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Article

Electronic Energy Self-Exchange with Macrocyclic Chromium(III) Complexes

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The luminescence lifetimes of N-deuterated Cr(III) complexes of macrocyclic tetraamine ligands, *trans*-$CrN_4X_2^{n+}$, are substantially longer than those of their undeuterated counterparts in room temperature solution. Thus, excited-state emission quenching of the longer lived species by the shorter lived species may be studied by analyzing the decay profile following pulsed excitation. Flash photolysis experiments were carried out for three deuterated/undeuterated pairs of *trans*-$CrN_4X_2^{n+}$ complexes (where X = CN^-, NH_3, and F^-). For the *trans*-$Cr(cyclam)(CN)_2^+$ system in H_2O, it was determined that energy transfer was occurring between the deuterated and undeuterated species. Although the rate constant of energy transfer was too fast to measure explicitly, it could be bracketed as $k_{et} \gg 7 \times 10^6$ M^{-1} s^{-1}. For this reaction it was possible to measure an equilibrium constant which was very near 1.0. For *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ in DMSO, it was also established that energy transfer was occurring and rate constants of 2.4×10^6 M^{-1} s^{-1} ($\mu = 0.1$) and 9.7×10^6 M^{-1} s^{-1} ($\mu = 1.0$) were determined by a Stern–Volmer analysis. For *trans*-$Cr(tet\ a)F_2^+$ in H_2O, no energy transfer was observed, which implies that the rate constant is $\ll 3 \times 10^5$ M^{-1} s^{-1}. Because these energy-transfer reactions represent self-exchange energy transfer and are thus thermoneutral, we are able to analyze the results using Marcus theory and draw some conclusions about the relative importance of nuclear reorganization and electronic factors in the overall rate.

Introduction

One of the most important developments in the field of electron transfer and perhaps in chemistry in general has been the theory developed independently by both Marcus and Hush to explain the dynamics of electron-transfer reactions.[1,2] Marcus–Hush theory presented a framework within which to analyze the effects of thermodynamics, nuclear reorganization, and electronic overlap on electron-transfer reaction rates. Over the last two decades this formalism has been applied to other reaction types, such as energy transfer,[3] proton transfer,[4] and hydride transfer,[5] an indication of the importance of this theory in understanding reaction dynamics in general.

For electron transfer, there is a significant nuclear rearrangement in the reactants, in terms of both bond lengths and more importantly the solvent shell, due to the differential charge on the reactants vs the products. This results in a significant reorganizational barrier, called the intrinsic barrier, which is usually the primary factor in determining the observed reaction rates. Thus, the effect of electronic interactions between reactants is frequently obscured. One advantage of studying *energy*-transfer rates (in addition to the fundamental knowledge gained about those processes) is that the contribution from the reorganization from the solvent is typically negligible.[3] This has allowed the determination of the role that internal reorganization and electronic

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[2] For a recent review see: Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148–13168.

[3] (a) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152–2163. (b) Scandola, F.; Balzani, V. *J. Chem. Educ.* **1983**, *60*, 814–823. (c) Parola, A. J.; Pina, F.; Ferreira, E.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1996**, *118*, 11610–11616.

[4] See for example: Guthrie, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 12886–12890 and references therein.

[5] Kreevoy, M. M.; Ostovic, D.; Lee, I. S. H.; Binder, D. A.; King, G. W. *J. Am. Chem. Soc.* **1988**, *110*, 524–530.

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factors have on the rate.[6−15] It has been suggested that energy-transfer reactions with very small reorganizational barriers may be used to probe general properties concerning electronic contributions to bimolecular reactions.[7,11]

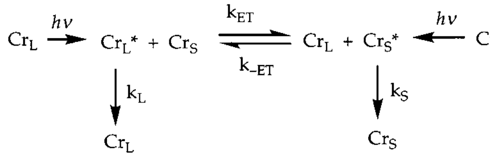
A number of studies of cross-exchange energy transfer have been analyzed with the objective of determining the relative importance of thermodynamics, electronic factors, and nuclear factors.[7−15] The majority of these studies have involved Cr(III) donors and/or acceptors due to the large body of existing knowledge on Cr(III) photophysics and photochemistry.[16,17] Electronic factors that have been explored include the charge and size of the complex, the nature of the solvent, and orbital overlap. Though it has been possible in some systems to deconvolute electronic factors from thermodynamic effects on the rate, it is our goal to find systems for which self-exchange energy transfer can be monitored, eliminating the effect of thermodynamics on the rate. Preferably these systems would be amenable to systematic variation so that a series of self-exchange and cross-exchange energy-transfer reactions could be analyzed in a manner similar to what has been done for electron transfer.

Unfortunately, measuring the rate of electronic energy self-exchange in fluid solution at room temperature has been more elusive than measuring the rates of electron-transfer self-exchange, but has been achieved for a few systems (vide infra).[18−21] Here we report our initial studies on electronic energy self-exchange in a series of closely related chromium(III) macrocyclic complexes using a method first described by Maharaj and Winnik[20] involving flash photolysis experiments on mixtures of two molecules which contain virtually identical chromophores. In this method, the molecules are chosen so that, for one of them, rapid intramolecular relaxation leads to a significantly shortened excited-state lifetime, relative to that of the other species, so that the shorter lived species serves as the quencher for the longer lived species.

Table 1. Emission Lifetimes of Chromium(III) Complexes (20 °C)

complex	solvent	τ_H (μs)	τ_D (μs)	ref
trans-$Cr(cyclam)(CN)_2^+$	H_2O	335	1500	23
trans-$Cr(cyclam)(NH_3)_2^{3+}$	H_2O	55	165	24
trans-$Cr(cyclam)(NH_3)_2^{3+}$	DMSO	135	1620	24
trans-$Cr(tet\ a)F_2^+$	H_2O	30	234	25

Scheme 1. Energy Transfer between Long-Lived (Cr_L) and Short-Lived (Cr_S) Components



We have had a long-standing interest in the photochemistry and photophysics of Cr(III) macrocyclic complexes. In our initial studies on the synthesis and photobehavior of the complexes *trans*-$Cr(cyclam)(NH_3)_2^{3+}$, *trans*-Cr(cyclam)-$(CN)_2^+$, and *trans*-$Cr(tet\ a)F_2^+$, we demonstrated that these systems were remarkably photoinert and exhibited unusually intense, long-lived phosphorescence in room temperature solution.[22−25] Especially noteworthy with respect to the present investigation, these were the first Cr(III) complexes to exhibit strong enhancements of their steady-state emission intensities and excited-state lifetimes in room temperature solution upon deuteration of the amine N−H protons.[23−25] As shown in Table 1, the lifetimes of the N-deuterated complexes are 4−12 times higher than those of their corresponding protio analogues in acidified room temperature solution (and essentially identical enhancements are observed for the corresponding steady-state emission signals). Furthermore, the strict similarity in the solution absorption and emission maxima of the deuterated and undeuterated species renders them essentially identical for the purposes of energy transfer. Arguably, energy transfer between isotopically labeled and unlabeled chromophores represents the closest model to self-exchange possible, and these molecules seemed ideally suited to such a study.

The procedure involves irradiating the mixture of virtually identical chromophores and then analyzing the excited-state decay. Parallel to the notation in Winnik's original paper,[20] let us denote the long-lived Cr(III) species as Cr_L and the short-lived species as Cr_S. Scheme 1 depicts the energy-transfer and relaxation processes. Here, $k_L = 1/\tau_L$ and $k_S = 1/\tau_S$ describe the sum of the rate constants of the processes which lead to the decay of Cr_L* and Cr_S*, respectively, exclusive of energy transfer.

For cases in which $k_{ET}[Cr_S]$ and $k_{-ET}[Cr_L]$ are comparable in magnitude with k_S, this scheme predicts a complex experimental situation. However, two limiting cases[20] and a

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third trivial case exist in which considerable simplifications can be made.

Case 1. $k_S \ll k_{-ET}[Cr_L]$.

Here the excitation energy will be transferred many times between Cr_L and Cr_S before deactivation of either excited state occurs. In this case, averaging of their two emission lifetimes occurs and only one excited state signal is experimentally observed, which decays exponentially with lifetime τ, where

$$1/\tau = k_L + K_{ET}([Cr_S]/[Cr_L])(k_S - 1/\tau) \qquad (1)$$

For this situation it is only possible to determine K_{ET}, the equilibrium constant for the self-exchange.

Case 2. $k_S \gg k_{-ET}[Cr_L]$.

Here energy transfer in the forward direction is essentially irreversible, since when Cr_S* is generated it will virtually always undergo deactivation prior to back energy transfer. Both excited-state decay signals will be experimentally observed with different lifetimes. If the experimental conditions are such that most of the light is absorbed by the longer lived species (i.e., $[Cr_S] \ll [Cr_L]$), then the quenching of this long-lived excited state may be followed using solutions containing different concentrations of Cr_S. Under such conditions, Cr_S simply acts as an excited-state lifetime quencher of the Cr_L emission signal, and the Stern−Volmer equation for the quenching of Cr_L* by Cr_S applies:

$$1/\tau = k_L + k_{ET}[Cr_S] \qquad (2)$$

Case 3. A third trivial case applies when $k_L \gg k_{ET}[Cr_S]$. In this circumstance, there will be no energy transfer and a biexponential decay will be observed with the lifetimes of the two components of the decay signal corresponding to the lifetimes of the pure protio and pure deuterio species.

Herein we report studies on energy transfer between the deuterated and undeuterated species of the three Cr(III) macrocyclic complexes listed above.

Experimental Section

Chemicals. The complexes *trans*-$Cr(cyclam)(NH_3)_2^{3+}$, *trans*-$Cr(cyclam)(CN)_2^+$, and *trans*-$Cr(tet\ a)F_2^+$ (including deuterated samples) were isolated as their perchlorate salts following literature methods.[23−25] The extent of amine deuteration (usually greater than 90%) was determined via IR spectroscopy by monitoring the relative areas of the absorption in the N−H and N−D stretching regions.

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with extreme caution and only in very small quantities. Trisperchlorates are particularly worrisome, and it is strongly recommended that deuterated trans-Cr(cyclam)-$(NH_3)_2^{3+}$ be isolated in the future as the PF_6^- salt.[24]

All other reagents were of reagent grade quality, and were used as received.

Measurements. Self-exchange energy-transfer studies for the complexes *trans*-$[Cr(cyclam)(CN)_2]ClO_4$ and *trans*-$[Cr(tet\ a)F_2]ClO_4$ were performed in acidified aqueous solution. For the *trans*-$[Cr(cyclam)(NH_3)_2](ClO_4)_3$ system, studies were performed in acidified dimethyl sulfoxide solution due to the much larger deuterium isotope effect in that solvent (Table 1). Solubility restrictions prevented DMSO solvent from being employed for the corresponding dicyano and difluoro complex systems. For each of the complexes it was initially established that the steady-state emission intensity and emission lifetime of the deuterated species did not decrease in mildly *acidified* solution over many hours at room temperature. This observation is consistent with efficient acid suppression of amine N−D exchange with solvent protons.

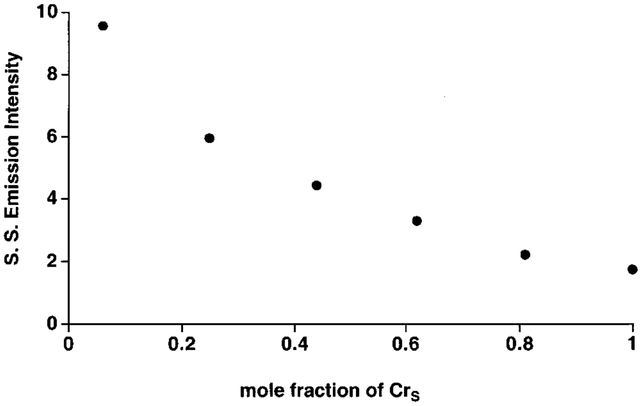

Figure 1. Steady-state emission intensity (arbitrary units) vs mole fraction of the protio species (Cr_S) for *trans*-$Cr(cyclam)(CN)_2^+$ in water, 20 °C.

The solution concentrations of the three Cr(III) complexes (deuterated and undeuterated) were determined by UV−vis spectroscopy (Cary 118C) using molar absorptivity values of $\epsilon_{414} = 63$ M^{-1} cm^{-1}, $\epsilon_{420} = 36$ M^{-1} cm^{-1}, and $\epsilon_{440} = 27$ M^{-1} cm^{-1}, respectively.[23a,24,25] The general procedure for solution preparations for studying energy self-exchange involved the initial preparation of acidified, absorbance-matched stock solutions of the deuterated and undeuterated samples. A series of solutions for analysis were produced by mixing the stock solutions in varying ratios. The concentrations of deuterated and undeuterated complexes in each test solution were corrected for the percent deuteration determined by IR for the deuterated solid sample. Each of these test solutions (thermostated at 20 °C) was then subjected to emission lifetime and steady-state emission spectral analysis using equipment and procedures described elsewhere.[24] Correlation coefficients for ln(intensity) vs time plots of the lifetime curves were typically 0.997 or greater, and the resultant lifetimes were reproducible to 10% or better. All studies were carried out under air-saturated solution conditions, since we have previously demonstrated that the emission intensities and excited-state lifetimes of the three complexes are insensitive to dissolved oxygen.[23−25]

Results

***trans*-$Cr(cyclam)(CN)_2^+$.** Mixtures of the *N*-protio and *N*-deuterio complexes with a total concentration of 2.24×10^{-3} M (0.01 M HCl, $\mu = 0.01$) were prepared with mole fractions of the protio species ranging from 0.06 to 1.00. The steady-state emission intensity of these solutions was *not* linear with respect to the mole fraction of the protio species (Figure 1). Such nonlinear behavior demonstrates that the protio and deuterio emissions are not independent and additive, and therefore is indicative of the presence of energy transfer.[20] The corresponding pulsed emission studies resulted in a single-exponential decay, indicative of case 1 behavior. Plotting the data according to eq 1 resulted in a straight line with a slope of 0.99, where the slope is the equilibrium constant for energy transfer (Figure 2). According to eq 1, the intercept of this plot corresponds to k_L (i.e., to the inverse

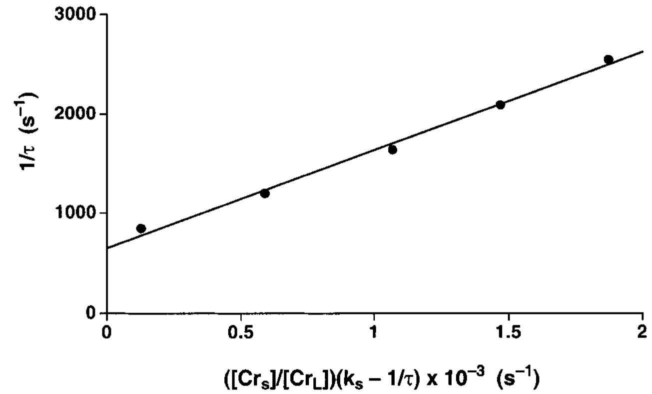

Figure 2. $1/\tau$ vs ($[Cr_S]/[Cr_L]$)($k_S - 1/\tau$) (eq 1) for *trans*-Cr(cyclam)$(CN)_2^+$ in water, 20 °C (slope 0.99, intercept 650 s^{-1}).

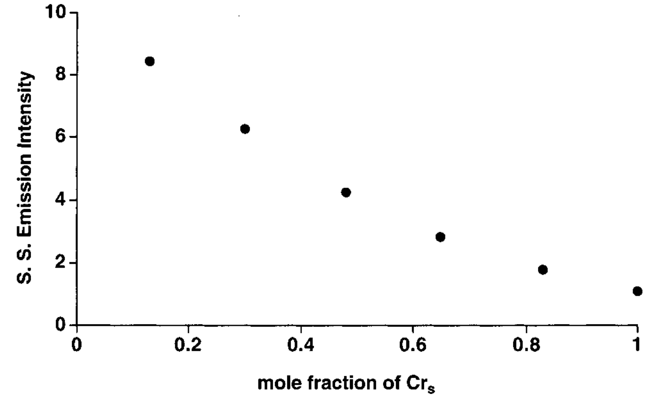

Figure 3. Steady-state emission intensity (arbitrary units) vs mole fraction of the protio species (Cr_S) for *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ in DMSO, 20 °C.

of the lifetime of the deuterated complex). An intercept value of 670 s^{-1} is thus anticipated (see Table 1), in good agreement with the experimental value of 650 s^{-1}. A similar experiment with an ionic strength of 1.0 (KCl as backing electrolyte) yielded an equilibrium constant of 1.1. These results confirm the thermoneutral nature of these self-exchange reactions.[26]

***trans*-Cr(cyclam)$(NH_3)_2^{3+}$.** Mixtures of the *N*-protio and *N*-deuterio complexes with a total concentration of 6.14 × 10^{-3} M in DMSO (0.1 M HNO_3, $\mu = 0.1$) were prepared with mole fractions of the protio species ranging from 0.13 to 1.00. The plot of the steady-state emission intensity of these solutions was again curved with respect to the mole fraction of the protio species, indicating that energy transfer was occurring (Figure 3). The same total concentration was used for the pulsed emission studies, but the mole fraction of the protio species ranged between 0.13 and 0.27. For this experiment, the concentration of the protio species was kept low to minimize absorption by the shorter lived quencher and to minimize the possibility of back energy transfer. The pulsed emission studies revealed a biexponential decay—indicative of the case 2 limit. A Stern−Volmer plot of the data in the longer decay time region (according to eq 2 with the protio complex as the quencher) yielded a straight line with a slope of 2.4 × 10^5 M^{-1} s^{-1} = k_{ET} (Figure 4). In this case, eq 2 predicts an intercept value of 620 s^{-1} (see Table 1), which is in accord with the experimental value of 580 s^{-1}. A similar experiment with an ionic strength of 1.0 (tetrabutylammonium perchlorate) yielded a k_{ET} value of 9.7 × 10^5 M^{-1} s^{-1}. The larger rate constant observed at higher ionic strength is consistent with reaction between positively charged species.[29]

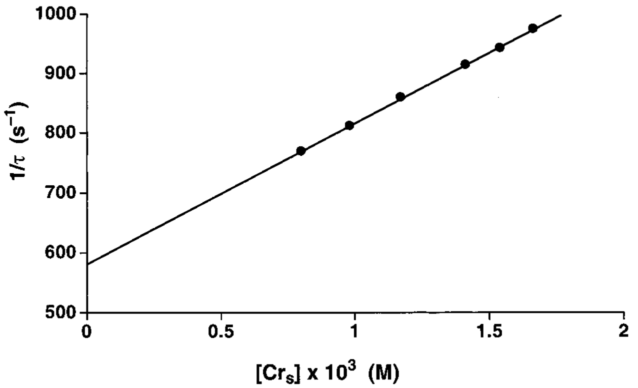

Figure 4. Stern−Volmer plot (eq 2) for the emission lifetime quenching of deuterated *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ by undeuterated *trans*-Cr(cyclam)-$(NH_3)_2^{3+}$ in DMSO, 20 °C (slope 2.4 × 10^5 M^{-1} s^{-1}, intercept 580 s^{-1}).

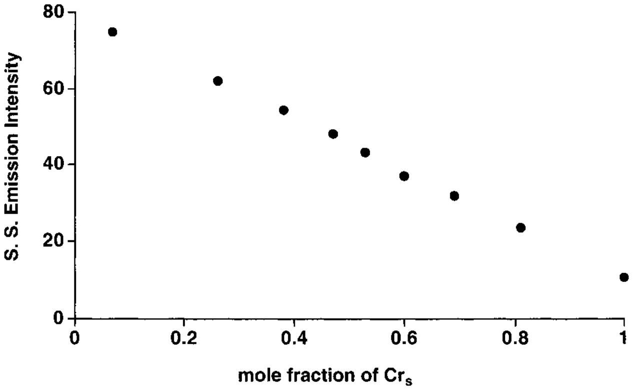

Figure 5. Steady-state emission intensity (arbitrary units) vs mole fraction of the protio species (Cr_S) for *trans*-Cr(cyclam)F_2^+ in water, 20 °C.

***trans*-Cr(tet a)F_2^+.** Mixtures of the *N*-protio and *N*-deuterio complexes with a total concentration of 3.73 × 10^{-3} M (0.01 M HCl, $\mu = 0.01$) were prepared with mole fractions of the protio species ranging from 0.07 to 1.00. The steady-state emission intensity of these solutions is linear with respect to the mole fraction of the protio species (Figure 5), indicating that *no* energy transfer was occurring (case 3 behavior). The pulsed emission studies revealed a biexponential decay, with the lifetime of the longer lived component essentially identical to that obtained for the pure deuterated sample, eliminating these pulse results from being associated with a case 2 limiting situation for energy transfer. An

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(26) Further support for the thermoneutrality of energy transfer from deuterated to undeuterated chromium(III) cyclam complexes is evident in that the $^2E_g \leftrightarrow {}^4A_{2g}$ (O_h) electronic origins for the deuterated and undeuterated species differ by less than 10 cm^{-1} for both *trans*-Cr-(cyclam)$(NH_3)_2^{3+}$,[27] and *trans*-Cr(cyclam)$(CN)_2^+$.[28]

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Table 2. Rate and Equilibrium Data Obtained from Kinetic Analysis

complex	solvent	μ	$[H^+]$	k_{ET} ($M^{-1}\,s^{-1}$)	K_{ET}
trans-$Cr(cyclam)(CN)_2^+$	H_2O	0.01	0.01		0.99
		1.00	0.01	$\gg 7 \times 10^6$	1.1
trans-$Cr(cyclam)(NH_3)_2^{3+}$	DMSO	0.10	0.10	2.4×10^5	
		1.00	0.10	9.7×10^5	
trans-$Cr(tet\ a)F_2^+$	H_2O	0.01	0.01	no observable ET $\ll 3 \times 10^5$	

additional experiment using total concentrations 5 times higher also failed to show evidence for energy transfer.

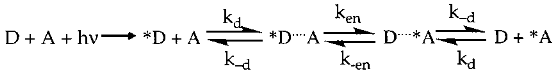
Although for the three complexes discussed above only one energy-transfer rate constant was directly measured, limits can be placed on the other two cases following the approach employed by Winnik.[20] Because *trans*-Cr(cyclam)-$(CN)_2^+$ falls in the case 1 limit, we know that $k_S \ll k_{-ET}[Cr_L]$. Given that no deviation from case 1 behavior occurred even at the lowest concentrations of the deuterio complex ($[Cr_L] = 0.4 \times 10^{-3}$ M), and that $k_S = 1/\tau_S$, where $\tau_S = 335\ \mu s$ for *trans*-$Cr(cyclam)(CN)_2^+$, we find that $k_{-ET} \gg 7 \times 10^6\ M^{-1}\ s^{-1}$. Given that this is a self-exchange process, $k_{ET} = k_{-ET}$. Therefore, $k_{ET} \gg 7 \times 10^6\ M^{-1}\ s^{-1}$.

Furthermore, because no energy transfer is observed for *trans*-$Cr(tet\ a)F_2^+$, we know that $k_L \gg k_{ET}[Cr_S]$. Given that no evidence of energy transfer was observed even at the highest quencher (protio species) concentration ($[Cr_S] = 1.5 \times 10^{-2}$ M), and that $k_L = 1/\tau_L$, where $\tau_L = 234\ \mu s$ for deuterio *trans*-$Cr(tet\ a)F_2^+$, we find that $k_{ET} \ll 3 \times 10^5\ M^{-1}\ s^{-1}$. The results are summarized in Table 2.

Discussion

Prior Studies. The complexes utilized in this study have indeed been amenable to self-exchange energy-transfer studies due to their relatively long excited-state lifetimes and the significant difference between the lifetimes of the deuterated and undeuterated species. To our knowledge, only one other example of exchange in solution between a deuterated and undeuterated species of the same molecule has been reported, and that was exchange between excited-state acetone and ground-state deuterated acetone in the elegant work by Lechtken and Turro.[18a] Unfortunately, that study was not amenable to systematic variation and further studies. Other examples of self-exchange involve exchange between “virtually identical chromophores”. The study by Maharaj and Winnik[20] involved energy transfer between differentially substituted diaryl ketones, while that of Encinas and Scaiano[19] involved triplet energy transfer between alkyl aryl ketones. The more recent report by Balzani and co-workers,[21] which perhaps bears the most relevance toward the present study, involved energy transfer between ruthenium(II) complexes with different bipyridine-based ligands. In Balzani’s work, they measured four different rate constants for exchange between differentially ligated ruthenium complexes. Since each pair is quite similar with respect to the others, the rate constants are all between 3.4×10^7 and $6.6 \times 10^7\ M^{-1}\ s^{-1}$. They attributed the sluggishness (relative to diffusion-controlled rates) of this reaction to poor electronic overlap, but do not have a large enough variance in rates to allow further comparison. For the case of the Cr(III) complexes discussed in this paper, we have the rare opportunity to compare self-exchange rate constants for three very different systems with similar structural motifs. To compare these rate constants, we need to understand the theoretical framework used to describe energy transfer.

Scheme 2. Kinetic Scheme of Bimolecular Energy Transfer



Kinetic Analysis. The treatment of energy-transfer dynamics using the same formalisms used to analyze electron-transfer rates has been presented in several papers by Balzani.[3] For bimolecular energy transfer occurring through collision (i.e., via an exchange mechanism), Scheme 2 describes the overall process, where D is the donor, A is the quencher or acceptor, k_d and k_{-d} are the forward and reverse rate constants for the formation of the encounter complex, and k_{en} and k_{-en} are the forward and reverse rate constants for the energy-transfer step. Quenching occurs in the encounter complex in a unimolecular reaction whose rate constant (k_{en}) depends on an electronic term (associated with k_{en}^0 in eq 3) and a nuclear term determined by Franck–Condon restrictions (associated with $\Delta G^{\ddagger}$ in eq 3). The experimental quenching rate constant, k_q, is given by

$$k_q = \frac{k_d}{1 + e^{\Delta G/RT} + (k_{-d}/k_{en}^0)e^{\Delta G^{\ddagger}/RT}} \qquad (3)$$

where k_{en}^0 is the preexponential factor and ΔG and $\Delta G^{\ddagger}$ are the standard free energy change and the activation free energy of the forward energy-transfer step. For the special case of energy-transfer self-exchange, ΔG is zero. Then eq 3 reduces to

$$k_q = \frac{k_d}{2 + (k_{-d}/k_{en}^0)e^{\Delta G^{\ddagger}/RT}} \qquad (4)$$

In all self-exchange cases where the rate constant is significantly below the diffusion-controlled value, the second term in the denominator of eq 4 must dominate and then eq 4 reduces to

$$k_q = \frac{k_d}{k_{-d}} k_{en}^0 e^{-\Delta G^{\ddagger}/RT} \qquad (5)$$

In such cases the energy-transfer rate is a function of both k_{en}^0 and $\Delta G^{\ddagger}$. For a self-exchange process, $\Delta G^{\ddagger}$, the intrinsic barrier, will depend only on the degree of distortion of the excited state, and it has been shown[3] that

$$\Delta G^{\ddagger} \leq (\text{Stokes shift})/4 \qquad (6)$$

Analysis of the Experimental Results. An analysis of our results therefore requires a consideration of the Stokes shifts of the three d^3 Cr(III) complexes investigated in this study. The Stokes shift is dependent on the extent of molecular distortion in the excited state. An assessment of this distortion, in turn, requires a knowledge of the orbital

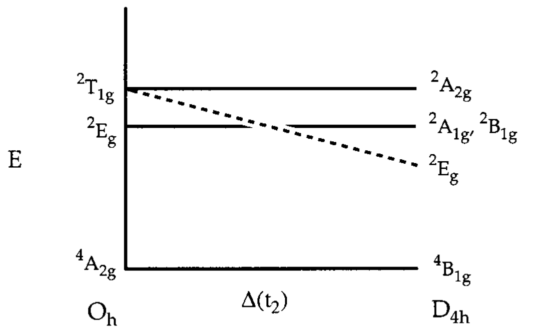


Figure 6. d^3 energy levels for O_h and D_{4h} geometries.

parentage of the ground state and lowest lying excited state of the three complexes. For the complexes *trans*-Cr(cyclam)(NH_3)$_2^{3+}$ and *trans*-Cr(cyclam)(CN)$_2^+$, spectral analysis has established that the lowest energy doublet excited state is of ^2E_g (O_h) origin (see Figure 6), and emission has been assigned as $^2E_g \rightarrow {}^4A_{2g}$ (O_h) phosphorescence.[16,23,24] Since excited states of ^2E_g (O_h) parentage have the same orbital occupation as the ground state, these D_{4h} *trans*-$CrN_4X_2^{n+}$ species are expected to show little or no geometric distortion relative to the ground state, and consequently should have very small Stokes shifts.[30] However, experimental values for Stokes shifts for Cr(III) complexes have been very difficult to obtain due to the spin-forbidden nature of the absorption. The Stokes shift can be estimated as twice the energy difference between the 0 → 0 line (frequently obtained from low-temperature studies) and the solution emission maximum.[31] Using available data for the 0 → 0 line,[27] and the solution emission maximum,[24] a value of approximately 200 cm^{-1} for the Stokes shift of the *trans*-Cr(cyclam)(NH_3)$_2^{3+}$ complex is obtained. Using corresponding data for *trans*-Cr(cyclam)(CN)$_2^+$,[23b,28] an estimated value of 170 cm^{-1} is obtained for this species.

However, unlike the sharp, well-resolved solution emission spectra observed for the diammine and dicyano complexes, the corresponding *trans*-Cr(tet a)F_2^+ species exhibits a broad structureless emission centered at 778 nm. We have previously attributed this signal to $^2T_{1g} \rightarrow {}^4A_{2g}$ (O_h) phosphorescence,[25] in accord with the spectral assignment for *trans*-Cr(en)$_2F_2^+$ by Flint and Matthews[32] and Forster and coworkers.[33] For these *trans*-$CrN_4F_2^+$ systems, the orbital occupations in the ground-state $^4B_{1g}$ and excited-state ^2E_g (D_{4h}) energy levels are no longer the same, and at sufficiently large Δt_2 the lowest energy doublet excited state is of $^2T_{1g}$ (O_h) parentage as depicted in Figure 6.[33] Because charge density in the lowest energy ^2E_g (D_{4h}) state is redirected from the axial antibonding orbitals into the *xy* plane, distortion is anticipated in the Cr−X and Cr−N bonds.[16,34] This has been experimentally established by Flint and Matthews for *trans*-Cr(en)$_2F_2^+$.[32] A substantial geometric distortion and a significant Stokes shift are therefore expected for *trans*-Cr(tet a)F_2^+. Though the Stokes shift for this species has not been measured, a value of 1200 cm^{-1} can be estimated for the related *trans*-[Cr(en)$_2F_2$]ClO_4 complex using the data of Flint and Matthews.[32] It is unlikely that the Stokes shift for *trans*-Cr(tet a)F_2^+ could be higher since the macrocycle will serve to reduce the extent of excited-state distortions. Thus, 1200 cm^{-1} can be taken as an upper limit for the Stokes shift. Recall that a significant Stokes shift corresponds to a substantial intrinsic barrier for self-exchange. Interestingly, Cr(tet a)F_2^+ was the only complex for which we observed no self-exchange, but is this entirely due to the intrinsic barrier or is much of its sluggishness due to electronic factors?

To answer that, let us compare the self-exchange rates of *trans*-Cr(tet a)F_2^+ and *trans*-Cr(cyclam)(CN)$_2^+$, both of which were measured in water, and both of which have the same overall complex charge and size. The rate of formation of the encounter complex should not differ significantly between the two, and any rate difference can be largely attributed to a combination of the differences in the intrinsic barrier and the difference in electronic overlap (see eq 5). Though neither rate was measured explicitly, the rate constants can be bracketed and it can be seen from Table 2 that the rate constant for self-exchange for *trans*-Cr(cyclam)(CN)$_2^+$ must be at least 500 times greater than that of *trans*-Cr(tet a)F_2^+ (assuming that the $\gg$ comparison indicates at least a conservative factor of 5). Equation 5 shows that the effect of the intrinsic barrier is to modify the rate constant by a factor of $e^{-\Delta G^{\ddagger}/RT}$. Using the values for the Stokes shifts calculated above, and eq 6, we estimate that the intrinsic barrier can account for no more than a factor of 5 in the rate, leaving at least a factor of 100 to electronic effects.

Concluding Remarks

Our experimental results, therefore, provide compelling evidence that electronic effects play a significant role in determining the rates of the self-exchange reactions for this series of complexes. As noted by several other authors, electronic energy transfer between Cr(III) complexes is expected to proceed by an exchange mechanism, due to the dipole and spin-forbidden nature of the electronic transitions for the donor and acceptor.[3b,11] The exchange interaction necessitates collisional interaction between the donor and acceptor molecules due to the requirement for overlap of two orbital pairs in the donor−acceptor couple. Various factors may influence the effectiveness of this orbital overlap, including contributions from donor/acceptor separation distance,[7,9] nephelauxetic effects,[8,10,14] or orbital symmetry. Although nephelauxetic parameters are not available for the *trans*-Cr(cyclam)(CN)$_2^+$ and *trans*-Cr(tet a)F_2^+ systems, the slower exchange rate observed for the difluoro species might

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(30) Forster, L. S. In *Concepts in Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; pp 1−35.

(31) This is likely an upper limit as it assumes that the potential well of the excited state has the same curvature as that of the ground state, whereas it is likely to be flatter. See for example: Hoggard, P. E.; Schmidtke, H. H. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 1013−1021.

(32) Flint, C. D.; Matthews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1307−1315.

(33) Fucaloro, A. F.; Forster, L. S.; Glover, S. G.; Kirk, A. D. *Inorg. Chem.* **1985**, *24*, 4242−4246.

(34) Flint, C. D.; Matthews, A. P. *Inorg. Chem.* **1975**, *14*, 1008−1014.

be associated in part with a poorer nephelauxetic effect for F^- versus CN^-. Separation distance effects may also play a role in this rate difference, in view of the bulkier nature of the tet a macrocycle (synthetic difficulties have prevented isolation of the *trans*-Cr(cyclam)F_2^+ species).[25] Although our present results are unable to resolve the relative importance of such contributions, we plan to continue work in this area by performing temperature dependence studies, searching for additional systems in which we can measure self-exchange rate constants, and also performing some cross-exchange reactions to common acceptors.

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