

^2E Relaxation in Mixed-Ligand $\text{Cr}(\text{NH}_3)_{6-n}\text{X}_n$ Complexes

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^2E relaxation rates in glassy solutions at 77 K for several complexes in each of the following groups have been determined: $\text{Cr}(\text{NH}_3)_{6-n}(\text{H}_2\text{O})_n^{3+}$, $\text{Cr}(\text{NH}_3)_{6-n}(\text{D}_2\text{O})_n^{3+}$, $\text{Cr}(\text{ND}_3)_{6-n}(\text{H}_2\text{O})_n^{3+}$, $\text{Cr}(\text{ND}_3)_{6-n}(\text{D}_2\text{O})_n^{3+}$, and $\text{Cr}(\text{NH}_3)_{6-n}(\text{NCS})_n^{3+}$. Except for $\text{Cr}(\text{NH}_3)_{6-n}(\text{D}_2\text{O})_n^{3+}$, the nonradiative rate for a mixed-ligand complex lies between the values for the homoligated complexes. NCS^- and ND_3 are characterized as nonquenching ligands, while NH_3 and H_2O are good quenchers. D_2O is a poor quencher, but not a nonquencher. The nonradiative relaxation rate in a $\text{Cr}(\text{III})$ complex with NCS^- , D_2O , or ND_3 ligands is markedly increased by substitution of two good quenching ligands. A satisfactory interpretation of the ligand effects must include consideration of promoting mode changes as well as the contributions of the accepting modes.

Introduction

The effect of molecular structure on radiationless transitions has been the subject of continuing interest (for reviews see ref 1-3). The most extensive data have been obtained with aromatic and heteroaromatic molecules and with rare-earth complexes. High-frequency vibrations (C-H and O-H) are mainly responsible for nonradiative relaxation in these molecules and progressive deuteration decreases the nonradiative rate.

In order to gain a deeper insight into the relative importance of the several factors that determine nonradiative rates, it is desirable to alter the molecular structure in a systematic manner. Varying the number of C-D or O-D bonds in a molecule represents one approach to this problem. Luminescent transition-metal complexes, in general, and $\text{Cr}(\text{III})$ complexes, in particular, are an attractive class of molecules for measuring nonradiative rates as a function of molecular structure. It is relatively easy to produce a sequence of $\text{CrA}_{6-n}\text{B}_n$ complexes with many different A and B pairs and to vary n for each pair over all or most of the range $n = 0$ to $n = 6$. Furthermore, most $\text{Cr}(\text{III})$ complexes luminesce at low temperatures in glassy solutions. We studied the ^2E decay behavior in the entire set of $\text{Cr}(\text{NH}_3)_{6-n}(\text{H}_2\text{O})_n^{3+}$ complexes⁴ and found that the nonradiative rate increases with n ; i.e., H_2O is a better ^2E quencher than NH_3 , but both ligands are good quenchers. Deuteration of NH_3 in $\text{Cr}(\text{NH}_3)_6^{3+}$ markedly reduces the ^2E relaxation rate and consequently ND_3 is not a good ^2E quencher.⁵ D_2O and NCS^- are also poor quenchers.⁶

In theoretical treatments of nonradiative processes, the rates depend upon the effectiveness of promoting and accepting vibrations.¹⁻³ By studying $\text{CrA}_{6-n}\text{B}_n$ complexes with A and B ligands that have markedly different quenching propensities, one may be able to sort out the factors responsible for the ^2E relaxation rates. We now report these rates for ligand pairs in the group NH_3 , ND_3 , H_2O , D_2O , and NCS^- .

Experimental Section

Materials. H-D exchange in H_2O is rapid at all reasonable pH values, but in NH_3 H-D exchange is much slower in acid solution;⁷ deuteration of coordinated NH_3 is base catalyzed. The complexes were prepared as follows.

$\text{Cr}(\text{ND}_3)_{6-n}(\text{D}_2\text{O})_n^{3+}$: Each fully deuterated complex was prepared by dissolving the solid containing the species of interest⁴ in D_2O and adding sodium acetate as specified to control the pH; $\text{Cr}(\text{ND}_3)_6^{3+}$ and $\text{Cr}(\text{ND}_3)_5(\text{D}_2\text{O})^{3+}$, 0.1 M; *cis*- and *trans*- $\text{Cr}(\text{ND}_3)_4(\text{D}_2\text{O})_2^{3+}$, 1.5 M. The solution, which changed color immediately upon addition of sodium acetate, was placed in the dark until full deuteration occurred, 3-5 h. The solution was then acidified with DCl and mixed with an equal volume of Me_2SO and the lifetime measured at 77 K. The criterion for complete deuteration was an exponential ^2E decay. The original color did not always return upon acidification, indicating a side reaction. The emission spectrum corresponded in each case to the species of interest. Apparently, the unwanted products are nonluminescent. The competition between the side reaction and deuterated complex formation becomes more serious with increasing n . In spite of repeated efforts, we were able to obtain an exponential decay from either *cis*- or *trans*- $\text{Cr}(\text{ND}_3)_2(\text{D}_2\text{O})_4^{3+}$. **$\text{Cr}(\text{NH}_3)_{6-n}(\text{D}_2\text{O})_n^{3+}$:** The solid perprotiated complex was added to acidified D_2O . After immediate mixing with Me_2SO , the solution was quickly frozen in liquid N_2 . **$\text{Cr}(\text{ND}_3)_{6-n}(\text{H}_2\text{O})_n^{3+}$:** The solution containing $\text{Cr}(\text{ND}_3)_{6-n}(\text{D}_2\text{O})_n^{3+}$ was acidified with HCl (pH < 3) and then diluted 10-fold with acetone. The resultant precipitate was separated, air dried by aspiration for several minutes, and then dissolved in acidified H_2O . **$\text{Cr}(\text{NH}_3)_{6-n}(\text{NCS})_n^{3+}$:** $\text{K}_3\text{Cr}(\text{NCS})_6$ and $\text{KCr}(\text{NH}_3)_2(\text{NCS})_4$ were recrystallized Alfa products. $[\text{Cr}(\text{NH}_3)_5(\text{NCS})](\text{NO}_3)_2$, *trans*- $[\text{Cr}(\text{NH}_3)_4(\text{NCS})_2]\text{ClO}_4$, and $\text{Cr}(\text{NH}_3)_3(\text{NCS})_3$ were prepared by literature methods.^{8,9}

Data Collection. The complexes, dissolved in Me_2SO - D_2O or Me_2SO - H_2O glasses (1:1 v/v) for aquoammines and

(1) Freed, K. F. "Topics in Applied Physics"; Springer-Verlag: New York, 1976; Vol. 15, Chapter 2.

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

(3) Englman, R. "Non-Radiative Decay of Ions and Molecules in Solids"; North-Holland Publishing Co.; Amsterdam, 1979.

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

(5) Flint, C. D.; Mathews, A. P. *Chem. Commun.* 1971, 954.

(6) Chatterjee, K. K.; Forster, L. S. *Spectrochim. Acta.* 1965, 20, 1603.

(7) Palmer, J. W.; Basolo, F. J. *Inorg. Nucl. Chem.* 1960, 15, 279.

(8) Zinato, E.; Lindholm, D.; Adamson, A. W. *J. Am. Chem. Soc.* 1969, 91, 1076.

(9) Kirk, A. D.; Wong, C. F. C. *Inorg. Chem. Acta.* 1978, 27, 265. (a) Werner, A.; Halbon, J. v. *Ber.* 1906, 39, 2668.

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TABLE I: τ^{-1} (s^{-1}) of $\text{Cr}(\text{III})$ Complexes in Glasses at 77 K

n	$\text{Cr}(\text{NH}_3)_{6-n}(\text{H}_2\text{O})_n^{3+}$	$\text{Cr}(\text{NH}_3)_{6-n}(\text{D}_2\text{O})_n^{3+}$	$\text{Cr}(\text{ND}_3)_{6-n}(\text{D}_2\text{O})_n^{3+}$	$\text{Cr}(\text{ND}_3)_{6-n}(\text{H}_2\text{O})_n^{3+}$	$\text{Cr}(\text{NH}_3)_{6-n}(\text{NCS})_n^{3-n}$
0	14 700	14 700	185	185	14 700
1	19 600	17 500	280	1600	14 300
2 (trans)	25 000	18 900	430	6290	7100
2 (cis)	23 800	19 200	405	3760	
3	29 400				6250
4 (trans)	33 000	10 000			2860
6	60 000	<2 000	<2000	60000	240

ethylene glycol- H_2O glasses (2:1 v/v) for (thiocyanato)-ammines, were excited at 337 nm by an N_2 laser or at longer wavelengths by an N_2 laser pumped dye laser and the decays recorded as described elsewhere.⁴ Emission spectra were determined by scanning a 0.25-m Jarrell-Ash monochromator (1-mm slits) and averaging with a PAR Model 160 Box-Car integrator. Samples were immersed directly in liquid N_2 for the 77 K data; 65 K was achieved by pumping on liquid N_2 .

Results

The 2E relaxation rates at 77 K (τ^{-1}), as monitored by the decay of the $^2E \rightarrow ^4A_2$ intensity, are collected in Table I. In $\text{Cr}(\text{NH}_3)_{6-n}(\text{H}_2\text{O})_n^{3+}$ complexes, the decay behavior in $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ and alcohol- H_2O glasses was the same. Also, 2E relaxation rates of both $\text{Cr}(\text{NH}_3)_6^{3+}$ and $\text{Cr}(\text{ND}_3)_6^{3+}$ are virtually identical in $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ and $\text{Me}_2\text{SO}-\text{D}_2\text{O}$ glasses. The decays were invariant to excitation wavelength.

Our purpose is to compare the low-temperature relaxation rates as a function of ligation. The term "low-temperature limit" needs clarification since 2E is split by the combined action of spin-orbit coupling and a low-symmetry ligand field. The decay rates of the two components of $^2E \rightarrow ^4A_2$ need not be the same. In ruby, where the radiative rate dominates, the decay rate does not reach a plateau as the temperature is reduced but passes through a minimum.¹⁰ However, except for $\text{Cr}(\text{D}_2\text{O})_6^{3+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, the lifetimes of the complexes studied here as well as most other $\text{Cr}(\text{III})$ complexes^{4,6,10,11} reach a definite plateau above 77 K. The value of τ^{-1} at this plateau is the low-temperature limit. The 2E splitting is negligible in $[\text{Cr}(\text{NH}_3)_6](\text{ClO}_4)_3$ ¹² and estimates of the 2E splitting in $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{ClO}_4)_3$ range from 20 ± 10^{13} to $\sim 200^{14,15} \text{ cm}^{-1}$. The near invariance of τ to temperature changes in the range -120 to -196°C for complexes with quite different 2E splittings indicate that the nonradiative relaxation rates are not very different for the two components of 2E . The existence of a plateau precludes any contribution from thermally activated photochemical processes.

The complexes are embedded in different solvent microenvironments and a distribution of $^2E \rightarrow ^4T_2$ energy separations prevails. When this energy gap is large enough to eliminate $^2E \rightarrow ^4T_2$ back transfer ($n < 4$), an exponential decay is observed in $\text{Cr}(\text{NH}_3)_{6-n}(\text{H}_2\text{O})_n^{3+}$ complexes.⁴ Similarly, the 2E decays in $\text{Cr}(\text{NH}_3)_5(\text{D}_2\text{O})_1^{3+}$ and $\text{Cr}(\text{NH}_3)_4(\text{D}_2\text{O})_2^{3+}$ were exponential, but the $\text{Cr}(\text{NH}_3)_2(\text{D}_2\text{O})_4^{3+}$ decay was slightly nonexponential. It was possible

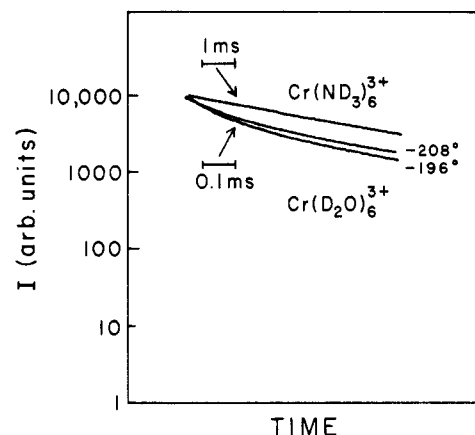


Figure 1. Decay profiles of $\text{Cr}(\text{ND}_3)_6^{3+}$ at -196°C and $\text{Cr}(\text{D}_2\text{O})_6^{3+}$ at -196 and -208°C in $\text{Me}_2\text{SO}-\text{D}_2\text{O}$ (1:1 v/v). Note change in time base.

to prepare $\text{Cr}(\text{ND}_3)_6^{3+}$ without appreciable contamination by partially deuterated complexes, but to minimize side reactions in the preparation of $\text{Cr}(\text{ND}_3)_5(\text{D}_2\text{O})_1^{3+}$ and $\text{Cr}(\text{ND}_3)_4(\text{D}_2\text{O})_2^{3+}$ the reaction was terminated before a completely exponential decay was achieved. Nevertheless, the deviation from exponentiality was small and good exponential tails were obtained. The Table I values were derived from these tails. In spite of some nonexponentiality, we feel that the difference between *cis*- and *trans*- $\text{Cr}(\text{ND}_3)_4(\text{H}_2\text{O})_2^{3+}$ is real. All of the $\text{Cr}(\text{NH}_3)_{6-n}(\text{NCS})_n^{3-n}$ decays were very exponential.

The decay profiles in $\text{Cr}(\text{D}_2\text{O})_6^{3+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ were very nonexponential at 77 K. As the temperature was decreased to 65 K, both the initial and the tail decays became slower (Figure 1). The tail lifetime in $\text{Cr}(\text{D}_2\text{O})_6^{3+}$ is increased from 450 μs at 77 K to 500 μs at 65 K. Thus, the 2000- s^{-1} value for $\text{Cr}(\text{D}_2\text{O})_6^{3+}$ is an upper limit for the 2E decay rate.

Discussion

In the low-temperature limit, the total decay rate (τ^{-1}) is the sum of the radiative $^2E \rightarrow ^4A_2$ (k_r) and nonradiative $^2E \rightarrow ^4A_2$ (k_{nr}) rates. Radiative rates in $\text{Cr}(\text{III})$ complexes range from 10 s^{-1} in centrosymmetric systems, e.g., $\text{Cr}^{3+}:\text{K}_3\text{Co}(\text{CN})_6$ ¹² to 250 s^{-1} in $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$.¹⁰ k_r for $\text{Cr}(\text{NH}_3)_6^{3+}$ has been estimated from the absorption intensity as 50 s^{-1} .¹¹ The near identity of τ^{-1} in $\text{Cr}(\text{ND}_3)_6^{3+}$ and $\text{Cr}(\text{NCS})_6^{3-}$ suggests that $k_{nr} \approx 0$ in these two complexes, and k_r is $\sim 200 \text{ s}^{-1}$ in all of the complexes considered here. The absence of an isomer effect in the $\text{Cr}(\text{ND}_3)_4(\text{D}_2\text{O})_2^{3+}$ complexes indicates that the radiative rates are insensitive to symmetry in aquoammine complexes. Some change in k_r with n is consistent with the results. In contrast, k_{nr} is large in $\text{Cr}(\text{NH}_3)_6^{3+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Consequently, ND_3 and NCS^- can be categorized as nonquenchers while NH_3 and H_2O are good quenching ligands. Oxalate and acetylacetonates are poor quenchers but CN^- , bipyridyl, and phenanthroline are nonquenchers.⁴ In the absence of a definite value for k_{nr} in $\text{Cr}(\text{D}_2\text{O})_6^{3+}$, the classification of

(10) Nelson, D. F.; Sturge, M. D. *Phys. Rev. A* 1965, 137, 1117.

(11) Zander, H. U. Doctoral Dissertation, Johann-Wolfgang-Goethe Universität, 1969, Frankfurt am Main.

(12) Flint, C. D.; Greenough, P. J. *Chem. Soc., Faraday Trans.* 1972, 2, 897.

(13) De Curtins, S.; Güdel, H. V.; Neuenschwander, K. *Inorg. Chem.* 1977, 16, 796.

(14) Flint, C. D.; Mathews, A. P. J. *Chem. Soc., Faraday Trans.* 1973, 2, 69, 419.

(15) Schönherr, T.; Schmidtke, H. H. *Inorg. Chem.* 1979, 18, 2726.

D₂O is less certain. τ increases progressively as the temperature is lowered in Cr³⁺:KAl(SO₄)₂·12D₂O, where Cr(D₂O)₆³⁺ is the emitting species, but does not exceed 1 ms, even at 4 K.¹⁶ In Cr³⁺:AlCl₃·6D₂O, τ approaches a limiting value of ~350 ms below 77 K.¹⁷ These results, coupled with the lifetimes of Cr(D₂O)₆³⁺ in a Me₂SO–D₂O glass at 77 and 65 K, suggest that the limiting τ^{-1} exceeds 1000 s⁻¹. Consequently, D₂O is a poor quencher, but a better quencher than ND₃ and NCS⁻. In La(D₂O)₉³⁺ complexes $\tau^{-1} \approx k_{nr}$.¹⁸ The division into quenching classes is arbitrary. Nonquenchers are characterized by $k_{nr} < 200$ s⁻¹ in homoliganded complexes, while k_{nr} for good quenchers exceeds 10 000 s⁻¹.

An examination of the literature indicates that k_{nr} in a mixed-ligand complex, CrA_{6-n}B_n, usually lies between the values for the homoliganded CrA₆ and CrB₆ complexes. Although the results for Cr(NH₃)_{6-n}(H₂O)_n³⁺, Cr(ND₃)_{6-n}(H₂O)_n³⁺, Cr(ND₃)_{6-n}(D₂O)_n³⁺, and Cr(NCS)_{6-n}(H₂O)_n³⁺, conform to this rule, the trend in the Cr(NH₃)_{6-n}(D₂O)_n³⁺ series stands in contrast to this generalization. Substitution of one or two poor quenchers (D₂O) for good quenchers (NH₃) actually increases k_{nr} . In addition, k_{nr} for Cr(NH₃)₆³⁺ and Cr(NH₃)₅(NCS)₂²⁺ are the same within experimental error.

k_{nr} depends upon electronic and vibrational factors. At low temperatures^{19,20}

$$k_{nr} = \beta \exp \left[-S - \frac{\Delta E}{h\nu_M} \left(\ln \frac{\Delta E}{Sh\nu_M} - 1 \right) \right] \quad (1)$$

where β is defined by

$$\beta = \frac{2\pi |H_{ba}'|^2}{h} \left(\frac{2\pi}{h\nu_M \Delta E} \right)^{1/2} \quad (2)$$

$|H_{ba}'|$ being the electronic matrix element of the radiationless transition between the electronic states a and b. ΔE is the effective energy gap and $S = 1/2 \sum_j \Delta_j^2$, Δ_j being the relative horizontal displacement of the potential minima along the j -th coordinate. In eq 1 and 2 ν_M represents an average frequency associated with the saddle-point method used in deriving eq 1 and is usually approximated by the frequency of the high-frequency accepting modes.^{19,20} Since ν_M is not very different in H₂O and NH₃, 3700 and 3400 cm⁻¹, an average $\bar{\nu}$ can be used for Cr(NH₃)_{6-n}(H₂O)_n³⁺ complexes.

If $(k_{nr})_n$ represents the nonradiative rate of Cr(NH₃)_{6-n}(H₂O)_n³⁺ and $(k_{nr})_0$ the nonradiative rate of Cr(NH₃)₆, we obtain

$$\frac{(k_{nr})_n}{(k_{nr})_0} = \exp \left[-(S_n - S_0) + \frac{\Delta E}{h\bar{\nu}} \ln \left(\frac{S_n - S_0}{S_0} + 1 \right) \right] \quad (3)$$

At high vibrational quantum numbers, a local mode approximation is good. For example, the $\Delta\nu = 6$ C–H transitions in C₆H₆ and C₆HD₅ have the same shapes and an intensity ratio of 6.²¹ In the local mode limit for Cr(NH₃)_{6-n}(H₂O)_n³⁺

$$S_n - S_0 = n(\Delta_{OH}^2 - \frac{1}{2}\Delta_{NH}^2) = n\Delta S \quad (4)$$

TABLE II

n	$\frac{[(k_{nr})_n]}{(k_{nr})_0} \text{ exptl}$	$\frac{[(k_{nr})_n]}{(k_{nr})_0}^n$
1	1.33	1.26 ^b
2 (trans)	1.70	
2 (cis)	1.62	1.59
3	2.00	2.00
4 (trans)	2.24	2.52
5 ^a	3.09	3.18
6	4.08	4.00

^a From ref 4. ^b Best value to fit data.

Since $\ln \{1 + (S_n - S_0)/S_0\} \approx (S_n - S_0)/S_0$ for $|S_n - S_0|/S_0 < 1$, eq 3 becomes

$$\frac{(k_{nr})_n}{(k_{nr})_0} = \exp \left[-(S_n - S_0) + \frac{\Delta E}{h\bar{\nu}} \frac{(S_n - S_0)}{S_0} \right] = \exp \left[n \left(-\Delta S + \frac{\Delta S \Delta E}{S_0 h\bar{\nu}} \right) \right] \quad (5A)$$

i.e.

$$(k_{nr})_n / (k_{nr})_0 = [(k_{nr})_1 / (k_{nr})_0]^n \quad (5B)$$

The Cr(NH₃)_{6-n}(H₂O)_n³⁺ results conform to eq 5 reasonably well (Table II). In the absence of a precise determination of k_{nr} , the applicability of eq 5 to Cr(ND₃)_{6-n}(D₂O)_n³⁺ complexes cannot be evaluated.

A similar analysis of the other series of complexes is complicated by the determination of ν_M . Thus, the ligand accepting modes in Cr(NH₃)_{6-n}(D₂O)_n³⁺ are 3400 and 2700 cm⁻¹. An even larger difference is encountered in the Cr(NH₃)_{6-n}(NCS)_n³⁻ⁿ series where the highest frequency NCS⁻ vibration is 2100 cm⁻¹. Furthermore, in contrast to the constancy of ΔE in Cr(NH₃)_{6-n}(H₂O)_n³⁺ and the deuterated analogues, a progressive decrease of ΔE with n obtains in Cr(NH₃)_{6-n}(NCS)_n³⁻ⁿ. If CrA_{6-n}B_n is composed of a good quencher (A), and a nonquencher (B), in the local mode limit eq 1 leads to²²

$$k_{nr} \propto (6 - n)^{\Delta E / h\nu_M} \quad (6)$$

providing that the electronic factor is constant.

Strek has fitted the ²E → ⁴A₂ emission intensity changes in Cr(H₂O)_{6-n}(NCS)_n³⁻ⁿ (ref 22) with eq 6. Clearly our Cr(NH₃)_{6-n}(NCS)_n³⁻ⁿ and Cr(NH₃)_{6-n}(D₂O)_n³⁺ data do not conform to this expression.

Aquo complexes of the lanthanides provide an interesting contrast to the transition-metal complexes. The decay rates of La(H₂O)₉³⁺ complexes are directly proportional to the number of OH bonds in the molecule.²³ This corresponds to an independent ligand model in which each ligand bond with a high-frequency OH vibration contributes additively to the relaxation, i.e., $k_{nr} = \sum_i k_{nr}^i$. This result cannot be explained only by changes in the vibrational factor in eq 1. The ligand-localized modes are little affected by $f \rightarrow f$ excitation in the rare-earth complexes. If there are no frequency differences and $\Delta_j = 0$ for all vibrations, $k_{nr} \rightarrow 0$, according to eq 2. The observed k_{nr} in La(H₂O)₉³⁺ is ~2000 s⁻¹, an order of magnitude smaller than in Cr(III) complexes with good quenching ligands. Bodunov and Sveshnikova suggest another quenching mechanism for this very weak coupling case in which the Franck–Condon factors do not appear and in which the good quenchers contribute additively to β and hence to k_{nr} .²⁴ This is an independent ligand model. Strek, in a

(16) Goldsmith, G. J.; Shallcross, F. V.; McClure, D. S. *J. Mol. Spectrosc.* **1965**, *16*, 296.

(17) Camassei, F. D.; Forster, L. S. *J. Chem. Phys.* **1969**, *50*, 2603.

(18) Haas, Y.; Stein, G. J. *Phys. Chem.* **1971**, *75*, 3668.

(19) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145.

(20) Lin, S. H. *J. Chem. Phys.* **1972**, *56*, 2645.

(21) Burberry, M. S.; Albrecht, A. C. *J. Chem. Phys.* **1979**, *70*, 147.

(22) Strek, W. *Acta Phys. Pol. A* **1981**, *60*, 707.

(23) Heller, A. *J. Am. Chem. Soc.* **1966**, *88*, 2058.

(24) Bodunov, E. N.; Sveshnikova, E. B. *Opt. Spectrosc.* **1974**, *36*, 196.

TABLE III: Deuterium-Induced Changes in k_{nr} ^a

<i>n</i>	Cr(NH ₃) _{6-n} (H ₂ O) _n ³⁺	Cr(ND ₃) _{6-n} (H ₂ O) _n ³⁺	Cr(H ₂ O) _{6-n} (NH ₃) _n ³⁺	Cr(D ₂ O) _{6-n} (NH ₃) _n ³⁺
1	2100	1300		
2 (trans)	6100	5900		
2 (cis)	4600	3400		
4 (trans)	23000		18 700	18 500
4 (cis)			20 000	18 800
5			18 000	17 200
6	58000	58000	14 500	14 500

^a $\Delta k = k_{nr}^H - k_{nr}^D$ (only the second ligand is deuterated in each column).

general treatment of f-f transitions, concludes that the number of promoting modes, which is proportional to the number of ligated H₂O molecules, plays the dominant role in aquolanthanide complex relaxation.²⁵

Robbins and Thomson proposed a linear correlation between k_{nr} and the number of NH and OH bonds in the Cr(III) complex.²⁶ This model, which is analogous to the independent ligand model applicable to the lanthanide aquo complexes, was explained in terms of the additive contributions of the promoting modes. The increase in k_{nr} with *n* in Cr(NH₃)_{6-n}(H₂O)_n³⁺ as well as the k_{nr} increase in Cr(NH₃)_{6-n}(D₂O)_n³⁺ (*n* = 0–2) are contrary examples. In the derivation of 5 only changes in the vibrational factor were included, but the trend in Cr(NH₃)_{6-n}(D₂O)_n³⁺ indicates that the electronic factor might also change with ligand. It is also possible that the other assumptions upon which eq 5 is based are invalid and that a more complicated dependence of k_{nr} on *n* obtains.

The deuterium isotope effects are much larger in metal complexes than in aromatic molecules. In the absence of an accurate value for k_{nr} , we can only estimate the deuterium isotope effect in Cr(NH₃)₆³⁺, but k_{nr} is decreased by at least a factor of 150. The corresponding deuterium effect in Rh(NH₃)₆³⁺ is 75.²⁷ In contrast, in aromatic hydrocarbons the decrease in the k_{nr} ratio for T₁ \rightarrow S₀ ranges from 1.7 in benzene to \sim 7 in pyrene and coronene.² If only changes in the vibrational factor are important^{19,20}

$$k_{nr}^H/k_{nr}^D = \exp[-(S_H - S_D) - \{\gamma_H/\nu_H - \gamma_D/\nu_D\}\Delta E/h] \simeq \exp[-\{\gamma_H/\nu_H - \gamma_D/\nu_D\}\Delta E/h] \quad (7)$$

where

$$\gamma = \ln \{\Delta E/(S_M h \nu_M)\} - 1$$

Since S_M (= S_H or S_D) is smaller for the ligand-localized vibrations in metal complexes than for the C–H modes in aromatic hydrocarbons, γ is larger in the complexes and a larger deuterium isotope effect is expected. However, deuteration can also affect the promoting-mode term in the electronic factor. Indeed, in the independent ligand model for the aquolanthanide complexes the deuterium isotope effect can only be explained by changes in the electronic factor and eq 7 is inapplicable.

If changes in the electronic factor were mainly responsible for the deuterium isotope effect in Cr(III) complexes, then the difference for a given *n*, $\Delta k = k_{nr}^H - k_{nr}^D$ would be proportional to *n*. The data in Table III do not support an independent ligand model. When H₂O \rightarrow D₂O in Cr(NH₃)_{6-n}(H₂O)_n³⁺ and Cr(ND₃)_{6-n}(H₂O)_n³⁺, Δk increases but not proportionally to *n* in the range *n* = 1–6. Even more striking is the nearly constant Δk for *n* = 4–6 when NH₃ \rightarrow ND₃ in Cr(H₂O)_{6-n}(NH₃)_n³⁺ and Cr(D₂O)_{6-n}(NH₃)_n³⁺. Although this contrast in the deuterium isotope

effect for H₂O and NH₃ is marked, in neither case is an independent ligand model applicable and we conclude that the deuterium isotope effect is not due mainly to changes in the electronic factor. This serves to emphasize the difference between the very weakly coupled lanthanide complexes and the weakly coupled Cr(III) complexes.

The behavior within the Cr(NH₃)_{6-n}(D₂O)_n³⁺ series is unusual in that k_{nr} passes through a maximum at *n* = 2. There are two possibilities to consider in this connection: (i) The electronic and vibrational factors both change when NH₃ \rightarrow D₂O and these changes are in opposite directions, and (ii) only the vibrational factor changes, but the assumptions invoked in eq 5 are invalid. In this latter event eq 3 can still be used to describe the trend in Cr(NH₃)_{6-n}(D₂O)_n³⁺ but the *n* dependence will be more complicated than suggested by eq 5.

Several points merit emphasis in connection with the deuterium effect results summarized in Table III. When four or five good quenching ligands are converted to poor quenchers (NH₃ \rightarrow ND₃), the quenching effectiveness of the remaining quencher (H₂O or D₂O) is of no consequence. Also, Δk is about the same for the deuteration of four, five, or six NH₃ ligands. Δk increases for H₂O \rightarrow D₂O in the presence of NH₃ or ND₃, but the deuteration effect is not proportional to *n*. Δk in this latter case is somewhat larger when NH₃ is the second ligand than for ND₃, but the absolute magnitudes of Δk are small and the difference is of marginal significance.

Summary and Conclusions

Although the simplified theory as embodied in eq 1 serves as a framework for discussing the effect of the vibrational factor on quenching efficiencies in homoligated complexes, it is only applicable to a limited class of mixed-ligand complexes where ν_M is nearly the same for both ligands. Furthermore, the dependence of the electronic factor on ligand cannot be ignored. The existence of a maximum for k_{nr} in the Cr(NH₃)_{6-n}(D₂O)_n³⁺ series underscores the role of the electronic factor. Nonetheless, some qualitative generalizations can be advanced. The division of ligands into nonquenchers and good quenchers provides a crude basis for interpreting the nonradiative rate data in metal complexes. However, the a priori classification of ligands by means of vibrational frequencies cannot always be made. While it is true that some good quenchers, e.g., NH₃ and H₂O, have large ν_M (>3000 cm⁻¹) and some nonquenchers, e.g., ND₃, CN⁻, and NCS⁻, have smaller ν_M , some notable exceptions exist. For example, bipyridyl and phenanthroline have large ν_M , but are very poor quenchers.

Two good quenchers in a complex are sufficient for fairly efficient nonradiative decay; the other ligands can be poor quenchers. Consequently, in a homoligated complex with good quenching ligands replacement of several ligands by poor quenchers has little effect on the decay rate.

Finally, large deuterium isotope effects will be the rule in transition-metal complexes.

(25) Strek, W. J. *J. Chem. Phys.* 1982, 70, 5856.

(26) Robbins, D. J.; Thomson, A. J. *Mol. Phys.* 1973, 25, 1103.

(27) Thomas, R. T.; Watts, R. J.; Crosby, G. A. *J. Chem. Phys.* 1973, 59, 2123.