

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(51) Jamieson, M. A.; Serpone, N.; Hoffman, M. Z. *Coord. Chem. Rev.* **1981**, *39*, 121.
(52) Kirk, A. D.; Namasivayam, C.; Riske, W.; Ristic-Petrovic, D. *Inorg. Chem.* **1989**, *28*, 972.
(53) Kirk, A. D.; Namasivayam, C. *Inorg. Chem.* **1988**, *27*, 1095.
(54) Serpone, N.; Jamieson, M. A.; Hoffman, M. Z. *Inorg. Chim. Acta* **1978**, *31*, L447.
(55) Brunschwig, B.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 7568.
(56) Pfeil, A. *J. Am. Chem. Soc.* **1971**, *93*, 5395.
(57) Serpone, N.; Jamieson, M. A.; Sriram, R.; Hoffman, M. Z. *Inorg. Chem.* **1981**, *20*, 3983.
(58) Sriram, R.; Hoffman, M. Z.; Jamieson, M. A.; Serpone, N. *J. Am. Chem. Soc.* **1980**, *102*, 1754.
(59) Nashiem, R. E. Ph.D. Dissertation, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, 1999.

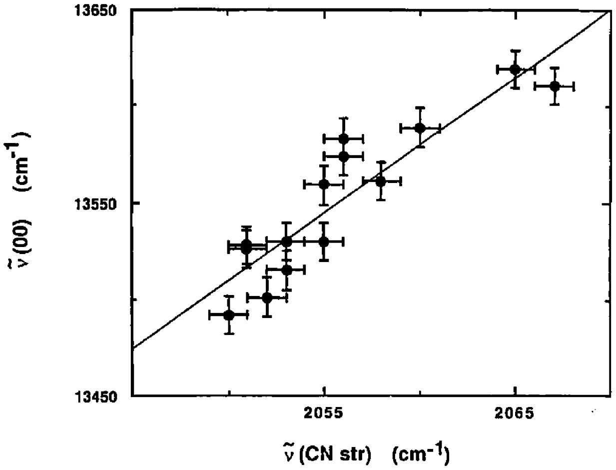

Figure 6. Plot of the wavenumber of the emission 0−0 band vs ν(CN) wavenumber. Slope of line = 7.07 (r^2 = 0.826).

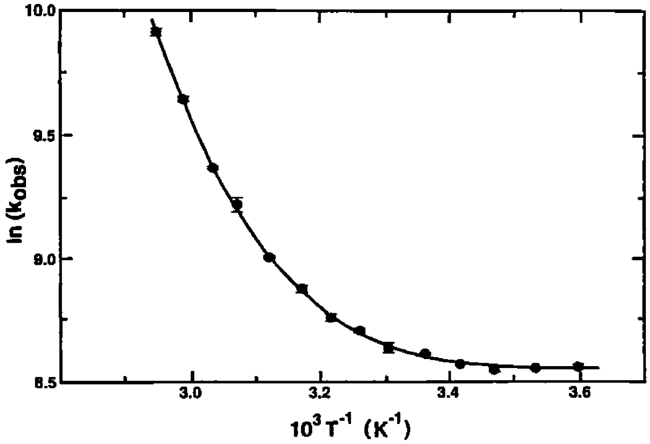

Figure 7. Temperature dependence of rate constant k_{obs} for doublet-state decay in an aqueous solution (0.015 M $HClO_4$). Conditions: [Cr] = 0.247 mM; λ_{ex} = 484 nm; λ_{em} = 735 nm; deoxygenated solution.

Table 3. Temperature Dependence of the Emission Decay, Fitted to Eq 1, $k_{obs} = k_0 + A\exp(-E_a/RT)$[a]

solvent	ln(A)	E_a (kJ mol^{-1})	$10^{-3}k_0$ (s^{-1})
acetonitrile	20.3 ± 0.7	36.4 ± 1.8	4.43 ± 0.05
nitromethane	23.0 ± 0.4	42.7 ± 1.0	6.01 ± 0.05
PC	25.8 ± 0.6	49.8 ± 1.7	5.19 ± 0.06
ACAN[b]	29.7 ± 0.1	50.5 ± 0.4	
pyridine	27.9 ± 0.6	52.3 ± 1.7	6.15 ± 0.20
NMF	32.5 ± 0.4	66.8 ± 1.2	5.48 ± 0.06
DMSO	33.1 ± 0.5	68.7 ± 1.4	5.56 ± 0.08
HMPA	34.6 ± 0.8	74.4 ± 2.2	5.72 ± 0.02
H_2O	36.8 ± 0.4	76.5 ± 1.0	5.14 ± 0.04
NMP	35.5 ± 0.7	77.1 ± 1.8	5.46 ± 0.02
DMF	35.6 ± 0.6	77.4 ± 1.5	5.37 ± 0.01
acetone[c]			4.70 ± 0.04
methanol[c]			5.70 ± 0.03

[a] [Cr] = 0.25 mM for all solutions. Temperature range = 4−66 °C, except acetonitrile (4−49 °C); pyridine and HMPA (10−66 °C); DMSO (20−66 °C); acetone (4−25 °C); methanol (4−30 °C). [b] Not enough points in the "low-temperature" region to determine k_0. [c] Not enough points in the "high-temperature" region to determine A and E_a.

Table 4. Concentration Dependence of the Emission Decay at 19.5 °C[a]

solvent	bp (K)[b]	η (cP)[c]	$10^{-3}k_n$ (s^{-1})	$10^{-5}k_q$ (M^{-1} s^{-1})
acetonitrile	354.8	0.358	4.47 ± 0.04	6.0 ± 0.3
acetone	329.2	0.320	4.53 ± 0.05	4.6 ± 0.4
nitromethane	374.4	0.647	6.11 ± 0.03	3.5 ± 0.3
H_2O	373.2	1.002	5.22 ± 0.02	3.3 ± 0.2
methanol	337.7	0.593	5.62 ± 0.02	3.0 ± 0.2
NMF	458	1.82	5.65 ± 0.03	1.6 ± 0.2
DMSO	462.2	2.216	5.72 ± 0.02	1.0 ± 0.1
NMP	475	1.666[d]	5.51 ± 0.02	0.6 ± 0.2
PC	514.9	2.76	5.45 ± 0.04	0.4 ± 0.2
DMF	426.2	0.924	5.41 ± 0.01	0.3 ± 0.1
HMPA	506	3.47	5.77 ± 0.02	0.0 ± 0.1

[a] Conditions: [Cr] range = 0.25−2.0 mM; λ_{ex} = 484 nm; λ_{em} = 735−740 nm. Values were calculated from $k_{obs} = k_n + k_q$[Cr]. [b] Boiling points at 1 atm.[60] [c] Viscosity coefficient values at 20 °C;[60] in some cases, these are values interpolated from those recorded for 15 and 25−30 °C. [d] η at 25 °C.

present study, the data show a satisfactory fit to the sum of a single-exponential function and a constant (eq 1).

$$k_{obs} = Ae^{-E_a/RT} + k_0 \qquad (1)$$

Values for E_a, A, and k_0 are given for various deoxygenated solvents in Table 3. All of these parameters are solvent-dependent, especially A and E_a. The lifetimes are also dependent on the concentration of the complex, with k_{obs} increasing in a linear fashion with the concentration of the complex ($k_{obs} = k_n + k_q$[trans complex]; Table 4). The values for k_q roughly correlate with the solvent boiling point and coefficient of viscosity, with a decrease in k_q being approximately parallel to an increase in the boiling point and viscosity coefficient, although k_q values are well below those expected for diffusion-controlled processes.

In contrast to many chromium(III) amine complexes, which show appreciable photosubstitutional quantum yields, *trans*-[Cr(cyclam)(NCS)$_2$]$^+$ shows a much decreased photoreactivity in 0.001 M $HClO_4$, similar to the cases for *trans*-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$ and *trans*-[Cr(cyclam)(CN)$_2$]$^+$.[18,61] At 22 °C, the quantum yield for thiocyanate release [ϕ_{rx}(NCS)] with 437 nm irradiation is ≤0.002, without a marked dependence on the presence of dissolved O_2. Time-resolved conductivity measurements at the same temperature have shown a prompt (τ < 1 μs) increase in conductivity upon pulsed irradiation of the ligand-field band in the visible region (530 nm) but *no further change* on the time scale of the decay of the doublet state.[62] This suggests that at this temperature the small amount of chemical reaction may proceed through a nascently populated Franck−Condon quartet state ("prompt reaction"), but the doublet state is photoinert. At 54 °C (where the higher-temperature region is dominant), ϕ_{rx}(NCS) is still minor (<0.02) upon ligand-field irradiation at 484 nm. Upon prolonged broad-band (310−640 nm) irradiation of pH 3 solutions of the complex, a small decrease in the solution pH is observed. This increase in the proton concentration is not supportive of heterolytic Cr−cyclam bond breakage with subsequent protonation of the free N atoms. It is, however, consistent with replacement of a thiocyanato ligand by a H_2O molecule, which subsequently releases a proton in an acid−base equilibrium

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(60) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.

(61) Kane-Maguire, N. A. P.; Crippen, W. S.; Miller, P. K. *Inorg. Chem.* **1983**, *22*, 696.

(62) Waltz, W. L.; Lilie, J., unpublished data.

reaction. Supportive of this interpretation is that *trans*-$[Cr(cyclam)(H_2O)_2]^{3+}$ has a pK_a for proton dissociation of approximately 3.05.[63]

Discussion

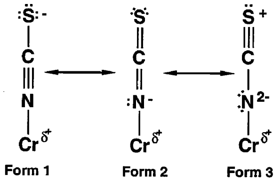
The foregoing kinetic and spectroscopic results bring forth the salient roles of environmental parameters (solvent, temperature, and O_2) influencing the photobehavior of the complex. For *trans*-$[Cr(cyclam)(NCS)_2]^+$, we can observe the effects of solvent interactions on two different types of ligands: the saturated cyclam ligand (in particular, the NH entities, which are directly bound to the Cr(III) center) and the unsaturated thiocyanate ligands (which are N-bound to the Cr(III) center).[64]

Solvent Effects on Spectroscopic Features. The correlation of the cyclam NH stretching frequency ν(NH) with the donor number for *trans*-$[Cr(cyclam)(NCS)_2]^+$ indicates that electron-pair donation from the solvent to the NH entities is substantial, as we also observed for *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ and $[Cr(NH_3)_6]^{3+}$.[19,38] According to the Gutmann bond-length variation rules, donation of electron density to the amine proton should weaken the NH bond and decrease the ν(NH) frequency.[40] This is confirmed by our data (Figure 1). Previous studies with *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ have also shown that there is an increase in the frequency of the Cr−N vibrational modes of these complexes, which is also consistent with the Gutmann model.[19,38] However, the decreased resolution of the emission spectrum did not allow us to investigate this aspect for *trans*-$[Cr(cyclam)(NCS)_2]^+$.

The uncomplexed thiocyanate anion is known to be sensitive to its environment, with the frequency of the NCS^- vibrational modes being solvent- and counterion-dependent, and they are especially influenced by adsorption of the ion onto surfaces.[31,32,65−72] The present work shows that NCS^- bound to a metal center is also remarkably sensitive to the nature of the solvent. The environmental dependence of the thiocyanate anion has been explained both by a simple valence-bond model[32,68] and by ab initio calculations.[69,70] Both models predict that the CN bond order, and therefore the ν(CN) frequency, increases when a more negative partial charge is present on the S atom of the NCS^- anion.

In valence-bond terms, the unsaturated thiocyanate anion can be represented as a resonance of canonical forms, each contributing a certain "percentage" of their character to the actual electron distribution of the anion (Scheme 2).[32,65,66] For uncomplexed thiocyanate, the triply bonded CN species (form 1) is considered to be the principal contributor;[32] however, coordination appears to favor increased contributions from the other resonance structures (i.e., forms 2 and 3).[31,32,65,66,73−75] Our results are consistent with this view. The solvents of high polarity (as measured by solvent strength P') stabilize enhanced electron density on the S atom. In turn, this increases the relative contribution of form 1 (increased CN bond order), as shown by increases in the ν(CN) wavenumber with increases in P' of the solvent (Figure 2).

Scheme 2



This qualitative picture also helps to explain the strong correlation between the wavenumber of the LMCT absorption and the wavenumber of the thiocyanato CN stretch, demonstrated in Figure 4. Here, the stabilization of additional electron density on the S atom with increasing solvent polarity decreases the electron density at the N atom. This makes the NCS^- ligand less prone to oxidation, thus shifting the LMCT maximum to higher frequencies.

In a related manner, the energy of the spin-forbidden 0−0 transition, as shown in Figure 6, also increases with increases in the ν(CN) wavenumber. The energy gap of the 0−0 transition depends strongly on the Racah electron repulsion parameters.[45,76,77] The decreased electron density at the N atom of Cr−NCS in high-polarity solvents gives decreasing electron delocalization in the Cr−N sphere. This shift will increase the interelectronic repulsion, thus increasing the energy of the 0−0 transition.

Solvent Effects on Photophysics. The low photochemical quantum yield for *trans*-$[Cr(cyclam)(NCS)_2]^+$ is a feature common to *trans*-$[Cr(cyclam)X_2]$ complexes, due partly to their stereochemistry.[18,61,78,79] The macrocyclic cyclam ligand inhibits trans to cis isomerization; by contrast, such isomerization generally occurs for nonmacrocyclic chromium(III) ammonia and ammine complexes.[8,12] The insignificant role of photochemistry here allows us to focus on the effects of solvent and temperature on the nonchemical aspects of the excited-state decay.

A potentially complicating feature is that the decay of the doublet electronically excited state is, in part, quenched by the ground-state form of *trans*-$[Cr(cyclam)(NCS)_2]^+$, and

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(63) Ferguson, J.; Tobe, M. L. *Inorg. Chim. Acta* **1970**, *4*, 109.

(64) Friesen, D. A.; Quail, J. W.; Waltz, W. L.; Nashiem, R. E. *Acta Crystallogr.* **1997**, *C53*, 687.

(65) Norbury, A. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 231.

(66) *Chemistry of Pseudohalides*; Golub, A. M., Kohler, H., Skopenko, V. V., Eds.; Elsevier: Amsterdam, The Netherlands, 1986; Chapter 5.

(67) Tadayyoni, M. A.; Farquharson, S.; Li, T. T.-T.; Weaver, M. J. *J. Phys. Chem.* **1984**, *88*, 4701.

(68) Chabanel, M.; Bencheikh, A.; Puchalska, D. *J. Chem. Soc., Dalton Trans.* **1989**, 2193.

(69) Schultz, P. W.; Leroi, G. E.; Harrison, J. F. *Mol. Phys.* **1996**, *88*, 217.

(70) Tielens, F.; Saeys, M.; Tourwe, E.; Marin, G. B.; Hubin, A.; Geerlings, P. *J. Phys. Chem. A* **2002**, *106*, 1450.

(71) Gonnissen, D.; Langenaeker, W.; Hubin, A.; Geerlings, P. *J. Raman Spectrosc.* **1998**, *29*, 1031.

(72) Li, X.; Gewirth, A. A. *J. Am. Chem. Soc.* **2003**, *125*, 11674.

(73) Takeuchi, Y.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 319.

(74) Fujita, J.; Nakamoto, K.; Kobayashi, M. *J. Am. Chem. Soc.* **1956**, *78*, 3295.

(75) Forster, D.; Horrocks, W. D., Jr. *Inorg. Chem.* **1967**, *6*, 339.

(76) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North Holland: Amsterdam, The Netherlands, 1971.

(77) Perumareddi, J. R. *Coord. Chem. Rev.* **1969**, *4*, 73.

(78) Kutal, C.; Adamson, A. W. *Inorg. Chem.* **1973**, *12*, 1990.

(79) Kane-Maguire, N. A. P.; Wallace, K. C.; Speece, D. G. *Inorg. Chem.* **1986**, *25*, 4650.

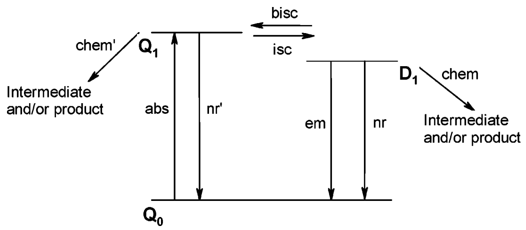

Figure 8. Simplified state diagram for a Cr(III) complex. The ground state is Q_0, and the lowest excited quartet and doublet states are Q_1 and D_1, respectively.

thus $k_{obs} = k_n + k_q[Cr]$, with the values of k_n and k_q being given in Table 4. In all studies of the temperature dependence of k_{obs} (Table 3), the concentration of the complex was 0.25 mM. At this concentration, analysis of the relative contributions of the two terms (k_n amd k_q[Cr]) to k_{obs} shows that the term k_q[Cr] is a minor contributor (<5% of k_{obs}) in all solvents studied. Therefore, we have taken the k_n value to be effectively that of k_{obs} in our discussions below of the effects of different solvents and temperatures. Of further note is that the values of the quenching constant k_q are many powers of 10 below those expected of diffusion-controlled reactions. Consequently, to what degree the quenching is a collisional process versus a static mechanism is unknown; however, the increased k_q values with the solvent boiling point and viscosity point to some possible collisional contribution. Variations of added perchlorate in methanol and DMF (15−30 mM) and in DMSO and H_2O (0.25−15 mM) had no effect on the k_q values, and such indicates, under our conditions, that it is unlikely that ion pairing plays a significant role.

Concentration-dependent lifetimes have also been observed for chromium(III) polypyridyl complexes, although the values for k_q are 1−3 orders of magnitude greater than those for *trans*-[Cr(cyclam)(NCS)$_2$]$^+$.[57,58] The mechanism is not known because emission corresponding to excimer formation is not observed;[80,81] however, the possibility cannot be ruled out. In any case, the presence of unsaturated ligands (NCS$^-$ or polypyridyls) may be important for effective interaction between the excited- and ground-state complexes. This is supported by a recent study that determined that the energy-transfer rate between protiated and deuterated *trans*-[Cr(cyclam)(CN)$_2$]$^+$ was much greater than that for the related complex *trans*-[Cr(tet a)F$_2$]$^+$.[82] This was attributed to electronic factors related to the interaction between energy donor−acceptor pairs (possibly a greater nephelauxetic effect for CN$^-$).

Absorption of visible light (350−550 nm) by the complex leads initially to vibronically excited levels of the excited quartet state (Figure 8). From the time-resolved conductivity results, a small fraction of the complexes undergoes photosubstitution, and this occurs just after laser excitation, so it likely arises from the nascent Franck−Condon excited state. This very quick change and the low overall photochemical quantum yields measured under steady-state conditions indicate that the major fraction of the system proceeds to the doublet state via intersystem crossing (isc). The isc yield here could approach unity, as was found for the congener *trans*-[Cr(cyclam)(CN)$_2$]$^+$.[83]

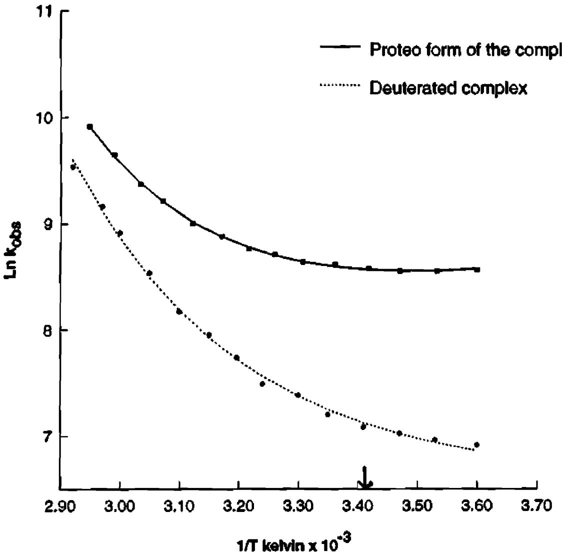

Figure 9. Comparison of the temperature dependence of k_{obs} for *trans*-[Cr(cyclam)(NCS)$_2$]$^+$ and *trans*-[Cr(cyclam-D$_4$)(NCS)$_2$]$^+$ in a deoxygenated acidic aqueous solution. The arrow corresponds to a temperature of 20 °C (figure from ref 59).

As shown in Figure 8, the long-lived doublet state can potentially exhibit several competitive decay routes: emissive (em), nonradiative (nr), and photochemical (chem). For our case, the photochemical contribution is negligible. Furthermore, the low emission quantum yield and long lifetime show (via the relationship $\phi_{em}\tau_{obs} = \eta_{isc}k_{em}$) that k_{em} is likely in the neighborhood of 20−30 s^{-1} in acidified H_2O at 22 °C. By contrast, the observed rate constant at the same temperature for doublet state decay is 5.3×10^3 s^{-1} in a deoxygenated acidified aqueous solution so the emissive pathway is also a very minor contributor. Therefore, the major decay pathway for the lowest doublet excited state must be nonradiative and nonchemical in nature.

The biphasic temperature dependence of the doublet-state lifetime is shown in Figure 7. The nearly temperature-independent component at lower temperatures (represented in eq 1 as "k_0") can be assigned to a weakly coupled nonradiative decay between the undistorted doublet and quartet ground states.[4,6,19] For the weakly coupled route, the decay rate constant depends on the frequencies of the high-energy accepting modes and on the energy gap between the excited doublet state and ground quartet state. For chromium(III) amine complexes, the NH stretching modes have been shown to act as the accepting modes.[4,6] Consistent with this interpretation, deuteration of the cyclam NH bonds leads to a marked increase in the emission lifetime below room temperature (Figure 9).[59]

Values for k_0 in the different solvents studied range between 4400 and 6200 s^{-1} (Table 3). They do *not* correlate with just any one parameter, neither the NH stretching

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(80) Farley, S. J.; Rochester, D. L.; Thompson, A. L.; Howard, J. A. K.; Williams, J. A. G. *Inorg. Chem.* **2005**, *44*, 9690.

(81) Connick, W. B.; Gray, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 11620.

(82) Wagenknecht, P. S.; Kane-Maguire, N. A. P.; Speece, D. G.; Helwic, N. *Inorg. Chem.* **2002**, *41*, 1229.

(83) Song, X.; Endicott, J. F. *Inorg. Chem.* **1991**, *30*, 2214.

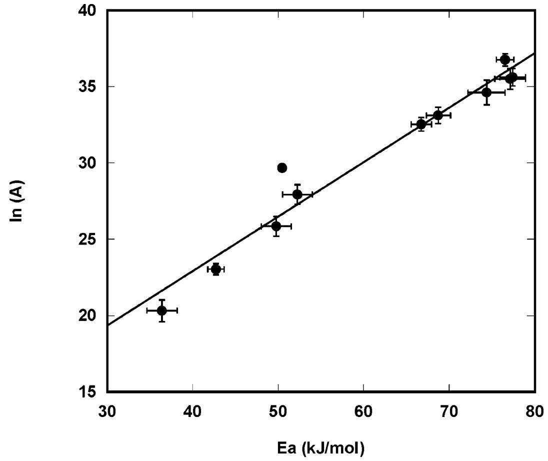

Figure 10. Barclay−Butler plot [ln(A) vs E_a] for *trans*-[Cr(cyclam)(NCS)$_2$]$^+$. Slope of line = 0.357 (r^2 = 0.954).

frequency nor the frequency of the 0−0 transition in the emission spectrum that equals the energy gap between the excited doublet and ground states. Because the rate of weakly coupled nonradiative decay depends *both* on the energy gap between the states (dominated by solvent effects on the NCS$^-$ ligand; Figure 6) and on the frequency of the acceptor modes (influenced by solvent effects on the NH stretches of the cyclam ligand; Figure 1), the absence of a straightforward correlation with either solvent scales or spectroscopic properties of the complex is not surprising.

Strongly temperature-dependent nonradiative decay at higher temperatures can be assigned to a strongly coupled transition, involving crossing from the doublet state either to the lowest excited quartet state or to a ground-state intermediate.[6,17] In this region, the rate constant for doublet-state decay displays Arrhenius-type behavior. The contribution of the strongly coupled decay to k_{obs} is represented as the first term in eq 1.

Fleischauer and co-workers have noted that the energy gap between the ground state and first excited quartet state for Cr(III) complexes can be estimated from the lowest-energy d−d absorption band (i.e., it is empirically related to the energy where absorption is 5% that of the peak maximum).[84] This method applied here provides a value of 19 280 cm^{-1} for the separation between ground and excited quartet states of *trans*-[Cr(cyclam)(NCS)$_2$]$^+$ in acidic aqueous solutions. Using a value of 13 610 cm^{-1} for the gap between the ground state and the excited doublet state (i.e., the energy of the 0−0 band for the emission spectrum in an aqueous solution), the gap between the excited doublet state and the first excited quartet state is estimated as approximately 67 kJ mol^{-1} in an aqueous solution. Thus, thermally activated back-isc to the excited quartet state ("bisc" in Figure 8) appears feasible for strongly coupled decay at higher temperatures because the observed activation energy E_a is ≥67 kJ mol^{-1} for many of the solvents studied here (Table 3). However, for several of the solvents (acetonitrile, nitromethane, propylene carbonate, acetic anhydride, and pyridine), the values for E_a are significantly less (30−45% less) than the energy gap estimated from the Fleischauer procedure. A detailed spectroscopic study for *cis*- and *trans*-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$ shows that the measured difference in energy between the excited quartet and doublet states is also considerably less than that obtained using the Fleischauer method.[50] Thus, our calculated excited quartet−doublet state gap of 67 kJ mol^{-1} for *trans*-[Cr(cyclam)(NCS)$_2$]$^+$ in an aqueous solution is likely an overestimate and should probably be considered as an upper limit. Furthermore, the Barclay−Butler plot of ln(A) vs E_a in Figure 10 lends considerable support to the likelihood for a *common* strongly coupled mechanism applying to the complex in all of the solvents studied here,[85] but the nature of the common mechanism remains an open question. Such may be back-isc to a thexi quartet excited state or surface crossing to a ground-state intermediate; both are known for similar Cr(III) complexes.[20,86]

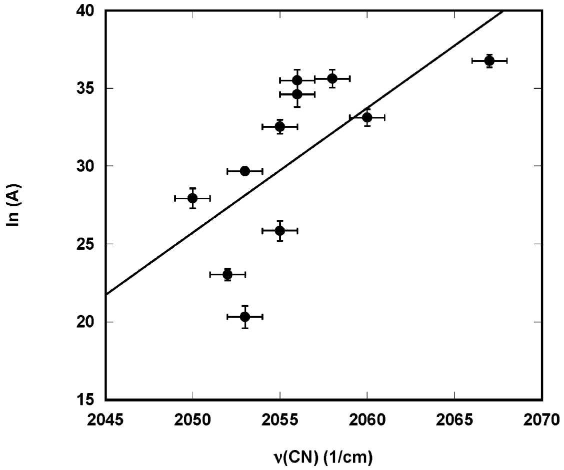

Figure 11. Plot of ln(A) vs ν(CN) wavenumber from data in Tables 1 and 3.

Strongly coupled nonradiative decay has often been interpreted according to the formalism of Englmann and Jortner.[87] In this formalism, the rate of radiationless decay is predicted to display a near-Arrhenius dependence on the temperature, with a preexponential factor that depends on the average frequency of all vibrational modes involved in the transition and an exponential term that depends on both the energy difference between the states involved (i.e., the excited doublet and quartet states) and the average vibrational frequency. As we have shown, solvent influences on these variables for the complex are ligand-dependent [i.e., the correlation of ν(CN) on P' vs the correlation of ν(NH) on the donor number].

Previous studies of the complexes *trans*-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$ and [Cr(NH$_3$)$_6$]$^{3+}$ have established the presence of linear correlations between the natural logarithm of the doublet decay rate constant [ln(k_{obs})] in the high-temperature region and the Gutmann donor number of the solvent.[19,38] These are interpreted as the dominance of a donor-type interaction at the NH bonds, which influenced the frequency

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[84] Fleischauer, P. D.; Adamson, A. W.; Sartori, G. *Prog. Inorg. Chem.* **1972**, *17*, 1.

[85] Li, C.; Hoffman, M. Z. *Inorg. Chem.* **1998**, *37*, 830.

[86] Irwin, G.; Kirk, A. D. *Coord. Chem. Rev.* **2001**, *211*, 25.

[87] Englmann, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145.

of the N−H and Cr−N vibrational modes and thus the nonradiative rate constant. In these cases, only one general type of ligand site (i.e., NH bonds) is readily available for solvent−solute, whereas for *trans*-[Cr(cyclam)(NCS)$_2$]$^+$, two potential sites exist (NH and NCS).

For the isothiocyanate complex, a positive trend between ln(A) [which approaches ln(k_{obs}) at an infinitely high temperature] and the wavenumber of ν(CN) is observed (Figure 11). By contrast, no trend is observed between ln(A) and the frequency of ν(NH), or the donor number. The relationship between ln(A) and ν(CN) (and between E_a and ν(CN) because E_a and ln(A) are correlated; Figure 9) is remarkable. It indicates that solvent effects on the NCS$^-$ ligands (which influence both the vibrational frequencies of the thiocyanato ligand and the energy gap between the quartet and doublet states) play a major role in influencing the rate of the nonradiative decay. Conversely, in this context, solvent effects on the NH sites of the cyclam ligand seem to be inconsequential.

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