Contribution from Istituto Chimico "G. Ciamician"
dell'Università and Istituto FRAE—CNR, Bologna, Italy

Role of Nuclear and Electronic Factors in the Electronic Energy Transfer from the ^2E_g Excited State of Tris(2,2′-bipyridine)chromium(III) to Cobalt(III) Complexes

MARIA TERESA GANDOLFI,[1a] MAURO MAESTRI,[1a,b] DIANA SANDRINI,[1a] and VINCENZO BALZANI*[1a,b]

Received April 26, 1983

The quenching of the phosphorescence emission of $(^2E_g)Cr(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) by $Co(NH_3)_6^{3+}$, $Co(NH_3)_5(H_2O)^{3+}$, $Co(en)_3^{3+}$, $Co(NH_3)_5X^{2+}$ (X = F, Cl, NCS, NO_2, HCOO), *cis*-$Co(en)_2(NH_3)Cl^{2+}$, *cis*-$Co(en)_2(H_2O)Cl^{2+}$, and *cis*- and *trans*-$Co(en)_2(XY)^+$ (X = Cl, NCS; Y = Cl, NCS) has been studied in 0.1 M H_2SO_4 aqueous solution. The bimolecular quenching constants are lower than diffusion and span a factor of ~400. On the basis of theoretical considerations it is shown that the only plausible quenching mechanism is electronic energy transfer. Calculations based on available spectroscopic data show that the intrinsic barriers to energy transfer are relatively high owing to the excited-state distortion of the Co(III) complexes but are canceled out by sufficiently large exoergonicities. Thus, nuclear factors are not responsible for the lower than diffusion quenching constants. It is suggested that the energy-transfer rate is controlled by electronic factors which depend on the nephelauxetic ability of the ligands and on those parameters (size, electric charge, geometrical configuration) that determine the intimate characteristics of the encounter complex.

Introduction

Quenching of electronically excited states by energy-[2-4] (eq 1) or electron-transfer (eq 2)[5-8] processes is a subject of great

$$^*D + A \rightarrow D + {}^*A \qquad (1)$$

$$^*D + A \rightarrow D^+ + A^- \qquad (2)$$

theoretical and practical interest, particularly for the photochemical conversion of solar energy.[9] In fluid solution, when transition-metal complexes are involved as donors and/or acceptors, energy transfer generally occurs by an exchange mechanism[2-4] and electron transfer by an outer-sphere mechanism.[5-8] It has been recently emphasized[10] that these two quenching mechanisms are conceptually related since both obey Franck–Condon restrictions and require spatial overlap between donor and acceptor orbitals. A general classical treatment has also been formulated which accounts for the rate constants of the two processes by means of the same algebraic formalism.[10] In such a treatment, quenching is considered to occur in an encounter (or precursor complex) by a unimolecular reaction whose rate constant depends on an electronic term related to orbital overlap and a nuclear term related to Franck–Condon restrictions.

In order to elucidate the role played by electronic and nuclear factors in determining the rate constants of quenching processes, systematic investigations must be performed on homogeneous families of donors and/or acceptors. Continuing our studies in the field of energy-transfer processes,[11-13] we report here the results of an investigation concerning the quenching of the ^2E_g excited state of $Cr(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) by 16 Co(III) complexes. It is shown that the quenching takes place by electronic energy transfer and that the lower than diffusion energy-transfer rate constants are caused by unfavorable electronic factors. This finding, together with some other recent results,[12-16] confirms the expectations[10] that a nonadiabatic regime is normal for energy-transfer processes involving metal-centered excited states. The results obtained also show that the electronic term is strongly dependent on the nephelauxetic ability of the ligands and on the geometrical configuration of the acceptor complex.

Experimental Section

Materials. $[Cr(bpy)_3](ClO_4)_3\cdot{}^1/_2H_2O$ was prepared and purified as reported in the literature.[17] The following Co(III) complexes were prepared according to literature procedures and their purity was checked by means of electronic absorption spectra: $[Co(NH_3)_6](NO_3)_3$,[18] $[Co(en)_3]Cl_3\cdot 3H_2O$,[18b,19] $[Co(NH_3)_5H_2O](ClO_4)_3$,[20] $[Co(NH_3)_5F](ClO_4)_2$,[21] $[Co(NH_3)_5Cl]Cl_2$,[18b,22] $[Co(NH_3)_5NO_2](NO_3)_2$,[23] $[Co(NH_3)_5(O_2CH)](ClO_4)_2$,[24] $[Co(NH_3)_5NCS](ClO_4)_2$,[24b,25] *cis*-$[Co(en)_2(H_2O)Cl]SO_4$,[26] *cis*-$[Co(en)_2(NH_3)Cl]Cl_2\cdot 2H_2O$,[27] *cis*-$[Co(en)_2Cl_2]Cl$,[28] *trans*-$[Co(en)_2Cl_2]Cl$,[28b,29] *cis*-$[Co(en)_2(NCS)Cl]Cl$,[30] *trans*-$[Co(en)_2(NCS)Cl]Cl$,[30b,31] *cis*-$[Co(en)_2(NCS)_2]Cl$,[32] *trans*-$[Co(en)_2(NCS)_2]Cl\cdot H_2O$.[32]

The purity of *cis*- and *trans*-$Co(en)_2(NCS)_2^+$ was also checked by IR spectroscopy. The ionic strength of the solution was controlled

---

(1) (a) Istituto "G. Ciamician". (b) Istituto FRAE—CNR.
(2) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321.
(3) Wilkinson, F. *Pure Appl. Chem.* **1975**, *41*, 661.
(4) Ermolaev, V. L.; Sveshnikova, E. G.; Shakhverdov, T. A. *Russ. Chem. Rev.* (*Engl. Transl.*) **1975**, *44*, 26.
(5) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.
(6) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717.
(7) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.
(8) Grätzel, M. *Acc. Chem. Res.* **1981**, *14*, 376.
(9) Connolly, J. S., Ed. "Photochemical Conversion and Storage of Solar Energy"; Academic Press: New York, 1981. Rabani, J., Ed. "Photochemical Conversion and Storage of Solar Energy"; Weizmann Science Press of Israel: Jerusalem, 1982; Part A.
(10) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.
(11) Bolletta, F.; Maestri, M.; Moggi, L.; Balzani, V. *J. Am. Chem. Soc.* **1973**, *95*, 7864.
(12) Balzani, V.; Indelli, M. T.; Maestri, M.; Sandrini, D.; Scandola, F. *J. Phys. Chem.* **1980**, *84*, 852.
(13) Maestri, M.; Sandrini, D. *J. Phys. Chem.* **1981**, *85*, 2050.
(14) Wilkinson, F.; Tsiamis, C. *J. Chem. Soc., Faraday Trans. 2*, **1981**, *77*, 1681.
(15) Wilkinson, F.; Tsiamis, C. *J. Phys. Chem.* **1981**, *85*, 4153.
(16) Endicott, J. F.; Heeg, M. J.; Gaswick, D. C.; Pyke, S. *J. Phys. Chem.* **1981**, *85*, 1777.
(17) Baker, B. R.; Mehta, B. D. *Inorg. Chem.* **1965**, *4*, 848.
(18) (a) Bjerrum, J.; McReynolds, J. P. *Inorg. Synth.* **1946**, *2*, 218. (b) Linhard, M.; Weigel, M. *Z. Anorg. Allg. Chem.* **1953**, *271*, 101.
(19) Work, J. B. *Inorg. Synth.* **1946**, *2*, 221.
(20) (a) Rutenberg, A. C.; Taube, H. *J. Chem. Phys.* **1952**, *20*, 825. (b) Taylor, R. S. *Inorg. Chem.* **1977**, *16*, 117.
(21) (a) Basolo, F.; Murmann, R. K. *Inorg. Synth.* **1953**, *4*, 171. (b) Sriram, R.; Endicott, J. F. *Inorg. Chem.* **1977**, *16*, 2766.
(22) Schlessinger, G. C. *Inorg. Synth.* **1967**, *9*, 160.
(23) (a) Basolo, F.; Murmann, R. K. *Inorg. Synth.* **1953**, *4*, 174. (b) Linhard, M.; Weigel, M. *Z. Anorg. Allg. Chem.* **1951**, *267*, 113.
(24) (a) Linhard, M.; Weigel, M. *Z. Anorg. Allg. Chem.* **1951**, *264*, 321. (b) Shimura, Y.; Tsuchida, R. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 311.
(25) Carlin, R. L.; Edwards, J. O. *J. Inorg. Nucl. Chem.* **1958**, *6*, 217.
(26) (a) Werner, A. *Justus Liebigs Ann. Chem.* **1912**, *386*, 123. (b) Baldwin, M. E.; Chan, S. C.; Tobe, M. L. *J. Chem. Soc.* **1961**, 4637.
(27) (a) Werner, A. *Justus Liebigs Ann. Chem.* **1912**, *386*, 165. (b) Pribush, R. A.; Wright, R. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1977**, *99*, 2495.
(28) (a) Bailar, J. C., Jr. *Inorg. Synth.* **1946**, *2*, 222. (b) Bifano, C.; Link, R. G. *Inorg. Chem.* **1968**, *7*, 908.
(29) Leverett, P.; Oliver, M. J. *J. Chem. Educ.* **1976**, *53*, 440.
(30) Werner, A.; Nyholm, R. S.; Tobe, M. L. *J. Chem. Soc.* **1956**, 1691.
(31) Werner, A. *Justus Liebigs Ann. Chem.* **1912**, *386*, 133.
(32) (a) Braünlich, F. Z. *Anorg. Chem.* **1900**, *22*, 123. Werner, A. *Justus Liebigs Ann. Chem.* **1912**, *386*, 192. (b) Shimura, Y. *J. Am. Chem. Soc.* **1951**, *73*, 5079.

0020-1669/83/1322-3435$01.50/0

Table I. Bimolecular Rate Constants for the Quenching of $(^2E_g)Cr(bpy)_3^{3+}$ by Co(III) Complexes[a]

quencher $z = 3+$[b]	$10^{-6}k_q$, $M^{-1}\ s^{-1}$	quencher $z = 2+$[b]	$10^{-6}k_q$, $M^{-1}\ s^{-1}$	quencher $z = 1+$[b]	$10^{-6}k_q$, $M^{-1}\ s^{-1}$
$Co(NH_3)_6^{3+}$	2	$Co(NH_3)_5F^{2+}$	2	*cis*-$Co(en)_2Cl_2^+$	180
$Co(NH_3)_5(H_2O)^{3+}$	1	$Co(NH_3)_5(OOCH)^{2+}$	3	*trans*-$Co(en)_2Cl_2^+$	10
$Co(en)_3^{3+}$	1	$Co(NH_3)_5(NO_2)^{2+}$	16	*cis*-$Co(en)_2(NCS)Cl^+$	360
		$Co(NH_3)_5Cl^{2+}$	20	*trans*-$Co(en)_2(NCS)Cl^+$	62
		$Co(NH_3)_5(NCS)^{2+}$	91	*cis*-$Co(en)_2(NCS)_2^+$	390
		cis-$Co(en)_2(H_2O)Cl^{2+}$	22	*trans*-$Co(en)_2(NCS)_2^+$	92
		cis-$Co(en)_2(NH_3)Cl^{2+}$	32		

[a] Conditions: aqueous solution; 22 °C; 0.1 M H_2SO_4 ($\mu = 0.12$). For the precision of the values reported in the table, see text. [b] z is the ionic charge of the quencher. The calculated (see text) diffusion-controlled rate constants and the corresponding dissociation constants are as follows: $z = 3+$, $k_d = 3.3 \times 10^9\ M^{-1}\ s^{-1}$, $k_{-d} = 1.3 \times 10^{10}\ s^{-1}$; $z = 2+$, $k_d = 5.2 \times 10^9\ M^{-1}\ s^{-1}$, $k_{-d} = 8.8 \times 10^9\ s^{-1}$; $z = 1+$, $k_d = 7.1 \times 10^9\ M^{-1}\ s^{-1}$, $k_{-d} = 5.0 \times 10^9\ s^{-1}$.

by 0.1 M H_2SO_4 (Merck Suprapur).

Apparatus. The UV and visible absorption spectra were recorded with a Perkin-Elmer 323 spectrophotometer. The IR spectra were performed on Nujol mulls with a Jasco DS-701G spectrophotometer using KBr disks. Luminescence measurements were carried out with a Perkin-Elmer MPF-3 spectrofluorimeter using an R955 photomultiplier tube. The emission lifetime of $Cr(bpy)_3^{3+}$ was measured by a JK System 2000 ruby laser; the estimated error is ~5%.

Procedures. All the experiments were carried out at room temperature (22 °C) in air-equilibrated aqueous solutions containing 0.1 M H_2SO_4. The $Cr(bpy)_3^{3+}$ concentration was 1.0×10^{-3} M, and the quencher concentration was in the range 5.0×10^{-4}–8.0×10^{-3} M. Photoexcitation was performed at 313 nm, corresponding to a maximum ($\epsilon = 25\,450\ M^{-1}\ cm^{-1}$) of $Cr(bpy)_3^{3+}$. The emitted light was collected at 45°. When necessary, appropriate corrections were performed to take into account the fraction of incident light absorbed by the quencher (≤10%). The phosphorescence emission, monitored at 728 nm, was not absorbed by the quenchers. Duplicate sets of quenching experiments were performed, each involving at least four different quencher concentrations.

The Stern–Volmer quenching constants for the two sets agreed to within 10% except for $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and $Co(NH_3)_5X^{2+}$ (X = H_2O, F, OOCH), where the agreement was within 25%.

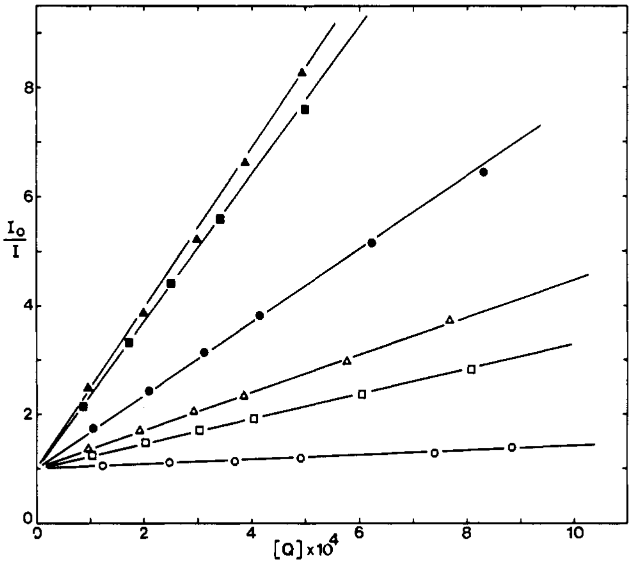

Figure 1. Stern–Volmer plots for the quenching of the $Cr(bpy)_3^{3+}$ phosphorescence by (○) *trans*-$Co(en)_2Cl_2^+$, (●) *cis*-$Co(en)_2Cl_2^+$, (□) *trans*-$Co(en)_2(NCS)Cl^+$, (■) *cis*-$Co(en)_2(NCS)Cl^+$, (△) *trans*-$Co(en)_2(NCS)_2^+$, and (▲) *cis*-$Co(en)_2(NCS)_2^+$.

Results

There was no evidence in the electronic spectra for the formation of any association between donor and acceptor. No spectral change was observed in our systems upon irradiation with the light of the spectrofluorimeter.

Linear Stern–Volmer plots were obtained (see, for example, Figure 1) for the quenching of the $Cr(bpy)_3^{3+}$ phosphorescence intensity by all the complexes used as quenchers. The bimolecular quenching constants (Table I) were obtained from the slopes of the Stern–Volmer plots with use of the value 38.0 μs for the $(^2E_g)Cr(bpy)_3^{3+}$ lifetime, measured in the absence of quencher under our experimental conditions. The diffusion-controlled rate constants and the corresponding dissociation rate constants for quenchers of charge 3+, 2+, and 1+ are reported in footnote *b* of Table I for comparison purposes (see Discussion).

The data previously obtained by Endicott et al.[16] for $Co(NH_3)_6^{3+}$ ($k_q = (3.5 \pm 0.8) \times 10^6\ M^{-1}\ s^{-1}$, $Co(NH_3)_5(H_2O)^{3+}$ ($k_q = (4.0 \pm 0.5) \times 10^6\ M^{-1}\ s^{-1}$), and $Co(en)_3^{3+}$ ($k_q = (1.5 \pm 0.6) \times 10^6\ M^{-1}\ s^{-1}$) are in fair agreement with our values (Table I) considering that they were obtained at higher ionic strengths ($\mu = 1.0$–1.5) and that the rate constants for these relatively inefficient quenchers are affected by considerable errors.

Discussion

Quenching Mechanism. In fluid solution the quenching of an excited state may take place by several distinct mechanisms,[2-5,33] the most important of which are (i) electronic energy transfer, (ii) electron transfer, (iii) chemical reaction involving atom transfer, (iv) exciplex formation, (v) spin-catalyzed deactivation, and (vi) external heavy-atom effect. In the specific case of the quenching of $(^2E_g)Cr(bpy)_3^{3+}$ by Co(III) complexes, spin-catalyzed deactivation, external heavy-atom effect, and atom transfer may be readily excluded. A small quenching effect ($k_q \simeq 1 \times 10^6\ M^{-1}\ s^{-1}$) on $(^2E_g)Cr(bpy)_3^{3+}$ by ground-state $Cr(bpy)_3^{3+}$ via some kind of exciplex formation has been reported in 5 M HCl, but no effect was found in media of lower acidity or ionic strength.[34] Thus, there is no reason why a similar mechanism should play a role in our systems. Electron transfer can also be excluded because the excited Cr complex is a strong oxidant but a very poor reductant ($Cr(bpy)_3^{4+}$ has never been obtained)[5] and the Co(III) complexes can only be reduced (Co(IV) is unknown, at least with usual ligands).[35] Even for the quenching of $(^2E_g)Cr(bpy)_3^{3+}$ by the very powerful oxidant $Co(H_2O)_6^{3+}$ electron transfer was ruled out.[16] On the other hand, quenching by energy transfer via an exchange mechanism (eq 3 and 4, where CoL^{z+} represents the complexes shown in Table

$$(^2E_g)Cr(bpy)_3^{3+} + (^1A_{1g})CoL^{z+} \rightarrow (^4A_{2g})Cr(bpy)_3^{3+} + (^3T_{1g})CoL^{z+} \quad (3)$$

$$(^2E_g)Cr(bpy)_3^{3+} + (^1A_{1g})CoL^{z+} \rightarrow (^4A_{2g})Cr(bpy)_3^{3+} + (^5T_{2g})CoL^{z+} \quad (4)$$

---

(33) Lamola, A. A. In "Energy Transfer and Organic Photochemistry"; Lamola, A. A., Turro, N. J., Eds.; Interscience: New York, 1969; p 17.

(34) Serpone, N.; Jamieson, M. A.; Sriram, R.; Hoffman, M. Z. *Inorg. Chem.* **1981**, *20*, 3983.

(35) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980.

I, assumed to have octahedral symmetry) is thermodynamically allowed because the zero–zero excited-state energy of (^2E_g)-$Cr(bpy)_3^{3+}$ is 13 800 cm^{-1} and the zero–zero energy of the $^3T_{1g}$ and $^5T_{2g}$ excited states of the Co(III) complexes is smaller than 10 800 cm^{-1} (for more details, see below). It should also be noted that both reactions 3 and 4 are spin allowed and exhibit unitary spin statistical factors.[14,36] Thus, energy transfer is expected to be the most important (if not the unique) quenching mechanism in our systems and we can assume that the experimental quenching constants reported in Table I refer to this type of process.

The upper limiting value for the energy-transfer quenching constant is the diffusion rate constant, k_d, because exchange energy transfer can only take place in an encounter complex:

$$^*D + A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} {}^*D\cdots A \underset{k_{-en}}{\overset{k_{en}}{\rightleftharpoons}} D\cdots{}^*A \underset{k_d}{\overset{k_{-d}}{\rightleftharpoons}} D + {}^*A \qquad (5)$$

The diffusion rate constant can be evaluated[37–39] by eq 6, where

$$k_d^{\mu=0} = \frac{8RT}{3000\eta}\,\frac{b/r}{e^{b/r}-1} \qquad (6)$$

μ, η, and r are the ionic strength, viscosity, and encounter distance, and the term b is given by

$$b = \frac{z_D z_A e^2}{\epsilon k T} \qquad (7)$$

where e is the electron charge, ϵ is the dielectric constant, and z_D, z_A are the electric charges of the two reactants. The ionic strength dependence of k_d is given by

$$\log k_d^{\mu} = \log k_d^{\mu=0} + \frac{1.02 z_D z_A \mu^{1/2}}{1 + Ar\mu^{1/2}} \qquad (8)$$

where A is $(8\pi Ne^2/1000k\epsilon T)^{1/2}$. The dissociation rate constant k_{-d} can be evaluated by the equation[40]

$$k_{-d} = \frac{2kT}{\pi r^3 \eta}\,\frac{b/r}{1-e^{-b/r}} \qquad (9)$$

where each symbol has the meaning previously seen. Taking 7 Å as the radius of $Cr(bpy)_3^{3+}$ and 4 Å as an average radius of the Co(III) complexes, one obtains the k_d and k_{-d} values reported in footnote b of Table I. From the same table, one can see that the values of the experimental quenching constant are lower than the diffusion-controlled limit and that they are also very different for the various complexes. In an attempt to establish which factors are responsible for the observed behavior, we will now apply the approach to energy-transfer processes discussed in detail in previous papers.

Approach to Energy-Transfer Processes.[10,12,13] The energy-transfer process (eq 1) is subdivided into elementary steps (eq 5), and the bimolecular quenching constant, k_q is expressed as a function of the rate constants of the various steps:

$$k_q = \frac{k_d}{1 + \dfrac{k_{-e}}{k_e} + \dfrac{k_{-d}}{k_e}} \qquad (10)$$

In the frame of the classical approach, the ratio k_{-e}/k_e is equal to exp $(\Delta G/RT)$, where ΔG is the free energy change of the energy-transfer step (taken as the difference between the zero–zero spectroscopy energies of the donor and acceptor, eq 11), and the rate constant of the forward energy transfer

$$\Delta G = -E^{00}(^*D,D) + E^{00}(^*A,A) \qquad (11)$$

step is given by eq 12, where $k^0{}_e$ is the preexponential factor,

$$k_e = k^0{}_e \exp\left(\frac{-\Delta G^*}{RT}\right) = \kappa\frac{kT}{h}\exp\left(\frac{-\Delta G^*}{RT}\right) \qquad (12)$$

κ is the electronic transmission coefficient, kT/h is the universal frequency of the transition-state theory (which should more correctly be replaced by an effective frequency for nuclear motion[39,41,42]), and ΔG^* is the free activation energy, which can be expressed by the free energy relationship given by eq 13.[43] In this equation, ΔG is the previously seen free

$$\Delta G^* = \Delta G + \frac{\Delta G^*(0)}{\ln 2}\ln\left(1 + \exp\left(-\frac{\Delta G \ln 2}{\Delta G^*(0)}\right)\right) \qquad (13)$$

energy change and $\Delta G^*(0)$ is the so-called intrinsic barrier to energy transfer, a parameter related to the amount of distortion of both the inner coordination spheres and the outer solvation shells accompanying the energy transfer. It is thus apparent that the classical equation, like the quantum-mechanical equation in the high-temperature limit, expresses the rate constant as a product of an electronic term associated with κ and a nuclear term associated with $\exp(-\Delta G^*/RT)$ (for a comparison between the classical and quantum mechanical models, see ref 39, 41, and 42).

Equation 10 can be rewritten as

$$k_q = \frac{k_d}{1 + \exp\left(\dfrac{\Delta G}{RT}\right) + \dfrac{k_{-d}}{k^0{}_e}\exp\left(\dfrac{\Delta G^*}{RT}\right)} \qquad (14)$$

which shows that the experimental quenching constant of an energy-transfer process may be lower than diffusion for three reasons: (i) the reaction is endoergonic; (ii) the preexponential term of the energy transfer step, $k^0{}_e$, is smaller than the dissociation rate constant, k_{-d}; (iii) the reaction is exoergonic but the activation energy term is positive because of a high intrinsic barrier (eq 13). Equations 14 and 13 can be used to correlate the quenching constants within homogeneous series of energy-transfer processes[10,14,15] and to elucidate the role of nuclear and electronic factors in determining the values of energy-transfer rate constants.[10,12–15]

Nuclear Factors. The role of the nuclear factors is contained in the $\exp(\Delta G^*/RT)$ term of eq 14, where ΔG^* is a function of the intrinsic barrier $\Delta G^*(0)$ and the free energy change ΔG according to eq 13. The intrinsic barrier to energy transfer can be taken as

$$\Delta G^*(0) = \tfrac{1}{2}(\Delta G^*{}_D(0) + \Delta G^*{}_A(0)) \qquad (15)$$

where $\Delta G^*{}_D(0)$ and $\Delta G^*{}_A(0)$ are the free energies of activation for the self-exchange energy transfer of donor and acceptor,[10] respectively. Each one of these terms receives contributions from changes in the inner nuclear coordinates of the molecule ("inner-sphere" reorganization energy, $\Delta G^*(0)_i$) and from

---

[36] Porter, G.; Wright, M. R. *Discuss. Faraday Soc.* **1959**, *27*, 18.

[37] Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.

[38] Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

[39] Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.

[40] Eigen, M. *Z. Phys. Chem.* (*Wiesbaden*) **1954**, *1*, 176.

[41] Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798.

[42] Balzani, V.; Scandola, F. In "Energy Resources by Photochemistry and Catalysis"; Grätzel, M., Ed.; Academic Press: New York, in press.

[43] Equation 13 is preferred to the classical Marcus equation, because it can better account for the behavior of highly exoergonic reactions.[44] In the case of slightly endoergonic or slightly exoergonic reactions, like those dealt with in this paper, the two equations give practically equivalent results.[44]

[44] Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1979**, *101*, 6140; **1980**, *102*, 3663.

changes in the solvent arrangement around the molecule ("outer-sphere" reorganization energy, $\Delta G^*(0)_o$).

Following the classical harmonic oscillator approach[10,39] the inner-sphere contribution to the intrinsic barrier of a self-exchange energy-transfer process can be calculated by the relation

$$\Delta G^*(0)_i = \frac{1}{2}\frac{f_1 f_2 (r_1 - r_2)^2}{(f_1 + f_2)} \qquad (16)$$

where f_1 and f_2 are the breathing force constants of the ground and excited state and $r_1 - r_2$ is the change in the bond length. The force constants are obtained from $f = 4\pi^2\nu^2\mu/N$, where ν is the frequency of the vibration and μ is the reduced mass of the oscillator. As far as the donor is concerned, the inner-sphere contribution is certainly negligible because it is well-known[45] that for Cr(III) complexes the ^2E_g excited state has practically the same size and vibrational frequency as the $^4A_{2g}$ ground state. The situation, however, is quite different for the acceptor Co(III) complexes because their low-energy excited states are obtained by promoting nonbonding $\pi(t_{2g})$ electron(s) to $\sigma^*(e_g)$ antibonding orbitals and are thus expected to have different equilibrium configuration and different vibrational frequency compared with those of the $^1A_{1g}$ ground state.[45] A complete picture of the excited-state situation is only known for $Co(NH_3)_6^{3+}$ [46] and *trans*-$Co(NH_3)_4(CN)_2^+$ [47] (the latter has not been used as a quencher in this paper). With use of eq 16 and the spectroscopic data reported in ref 46 and 47, $\Delta G^*(0)_i$ values ranging from 950 to 2290 cm^{-1} are obtained for the following self-exchange reactions:

$Co(NH_3)_6^{3+}$

$$^1A_{1g} + {}^5T_{2g} \rightarrow {}^5T_{2g} + {}^1A_{1g} \qquad \Delta G^*(0)_i = 2290\ \text{cm}^{-1} \quad (17)$$

$$^1A_{1g} + {}^3T_{1g} \rightarrow {}^3T_{1g} + {}^1A_{1g} \qquad \Delta G^*(0)_i = 1420\ \text{cm}^{-1} \quad (18)$$

$$^1A_{1g} + {}^1T_{1g} \rightarrow {}^1T_{1g} + {}^1A_{1g} \qquad \Delta G^*(0)_i = 1540\ \text{cm}^{-1} \quad (19)$$

trans-$Co(NH_3)_4(CN)_2^+$

$$^1A_{1g} + {}^1A_{2g} \rightarrow {}^1A_{2g} + {}^1A_{1g} \qquad \Delta G^*(0)_i = 950\ \text{cm}^{-1} \quad (20)$$

For $Co(NH_3)_5X^{2+}$ (X = F, Cl, Br) and *trans*-$Co(NH_3)_4X_2^+$ (X = Cl, Br) high-resolution spectra are also available[48] and, although their detailed interpretation does not seem possible, it is evident that the geometrical situation for these complexes must be quite similar to that of $Co(NH_3)_6^{3+}$ and *trans*-$Co(NH_3)_4(CN)_2^+$. Thus, the $\Delta G^*(0)_i$ values of eq 17–20 can be taken as representative for all the Co(III) complexes used in this paper.

In evaluating the outer-sphere contribution to the intrinsic barrier, it should be noted that in energy-transfer processes the electric charges of the reaction partners do not change (unlike the electron-transfer case[39]); thus this contribution must be small because it is only due to changes in dipole moment, polarizability, and molecular size. Since we are dealing with energy transfer involving metal-centered excited states, no important change in dipole moment and polarizability is expected. For the donor Cr complex, there is also no change in size (see above). For the acceptor Co(III) complexes there is a small increase in size in going from the ground state to the excited states[46] (mean radii for $Co(NH_3)_6^{3+}$: $^1A_{1g}$, 3.30 Å; $^5T_{2g}$, 3.44 Å; $^3T_{1g}$, 3.38 Å; $^1T_{1g}$, 3.39 Å). The corresponding contribution to $\Delta G^*(0)_o$, however, is expected to be negligible, as shown by the practically identical values obtained for $\Delta G^*(0)_o$ for the self-exchange electron-transfer processes of $Fe(H_2O)_6^{3+/2+}$ (Δr = 0.14 Å) and $Ru(NH_3)_6^{3+/2+}$ (Δr = 0.04 Å).[49,50]

In conclusion, the only important contribution to the intrinsic barrier $\Delta G^*(0)$ of reactions 3 and 4 comes from the inner-sphere reorganization of the acceptor. On the basis of eq 15 and of the values estimated for $\Delta G^*{}_A(0)_i$ (eq 17–20), such a barrier should be on the order of 500–1000 cm^{-1}.

The effect of the intrinsic barrier in slowing down k_e is moderated by the exoergonicity of the reaction according to eq 12 and 13. As we have seen above, the free energy changes of an energy-transfer process is approximately given by the difference between the zero–zero spectroscopic energies of the donor and acceptor (eq 11). For our systems $E^{00}(^*D,D)$ is equal to 13 800 cm^{-1}. As for the acceptors, from the paper of Wilson and Solomon[46] values of 10 580 and ~8300 cm^{-1} can be obtained for the zero–zero energy of the $^3T_{1g}$ and $^5T_{2g}$ excited states of $Co(NH_3)_6^{3+}$. On the basis of ligand field arguments, Endicott et al.[16] obtained a value of 10 800 cm^{-1} for the $^3T_{1g}$ excited state of $Co(en)_3^{3+}$, and on the same basis, slightly lower values can be predicted for the energies of the correspondent excited states of the other quenchers. From the above estimations of exoergonicities and intrinsic barriers we can now estimate the free activation energies of reactions 3 and 4 by eq 13. For $Co(NH_3)_6^{3+}$, reaction 3 is exoergonic by 3220 cm^{-1} and the intrinsic barrier (eq 15 and 18) is on the order of 700 cm^{-1}. If it is assumed that the value of the intrinsic barrier might be underestimated by as much as 70%,[51] ΔG^* is found to be in the range 41–245 cm^{-1}.[52] In the same way for reaction 4, taking $\Delta G = -5500$ cm^{-1} and $\Delta G^*(0)$ = 1100–1900 cm^{-1}, one gets ΔG^* ranging from 50 to 330 cm^{-1}. As previously mentioned, for the other quenchers used, reactions 3 and 4 are expected to be a little more exoergonic and to exhibit comparable (or a little smaller[50]) intrinsic barriers. Thus, the values ~50 to ~300 cm^{-1} estimated for the free activation energy in the case of $Co(NH_3)_6^{3+}$ are representative for all the quenchers used. This means the term $\exp(-\Delta G^*/RT)$ in eq 12 is not far from unity (0.2–0.8) so that, if κ were equal to unity, k^0_e would be about equal to kT/h, i.e. much higher than k_{-d}, and k_q (eq 14) would have been diffusion controlled. In other words, *in all cases energy transfer is sufficiently exoergonic to make up for the intrinsic barrier*. Thus, nuclear factors cannot be responsible for the observed lower than diffusion quenching constants and for the differences in the k_q values for the various complexes.

Electronic Factors. From the above discussion it is apparent that the quenching constants are controlled by the transmission coefficient κ, i.e. by electronic factors. When, as in our case, ΔG is large and negative and ΔG^* is very small, eq 14 reduces to

$$k_q = \frac{k_d}{k_{-d}}\kappa\frac{kT}{h} \qquad (21)$$

and κ values ranging from 6.3×10^{-7} for $Co(NH_3)_5H_2O^{3+}$ to

---

(45) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: London, 1970.

(46) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.

(47) Urushiyama, A.; Kupka, H.; Degen, J.; Schmidtke, H. H. *Chem. Phys.* **1982**, *67*, 65.

(48) Fukuda, K.; Urushiyama, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1946.

(49) Sutin, N. In "Tunneling in Biological Systems"; Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds.; Academic Press: New York, 1979; p 201.

(50) Endicott et al.[16] have used a simple Born charging model to estimate $\Delta G^*(0)_o$. With this approach, $\Delta G^*(0)_o$ values of ~1000 and ~100 cm^{-1} are obtained for complexes having 3+ and 1+ ionic charges, respectively. The conclusions reported in this paper would not be affected by using such values. We would like to note, however, that it is not clear how actual activation energies can be estimated by the Born charging model.

(51) In this way, the value of $\Delta G^*(0)_o$ estimated from the Born charging model[50] would be included.

(52) Using the Marcus quadratic equation instead of eq 13,[43] one obtains quite similar values: ΔG^* = 16–125 cm^{-1}.

4.3×10^{-5} for *cis*-$Co(en)_2(NCS)_2^+$ can be obtained from the data reported in Table I, showing that energy transfer from $(^2E_g)Cr(bpy)_3^{3+}$ to Co(III) complexes is strongly *nonadiabatic*. This important feature of energy-transfer processes involving metal-centered excited states of transition-metal complexes has already been observed in this[10-13] and other[14-16] laboratories. As discussed in more detail elsewhere,[12] the electronic interaction between initial and final states in energy-transfer processes has the form of an exchange integral between donor and acceptor orbitals. To a first approximation, the donor–acceptor orbitals involved in the energy-transfer process (eq 3 and 4) are centered on the different metals and thus they are shielded by the ligands. This reduces the overlap between the metal orbitals and causes the lower than unity κ values. Different ligands, however, and different geometrical structures may exhibit different shielding effects, causing the observed variations in the quenching constants (Table I).

The Co(III) complexes used as quenchers (Table I) differ from one another for one or more of these four parameters: (i) electric charge, (ii) size, (iii) nature of the ligands, and (iv) geometrical configuration. In order to understand the role played by each one of these parameters, one should compare the results obtained with complexes which are identical as far as the other parameters are concerned. In Table I, the quenchers are grouped according to their charge. At first glance, it would appear that the quenching constants increase with decreasing electric charge, as is expected in view of the positive charge of the donor. Upon closer examination, however, it is clear that such a conclusion is not firm because a change in the electric charge is always accompanied by a change in the nature of the ligands.

Concerning the size of the quenchers, Endicott et al.[16] reported that for a series of 3+ Co(III) complexes there is a consistent decrease in k_q with increasing size of the complex, as expected on the basis of orbital overlap arguments. In agreement with these authors,[16] we find that $Co(NH_3)_6^{3+}$ is a slightly better quencher than $Co(en)_3^{3+}$. However, it should again be emphasized that a change in size always involves a change in the nature of the ligands. Thus, other effects can predominate, as shown, for example, by the higher quenching constants of the complexes containing 2 NCS^- compared with those of the analogous, smaller complexes containing 2 Cl^-.

More reliable conclusions can be drawn as far as the nature of the ligands is concerned. The quenching of the couples $Co(NH_3)_6^{3+}$–$Co(NH_3)_5(H_2O)^{3+}$ and $Co(en)_2(H_2O)Cl^{2+}$–$Co(en)_2(NH_3)Cl^{2+}$ shows that NH_3 has a slightly better quenching ability than H_2O. Comparison among the quenching constants of the $Co(NH_3)_5X^{2+}$ complexes, which may be assumed to have approximately the same size, allows classification of the X^- ligands according to the following series: $F^- < HCOO^- < NO_2^- < Cl^- < NCS^-$. The better quenching ability of NCS^- compared with that of Cl^- (in spite of the larger size) is fully confirmed by the $Co(en)_2X_2^+$ complexes. The ligand series above coincides (except for the position of NCS^- with respect to Cl^-) with the nephelauxetic series,[53] which is related to the delocalization of the metal orbitals as measured from spectroscopic parameters. A strict correlation between the preexponential factor of the energy transfer rate constant and the nephelauxetic parameter β has already been found for energy transfer to Cr(III) complexes.[12,13] Interestingly, the inversion between Cl^- and NCS^- compared to the nephelauxetic series was already found for the quenching of $^*Ru(bpy)_3^{2+}$ by $Cr(en)_2X_2^+$ complexes.[11]

The effect of geometrical structure is extremely clear: the cis isomers are better quenchers than the trans isomers. This is again in agreement with previous findings[11] concerning the quenching of $^*Ru(bpy)_3^{2+}$ by $Cr(en)_2X_2^+$ complexes. The most likely explanation of this effect is the following: the cis acceptors may interact better with the positively charged donor because they have a dipolar distribution of the electric charge, with the less positive region corresponding to the 2 X ligands, which are more nephelauxetic than en. The effect of the geometrical structure is very strong, and it seems to overcome the effects of ligand and electric charge, as one can see on comparing the rate constants of cis-$Co(en)_2(NH_3)Cl^{2+}$ and trans-$Co(en)_2Cl_2^+$. Other, minor details on the behavior of the quenching constants appear in the data of Table I, but their interpretation is difficult because of the small number of cases examined.

Conclusion. Quenching of $(^2E_g)Cr(bpy)_3^{3+}$ by Co(III) complexes takes place by an exchange energy transfer mechanism. The intrinsic barriers are relatively high because of the strong distortion of the acceptor excited states, but their effects are canceled out by a sufficiently large exoergonicity. The low values of the rate constants are controlled by electronic factors which depend on the ability of the ligands to delocalize the metal orbitals (nephelauxetic effect) and on those parameters (size, electric charge, geometrical configuration) which determine the intimate characteristics of the encounter complex.

In view of the analogy between energy transfer via an exchange mechanism and outer-sphere electron transfer, it seems likely that the nephelauxetic properties of the ligands and the geometrical configuration of the complex can play some role in outer-sphere electron transfer processes involving transition-metal complexes.

Acknowledgment. Financial support from MPI is gratefully acknowledged.

Registry No. $Cr(bpy)_3^{3+}$, 15276-15-0; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(NH_3)_5(H_2O)^{3+}$, 14403-82-8; $Co(en)_3^{3+}$, 14878-41-2; $Co(NH_3)_5F^{2+}$, 15392-06-0; $Co(NH_3)_5(OOCH)^{2+}$, 19173-64-9; $Co(NH_3)_5(NO_2)^{2+}$, 14482-68-9; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5(NCS)^{2+}$, 14970-18-4; *cis*-$Co(en)_2(H_2O)Cl^{2+}$, 15693-74-0; *cis*-$Co(en)_2(NH_3)Cl^{2+}$, 15392-82-2; *cis*-$Co(en)_2Cl_2^+$, 14875-15-1; *trans*-$Co(en)_2Cl_2^+$, 14403-91-9; *cis*-$Co(en)_2(NCS)Cl^+$, 24912-92-3; *trans*-$Co(en)_2(NCS)Cl^+$, 16997-24-3; *cis*-$Co(en)_2(NCS)_2^+$, 21169-85-7; *trans*-$Co(en)_2(NCS)_2^+$, 24988-19-0.

---

(53) Jørgensen, C. K. "Modern Aspects of Ligand Field Theory"; North-Holland Publishing Co.: Amsterdam, 1971; p 310.