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Solvent Influence on Emitting States in Quadrate Chromium(III) Complexes

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The effect of hydroxylic and non-hydroxylic glassy solvents on the emission spectra of CrN_4XY complexes has been determined at 77 K. When X or Y is F^- or OH^-, the splitting of the ${}^2T_1$ level is reduced in hydrogen-bonding solvents. When the lowest component of ${}^2T_1({}^2E^Q)$ is above ${}^2E$ in all solvents, the emission spectrum is sharp and is only slightly affected by the solvent. If ${}^2E^Q$ is below ${}^2E$ in all solvents, the broad emission spectrum is shifted to shorter wavelengths in hydroxylic solvents. In some cases, e.g., *cis*-$CrN_4(OH)_2^+$, ${}^2E^Q$ is below ${}^2E$ in non-hydroxylic solvents, but the state order is reversed in hydroxylic solvents. This leads to a marked narrowing of the spectrum in hydroxylic media. Solvent effects can be useful in assigning Cr(III) emission spectra.

Introduction

Transition energies in metal complexes are often solvent dependent. The largest effects are seen in charge-transfer transitions,[1] but small shifts in both the spin-allowed and spin-forbidden Cr(III) d–d band positions have been reported.[2] In the case of *trans*-CrN_4FX (X = F^-, NCS^-, H_2O, and NH_3) where the N-coordination is due to NH_3 or ethylenediamine (en), differential movements of the ${}^4T_2 \leftarrow {}^4A_2$ and ${}^4T_1 \leftarrow {}^4A_2$ components are observed when the solvent is changed from water to DMF or tetrahydrofuran.[3] The transition energy changes in Cr(III) fluoro–amine complexes were attributed to the alteration in the hydrogen bonding between the coordinated F atoms and the solvent; the σ- and π-donation of F^- to Cr(III) varies with solvent.

As the quadrate field strength is increased, some of the level degeneracies are reduced. The ${}^4T_2$ and ${}^4T_1$ splittings depend upon the differences in the σ- and π-bonding parameters of the axial and equatorial ligands.[4] In contrast, the ${}^2T_1$ splitting is a function only of the π-bonding parameters. The ${}^2E$ components are insensitive to quadrate fields (Figure 1). In sufficiently large fields, the ${}^2E^Q$ component of ${}^2T_1$ will be depressed below the ${}^2E$ components.[5] The superscript Q designates the symmetry label in quadrate symmetries. When this superscript is omitted, the cubic symmetry symbol is implied. Emission arises from the lowest doublet state or levels that are thermally populated from the lowest excited state. In a previous study of emission from quadrate Cr(III) complexes the emission was assigned as ${}^2E$ or ${}^2T_1$, depending upon the nature of the lowest excited level, ${}^2E$ or ${}^2E^Q$, respectively.[6] ${}^2E \rightarrow {}^4A_2$ emission is characterized by sharp emission spectra in the 650–710-nm region, while the ${}^2E^Q \rightarrow {}^4A_2$ spectra are broad and are shifted, in most cases, to longer wavelengths. Delocalization of the d electrons onto the π^*-ligand orbitals leads to a red shift of the ${}^2E \rightarrow {}^4A_2$ emission, but the spectrum remains narrow.

The emission of three complexes has been established as ${}^2E^Q \rightarrow {}^4A_2$ in crystalline media, *trans*-$Cr(py)_4F_2^+$,[7] $Cr(NH_3)_5(OH)^{2+}$,[8] and *trans*-$Cr(en)_2F_2^+$.[9] While the emission spectrum of $Cr(NH_3)_5(H_2O)^{3+}$, a ${}^2E$ emitter, is essentially the same in glassy and crystalline environments, the spectrum of the ${}^2T_1$ emitter $Cr(NH_3)_5(OH)^{2+}$ is markedly red shifted in the solid compared to that of the glassy solution.[10] In this work we relate spectral shifts and excited-state decay kinetics to the relative disposition of the ${}^2T_1$ and ${}^2E$ components in hydroxylic and non-hydroxylic solvents.

Experimental Section

Syntheses of the $Cr(NH_3)_4XY$, $Cr(en)_2XY$, and *trans*-$Cr(py)_4F_2^+$ (py = pyridine) complexes have been described.[6] $Cr(cyca)F_2^+$ (cyca = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) was a gift from O. Mønsted (University of Copenhagen). All solvents were reagent or spectral grade and were used as supplied.

For the low-temperature spectra, samples were immersed directly in liquid N_2 and excitation was obtained with an N_2 laser or by dye lasers, N_2 laser or flashlamp pumped. Spectra were recorded with an RCA C31034 photomultiplier–0.25-M Jarrell-Ash monochromator (4.4-nm bandwidth) combination and were not corrected for the wavelength variation of the detector–monochromator sensitivity. The signal was averaged at different delay times with a boxcar averager. Lifetimes were measured at fixed wavelengths by digiziting the signal with a Biomation Model 805 transient recorder and averaging for 1024 sweeps.

Room-temperature emission spectra were excited by a 250-W compact Hg arc–Bausch and Lomb high-intensity monochromator combination, suitably filtered and time-averaged with a PDP-11 computer that applied corrections for the spectral sensitivity of the detection system.

Results

Three solvent systems were employed, DMF–H_2O, Me_2SO–H_2O, and tetrahydrofuran–H_2O. The composition was varied over the range X_{H_2O} = 0–1. The results were compared with those obtained in alcohol–H_2O glasses.[6,11]

***trans*-$Cr(py)_4F_2^+$.** The emission spectra in DMF–H_2O and Me_2SO–H_2O solutions are dependent on the water content of the glass (Figure 2). These spectra were recorded at short delay times (20 μs), but there is little spectral change with delay. The spectra in pure DMF and Me_2SO are nearly the same. As the water level is increased, the intensity in the 805-nm region increases relative to the 850-nm band. At $X_{H_2O} = 0.80$, the spectrum resembles that in an alcohol–water glass, albeit red-shifted. Decays monitored at 845 nm are nearly exponential in all solutions with the lifetime increasing from 90 μs in pure Me_2SO and DMF to 130 μs at $X_{H_2O} = 0.80$. The 795-nm decays are slightly nonexponential but are close to the 200-μs value that prevails in alcohol–water at 800 nm.

Fluoro–Amine Complexes. The emission spectrum of $Cr(NH_3)_5F^{2+}$ is nearly invariant to solvent (Figure 3). The solvent effects on the sharp spectra of *cis*-$Cr(en)_2F_2^+$ and *cis*-$(NH_3)_4F_2^+$ are likewise small. The broad *trans*-$Cr(NH_3)_4F_2^+$ emission is very sensitive to solvent (Figure 4); the shifts are comparable to those in *trans*-$Cr(py)_4F_2^+$. Again no variation with delay time is evident. The relatively small solvent effect on the spectrum of *trans*-$Cr(en)_2F_2^+$ is noteworthy (Figure 5). The *trans*-$Cr(en)_2F_2^+$ decay, which is exponential in alcohol–water, becomes nonexponential in DMF. The emission of *trans*-$Cr(en)_2(H_2O)F^{2+}$ resembles that of *trans*-$Cr(NH_3)_4F_2^+$ in breadth, but the solvent sensitivity of the fluoro–aquo complex is much less (Figure 6). The lifetime

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(1) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.
(2) Adamson, A. W. *J. Inorg. Nucl. Chem.* **1966**, *28*, 1955.
(3) Glover, S.; Kirk, A. D. *Inorg. Chim. Acta* **1982**, *137*, L1982.
(4) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399.
(5) Flint, C. D.; Mathews, A. P.; O'Grady, P. J. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 655.
(6) Forster, L. S.; Fucaloro, A. F.; Rund, J. V. *J. Phys. Chem.* **1984**, *88*, 5012.
(7) Flint, C. D.; Mathews, A. P. *Inorg. Chem.* **1975**, *14*, 1008.
(8) Decurtins, S.; Gudel, H. U.; Neuenschwander, K. *Inorg. Chem.* **1977**, *16*, 796.
(9) Flint, C. D.; Mathews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1307.
(10) Schläfer, H. L.; Martin, M.; Gausmann, H.; Schmidtke, H. H. *Z. Phys. Chem. (Munich)* **1971**, *76*, 61.
(11) Forster, L. S.; Fucaloro, A. F.; Rund, J. V.; Lin, S. H. *J. Phys. Chem.* **1984**, *88*, 5017.

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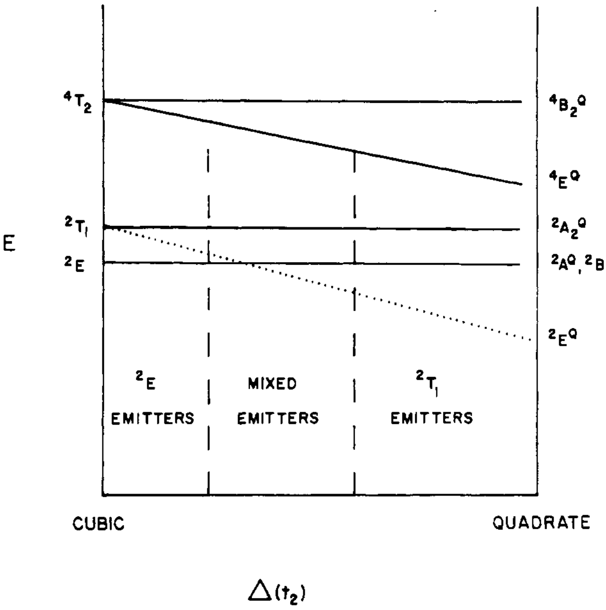

Figure 1. d^3 energy levels in quadrate fields (schematic). Symmetry labels on the left refer to cubic symmetry and those on the right to quadrate symmetry.

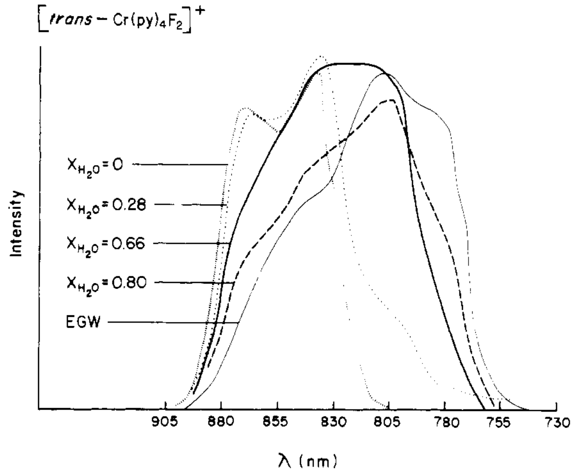

Figure 2. 77 K emission spectra of *trans*-$Cr(py)_4F_2^+$ in Me_2SO-H_2O mixtures of the indicated composition. EGW is ethylene glycol-H_2O ($X_{H_2O} = 0.6$).

of *trans*-$Cr(NH_3)_4F_2^+$ is reduced from 49 μs in alcohol-water to 30 μs in $DMF-H_2O$, but the decay times of $Cr(NH_3)_5F^{2+}$, *cis*-$(NH_3)_4F_2^+$, and *cis*-$Cr(en)_2F_2^+$ are insensitive to solvent.

Aquo- and Hydoxy-Amine Complexes. The emission decays of *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ are exponential in alcohol-water and $DMF-H_2O$ glasses (τ = 40 μs), and except for some changes in the relative vibronic intensities, the emission spectra are not markedly affected by solvent (Figure 7). This invariance to environment extends to the crystalline state.[10] The spectral and decay behavior of *cis*-$Cr(NH_3)_4(OH)_2^+$ and *cis*-$Cr(en)_2(OH)_2^+$ are quite different from that of *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ (Figure 8). In the first place the *cis*-$CrN_4(OH)_2^+$ spectra are broad in $DMF-H_2O$ but narrow in alcohol-water, whereas the *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ spectrum is narrow in all solvents. Secondly, the decay of *cis*-$Cr(NH_3)_4(OH)_2^+$, which is nearly exponential in alcohol-water, becomes markedly nonexponential in $DMF-H_2O$. Finally, there is a significant narrowing of the *cis*-$CrN_4(OH)_2^+$ spectra with delay time. At long delays the emission resembles the spectrum in alcohol-water in shape but is shifted somewhat to lower energies.

A distinct solvent shift obtains in the spectra of $Cr(NH_3)_5(OH)^{2+}$ and *trans*-$Cr(NH_3)_4(H_2O)(OH)^{2+}$ (Figure 9). The decays of $Cr(NH_3)_5(OH)^{2+}$ are much shorter in DMF (10 μs) than in alcohol-water (27 μs). The emission spectra of $Cr(NH_3)_5(OH)^{2+}$ in DMF and $DMF-H_2O$ are independent of delay time.

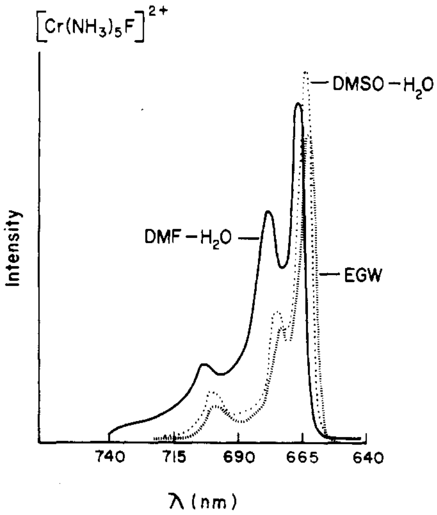

Figure 3. 77 K emission spectra of $Cr(NH_3)_5F^{2+}$ in different solvents: $DMF-H_2O$ ($X_{H_2O} = 0.30$); Me_2SO-H_2O ($X_{H_2O} = 0.80$); ethylene glycol-H_2O ($X_{H_2O} = 0.6$) (EGW).

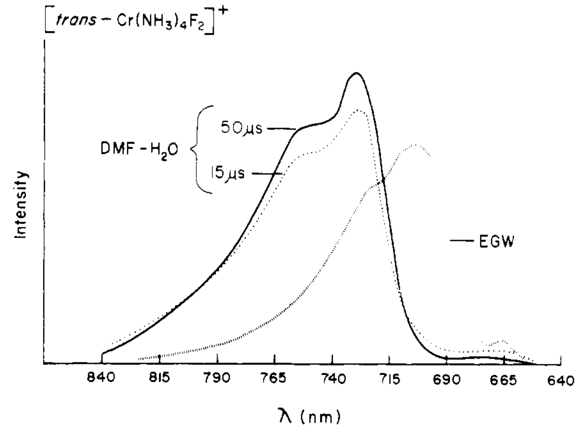

Figure 4. 77 K emission spectra of *trans*-$Cr(NH)_4F_2^+$ as a function of solvent and delay time: $DMF-H_2O$ ($X_{H_2O} = 0.30$); ethylene glycol-H_2O ($X_{H_2O} = 0.6$) (EGW).

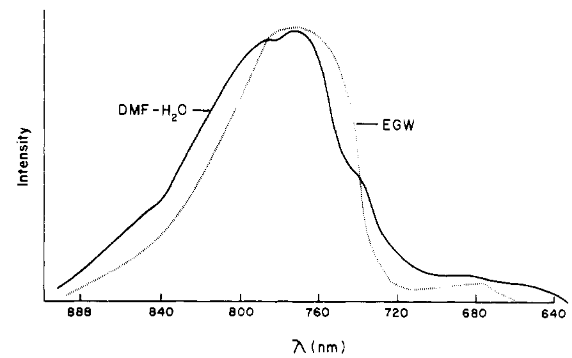

Figure 5. 77 K emission spectra of *trans*-$Cr(en)_2F_2^+$ in different solvents: $DMF-H_2O$ ($X_{H_2O} = 0.30$); ethylene glycol-H_2O ($X_{H_2O} = 0.6$) (EGW).

Discussion

We have previously divided quadrate Cr(III) complexes into two groups, ^2E and $^2T_1$ emitters, depending upon the character of the lowest excited state.[6] On the basis of spectral position and breadth as well as lifetime in alcohol-H_2O solution, the complexes studied here were classified as follows: ^2E emitters $Cr(NH_3)_5F^{2+}$, *cis*-$Cr(en)_2F_2^+$, *cis*-$Cr(en)_2(OH)_2^+$, and *cis*-$Cr(NH_3)_4(OH)_2^+$; $^2T_1$ emitters *trans*-$Cr(py)_4F_2^+$, $Cr(NH_3)_5(OH)^{2+}$, *trans*-$Cr(NH_3)_4F_2^+$, *trans*-$Cr(en)_2F_2^+$, *trans*-$Cr(en)_2F(H_2O)^{2+}$, and *trans*-Cr-

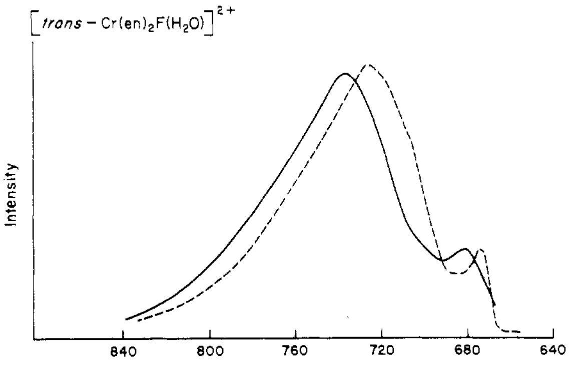

Figure 6. 77 K emission spectra of *trans*-Cr(en)$_2$F(H$_2$O)$^{2+}$ in different solvents: (—) DMF; (---) ethylene glycol–H$_2$O (X_{H_2O} = 0.6).

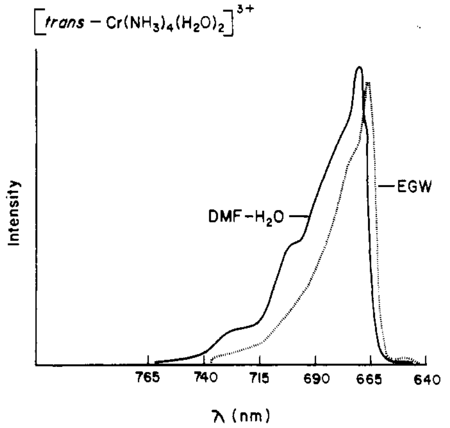

Figure 7. 77 K emission spectra of *trans*-Cr(NH$_3$)$_4$(H$_2$O)$_2$$^{3+}$ in different solvents: DMF–H$_2$O (X_{H_2O} = 0.6); ethylene glycol–H$_2$O (X_{H_2O} = 0.6) (EGW).

(NH$_3$)$_4$(H$_2$O)(OH)$^{2+}$. Clearly, a two-valued scheme is an oversimplification since the ^{2}E and ^{2}E^Q energies cross and will be nearly equal in some quadrate fields (Figure 1). We designate complexes in this intermediate domain as mixed emitters.

Since the individual vibronic transitions are not resolved, the solvent-induced shifts cannot be readily quantified. Nonetheless, the qualitative results provide considerable information about the relative disposition of the ^{2}E and ^{2}E^Q levels. A model that explains most of the results is as follows: (i) In low quadrate fields, where the difference in π-donation between axial and equatorial ligands is small, ^{2}E emission occurs. For cis complexes, holohedrized symmetry is assumed whereby the π-donating ability for both ligands on an axis is an average of the individual ligand characteristics.[4] The sharp spectrum and lifetime of a ^{2}E emitter are nearly the same in hydroxylic and non-hydroxylic solvents.

(ii) The emission in high quadrate fields in ^{2}T$_1$. The transition energy and lifetime are larger in hydroxylic solvents, but the spectra are broad in all solvents.

(iii) At intermediate quadrate field strengths mixed emission is observed. The influence of solvent on mixed emission depends on the relative energies of the ^{2}E and ^{2}E^Q levels and on the change in π-bonding with solvent.

The preponderance of Cr(III) complexes are ^{2}E emitters. ^{2}E, ^{2}T$_1$, and ^{4}A$_2$ are derived from the same configuration, t_2^3, in O_h and the small relative displacement of the potential minima leads to sharp ^{2}E → ^{4}A$_2$ and ^{2}T$_1$ → ^{4}A$_2$ emission spectra. The intraconfigurational character of ^{2}E → ^{4}A$_2$ persists in quadrate symmetry.[12] The ^{2}E energy depends upon the interelectronic repulsion, a quantity that varies with the ligands. In CrN$_4$XY complexes, the ^{2}E → ^{4}A$_2$ emission moves progressively to lower energies as the number of NH bonds is decreased, i.e., in the sequence NH$_3$ > en. Except in centrosymmetric complexes, the 0–0 band is the most intense feature and many ^{2}E emission spectra resemble the Cr(NH$_3$)$_5$F^{2+} spectrum (Figure 3). Unless the repulsion between the metal-centered t$_2$ electrons is reduced by delocalization onto the ligands, the ^{2}E → ^{4}A$_2$ origin lies between 650 and 710 nm. Coordination by ligands with multicenter π-orbitals, e.g. NCS$^-$, CN$^-$, and acetylacetonate, shifts the emission to longer wavelengths, and the Cr(CN)$_6$$^{3-}$ emission is in the 800-nm region.

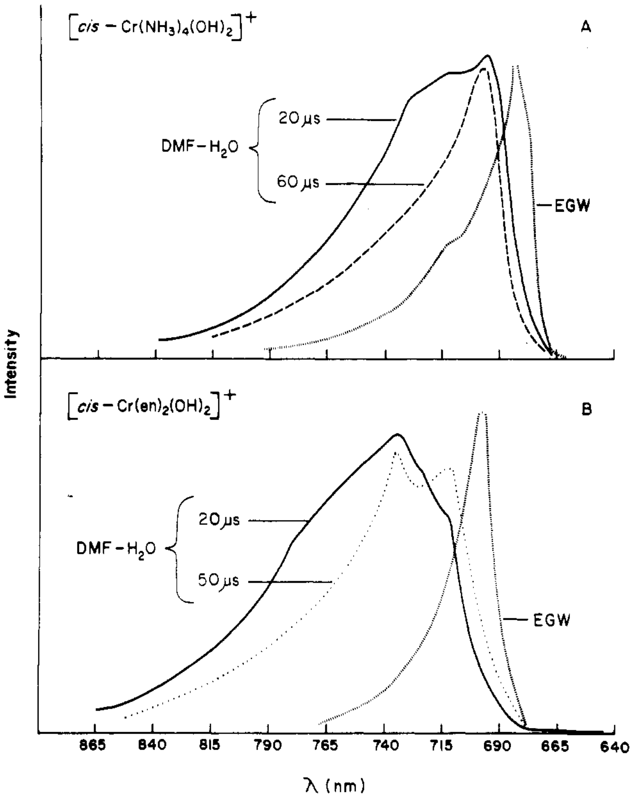

Figure 8. 77 K emission spectra of (A) *cis*-Cr(NH$_3$)$_4$(OH)$_2$$^+$ and (B) *cis*-Cr(en)$_2$(OH)$_2$$^+$ at different delay times in DMF–H$_2$O (X_{H_2O} = 0.30) and ethylene glycol–H$_2$O (X_{H_2O} = 0.6) (EGW).

The ^{2}E^Q → ^{4}A$_2$ transition involves a configuration change in D_{4h},[12] and the Franck–Condon factors point to a substantial shift in the potential minima. The 0–0 bands are then weak, and the more intense vibronic bands span a large range. If the individual vibronic transitions are not resolved, the emission band envelope is much broader than the typical ^{2}E → ^{4}A$_2$ emission.

The ^{2}E^Q energies of the *trans*-CrN$_4$F$_2$$^+$ complexes in DMF–H$_2$O vary with ligand in the same order as the ^{2}E energies in *trans*-CrN$_4$XY complexes, NH$_3$ > en > cyca. The correlation of the energy decrease in both states might be due to the nephelauxetic effect. Geometry may also play a role since ligand distortions in a five-membered ring would affect ^{2}E^Q more than ^{2}E.[13] The ^{2}E–^{2}T$_1$ splitting is due to configuration interaction whose extent, in turn, depends upon the interelectronic repulsion. The relative position of ^{2}E and ^{2}E^Q is determined by the interplay of quadrate field, geometric distortions, and configuration interaction.

The solvent shift in hydroxylic solvents is smaller for *trans*-Cr(en)$_2$F$_2$$^+$ than for *trans*-Cr(cyca)F$_2$$^+$ (Figure 10) and *trans*-Cr(NH$_3$)$_4$F$_2$$^+$. The vibronic envelope in the emission of solid *trans*-[Cr(en)$_2$F$_2$]I exhibits a maximum near 810 nm.[9] The solvent shift in the room-temperature emission of *trans*-Cr(en)$_2$F$_2$$^+$ is shown in Figure 11. The emission maximum hardly changes from pure H$_2$O to X_{H_2O} = 0.6 in THF–H$_2$O solutions. Small red shifts are observed as the water content is diminished to X_{H_2O} = 0.2, but in pure THF the maximum of the very weak emission occurs beyond 850 nm. Identical results obtain in DMF–H$_2$O solutions. The marked difference between the low-temperature and room-

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(12) Schmidtke, H. H.; Hoggard, P. E. *Chem. Phys. Lett.* **1973**, *19*, 119.

(13) Wallace, W. M.; Hoggard, P. E. *Inorg. Chem.* **1983**, *22*, 491.

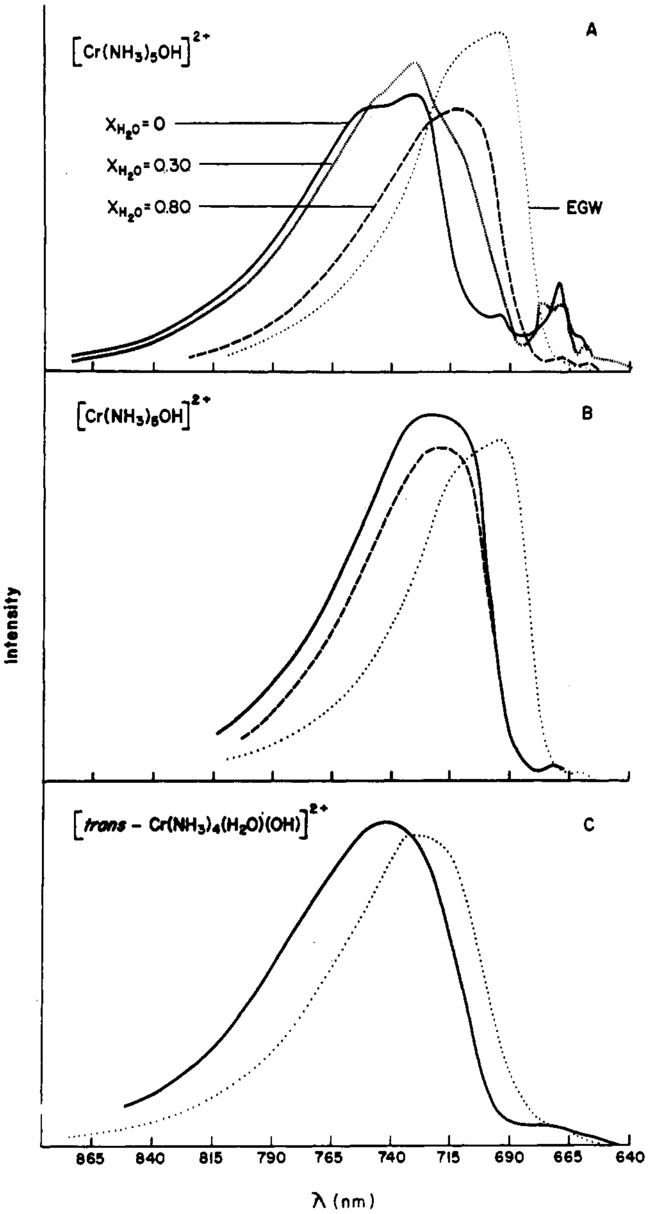

Figure 9. 77 K emission spectra in different solvents. (A) $Cr(NH_3)_5OH^{2+}$ in DMF–H_2O solutions at the indicated compositions EGW is ethylene glycol–H_2O (X_{H_2O} = 0.6). (B) $Cr(NH_3)_5OH^{2+}$: (—) Me_2SO–H_2O (X_{H_2O} = 0.80), 5-μs delay; (---) Me_2SO–H_2O (X_{H_2O} = 0.80), 25-μs delay; (···) ethylene glycol–H_2O (X_{H_2O} = 0.6). (C) *trans*-$Cr(NH_3)_4(H_2O)(OH)^{2+}$: (—) Me_2SO–H_2O (X_{H_2O} = 0.80); (···) ethylene glycol–H_2O (X_{H_2O} = 0.6).

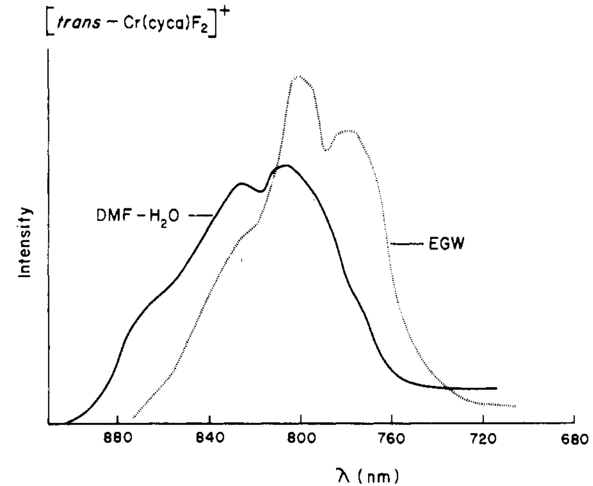

Figure 10. 77 K emission spectra of *trans*-$Cr(cyca)F_2^+$ in different solvents: DMF–H_2O (X_{H_2O} = 0.30); ethylene glycol–H_2O (X_{H_2O} = 0.6) (EGW).

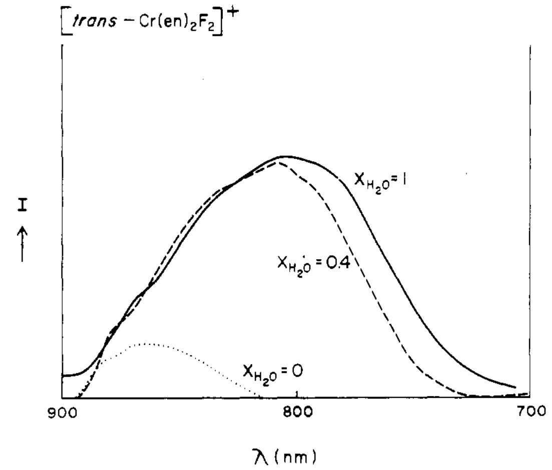

Figure 11. Room-temperature emission spectra (corrected) of *trans*-$Cr(en)_2F_2^+$ in THF–H_2O mixtures.

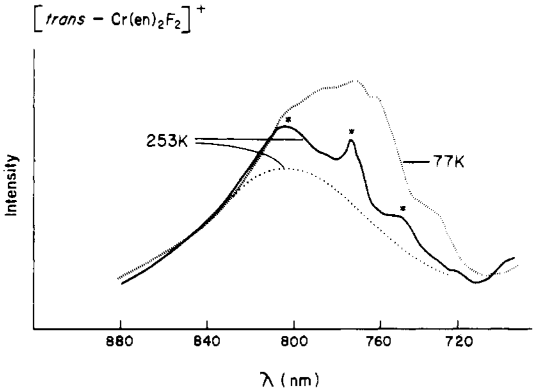

Figure 12. Emission spectra of *trans*-$Cr(en)_2F_2^+$ in DMF as a function of temperature. The asterisks denote spurious peaks arising from solvent emission. A 253 K spectrum, approximately corrected for solvent emission, is also shown (···).

temperature emissions in pure DMF might be partially artifactual since the room-temperature spectra were recorded with a different detection system and are corrected, but the 60-nm solvent shift in the room-temperature emission is much larger than in the low-temperature emission. There is a definite temperature effect in pure DMF as evidenced by the 77 and 253 K spectra (Figure 12). It is possible that the room-temperature DMF emission is fluorescence ($^4E^Q \rightarrow {}^4A_2$) rather than $^2E^Q \rightarrow {}^4A_2$. The energy difference between the 0–0 line of $^2E^Q \rightarrow {}^4A_2$ and the band maximum of $^4E^Q \rightarrow {}^4A_2$ is 5500 cm^{-1}.[9] These data suggest an energy gap <4000 cm^{-1} for back-transfer, which makes room-temperature fluorescence possible.

In the angular-overlap model, the $^2T_1$ splitting is a quadratic function of the t_2 orbital splitting, $|\Delta(t_2)|$. The global $\Delta(t_2)$ parameter can be related to the local ligand parameters.[4] In *trans*-CrN_4XY complexes with linear ligators

$$\Delta(t_2) = -\tfrac{1}{4}(\Delta'_{\pi X} + \Delta'_{\pi Y}) \qquad (1)$$

where $\Delta'_{\pi X}$ represents the π-donor tendency of the X ligand. In eq 1, it is assumed that the equatorial ligands are incapable of π-bonding. In *cis*-CrN_4X_2 and $Cr(NH_3)_5X$ complexes

$$|\Delta(t_2)| = \tfrac{1}{4}(\Delta'_{\pi X}) \qquad (2)$$

If the π-donor ability of the axial ligands is reduced by H-bonding, $\Delta(t_2)$ would be decreased in hydroxylic solvents. Within the group of CrN_4XY complexes, coordination by F^- or OH^- ligands often leads to $^2T_1$ emission and these are the ligands that are most affected by H-bonding. The ^2E energy is not a function of $\Delta(t_2)$, and solvent effects on ^2E emission are also minimal. The $^2T_1$

splitting is smaller in hydroxylic solvents if $\Delta(t_2)$ is decreased by H-bonding. The concomitant increase in the $^2E^Q$ energy then leads to a blue shift of the $^2E^Q \rightarrow {}^4A_2$ emission band. In the mixed-emission regime three possibilities can be imagined: (i) $^2E^Q$ is lower than ^2E in all solvents and the spectra are all broad; (ii) ^2E is lower in all solvents and the $^2E \rightarrow {}^4A_2$ emission is slightly broadened by ^2E–$^2E^Q$ mixing; (iii) $^2E^Q$ is lower than ^2E in non-hydroxylic solvents and higher in hydroxylic media. In the last case the spectrum is not only blue-shifted in hydroxylic solvents but also narrows.

The components of ^2E and $^2E^Q$ mix under spin–orbit coupling.[5,14] Ligand field calculations, using the full 30 × 30 matrices for each of the two double group representations in $D_4{}^*$,[14] suggest that this mixing is small, 14% when the unperturbed levels are equienergetic. Thus, except for some broadening of the $^2E \rightarrow {}^4A_2$ spectra, the emission from either level can be reasonably well described without reference to spin–orbit mixing between them. However, the relative populations of ^2E and $^2E^Q$ will be sensitive to $\Delta(t_2)$ if the separation of the two levels approximates the thermal energy. The energy difference between the two levels will vary with the solute–solvent interaction, and in a glassy solvent where a distribution of such interactions exist, nonexponential decay can be the result.[15] We suggest that ^2E and $^2T_1$ emission decays will be exponential but that mixed emission might be nonexponential.

According to eq 2 the $^2T_1$ splitting in $Cr(NH_3)_5F^{2+}$ and *cis*-$Cr(NH_3)_4F_2{}^+$ should be the same. The assignment of the emission from both complexes as ^2E is consistent with this prediction. In alcohol–water, the spectra of *cis*-$Cr(NH_3)_4(OH)_2{}^+$ and *cis*-cr-$(en)_2(OH)_2{}^+$ resemble the emission of *trans*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$, a ^2E emitter. However, the previous designation of the *cis*-$CrN_4(OH)_2{}^+$ emission as ^2E in alcohol–water was problematical in view of the assignment of the $Cr(NH_3)_5(OH)^{2+}$ emission in alcohol–water as $^2T_1$.[6] The solvent effect on the $Cr(NH_3)_5(OH)^{2+}$ emission is normal for a $^2T_1$ emitter. On the other hand, both *cis*-$Cr(NH_3)_4(OH)_2{}^+$ and *cis*-$Cr(en)_2(OH)_2{}^+$ behave as mixed emitters in which the emission is mainly $^2T_1$ in a non-hydroxylic solvent but ^2E in hydroxylic media. In alcohol–water, $^2E^Q$ is slightly above ^2E but not appreciably populated at 77 K. In DMF–H_2O both levels are populated but to a degree that varies with the microenvironment of the complexes. At short times the emission originates from species in which the $^2E^Q \rightarrow {}^4A_2$ component is dominant. At long times the emission is mainly due to species with predominently $^2E \rightarrow {}^4A_2$ spectra. These results indicate that the difference in the behavior of $Cr(NH_3)_5(OH)^{2+}$ and *cis*-$CrN_4(OH)_2{}^+$ in hydroxylic solvents is not due to a serious defect in the angular-overlap model, since eq 2 correctly predicts the behavior in nonhydroxylic solvents. When $^2E^Q$ and ^2E are nearly coincident in energy, the solvent effects can be dramatic.

On the basis of spectral position and width as well as the $\Delta(t_2)$ value, *trans*-$Cr(en)_2(H_2O)F^{2+}$ was assigned as a $^2T_1$ emitter.[6] The emission from the cis isomer is sharp and at much shorter wavelength, indicating ^2E emission for the cis species. The emission spectrum and lifetime (τ = 50 μs) of *cis*-$Cr(en)_2(H_2O)F^{2+}$ is solvent independent, but the *trans*-$Cr(en)_2(H_2O)F^{2+}$ spectrum does exhibit the characteristic $^2T_1$ solvent shift (Figure 6) and the lifetime, which is 50 μs in DMF–H_2O, increases to 66 μs in alcohol–water. The solvent shifts in the monofluoro and monohydroxy species are small compared to their difluoro and dihydroxy counterparts. This is consistent with the belief that changes in H-bonding between the solvent and the F^- and OH^- ligands are responsible for the solvent effect.

trans-$Cr(py)_4F_2{}^+$ differs from *trans*-$Cr(NH_3)_4F_2{}^+$ and *trans*-$Cr(en)_2F_2{}^+$ in two respects: $\Delta'_{\pi_{py}} < 0$ and delocalization of the d electrons onto the ligands. The putative negative $\Delta'_{\pi_{py}}$ parameter has been the subject of dispute,[16,17] and this question will be treated elsewhere. Equation (2) must be modified if π-donation of the equatorial ligands does not vanish, and $\Delta'_{\pi_{py}} < 0$ leads to an increased $\Delta(t_2)$.

Environment and Decay Times. Excited-state lifetimes of many Cr(III) complexes have been reported. The environments vary from pure crystals to glassy solutions, and comparison of the intramolecular excited-state relaxation rates can be made only if there is confidence that the low-temperature limiting lifetimes are not affected by solute–environment interactions. Since the lifetime of a complex in an undiluted crystal is often less than in an isostructural crystalline host or a glassy matrix,[18] data from pure crystalline solids must be regarded with suspicion.

When pure dry DMF is plunged into liquid N_2 an opaque mass results. The addition of very small amounts of water leads to a cracked but translucent glass. Ofter the dissolved complex concentration is sufficiently high to prevent crystallization. Much higher water levels ($X_{H_2O} > 0.40$) are required to produce translucent Me_2SO–H_2O glasses. Frozen Me_2SO has been used as a solvent in some measurements of Cr(III) lifetimes.[19] X-ray diffraction patterns of frozen Me_2SO indicate considerable crystallinity, which disappears in Me_2SO–H_2O mixtures. Nonetheless, the lifetime and spectral data do not reveal any discontinuity in behavior between the glassy and the frozen pure solvent.

Solvent-induced red shifts in the $^2T_1$ emission are accompanied by a decreased lifetime. Although the influence of specific interactions cannot be excluded, much of the lifetime variation experienced by a given complex when the environment changes is probably due to the changing energy gap.[20] Since the energy gap is not changed in the ^2E emitters, the solvent will make little difference and, subject to the caveat discussed below, pure solvents are as suitable for low-temperature ^2E lifetime measurements as glassy solvent mixtures.

$Cr(NCS)_6{}^{3-}$ is a ^2E emitter whose sharp spectrum is at 780 nm in both alcohol–water glass and frozen DMF. However, the lifetime varies from 4.3 ms in alcohol–water to 10 ms in pure DMF. In the theory of radiationless transitions the nonradiative decay rate (k_{nr}) increases as the energy gap decreases[20] and the 77 K lifetime variation for $Cr(NCS)_6{}^{3-}$ in a group of pure frozen alcohols was attributed to the small changes in the $^2E \rightarrow {}^4A_2$ energy.[21] This interpretation is at odds with our observation that the $Cr(NCS)_6{}^{3-}$ decay is very different in DMF and alcohol–water, solvents in which the energy gap is the same. Furthermore, in this instance the changes in the measured lifetime are not a direct measure of the solvent effect on k_{nr}. $\tau^{-1} = k_r + k_{nr}$, where k_r is the radiative rate. In Cr(III) complexes k_r = 100–200 s^{-1}. The major influence of solvent on the $Cr(NCS)_6{}^{3-}$ lifetime is on the radiative rather than on the nonradiative contribution.

Summary and Conclusions

The largest $^2T_1$ splittings in CrN_4XY complexes are associated with F^- and OH^- ligands. The interaction between these two ligands and hydroxylic solvents leads to increases in the $^2E^Q$ energies. If $^2E^Q$ is sufficiently above ^2E, a sharp $^2E \rightarrow {}^4A_2$ emission spectrum that varies little with solvent obtains. In this case, the $^2E \rightarrow {}^4A_2$ energies are not very different in the cis and trans isomers. When $^2E^Q$ is much lower than ^2E, the $^2E^Q \rightarrow {}^4A_2$ emission is blue-shifted in hydroxylic solvents but remains broad in all solvents. Since the $^2T_1$ splitting is much larger in trans than in cis isomers, there will be a marked isomer effect on the spectrum. An intermediate situation prevails when $^2E^Q$ is only slightly below ^2E in nonhydroxylic solvents. The level order can then be reversed in hydroxylic solvents and the broad $^2E^Q \rightarrow {}^4A_2$ emission will then be transformed to the sharper $^2E \rightarrow {}^4A_2$ when the solvent is changed.

Our results suggest that solvent effects can be useful in the assignment of the emission spectra of quadrate Cr(III) complexes.

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(14) Hoggard, P. E. *Z. Naturforsch., A* **1981**, *36*, 1276.

(15) Forster, L. S.; Rund, J. V.; Castelli, F.; Adams, P. *J. Phys. Chem.* **1982**, *86*, 2395.

(16) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1980**, *19*, 2855.

(17) Gerloch, M.; Wooley, R. G. *Prog. Inorg. Chem.* **1984**, *31*, 371.

(18) Forster, L. S. *Adv. Chem. Ser.* **1976**, *No. 150*, 172.

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

(20) Avouris, P.; Gelbart, W. M.; El-Sayed, M. A. *Chem. Rev.* **1977**, *77*, 793.

(21) Lukowiak, E.; Strek, W.; Jezowska-Trzebiatowska, B. *Z. Naturforsch, A.* **1981**, *36*, 996.