Multiple Decays of $Cr(CN)_6^{3-}$ Emission in Rigid Glass Solutions[1]

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Abstract: $^2E \rightarrow {}^4A_2$ emission from $Cr(CN)_6^{3-}$ in rigid glass solution exhibits a nonexponential decay when excited at 398, 418, and 436 nm. The decay becomes exponential under 337- and 366-nm excitation. In fluid media, only a single exponential decay is evident at all excitation wavelengths. The dependence of the steady-state emission spectra on excitation wavelength, which is observed in rigid media, also disappears when the solvent becomes fluid. The results are ascribed to microenvironmental heterogenity. Species excited by wavelengths on the red side of the $^4T_{2g} \leftarrow {}^4A_{2g}$ band maximum exhibit different lifetimes and spectra from those excited in the main portion of the absorption spectrum.

The validation of mechanistic schemes for photochemical reactions involving Cr^{3+} complexes requires information about the lifetimes of the several excited states. In particular, controversies about the relative importance of the $^4T_2$ and ^2E states in a given photoreaction may hinge upon the magnitude of the $^4T_2$ lifetime.[2] Even when the $^4T_2$ state is definitely implicated, the decision between unimolecular and bimolecular primary processes leans heavily on the lifetime of the $^4T_2$ state.

Most Cr^{3+} complexes phosphoresce ($^2E \rightarrow {}^4A_2$) and many ^2E lifetimes have been reported.[3] Fluorescence ($^4T_2 \rightarrow {}^4A_2$) is a less common occurrence. According to Schläfer's rule,[4] when $^4T_2$ lies sufficiently above ^2E, $^4T_2$ is thermally inaccessible from ^2E and no fluorescence is expected. An apparent exception to this generalization was reported by Chen and Porter,[5] who observed a nonexponential decay from $Cr(CN)_6^{3-}$ dissolved in a rigid glass. They interpreted this decay in terms of a short-lived fluorescence (~50 μsec) superimposed upon the normal long-lived phosphorescence (~3 msec). The fluorescence and the phosphorescence emissions were assumed to overlap. Consequently, the fluorescence would have to be Stokes shifted some 14,000 cm^{-1}. Such a large Stokes shift could arise from large distortions in the $^4T_2$ state, a phenomenon postulated by Adamson as a possible mechanism for prolonging the lifetime of $^4T_2$ states.[2]

In view of the significance of the Chen and Porter results, we have reinvestigated the emission of $Cr(CN)_6^{3-}$ with varying excitation wavelengths. Our results suggest a different interpretation of the nonexponential decay.

Experimental Section

Emission decays were excited by a N_2 pulsed laser (Avco C-950) for 337 nm, N_2 laser pumped αNPO, POPOP, and BBOT dye lasers for 398, 418, and 436 nm, respectively. The pulse widths were 10 nsec or less. The dye lasers were operated in the superradiant mode with line widths of ~3 nm. The $Cr(CN)_6^{3-}$ emission, filtered through 3 cm of a saturated $K_2Cr_2O_7$ solution and a 2-59 Corning filter, was focussed onto the slit of a 0.25-m Jarrell-Ash monochromator (3.3 nm/mm), with a bandwidth of ~40 nm, whose output was detected by an uncooled Centronic photomultiplier (Q4283SA, red-extended S-20 response). The output of this tube was fed through a 27 kΩ load directly to the probe of a Tektronix 7904 oscilloscope with a 7A11 amplifier. The overall response time of the detection system was less than 1 μsec. Time resolved spectra were obtained with the same arrangement except the oscilloscope output was fed into a PAR Model 60 box car integrator and 2-mm slits were employed on the Jarrell-Ash monochromator. The averaged signal was then displayed on a strip chart recorder. Steady-state spectra were recorded with 90° geometry and excitation was furnished by a 100-W PEK Hg lamp–250 mm Bausch and Lomb monochromator combination. A 75-W PEK Xe lamp was used for the excitation spectra. The emission was passed through the Jarrell-Ash monochromator to the Centronic photomultiplier which was cooled to $-78°$. Cooling the photomultiplier changed the red sensitivity slightly and spectra obtained with the cooled and uncooled detectors are not identical.

The $Cr(CN)_6^{3-}$ solutions were prepared by dissolving recrystallized $K_3Cr(CN)_6$ in a H_2O, ethylene glycol, methyl alcohol (3:2:2 v/v) solvent.

Results

The decay curves of $Cr(CN)_6^{3-}$ in rigid glass solution at $-196°$ are shown in Figure 1 for several excitation wavelengths. For excitation at 418 nm, the decay is definitely nonexponential (Figure 2) with short-lived components and a long-lived component (3.9 msec). Chen and Porter obtained a similar result and computed lifetimes of 50 μsec and 3.45 msec for the short- and long-lived components, respectively.[5] However, as the excitation wavelength is reduced to 398 nm, the contribution of the short-lived emission decreases markedly, and under 337- and 366-nm excitation only a single decay is observed. This latter decay is quite exponential with $\tau = 3.95$ msec. With 436-nm excitation, the 3.95-msec component disappears, and only fast decay processes persist. This decay consists of many components with lifetimes in the range 50–1000 μsec.

As expected, when the temperature is increased and the solvent becomes fluid ($T \simeq -110°$), the lifetime decreases. This temperature dependence compares favorably with that obtained by Pfeil[6] for air-saturated solutions. Moreover, in fluid media, the τ values are identical and the decays are strictly exponential at all excitation wavelengths.

Time resolved spectra have been recorded for rigid solutions at $-196°$ (Figure 3). For 418- and 436-nm excitation, the spectra at 10 μsec and 2 msec are quite different in shape. Furthermore, the position of the

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[1] This research has been supported by National Science Foundation Grant GP20120. The laser was provided by a National Science Foundation equipment grant to the University of Arizona Chemistry Department (GP-29179).

[2] A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

[3] L. S. Forster, *Transition Metal Chem.*, 5, 1 (1969).

[4] H. L. Schläfer, H. Gausmann, and H. Witzke, *J. Chem. Phys.*, 46, 1423 (1967).

[5] S. N. Chen and G. B. Porter, *J. Amer. Chem. Soc.*, 92, 2189 (1970).

[6] A. Pfeil, *J. Amer. Chem. Soc.*, 93, 5395 (1971).

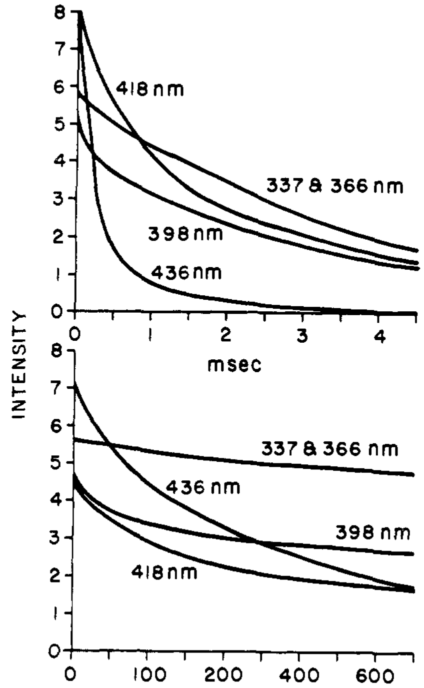

Figure 1. Decay curves of $Cr(CN)_6^{3-}$ in rigid glass at −196° at various excitation wavelengths.

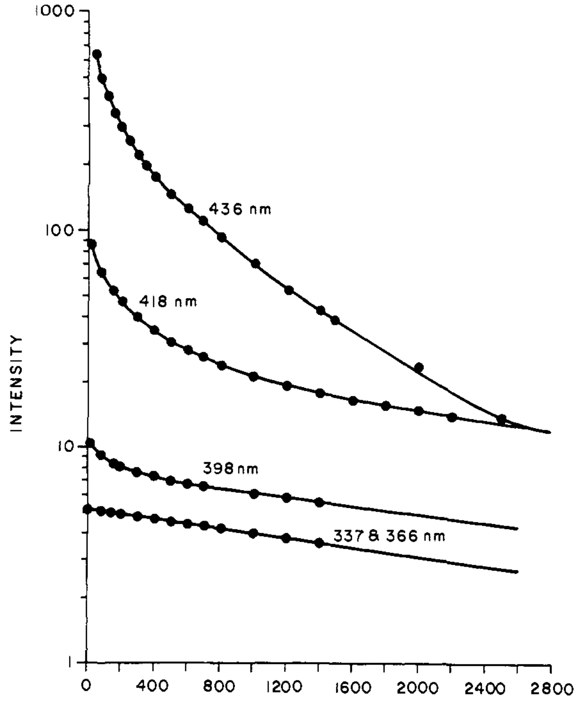

Figure 2. Semilog plots of $Cr(CN)_6^{3-}$ decays in rigid glass at −196°.

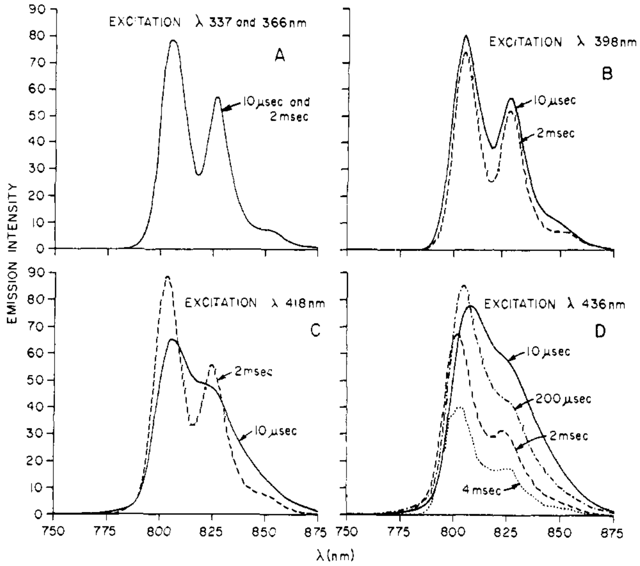

Figure 3. Time-resolved emission spectra of $Cr(CN)_6^{3-}$ in rigid glass at −196° at different excitation wavelengths. The gain was increased at longer times.

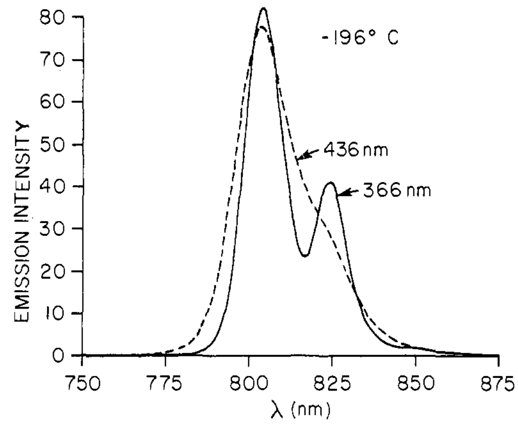

Figure 4. Steady-state emission spectra of $Cr(CN)_6^{3-}$ in rigid glass at −196° at different excitation wavelengths. The spectra excited at 405 and 366 nm are identical.

maximum shifts to shorter wavelengths at longer times. This difference decreases when the excitation wavelength is reduced to 398 nm and disappears entirely for 337- and 366-nm excitation. The 2-msec spectra are the same for 337-, 366-, 398-, and 418-nm excitation.

Emission spectra have also been obtained under conditions of steady illumination. At −196° the steady-state spectra vary markedly with excitation wavelength (Figure 4). Spectra excited by 405, 366, and shorter wavelengths are identical but differ substantially from those observed with excitation at 436 nm. The excitation spectrum for 815-nm emission clearly shows an enhancement of the red tail when compared with excitation spectrum for 803-nm emission (Figure 5). As the temperature is increased, the 826-nm peak in the 366-nm excited spectrum decreases progressively (Figure 6). At 436-nm excitation the spectral shape is hardly changed in a temperature range −196 to −140°. As the solvent rigidity decreases rapidly above −130°, the 436-nm spectrum actually sharpens and the 826-nm shoulder is more clearly resolved (Figure 6). At −78° the 436- and 366-nm spectra are identical. Furthermore, at −78° the spectra are the same in air-saturated and deoxygenated solutions.

Microcrystallite emission can be ruled out as the source of the spectral and lifetime changes. The emission spectrum of microcrystallites, deliberately induced, is quite different from the solution spectrum.

Discussion

The absorption spectrum and energy level diagram of $Cr(CN)_6^{3-}$ are shown in Figure 7. After excitation

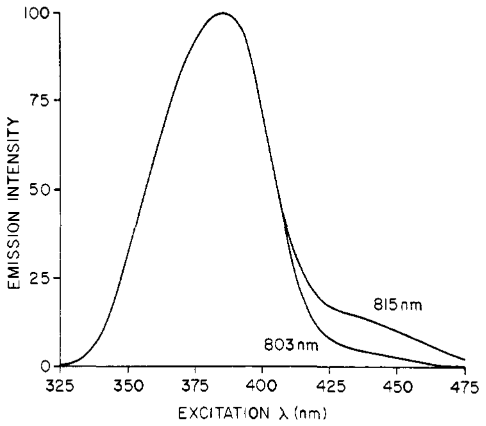

Figure 5. Excitation spectra of $Cr(CN)_6{}^{3-}$ in rigid glass at −196° for different emission wavelengths.

into $^4T_2$, vibrational relaxation within $^4T_2$ competes with intersystem crossing to the doublet manifold. According to the Chen and Porter interpretation, the luminescence of $Cr(CN)_6{}^{3-}$ consists of both fluorescence and phosphorescence. In their model, our result that the short-lived fluorescence is absent under 337- and 366-nm illumination would be due to a more efficient intersystem crossing at higher energies.

The evidence against the fluorescence interpretation may be summarized as follows.

(i) The short-lived component disappears when the solvent becomes fluid.

(ii) No short-lived component due to $Cr(CN)_6{}^{3-}$ is detectable in crystals of $Cr^{3+}:K_3Co(CN)_6$ at any of the excitation wavelengths.

(iii) The decay at short times consists of many components with different lifetimes.

On the basis of the foregoing, we rule out fluorescence as the source of the short-lived emission. We also exclude impurities as the origin of the observed wavelength dependence since the impurity emission would then have to be completely absent in fluid solvents. In addition, the multiplicity of emission components would require contributions from many different impurities. Instead, we ascribe the wavelength dependence in rigid media to microenvironmental heterogeneity. This phenomenon has been implicated by Galley and Purkey as the origin of the wavelength dependence of indole fluorescence in rigid media.[7] According to this model each absorbing species (A_i) has a particular arrangement of solvent dipoles at the instant of absorption. In a rigid environment this arrangement cannot change during the lifetime of the excited states, *i.e.*, the solvent–solute relaxation time is much longer than the excited-state lifetime. The long wavelength tail of the absorption band is due mainly to species with the smallest transition energies.

No variation in the lifetime of a single excited state due to environmental heterogeneity has to our knowledge been reported. If the lifetime is not sensitive to solute–solvent interaction, all A_i have nearly the same lifetimes and an exponential decay results, a common observation in glassy systems. However, if the interaction is strong, the lifetimes, τ_i, would differ from one species to another and a nonexponential decay would obtain. Our results indicate that some of the species excited by irradiation into the long wavelength tail of the $^4T_{2g} \leftarrow {}^4A_{2g}$ band are shorter lived than those responsible for the bulk of the absorption band. In fact, the shorter lived species span a range of decay constants.

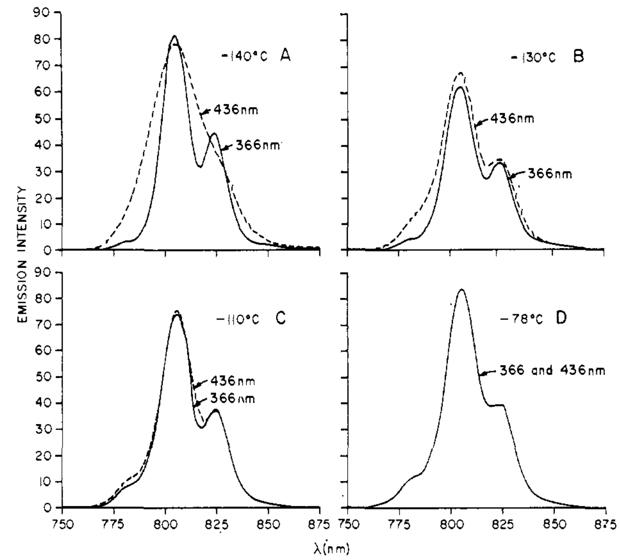

Figure 6. Steady-state emission spectra of $Cr(CN)_6{}^{3-}$ solutions at different temperatures and excitation wavelengths.

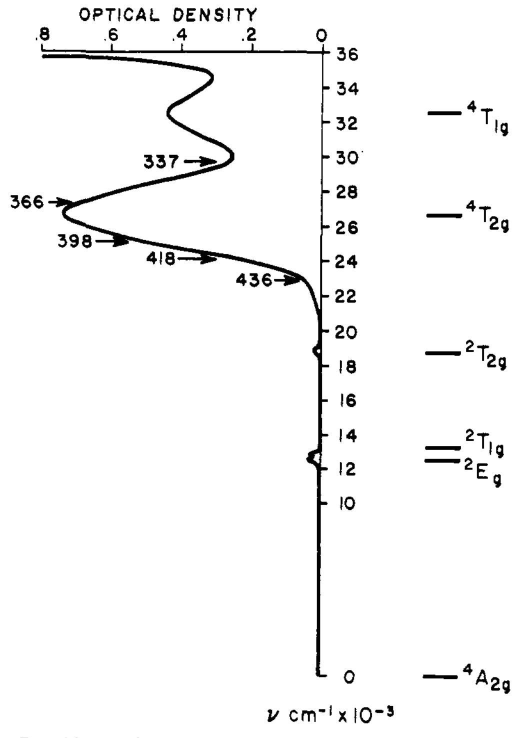

Figure 7. Absorption spectrum and energy level scheme of $Cr(CN)_6{}^{3-}$. The intensities of the spin-forbidden transitions are enhanced for clarity.

The emission spectrum of the short-lived species is broadened and shifted to longer wavelengths (Figure 3). This spectral shift is analogous to that reported for indole. The 436-nm steady-state spectrum is different in shape from that excited at shorter wavelengths but is not red shifted. The difference between the 436-nm time-resolved and steady-state spectra is attributed to the greater weighting of the shorter lived species in the pulsed spectrum. The relative emission intensity,

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[7] W. C. Galley and R. M. Purkey, *Proc. Nat. Acad. Sci. U. S.*, **67**, 1116 (1970).

pulsed to steady state, of any species is increased by the ratio of the lifetimes, a factor that approaches 80 in this case.

It is reasonable to associate the short-lived species with a solvent orientation that leads to the strongest solute–solvent interaction. The emission spectrum of $Cr(CN)_6^{3-}$ is unusually sensitive to environment; the ratio of the 803- and 826-nm peak heights varies considerably with the counterion in $M_3Cr(CN)_6$ crystals.[8] Furthermore, the ^2E lifetime varies from 150 msec in $Cr^{3+}:K_3Co(CN)_6$ to 4 msec for $Cr(CN)_6^{3-}$ dissolved in a rigid glass at 77°K.[9] It is, therefore, not surprising to find a range of lifetimes in rigid glass environments. Apparently only a small fraction of the $Cr(CN)_6^{3-}$ is in a strongly interacting environment. The lifetimes associated with the bulk of the ions must lie in a small range near 4 msec.

In fluid solvents, the solvent relaxation time is short compared with the $Cr(CN)_6^{3-}$ lifetime, and each $Cr(CN)_6^{3-}$ can sample the entire range of solute–solvent configuration, *i.e.*, sees an average environment. This leads to exponential decay with identical lifetimes at all excitation wavelengths, and the excitation wavelength dependence of the emission spectrum disappears.

Thus, all of our results appear to be explicable in terms of environmental heterogeneity. As further support for this interpretation, we cite the properties of $[(C_4H_9)_4N]_3Cr(CN)_6$, a salt which is more soluble than $K_3Cr(CN)_6$ in nonaqueous media. This salt exhibits the same behavior as $K_3Cr(CN)_6$ in rigid H_2O, ethylene glycol, and methyl alcohol solvent. When dissolved in ethanol at low temperature, $[(C_4H_9)_4N]_3Cr(CN)_6$ shows the same lifetime behavior (nonexponential decay, wavelength dependence of decay), but the steady-state and time-resolved spectra are different in the two solvents at all excitation wavelengths, including 366 nm. This again documents the sensitivity of $Cr(CN)_6^{3-}$ emission to environment.

It is now clear that the $^4T_{2g}$ lifetime is much shorter than 50 μsec. In fact, at room temperature, the rise-time of the $^2E \rightarrow {}^4A_2$ $Cr(CN)_6^{3-}$ emission is less than 10^{-9} sec (under 398-nm excitation).[10] Thus, the $^4T_{2g}$ lifetime in $Cr(CN)_6^{3-}$ is very short and excited-state distortions, if present, do not lead to a substantial lifetime prolongation.

The red-edge effect has been observed for polar molecules dissolved in polar glasses.[7] A comparable effect with symmetric molecules was not anticipated. Care should be exercised in analyzing spectral and lifetime data in rigid media when excitation beyond the absorption maximum is involved. Precautions are particularly important under pulsed conditions when the lifetimes of "normal" and "red-edge" species may be quite different.

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(9) F. Diomedi Camassei and L. S. Forster, *J. Chem. Phys.*, **50**, 2603 (1969).

(10) F. Castelli and L. S. Forster, to be published.

Interactions of Divalent Metal Ions with Inorganic and Nucleoside Phosphates. III. Temperature Dependence of the Magnesium(II)–Adenosine 5'-Triphosphate, –Adenosine 5'-Diphosphate, and –Cytidine 5'-Diphosphate Systems

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Abstract: Kinetic data as a function of temperature over the range 5–35° are reported for the reactions of Mg^{2+} with ATP^{4-}, ADP^{3-}, and CDP^{3-}. The results for all three systems are compatible with a mechanism involving complexation with the phosphate moiety, the rate-determining step being the expulsion of a water molecule(s) from the inner hydration sphere of Mg^{2+}. The rate constants at 25° and the activation parameters are compared with the analogous quantities for the nmr water exchange rate. Our results are completely consistent with an SN1 complexation mechanism. We conclude that the activation enthalpy is a more reliable mechanistic criterion than rate constants.

Considerable evidence has been accumulated to indicate that simple metal complexing reactions occur *via* a two-step process. The first step entails the diffusion-controlled formation of an outer sphere complex in which the reaction partners are separated by an interposed solvent layer. The second step, which is rate limiting, involves the penetration of the ligand into the inner coordination sphere of the metal ion.

From a compilation[2] of a large number of results it has been concluded that many reactions involving, *e.g.*, Ni^{2+}, Co^{2+}, and Mg^{2+}, are characterized by a ligand penetration rate constant which is a function of the metal ion but is essentially independent of the nature of

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(1) National Institutes of Health Career Development Awardee (17834).

(2) M. Eigen and R. Wilkins, *Advan. Chem. Ser.*, No. **49**, 55 (1965).