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Excited State Relaxation in $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ Complexes

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Abstract

The emission spectra and excited state decay rates have been recorded for $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ (n = 0–6) complexes. Both the transition energy and relaxation rates increase with n but the large changes in transition energies are not sufficient to account for the failure of the displaced coordinate to explain the relaxation rate results.

Introduction

One approach to exploring the systematics of emission in Cr(III) complexes is to determine the $^2E \rightarrow {}^4A_2$ decay rates in a $CrA_{6-n}B_n$ series with $n = 0$–6. In previous work, $Cr(NCS)_{6-n}(DMSO)_n^{n-3}$ [1], $Cr(NH_3)_{6-n}(H_2O)_n^{3+}$ [2], $Cr(NCS)_{6-n}(NH_3)_n^{n-3}$ [2] and $Cr(D_2O)_{6-n}(NH_3)_n^{3+}$ [2] have been studied. Ligands can be classified as good or poor quenchers according to the lifetime of the CrA_6 species. Radiative rates in Cr(III) complexes are 100–300 s^{-1} and when $\tau = 1/(k_r + k_{nr}) > 4$ ms, $k_{nr} \simeq 0$. Homoliganded complexes with these long lifetimes contain the poor quenchers ND_3, 2,2′-bipyridine, 1,10-phenanthroline, CN^-, and NCS^-.

Non-radiative rates for ^2E relaxation have been interpreted theoretically [3–7]. Strek found that a displaced coordinate model was sufficient to describe the variation of the relaxation rates with n in $Cr(NCS)_{6-n}(H_2O)_n^{n-3}$ and $Cr(NCS)_{6-n}(DMSO)_n^{n-3}$ complexes [1, 3]. However, the $Cr(NCS)_{6-n}(NH_3)_n^{n-3}$ results did not conform to this simple model [2]. We now examine the relationship between the number of good and poor quenching ligands and the excited state decay rate in the mixed ligand complexes $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ (n = 0–6).

Experimental

$K_3Cr(CN)_6$ was synthesized by the method of Schaap *et al.* [8]. The $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ complexes with n = 1–5 were synthesized in aqueous solutions as described by Jimerson [9]. Jimerson's method for the preparation of $Cr(CN)_5(H_2O)^{2-}$ yielded a solution with an incorrect absorption spectrum. When the solution was passed through an anion exchange column in a cold room, an unknown species which absorbed strongly at 300 nm was eluted after *cis*-$Cr(CN)_4(H_2O)_2^-$. Upon further elution $Cr(CN)_5(H_2O)^{2-}$ was collected. With this exception, the preparations went smoothly and the spectra agreed well with those published.

A sample was prepared for emission by the addition of two parts of ethylene glycol to one part of the aqueous solution, by volume, and was then kept at 77 K until the measurements were made. 337 nm excitation was obtained with an N_2 laser and longer wave lengths with a dye laser pumped by the N_2 laser. The decays were analyzed as described elsewhere [10]. Box-car detection was used for the spectral recording.

Results and Discussion

The $^2E \rightarrow {}^4A_2$ energy is a monotonic function of n (Fig. 1). Similar behavior prevails in $Cr(NCS)_{6-n}(NH_3)_n^{n-3}$ and $Cr(NCS)_{6-n}(DMSO)_n^{n-3}$ and is due to d-electron delocalization onto the CN^- and NCS^- ligands which have low-lying anti-bonding orbitals. The nephelauxetic effect increases progressively with the number of π-acceptor ligands.

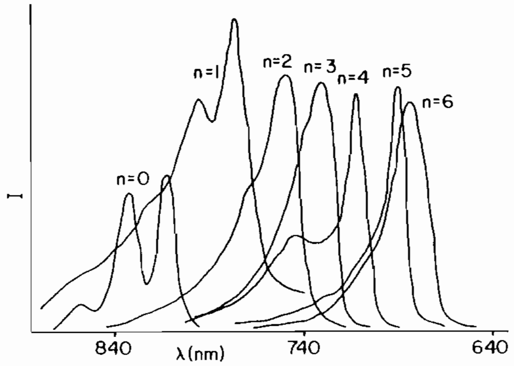

Fig. 1. 77 K emission spectra $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ complexes in ethylene glycol–H_2O (2:1 v/v)

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TABLE I. $^2E \rightarrow {}^4A_2$ Transition Energies and Lifetimes for $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ Complexes in Ethylene Glycol–H_2O at 77 K

n	ΔE (μ m^{-1})	$\tau \times 10^{-6}$ (s)	k_{nr} (s^{-1})^a
0	1.238	4200	0
1	1.290	1500–2500	200–400
2	1.328	150–230	4150–6450
3	1.370	180	5300
4	1.408	110	8900
5	1.455	55	17900
6	1.468	17^b	<60000

$^a k_{nr} = \tau^{-1} - 240$. ^{b}Ref. 2.

^2E lifetimes at 77 K are listed in Table I. The $Cr(CN)_5H_2O^{2-}$ and $Cr(CN)_4(H_2O)_2^-$ decays were somewhat non-exponential and a range of lifetimes are indicated. With one exception, 77 K is sufficiently low to achieve the low temperature limiting value for the lifetime. The low temperature limit is not quite reached at 77 K for $Cr(H_2O)_6^{3+}$ and the tabulated rate is an upper limit [2]. These uncertainties do not vitiate the following discussion.

The small k_{nr} in $Cr(CN)_6^{3-}$ and $Cr(NCS)_6^{3-}$ are ascribed to the absence of high frequency intraligand modes that can function as effective accepting vibrations. The highest energy vibrations in CN^- and NCS^- are approximately 2100 cm^{-1} [11]. In contrast, the energies of O–H stretching modes are near 3400 cm^{-1}, making H_2O a good quenching ligand. Successive replacement of a poor quencher by a good quencher in $CrA_{6-n}B_n$ usually leads to an increase in k_{nr}.

The low temperature non-radiative decay rate can be expressed as [12]

$$k_{nr} = (2\pi/\hbar)\langle {}^2E|H'|{}^4A_2\rangle^2 F \tag{1}$$

where the electronic factor depends upon $\langle {}^2E|H'|{}^4A_2\rangle$ (H' represents the vibronic and spin–orbit coupling perturbations) and F is a sum of the squared Franck–Condon factors for all the combinations of accepting and promoting modes that satisfy the energy conservation requirement. The modes responsible for the vibronic perturbation are termed promoting [12]. In the displaced coordinate approximation the weak coupling limit at low temperatures yields [4].

$$F \alpha \exp[-S - (\Delta E/h\nu_M)(\ln(\Delta E/S_M h\nu_M) - 1)] \tag{2}$$

where ΔE is the $^2E \rightarrow {}^4A_2$ transition energy less the energy of the promoting mode and ν_M is the frequency of the high energy accepting mode. S is a measure of the total horizontal displacement between the minima of the potential surfaces while S_M refers to the displacement along the accepting mode coordinates.

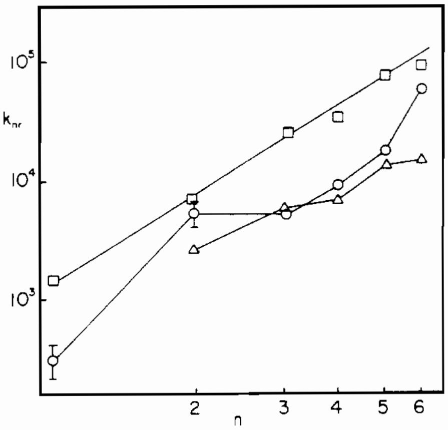

Fig. 2. $k_{nr} = \tau^{-1} - 240$ (s^{-1}) at 77 K: ○ $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ in ethylene glycol–H_2O; △ $Cr(NCS)_{6-n}(NH_3)_n^{n-3}$ (from ref. 2); and □ $Cr(NCS)_{6-n}(DMSO)_n^{n-3}$ in DMSO (from ref. 3).

Strek [1] suggested that in $CrA_{6-n}B_n$ complexes with poor quenchers A and good quenchers B, S_M is proportional to n and that eqn. (2) reduces to

$$F \alpha (n)^{(\Delta E/h\nu_M)} \tag{3}$$

Equation (3) is based on the assumption that the transition energy is fixed. The $Cr(CN)_{6-n}(H_2O)_n^{n-3}$-$k_{nr}$ are compared to the $Cr(NCS)_{6-n}(DMSO)_n^{n-3}$ and $Cr(NCS)_{6-n}(NH_3)_n^{n-3}$ values in Fig. 2 (log–log plot). Although the $Cr(NCS)_{6-n}(DMSO)_n^{n-3}$ results are consistent with eqn. (3) if $k_{nr} = \tau^{-1} - 300$ s^{-1}, k_{nr} decreases with ΔE (the energy gap law) and correction for the 1200 cm^{-1} transition energy shift would lead to an upward curvature in the plot. The corresponding energy difference within the $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ series is 2300 cm^{-1}. Thus, $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ is another example of a group whose behavior is not described by eqn. (3).

The most obvious reasons for the failure of eqn. (3) are: (1) the inadequacy of the displaced coordinate model for the calculation of F; and (2) changes in the electronic factor. Surely, $\langle {}^2E|H'|{}^4A_2\rangle$ will vary with n. Kupka has included changes in ν_M between the ^2E and $^4A_2$ levels in the analysis and finds that the frequency changes dominate when the coordinate displacement is small [13], as in the Cr(III) $^2E \rightarrow {}^4A_2$ transition. It is not surprising that the displaced coordinate model is not successful here.

An additional feature is the contrast between the smooth dependence of the $Cr(NCS)_{6-n}(DMSO)_n^{n-3}$-$k_{nr}$ upon n and the kinks in the $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ and $Cr(NCS)_{6-n}(NH_3)_n^{n-3}$ plots. In the former group little change is observed between $n = 2$ and $n = 3$, while in the latter plateaus occur from $n = 3$ to $n = 4$ and $n = 5$ to $n = 6$. Kupka has extended his treatment to encompass $MA_{6-n}B_n$ complexes and has made calculations for a range of coordinate displacements and frequency changes [14]. These calculations indicate that in the presence of the good quenchers H_2O ($\nu_M = 3400$ cm^{-1}) and NH_3 ($\nu_M = 3200$ cm^{-1}), the contribution of the poor quenchers CN^- and NCS^- ($\nu_M = 2100$ cm^{-1}) to k_{nr} is small, <15%. The low frequency ligand modes as well as the skeletal modes must function to some extent as acceptors in order to satisfy the energy conservation requirement. As the transition energy is decreased, the number of 3200–3400 cm^{-1} quanta needed to bridge the ΔE gap might decrease discontinuously and the $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ plateau could be due to this phenomenon, but it is difficult to ascribe the shape of the $Cr(NCS)_{6-n}(NH_3)_n^{n-3}$ curve to this source.

The nephelauxetic red-shift induced in $^2E \rightarrow {}^4A_2$ transitions by delocalizing the d-electrons onto π-accepting ligands leads to a nearly linear increase in energy with n for $Cr(CN)_{6-n}(H_2O)_n^{n-3}$ and $Cr(NCS)_{6-n}(DMSO)_n^{n-3}$. In $Cr(NCS)_{6-n}(NH_3)_n^{n-3}$ the transition energy is a monotonic but not a linear function of n. However, the deviation from linearity is not too large and as a first approximation, each π-accepting ligand can be assigned a nephelauxetic parameter independent of the other coordinated groups.

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