Low-Temperature Emission and Absorption Spectra of *trans*- and *cis*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) Salts

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The $^2E_g \leftarrow {}^4A_{2g}$ and $^4T_{2g} \leftarrow {}^4A_{2g}$ electronic absorption spectra of single crystals of *trans*-[Cr(cyclam)(NH$_3$)$_2$](ClO$_4$)$_3$ and the $^2E_g \rightarrow {}^4A_{2g}$ emission spectra of powder samples of *trans*-[Cr(cyclam)(NH$_3$)$_2$](NO$_3$)$_2$(ClO$_4$) and their deuterated analogues have been measured at temperatures down to 5 K. Similar measurements on the cis isomer employed powder samples and KBr pellets of the diperchlorate nitrate. The weak $^2E_g \leftrightarrow {}^4A_2$ electronic origins of the trans complex lie at 14 921 and 14 965 cm^{-1} and move to 14 925 and 14 974 cm^{-1} on deuteration of the am(m)ine groups. For both trans compounds, most of the intensity is in five strong and a number of weaker vibronic origins. In contrast, the cis isomer has a strong electronic origin with weaker vibronic origins and a somewhat larger ^2E splitting of 64 cm^{-1} with the lower energy component at 14 786 cm^{-1}. Neither isomer shows any structure on the quartet absorption bands, but the origin of the $^4T_2 \leftarrow {}^4A_2$ band can be estimated to be close to 18 800 cm^{-1} in both isomers. This leads to solid-state quartet/doublet zero/zero spacings of about 3900 cm^{-1} (~47 kJ mol^{-1}) in the two isomers. The significance of these results for the pathway of reaction and deactivation of the ^2E state is discussed.

Introduction

There has been considerable interest in the photochemical and photophysical properties of complexes with macrocyclic ligands, prominently those of Cr(III).[1-6] Such molecules are being used to explore the effects of ligand constraints and geometry on the photochemistry and the photophysical properties of excited states such as $^4T_2$ and ^2E of Cr(III). Frequently, large ligand effects on doublet lifetimes have been observed, but it has not always been clear whether the origin of these lies in static distortions[6] of the ligand coordination geometry or in dynamic effects[7] associated with the ligand strain that often exists.

The trans and cis isomers of the title compound are an important pair of such complexes. The trans isomer is photochemically inert[2] while the cis isomer photoaquates with a quantum yield of 0.16. The photoinertness of the trans material is particularly striking when viewed in the context of the efficient photochemistry of its non-macrocyclic analogues. This has been considered[2,3,8] as confirming a requirement for stereochemical change to accompany photoreaction.

The title complexes also differ in some characteristics of the doublet state. For example the trans isomer shows a much larger activation energy for the dominant process depopulating the doublet state in competition with radiative decay. Thus, values of 59 and 36 kJ mol^{-1} have recently been reported[1] for the trans and cis isomers, respectively. The trans isomer also contrasts with the cis isomer in showing a significant temperature dependence of the volume of activation for the process deactivating the doublet state, but at 58 °C when the trans complex achieves its ambient temperature limiting value, their volumes of activation are equal. The 7 cm^3 mol^{-1} value for these conditions shows there is a significant increase in volume associated with the route for return to the ground state in both complexes.

These studies of complexes of macrocyclic ligands are useful and important. There are no studies, however, of the effect of such ligands on the high-resolution emission and absorption spectroscopy of such molecules. It therefore remains an open question as to whether they can be expected to be spectroscopically similar to non-macrocyclic analogues[9,10] such as $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$ etc., particularly when recognition is given to the steric distortions that are present at Cr in the cis isomer of the title cation but not in the trans. This study was undertaken to address such questions.

It is also of considerable interest to estimate the low-temperature, solid-state spectroscopic quartet/doublet splittings and to compare these values to the reported activation energies for the temperature dependence of the doublet emission lifetime in solution.[1,2] These, together with the activation volume results,[1] carry important implications regarding the dominant pathways of doublet relaxation. It was therefore an objective of the study to identify the positions of the quartet and doublet states by single-crystal low-temperature emission and absorption spectroscopy. It was recognized, however, that the complexity of the molecules made it probable that the quartet absorption band would not show any resolved vibrational structure to assist in locating the lowest $^4T_2 \leftarrow {}^4A_2$ origin in absorption. Wilson and Solomon reported[11] major problems in finding a crystalline environment for the simpler $Cr(NH_3)_6^{3+}$ that revealed structure in this region.

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Table I. Solution Absorption Spectral Data[a]

compd	${}^4T_{2g}(O_h)$ $\nu(\epsilon)$	${}^4T_{1g}$ $\nu(\epsilon)$	NO_3^- $\nu(\epsilon)$	ref
trans	21.6 (26, sh), 24.0 (30)	29.7 (41)	49.0 (11)	
	22.5 (32, sh), 23.8 (36)	29.9 (50)		2
cis	21.5 (115)	28.1 (80)	49.0 (22)	
	21.4 (115)	28.2 (80)		2

[a] Frequencies in 10^3 cm^{-1}.

Experimental Section

Compounds. *trans*- and *cis*-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$ were prepared and characterized as described in the literature.[2,8] UV–vis spectra discussed later showed that the powder samples consisted of the diperchlorate nitrate of the trans and the monoperchlorate dinitrate of the cis.

Single crystals of the trans isomer were grown by slow evaporation in the dark of a saturated solution of the compound in 0.1 M HClO$_4$. Deuterated crystals were prepared by similar growth from 0.1 M HClO$_4$ solution of the protonated compound in heavy water. KBr pellet infrared spectra of such a crystal showed that the level of N–H deuteration by this simple procedure was better than 95%. Also, the nitrate band at 1308 cm^{-1} was absent, showing that the crystal growth from the perchloric acid medium gave crystals of the triperchlorate. Unfortunately, single crystals of the cis isomer of suitable size and quality for spectroscopy were not formed by similar solution growth procedures.

Spectroscopic Measurements. Powder samples in glass capillaries or single crystals mounted on thin aluminum plates were cooled by helium gas in a flow tube. High-resolution absorption spectra were obtained using a double-beam instrument with tungsten/halogen light source, a Spex 1402 double monochromator, and a Hamamatsu R928 photomultiplier detector, while emission spectra were obtained with a Spex 1402 double monochromator, RCA 31034 GaAs photomultiplier, and photon counting detection (SRI), irradiating with about 40 mW of 457-nm unfocused light from an argon ion laser.

Results

Solution Absorption Spectra. The spectral data are listed and compared with literature values in Table I. Both isomers show three absorption bands in the accessible range. The highest energy band seen at 49 × 10^3 cm^{-1} is at the correct energy[12] for the nitrate ion present in the compounds, and the molar absorptivities found are consistent with the presence of 1 mol of nitrate ion in the trans compound and 2 mol in the cis, supporting the formulations given above.

The lowest energy pair of bands can be assigned as the transitions to the lowest ligand field quartet states on the basis of their positions and intensities. The wavelength maxima of these bands are in agreement with literature values. The molar absorptivities agree for the cis compound, but for the trans they are about 20% lower than reported earlier.[2] The lowest energy band in the trans shows evidence of the usual D_{4h} splitting of ${}^4T_{2g}$ into ${}^4B_{1g}$ and ${}^4E_g$, which appear as the peak at 24.0 × 10^3 and the shoulder at 22.5 × 10^3 cm^{-1}, respectively.

The ${}^4T_1$ transitions for the two isomers are found at 30 × 10^3 and 28 × 10^3 cm^{-1} for trans and cis, respectively, with no further splitting observed. The third ligand field band is expected around 45 × 10^3 cm^{-1} and is usually weak. It can not be seen and is undoubtedly buried in the tail of the nitrate absorption band in these salts.

Solid-State Emission and Absorption Spectra. *trans*-[Cr(cyclam)(NH$_3$)$_2$](ClO$_4$)$_2$(NO$_3$). Figure 1 shows the 6 and 62 K powder emission of *trans*-[Cr(cyclam)(NH$_3$)$_2$](ClO$_4$)$_2$(NO$_3$) and 5 K single-crystal absorption spectra for *trans*-[Cr(cyclam)(NH$_3$)$_2$](ClO$_4$)$_3$. A striking feature of all these spectra is the weak, split origin and the prominence of the vibronic sidebands, which, in higher temperature emission spectra, show the electronic origin splitting repeated throughout the spectrum. This and the coincidence of the electronic origins in absorption and emission removes any uncertainty about their assignment. The feature at 14 921 cm^{-1} (uncertainty of these figures is about ± 2 cm^{-1}) is the lowest energy component of the split ${}^2E$ state, R$_1$, and as the temperature is raised the upper component, R$_2$, at 14 965 cm^{-1} is populated, as shown for 62 K in emission. Because there are several closely spaced vibronic sidebands, the higher temperature spectra show significant overlap of bands based on the two electronic origins. In several instances this results in composite peak wavenumber maxima that are misleading. These effects can be seen clearly by reference to the main body of Figure 1 where vertical markers indicate the line spacings taken from the 6 K spectrum and relocated to start on the higher energy origin. The correspondence of these markers with many of the bands that have grown in with increasing temperature can be seen, and the overlap of components from the two sets of lines is obvious.

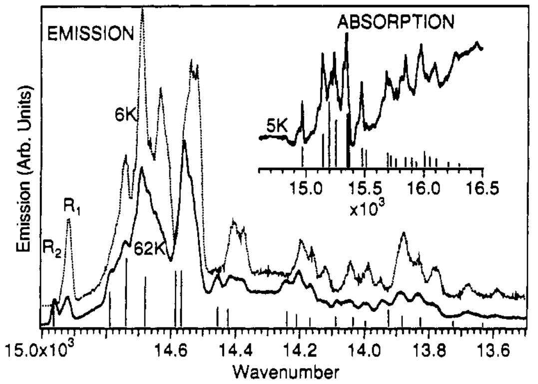

Figure 1. Emission (powder, nitrate diperchlorate) and absorption (crystal, triperchlorate, unpolarized) spectra of *trans*-Cr(cyclam)(NH$_3$)$_2$$^{3+}$. Doublet origins R$_1$ and R$_2$ are at 14 921 and 14 965 cm^{-1}, respectively. The vertical lines on the emission spectra show the 6 K vibronic sideband spacings and relative intensities displaced to originate on the higher energy component of the split ${}^2E$ state at 14 965 cm^{-1}. The inset absorption spectrum is similarly marked. This makes clear that the main observable intensity in absorption derives from the higher energy origin.

The inset in Figure 1 shows the single-crystal absorption spectrum at 5 K. The 6 K emission line spacings and relative intensities are shown, again originating on the higher energy doublet component. A correspondence both in energy and intensity with many of the bands in the absorption spectrum is visible. An interesting feature of this absorption spectrum is that the higher energy doublet component is the sharper (or stronger?) of the two, both in the origin and in the vibronic sidebands.

Collectively, the absorption spectrum, the emission spectra, and their temperature dependence establish the identity of the electronic origins. There is no possibility that the doublet splitting in the emission data arises because of emission from impurity sites in the lattice after energy transfer to those sites, as has been observed in other systems.[13]

***trans*-[Cr(cyclam-d_4)(ND$_3$)$_2$](ClO$_4$)$_3$.** Figure 2 shows analogous results obtained for the deuterated trans isomer. The electronic origins, R$_1$ and R$_2$, are now located at 14 925 and 14 974 cm^{-1}; i.e., their blue shifts on deuteration are only 4 and 10 cm^{-1}, respectively. This is consistent with the expectation of similar vibrational frequencies for the ground and excited states involved in the transition. The doublet splitting of 49 cm^{-1} is slightly greater than the 44 cm^{-1} found for the undeuterated compound. The vibronic structures for the two systems are similar, and only a few differences are seen in the detailed comparison of line spacings and IR frequencies (shown only up to 1040 cm^{-1}) of Table II. The most notable of these is the band corresponding to the ND vibration which appears at a spacing of 2453 cm^{-1} in the deuterated species, shown in the inset to Figure 2. The equivalent NH band in the undeuterated molecule is much harder to see as it falls close to the end of the sensitivity range of the photomultiplier. Except for the 398-cm^{-1} vibronic origin of the

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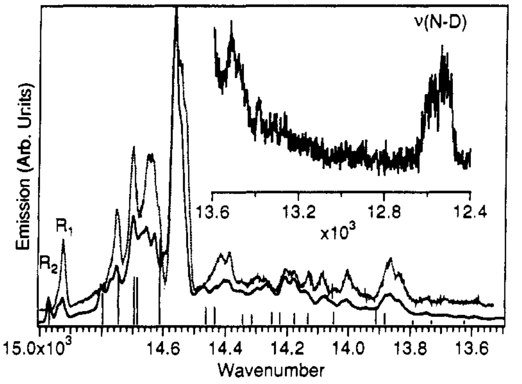

Figure 2. Emission spectra of deuterated *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ (powder, nitrate diperchlorate). Doublet origins R_1 and R_2 are at 14 925 and 14 974 cm^{-1}, respectively. The marking scheme is the same as for Figure 1.

undeuterated compound, the transitions at lower frequencies are little altered by deuteration showing that the NH vibration is not an important contributor to most of these modes.

***cis*-[Cr(cyclam)$(NH_3)_2$]$(ClO_4)(NO_3)_2$.** For this compound, we did not obtain crystals of sufficient size or quality to run absorption spectra. Therefore, Figure 3 shows a comparison of emission data at low and high temperature with the absorption data for the cis isomer, both taken for the same KBr pellet. The doublet origins at 14 786 and 14 850 cm^{-1} coincide in absorption and emission, and this minimizes uncertainty about the assignment of the 64-cm^{-1} spacing to the electronic ^2E splitting. Emission spectra on microcrystalline powder samples were also collected, and these revealed that a red shift of the transitions of about 40 cm^{-1} occurs in the KBr pellet. In the powder samples there is an additional 20-cm^{-1} splitting of all the emission lines, which most probably arises from the presence of two different crystal sites. In the KBr spectra, the lines are inhomogeneously broadened, and this splitting is no longer resolved.

From a comparison with Figures 1 and 2, it is immediately evident that the intensity distribution both in emission and absorption is quite different from that of the trans isomer. Most of the transition strength is in the electronic origins and the vibronic structure is weak, though the bands extend over similar ranges of frequencies in the two isomers.

Table II gives the line spacings based on the powder emission spectra (which have higher resolution) and the KBr pellet absorption and IR frequencies. Several of the low-frequency spacings are similar to those seen in the trans isomer and the hexaammine compound and are assigned by Flint to Cr–N distortions.[9,14] For example, the strongest cis lines, spaced at 184, 268, and 468 cm^{-1} from the lower energy origin, match the 212, 264, and 476 cm^{-1} spacings reported by Flint for the hexaammine perchlorate salt. No progressions are seen, consistent with there being similar excited- and ground-state geometries.

Quartet Absorption Spectra. Figure 4 shows the onset of the $^4T_2 \leftarrow {}^4A_2$ absorption spectrum of a thin single crystal of the trans isomer and of the KBr pellet of the cis isomer at 5 and 7 K, respectively. Neither compound shows any fine structure in this region. It is therefore not possible to obtain an exact $^4T_2 \leftarrow {}^4A_2$ origin energy. However, it is clear that the absorption extends below 19 500 cm^{-1} in both spectra. We estimate origin energies of 18 800 ± 300 cm^{-1} and 18 800 ± 500 cm^{-1} for the trans and cis isomers, respectively.

Discussion

Quartet/Quartet Solution Absorption Spectra. No quadrate splitting is evident in the $^4T_{1g} \leftarrow {}^4A_{2g}$ transition of *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ or in either of the two d–d transitions in the cis isomer. The intensities of the cis absorption bands are greater than those of the trans as expected from the lack of an inversion center in the cis isomer. For this pair of isomers, however, the intensity difference is larger than usually observed. Although crystal structures are not available for these isomers, it can be anticipated from analogues that the Cr center in the trans isomer will be only slightly distorted from octahedral symmetry by the constraints of the cyclam ligand. In contrast, in the cis isomer, the Cr(III) coordination geometry is expected to be particularly asymmetric because of the steric problems associated with folding the macrocyclic ligand.[15-18] The crystal structure of the analogous Cr(cyclam)en^{3+} cation shows[15] that the cis cyclam ligand folds so as to give two N–Cr–N angles of 96° at the Cr center, while the angle of the other N–Cr–N axis which forms the "hinge" of the fold is reduced from 180 to 172°.

A peculiar aspect of these spectra noted also by other authors[2,19] is the apparently smaller ligand field strength of the ligands in the cis isomer. The position of the first absorption band is almost exactly the same as in the hexaammine, with no obvious broadening because of band splitting. This implies that the secondary nitrogen atoms in the cis cyclam ligand have about the same angular overlap ligand field parameters as the ammine ligands (ϵ_σ = 7183, ϵ_π = 0 cm^{-1}). Apparently a reduction in σ-donor strength occurs because of steric strains present for the cis conformation of the cyclam ligand. Such strain does not occur in the trans isomer, for which the spectrum is consistent with expectation for a D_{4h} system having stronger equatorial ligands. The position of the $^4B_{1g}$ ($^4T_{2g}$) component in the trans isomer implies that ϵ_σ = 8000 cm^{-1} for the secondary nitrogens of the unstrained cyclam ligand, on the basis of the expectation that ϵ_π = 0 cm^{-1}. Similar trans/cis differences occur in the $^4T_1 \leftarrow {}^4A_2$ band and probably have the same origin, but the analysis is not so clear because the energies now also depend on the Racah parameters *B* and *C*.

^2E_g–$^4A_{2g}$ Spectra. The emission and absorption spectra of the protiated and deuterated trans isomer in the doublet region show a parallel to those reported by Flint and co-workers for $Cr(NH_3)_6^{3+}$. As the perchlorate salt, the latter complex shows four strong vibronic origins spaced at 212, 264, 670, and 741 cm^{-1} above the zero phonon lines. For our protiated complex, the overall band profile is similar, but the major components now lie 175, 227, 285, and 384/395 cm^{-1} above the zero phonon line. The prominent sidebands observed both in absorption and emission in the energy range 150–400 cm^{-1} are identified as vibronic origins involving one quantum of an enabling mode, and there is no evidence of progressions. The important conclusion here is that no dramatic new effects occur for this compound as a result of the macrocyclic nature of the ligands. There appears to be a lowering of the frequency of the vibronic origins, likely originating in an increase in the effective mass of the coordinated nitrogen atoms because of their incorporation into the ligand rings. But it is clear that there is no great involvement of ring vibrational modes in the doublet spectrum.

The situation is a little different for the cis isomer, which more closely parallels $Cr(en)_3^{3+}$. While the vibronic spacings are very similar to those in the trans and there is again no great involvement of cyclam ring modes, the intensity distribution is very different from that in the trans isomer, showing a strong electronic origin and weaker vibronic sidebands. This is connected with the overall higher intensity of the quartet bands in the cis isomer. Both phenomena have their origin in the lack of an inversion center in the cis isomer, providing a source of electric dipole intensity

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Table II. Frequency Differences in Absorption and Emission[f]

trans			deuterated trans			cis		
ν_{ab}[a]	ν_{em}[b]	ν_{IR}	ν_{ab}[c]	ν_{em}[d]	ν_{IR}	ν_{ab}[e]	ν_{em}[e]	ν_{IR}
–405						0		
0						–64		
144			133				(101)	
175	175		168	172			184	
246	227		232	224				
273	285		283	279			268	
376	384	378	371	363	359		331	
	398					393		
504	513	499	492	508	497		468	495
	540	530		536			532	527
			570	575	565			570
				653		619	635	
721	725	731		720	698		730	
745	779			748				
799	797	789	790	793	780			
844			822	837	830		833	832
881	876	878	877	880	886			
	930			922	913			
	965	963						
1012	1039	1040		1057	1040		1039	1040

[a] Based on 14 965-cm^{-1} doublet origin (R$_2$). [b] Based on 14 921-cm^{-1} doublet origin (R$_1$). [c] Based on 14 974-cm^{-1} doublet origin (R$_2$). [d] Based on 14 925-cm^{-1} doublet origin (R$_1$). [e] Based on 14 786-cm^{-1} doublet origin (R$_2$). Line in parentheses likely belongs to the other origin. [f] Only frequencies up to 1040 cm^{-1} have been included.

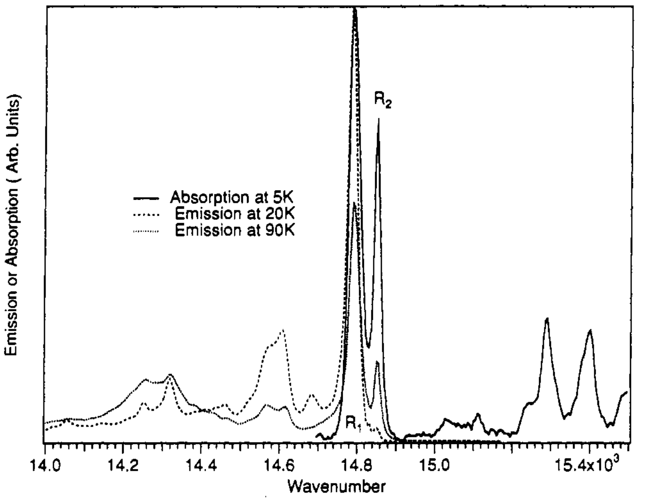

Figure 3. Emission and absorption spectra of a KBr pellet containing *cis*-[Cr(cyclam)(NH$_3$)$_2$](NO$_3$)$_2$ClO$_4$. Doublet origins R$_1$ and R$_2$ coincide in emission and absorption and are at 14 786 and 14 850 cm^{-1}, respectively.

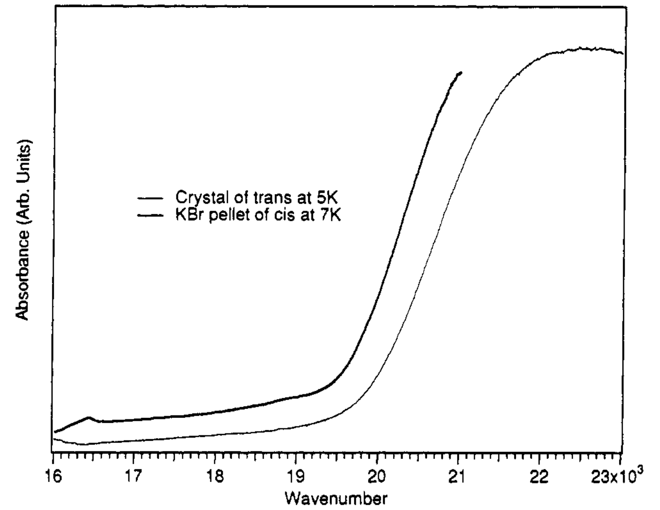

Figure 4. Absorption spectra of *trans*-[Cr(cyclam)(NH$_3$)$_2$]NO$_3$(ClO$_4$)$_2$ (crystal) and *cis*-[Cr(cyclam)(NH$_3$)$_2$](NO$_3$)$_2$ClO$_4$ (KBr pellet) at 5 and 7 K, respectively.

to the nominally g ↔ g electronic origins. Similar behavior has been found[20] in other cis isomers of Cr(III) salts. Compared to that in Cr(en)$_3$$^{3+}$, this effect may be amplified by the significant angular distortions in *cis*-Cr(cyclam)(NH$_3$)$_2$$^{3+}$, which will increase the odd-parity ligand field potential at Cr(III). Qualitative observations that the emission from the cis compound is significantly brighter than that from the trans also support a larger radiative rate constant for the cis isomer, which therefore competes more effectively with nonradiative pathways of excited-state decay.

The results show that the intensity distribution between the electronic origins and the vibronic sidebands in doublet emission or absorption can be a useful criterion to distinguish trans and cis isomers.

Doublet Splittings. The electronic origins are significantly split, by 45 and 64 cm^{-1}, for *trans*- and *cis*-Cr(cyclam)(NH$_3$)$_2$$^{3+}$, respectively. This is considerably larger than the value of 11 cm^{-1} reported for the analogous hexaammine perchlorate salt. We attribute this difference to the distortion of the Cr(III) site from O_h in our complexes, since the ^{2}E splitting arises from the combined action of spin–orbit coupling and low-symmetry ligand field potential. Flint and co-workers found for Cr(en)$_3$$^{3+}$ that this splitting depended on the counterion, presumably because of its influence on the site symmetry. They found a splitting of 48 cm^{-1} for the triperchlorate, which is comparable to our value. We conclude that the factors determining the magnitude of this splitting are subtle and include the effects of both the coordination environment and the environment provided by the crystal lattice. Hoggard and co-workers have investigated the effect of geometrical distortions on this splitting by using an angular overlap model[21] and also considered the effects of the second coordination sphere.[22]

Quartet/Doublet Spacing and Mechanism of Doublet-State Photoreactivity. One reason for undertaking the present work was to obtain estimates of the lowest quartet/doublet zero/zero spacing that would help assess the importance of various pathways proposed for reaction and relaxation of the Cr(III) doublet state back to the ground state. The three candidate pathways are direct doublet reaction or decay, thermally activated reverse

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intersystem crossing followed by quartet reaction or decay, and tunneling to a ground-state intermediate or transition state for reaction. The experimental background and the rather complex detailed arguments have been well presented in previous work.[1,2,4,5] They favor a choice between the latter two mechanisms, where the deactivation/reaction process is strong-coupled, and only the choice between these two will be considered further here.

The absence of fine structure in the $^4T_2 \leftarrow {}^4A_2$ absorption band is the usual situation which arises because of inhomogeneous broadening. Nevertheless, our data for the absorption bands, Figure 4, shows that there can not be a great difference in the frequencies of the onset of absorption for the two isomers. Both occur around 18 800 cm^{-1} with uncertainties of ±300 and ±500 cm^{-1} for trans and cis, respectively; these $^4T_2 \leftarrow {}^4A_2$ origin energies are smaller than the 20 000 cm^{-1} reported[11] for $Cr(NH_3)_6^{3+}$. Combining these values with the doublet origin positions given above, one obtains estimates of the $^2E/^4T_2$ zero/zero spacings of 47 ± 4 and 48 ± 6 kJ mol^{-1}, respectively, in units appropriate for comparison with kinetic data.

These values can be compared to the activation energy, E_a, of the main process depopulating the doublet state in room-temperature aqueous solutions. Such values have been derived from Arrhenius plots of reciprocal emission lifetime for temperature ranges near ambient, and several values are in the literature. Those reported for the trans isomer were E_a = 73[2] and 59[1] kJ mol^{-1}, and those for the cis isomer, 43,[2] 36,[1] and 37[8] kJ mol^{-1}. The apparent disagreement in the values for the trans isomer probably arises because of room-temperature nonlinearities in the Arrhenius plot for this compound and differences in the method of evaluation of the data. Since the procedure that led to the more recent value of 59 kJ mol^{-1} was clearly set out and theoretically justifiable it will be accepted here, as will the lowest value for the cis.

For the trans isomer, the spectroscopic $^2E/^4T_2$ zero/zero energy spacing is 12 kJ mol^{-1} smaller than E_a. This can be rationalized in a single configuration coordinate (SCC) model. Classically, the activation energy is determined by the energy gap from the $v = 0$ level of the doublet state to the crossing point of the ^2E and $^4T_2$ potentials, which lies above the $v = 0$ level of $^4T_2$. In reality, the potential surface is more complex, as Wilson and Solomon[11] have shown that the upper state equilibrium geometry corresponds to distortion in both a_{1g} and e_g coordinates, but this does not alter the essence of the situation.

For the cis compound, however, the experimental situation is reversed, with E_a smaller than the $^2E/^4T_2$ zero/zero spacing by 12 kJ mol^{-1}. Obviously this cannot be accounted for in an SCC model. In the following we will therefore introduce an additional coordinate and in doing so we will be guided not only by the spectroscopic results presented here but also by the results of photochemical and photophysical studies.

There is a significant body of evidence that the reaction via the doublet state gives the same products in the same ratios with the same stereochemistry (different from the stereochemistry of the ground-state reaction) as the unquenchable reaction which occurs via the quartet state. See, for example, refs 8 and 23–25. Our findings here for the unreactive trans isomer are nicely consistent with reverse intersystem crossing as the pathway of doublet decay, and to us, the idea of parallel mechanisms for the two isomers has an intuitive appeal. Finally, the unusually low activation barriers seem to be a general feature shown by reactive systems.

This body of evidence suggests to us that previous arguments against the reverse intersystem crossing mechanism have failed to give adequate weight to a potentially crucial aspect. Namely, the barrier to reverse intersystem crossing could reasonably be expected to be lowered significantly in reactive systems because of the strong interaction that can occur in the excited state (but not in the ground state) with the nucleophilic solvent.

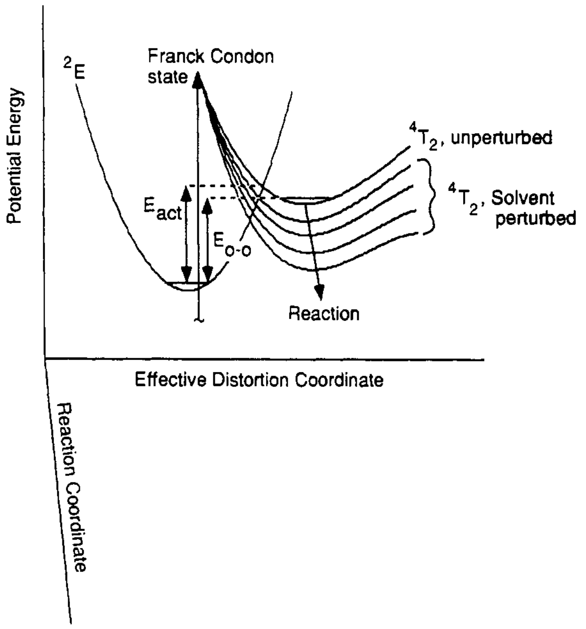

Figure 5. Excited-state potential energy curves for Cr(III) showing the relationship between E_{0-0} and E_{act} for reverse intersystem crossing and the possible change in this activation energy as a result of perturbation of the excited quartet state by solvent interaction. The figure shows how the energy of the quartet state should decrease along a reaction coordinate while the doublet-state surface should remain unchanged (and therefore represented by a trough, omitted for clarity). See text for further details.

In Figure 5 we have attempted to show qualitatively how a lowering of the activation energy could be expected to arise. In the reactive excited quartet state, the vacant t_{2g} orbital allows an interaction with Lewis base solvents that leads to photoreaction.[26] For *cis*-$Cr(cyclam)(NH_3)_2^{3+}$, this excited-state reaction is somewhat unusual in that it occurs via a seven-coordinate intermediate,[1] but this does not alter the situation. The consequent distortion along a coordinate for chemical reaction, shown as a motion out of the plane of the paper, lowers the energy of the vibrationally relaxed quartet excited state but not of the doublet excited state (which is therefore a trough coming out of the plane of the paper, omitted for clarity). Consequently, for reverse intersystem crossing to quartet states that are strongly interacting with the solvent, there will be lower lying intersection points between the doublet and quartet potential energy surfaces which will serve to reduce the activation energy for reverse intersystem crossing significantly below the solid-state "spectroscopic" value. Such effects would be prevented in the trans isomer because of the steric barriers along the potential reaction coordinates which render it photoinert.

We have also tried to illustrate that this could occur without being obvious in the solution absorption spectrum. A guide to the nature and magnitude of the spectral effects to be expected is, for example, the detailed understanding of the absorption and emission of ammonia[27] based upon the time-dependent perturbation theory of Heller.[28]

For Cr(III) complexes, the energy of the Franck–Condon transition should be unaffected because there is no solvent interaction in the ground state. The major effect expected is an increase in the gradient of the upper state potential surface at ground-state geometry. This would increase the rate at which

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the wave packet evolves on the excited-state potential surface, leading to a broadening of the component transitions making up the absorption band. Since the overall spectral envelope for the $^4T_2 \leftarrow {}^4A_2$ transition is already very broad, however, with a width at half-height of greater than 2500 cm^{-1} in the *cis*-Cr(cyclam)$(NH_3)_2^{3+}$, we would not expect this broadening to be observable; it amounts to only 50 cm^{-1} for an assumed excited-state lifetime of only 10^{-13} s.

We are aware that this model is somewhat speculative, but it is not in contradiction with any of the experimental observations. Furthermore we believe that such effects could account for other measurements of room-temperature activation energies for doublet depopulation that are smaller than predicted from spectroscopic measurements or from other estimates of the doublet quartet spacing, as well as the many observations that such experimental activation energies vary dramatically depending on solvent or medium.[4,29]

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Registry No. *trans*-[Cr(cyclam)$(NH_3)_2$]$^{3+}$, 94484-08-9; *cis*-[Cr(cyclam)$(NH_3)_2$]$(NO_3)_2ClO_4$, 143343-56-0; *trans*-[Cr(cyclam)$(NH_3)_2$]$NO_3(ClO_4)_2$, 143293-09-8; *trans*-[Cr(cyclam-d_4)$(ND_3)_2$]$NO_3(ClO_4)_2$, 143266-38-0; D_2, 7782-39-0.

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