likely energy result from deprotonation of HDPA as suggested previously. The deprotonated complexes in particular are excellent candidates for more extensive investigation as the low-energy charge-transfer bands and indications of increased metal–ligand interactions make these species unique members of the class of Ru(II) tris(diimine) complexes.

Acknowledgment. We wish to express gratitude to Charles T. Vance of this department for helpful discussions concerning the isolation of K(DPA). This research was supported by NSF Grants CHE-81-19702 and CHE-80-14183.

Registry No. $[Ru(HDPA)_3]^{2+}$, 84052-35-7; $[Ru(HDPA)_2(bpy)]^{2+}$, 91295-39-5; $[Ru(HDPA)(bpy)_2]^{2+}$, 91295-40-8; $[Ru(bpy)_3]^{2+}$, 15158-62-0; $[Ru(DPA)(bpy)_2]^{+}$, 91295-41-9; $[Ru(DPA)_2(bpy)]$, 91295-42-0; $[Ru(HDPA)_3]^{3+}$, 91295-43-1; $[Ru(HDPA)_3]^{+}$, 91295-44-2; $[Ru(HDPA)_2(bpy)]^{3+}$, 91295-45-3; $[Ru(HDPA)_2(bpy)]^{+}$, 91295-46-4; $[Ru(HDPA)_2(bpy)]$, 91295-47-5; $[Ru(HDPA)(bpy)_2]^{3+}$, 91295-48-6; $[Ru(HDPA)(bpy)_2]^{+}$, 91295-49-7; $[Ru(HDPA)(bpy)_2]$, 91295-50-0; $[Ru(HDPA)(bpy)_2]^{-}$, 91295-51-1; $[Ru(bpy)_3]^{3+}$, 18955-01-6; $[Ru(bpy)_3]^{+}$, 56977-24-3; $[Ru(bpy)_3]$, 74391-32-5; $[Ru(bpy)_3]^{-}$, 56977-23-2; $[Ru(bpy)_3]^{2-}$, 87279-34-3; $[Ru(DPA)(bpy)_2]^{2+}$, 91295-52-2; $[Ru(DPA)(bpy)_2]^{3+}$, 91295-53-3; $[Ru(DPA)(bpy)_2]$, 91295-54-4; $[Ru(DPA)(bpy)_2]^{-}$, 91295-55-5; $[Ru(DPA)(bpy)_2]^{2-}$, 91295-56-6; $[Ru(DPA)_2(bpy)]^{+}$, 91295-57-7; $[Ru(DPA)_2(bpy)]^{2+}$, 91295-58-8; $[Ru(DPA)_2(bpy)]^{3+}$, 91295-59-9; $[Ru(DPA)_2(bpy)]^{-}$, 91295-60-2; $[Ru(DPA)_2(bpy)]^{2-}$, 91295-61-3; $[Ru(HDPA)(bpy)_2](ClO_4)_2$, 91295-64-6; $[Ru(bpy)_2Cl_2]$, 15746-57-3; $[Ru(DPA)(bpy)_2](ClO_4)$, 91311-03-4; $[Ru(HDPA)_2(bpy)](ClO_4)_2$, 91295-65-7; $K[Ru(DPA)_3]$, 91295-67-9; K(DPA), 91295-66-8; DPA^{-}, 91295-68-0; HDPA, 1202-34-2; $HDPA^{+}$, 91295-62-4; $HDPA^{-}$, 91382-95-5; bpy, 366-18-7; bpy^{-}, 34475-06-4; bpy^{2-}, 91295-63-5.

Contribution from the Istituto Chimico "Ciamician"
dell'Università and Istituto FRAE-CNR, Bologna, Italy

Electron-Transfer Quenching of the Luminescence of Ruthenium and Osmium Polypyridine Complexes by Cobalt(III) Complexes

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The quenching of the luminescence of $Ru(bpy)_3^{2+}$, $Os(phen)_3^{2+}$, and other Ru polypyridine complexes by 17 Co(III) complexes has been studied in aqueous solution. The quenching rate constants correlate with the rate constants available for reduction of the same Co(III) complexes by $Ru(NH_3)_6^{2+}$ or $Cr(bpy)_3^{2+}$, as expected for an electron-transfer quenching mechanism. Conversely, there is no correlation with the rate constants for the quenching of the luminescence of $Cr(bpy)_3^{3+}$, which was previously shown to occur by energy transfer. The rate constants obtained in this paper and other homogeneous data taken from the literature for outer-sphere electron-transfer reactions of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$, $Co(en)_3^{3+}$, $Co(bpy)_3^{3+}$, and $Co(phen)_3^{3+}$ have been examined by the approach based on the log k_{cor} vs. ΔG plot in an attempt to disentangle the effects of nuclear and electronic terms on the rate constants. This analysis has led to the following values for the electronic transmission coefficient $\mathbf{k}$ and for the intrinsic barrier ΔG^* of the self-exchange reactions: $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5H_2O^{3+}$, $\mathbf{k} = 10^{-1\pm1}$, $\Delta G^* = 24 \pm 2$ kcal/mol; $Co(en)_3^{3+}$, $\mathbf{k} = 10^{-3\pm1}$, $\Delta G^* = 17 \pm 2$ kcal/mol; $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$, $\mathbf{k} = 10^{-5\pm1}$, $\Delta G^* = 13 \pm 2$ kcal/mol.

Introduction

Outer-sphere electron-transfer reactions continue to be the object of many theoretical and experimental studies.[2-9] The aim of these studies is to understand the role played by nuclear and electronic factors in determining the observed rate constants and eventually to correlate these factors to fundamental molecular parameters such as chemical composition, geometrical structure, and electric charge.

The behavior of the Co(III)–Co(II) complexes has always been the object of much interest because of two features that are expected to cause very low rate constants:[4-8,10-14] (i) the electron-transfer process involves $\sigma^*(e_g)$ antibonding orbitals with a consequent strong change in the nuclear coordinates; (ii) the electron-transfer process is spin forbidden, and thus it can only occur by mixing of excited-state and ground-state wave functions. Furthermore, recent studies have suggested that orbital-overlap problems might also be responsible for the low rate constants.[8,15-20]

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(1) (a) Istituto Chimico "Ciamician". (b) Istituto FRAE-CNR.
(2) Chance, B., De Vault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds. "Tunneling in Biological Systems"; Academic Press: New York, 1979.
(3) Ulstrup, J. "Charge Transfer Processes in Condensed Media"; Springer-Verlag: West Berlin, 1979.
(4) Cannon, R. D. "Electron Transfer Reactions"; Butterworths: London, 1980.
(5) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.
(6) Rorabacher, D. B., Endicott, J. F., Eds. "Mechanistic Aspects of Inorganic Reactions"; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 198.
(7) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.
(8) Endicott, J. F.; Kumar, K.; Ramasani, T.; Rotzinger, F. P. *Prog. Inorg. Chem.* **1983**, *30*, 141.
(9) Balzani, V.; Scandola, F. In "Energy Resources by Photochemistry and Catalysis"; Grätzel, M., Ed.; Academic Press: New York, 1983; Chapter 1, p 1.
(10) Sutin, N. In "Bioinorganic Chemistry"; Eichhorn, G. L., Ed.; American Elsevier: New York, 1973; Vol. 2, Chapter 19, p 611.
(11) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.
(12) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979**, *18*, 2014.
(13) Endicott, J. F.; Durham, B.; Glick, D. M.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 1431.
(14) Endicott, J. F.; Durham, B.; Kumar, K. *Inorg. Chem.* **1982**, *21*, 2437.
(15) Endicott, J. F.; Heeg, M. J.; Gaswick, D. C.; Pyke, S. *J. Phys. Chem.* **1981**, *85*, 1777.
(16) Buhks, E.; Wilkins, R. G.; Isied, S. S.; Endicott, J. F. In ref 6, p 213.

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Table I. Quenching Constants[a]

no.	quencher ($E°$, V)[b]	excited state	$10^{-7}k_{\text{exptl}}$, M^{-1} s^{-1} [c]
1	$Co(NH_3)_6^{3+}$ (0.1)	$Ru(bpy)_3^{2+}$	4.0[d,e]
		$Ru(phen)_3^{2+}$	1.2[e]
		$Ru(DM\text{-}phen)_3^{2+}$	2.3
		$Ru(DM\text{-}bpy)_3^{2+}$	0.9
		$Os(phen)_3^{2+}$	10
2	$Co(en)_3^{3+}$ (−0.18)	$Ru(bpy)_3^{2+}$	2.0
		$Os(phen)_3^{2+}$	10
3	$Co(phen)_3^{3+}$ (0.4)	$Ru(bpy)_3^{2+}$	190[f]
4	$Co(NH_3)_5H_2O^{3+}$ (0.37)	$Ru(bpy)_3^{2+}$	7.5[g]
		$Os(phen)_3^{2+}$	37
5	$Co(NH_3)_5F^{2+}$	$Ru(bpy)_3^{2+}$	8.0
		$Os(phen)_3^{2+}$	29
6	$Co(NH_3)_5Cl^{2+}$	$Ru(bpy)_3^{2+}$	58[h]
		$Os(phen)_3^{2+}$	93
7	$Co(NH_3)_5NCS^{2+}$	$Ru(bpy)_3^{2+}$	30
		$Os(phen)_3^{2+}$	68
8	$Co(NH_3)_5(O_2CH)^{2+}$	$Ru(bpy)_3^{2+}$	4.7
		$Os(phen)_3^{2+}$	41
9	$Co(NH_3)_5(NO_2)^{2+}$	$Ru(bpy)_3^{2+}$	10
10	c-$Co(en)_2(H_2O)Cl^{2+}$	$Ru(bpy)_3^{2+}$	60
		$Os(phen)_3^{2+}$	96
11	c-$Co(en)_2(NH_3)Cl^{2+}$	$Ru(bpy)_3^{2+}$	42
		$Os(phen)_3^{2+}$	93
12	c-$Co(en)_2Cl_2^{+}$	$Ru(bpy)_3^{2+}$	143
		$Os(phen)_3^{2+}$	225
13	t-$Co(en)_2Cl_2^{+}$	$Ru(bpy)_3^{2+}$	200
		$Os(phen)_3^{2+}$	265
14	c-$Co(en)_2(NCS)Cl^{+}$	$Ru(bpy)_3^{2+}$	155
		$Os(phen)_3^{2+}$	212
15	t-$Co(en)_2(NCS)Cl^{+}$	$Ru(bpy)_3^{2+}$	107
		$Os(phen)_3^{2+}$	160
16	c-$Co(en)_2(NCS)_2^{+}$	$Ru(bpy)_3^{2+}$	76
		$Os(phen)_3^{2+}$	190
17	t-$Co(en)_2(NCS)_2^{+}$	$Ru(bpy)_3^{2+}$	48
		$Os(phen)_3^{2+}$	170

[a] Conditions: 0.1 M H_2SO_4 ($\mu = 0.12$), ~22 °C. [b] Standard reduction potential, from ref 32. [c] Mean values of two or three sets of experiments. For precision, see text. Data obtained by other authors are reported in footnotes. [d] $\sim 1 \times 10^7$ M^{-1} s^{-1} (0.5 M H_2SO_4), 25 °C.[27] [e] $< 3 \times 10^6$ and $\sim 3 \times 10^6$ M^{-1} s^{-1} for $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$, respectively (H_2O, $\mu \to 0$); 21 °C.[23] [f] 2.18×10^9 M^{-1} s^{-1} (1 M SO_4^{2-}), 25 °C;[38] 2.3×10^9 M^{-1} s^{-1} (0.17 M NaCl), 25 °C (Lin, C. T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97). [g] 1.5×10^8 M^{-1} s^{-1} (0.5 M H_2SO_4), 25 °C.[27] [h] 9.3×10^8 M^{-1} s^{-1} (0.5 M H_2SO_4), 25 °C;[27] 7.2×10^7 M^{-1} s^{-1} (H_2O, $\mu \to 0$), 21 °C.[23]

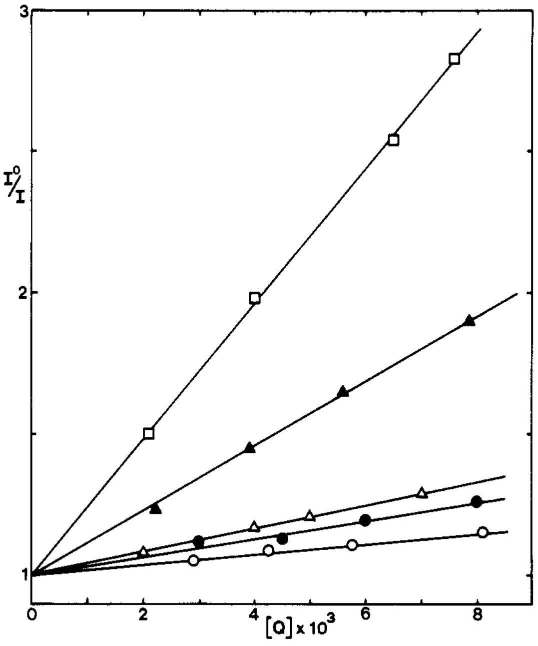

Figure 1. Stern–Volmer plots for the quenching of $^*Ru(bpy)_3^{2+}$ by $Co(NH_3)_5X^{2+}$ complexes: (●) F^-; (□) Cl^-; (▲) NCS^-; (○) $HCOO^-$; (△) NO_2^-.

As a part of our effort to elucidate the role played by the nuclear and electronic factors in determining the rate constant of energy- and electron-transfer processes, we have studied the quenching reactions of $^*Ru(bpy)_3^{2+}$, $^*Os(phen)_3^{2+}$ and related complexes (the asterisk indicates the lowest excited state) by 17 Co(III) complexes (Table I). It is shown that the quenching takes place via electron transfer, whereas the quenching of $^*Cr(bpy)_3^{3+}$ by the same Co(III) complexes was previously found[18] to occur via energy transfer. The results obtained in this paper as well as other data available from the literature for electron-transfer reactions of Co(III) complexes have been analyzed by an approach previously described[9,21,22] in order to disentangle the effects of the nuclear and electronic terms.

Experimental Section

Materials. The Co(III) complexes were available from previous investigations,[18] and their purity was checked by means of electronic absorption spectra. $Ru(bpy)_3^{2+}$, $Ru(DM\text{-}bpy)_3^{2+}$, $Ru(phen)_3^{2+}$, $Ru(DM\text{-}phen)_3^{2+}$, and $Os(phen)_3^{2+}$ (bpy = 2,2′-bipyridine, DM-bpy = 4,4′-$(CH_3)_2$bpy, phen = 1,10-phenanthroline, DM-phen = 4,7-$(CH_3)_2$phen) were prepared according to procedures indicated in the literature,[23] and their purity was checked by absorption spectra, emission spectra, and emission lifetimes.[24] Hereafter these complexes will be indicated by $M(LL)_3^{2+}$.

Apparatus. The electronic absorption spectra were recorded with a Cary 19 spectrophotometer. Luminescence intensity measurements were carried out by a Perkin-Elmer MPF 3 spectrofluorimeter using an R 955 photomultiplier tube. Emission lifetimes were measured by a JK System 2000 neodymium Yag DLPY 4 laser, exciting with the second harmonic at 532 nm.

Procedure. All experiments were carried out in aqueous solution at room temperature (~22 °C). The concentration of the Ru or Os complexes was usually 5.0×10^{-4} M, and the quencher concentration was in the range 1.0×10^{-3}–8.0×10^{-3} M. The ionic strength of the solution was controlled by the presence of 0.1 M H_2SO_4. All solutions were air equilibrated. Excitation was carried out in the visible band of the Ru or Os complexes at wavelengths where absorption by the quencher was minimized. Appropriate correction was made for the fraction of light absorbed by the cobalt complexes, which did not exceed 10% of total light absorption. Emission was monitored at wavelengths where the cobalt complexes do not show appreciable absorption.

No spectral change was observed on mixing solutions of ruthenium and cobalt complexes or of $Os(phen)_3^{2+}$ and the following cobalt complexes: $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, $Co(NH_3)_5H_2O^{3+}$, $Co(NH_3)_5F^{2+}$, $Co(NH_3)_5(O_2CH)^{2+}$, *cis*- and *trans*-$Co(en)_2(NCS)_2^+$. In contrast, when $Os(phen)_3^{2+}$ solutions were mixed with solutions of the other cobalt complexes, the spectra were not additive. More specifically, there was a decrease in the visible absorption of $Os(phen)_3^{2+}$, corresponding to a 5–15% disappearance of the original $Os(phen)_3^{2+}$

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(17) (a) Endicott, J. F.; Ramasami, T. *J. Am. Chem. Soc.* **1982**, *104*, 5252. (b) Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301.

(18) Gandolfi, M. T.; Maestri, M.; Sandrini, D.; Balzani, V. *Inorg. Chem.* **1983**, *22*, 3435.

(19) Endicott, J. F.; Brubaker, G. R.; Ramasami, T.; Kumar, K.; Dwarakanath, K.; Cassel, J.; Johnson, D. *Inorg. Chem.* **1983**, *22*, 3754.

(20) Borchardt, D.; Pool, K.; Wherland, S. *Inorg. Chem.* **1982**, *21*, 93.

(21) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.

(22) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 3370.

(23) Demas, J. N.; Addington, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5800.

(24) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

concentration owing to thermal oxidation by the Co(III) complexes. Since the concentration of the Co(III) complexes was at least 20 times higher than that of $Os(phen)_3^{2+}$, no correction was needed for the decrease in the quencher concentration while an appropriate correction was made for the fraction of light actually absorbed by $Os(phen)_3^{2+}$ in each solution.

As previously noted by Gafney et al.[25,26] and Navon and Sutin,[27] solutions containing $M(LL)_3^{2+}$ and the Co(III) complexes were more or less photosensitive because of the electron-transfer quenching reaction. For this reason, the emission light intensity of the various solutions was measured only at the emission maximum, limiting to a few seconds the exposure time to the exciting light.

After the above described corrections, linear Stern–Volmer plots were obtained in all cases for the quenching of the luminescence emission of the ruthenium or osmium complexes by the cobalt complexes. Duplicate or triplicate sets of quenching experiments were performed, each involving at least four different quencher concentrations. The Stern–Volmer quenching constants agreed to within 10% except for $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$, where the agreement was within 25%.

Results

Figure 1 shows typical Stern–Volmer plots obtained for the quenching of the $^*M(LL)_3^{2+}$ luminescence by Co(III) complexes. Under the experimental conditions used, the excited-state lifetimes were as follows: $^*Ru(bpy)_3^{2+}$, 400 ns; $^*Ru(DM\text{-}bpy)_3^{2+}$, 240 ns; $^*Ru(phen)_3^{2+}$, 510 ns; $^*Ru(DM\text{-}phen)_3^{2+}$, 520 ns; $^*Os(phen)_3^{2+}$, 75 ns. The estimated error is about 5%.

The values of the bimolecular quenching constants (Table I) were obtained from the slopes of the Stern–Volmer quenching plots by using the above reported lifetime values. The data previously obtained by other authors for some excited-state–quencher couples (see footnotes of Table I) are in fair agreement with our values considering that they refer to different ionic strengths.

Discussion

Quenching Mechanism. As discussed in more detail elsewhere,[18,24,28-30] in fluid solution the deactivation of an excited state by a quencher may take place by several distinct mechanisms. When the bimolecular quenching constants are, as in our case (Table I), larger than $10^7\ M^{-1}\ s^{-1}$, only energy- or electron-transfer processes have to be considered. Energy transfer (eq 1, where Co(III) represents the quencher used,

$$^*M(LL)_3^{2+} + (^1A_{1g})Co(III) \rightarrow M(LL)_3^{2+} + (^3T_{1g}\ \text{or}\ ^5T_{2g})Co(III) \quad (1)$$

assumed for simplicity to have octahedral symmetry) is spin allowed and is also thermodynamically allowed in all cases since the zero–zero energy of the emitting excited state of the $M(LL)_3^{2+}$ complexes lies in the range 14 000–17 500 cm^{-1} [24] and the zero–zero energies of the $^3T_{1g}$ and $^5T_{2g}$ excited states of the Co(III) complexes are smaller than 11 000 cm^{-1}.[15,18] Oxidative electron transfer (eq 2) is also thermodynamically

$$^*M(LL)_3^{2+} + Co(III) \rightarrow M(LL)_3^{3+} + Co(II) \quad (2)$$

allowed since the standard reduction potentials of the $M(LL)_3^{3+}/^*M(LL)_3^{2+}$ couples vary from −0.83 to −1.03 V[24] and the Co(III) complexes can be easily reduced.[31]

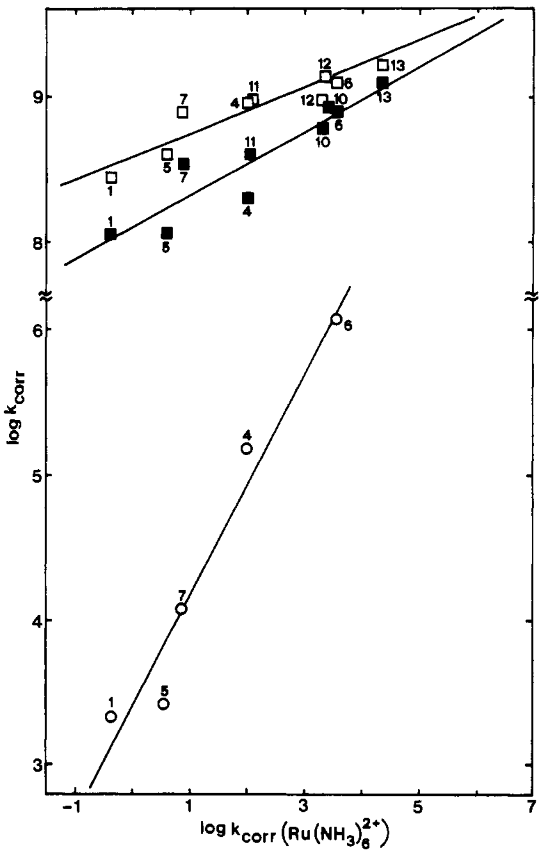

Figure 2. Plot of the logarithm of the rate constant for the quenching of $^*Ru(bpy)_3^{2+}$ (■) and $^*Os(phen)_3^{2+}$ (□) and the oxidation of $Cr(bpy)_3^{2+}$ (○) by Co(III) complexes vs. the logarithm of the rate constants for the oxidation of $Ru(NH_3)_6^{2+}$ by the same Co(III) complexes. The cobalt complexes are numbered as in Table I. The rate constants for the reactions of the Co(III) complexes with $Cr(bpy)_3^{2+}$ [40] and $Ru(NH_3)_6^{2+}$ [39] have been taken from the literature. All the rate constants have been made homogeneous (2+, 2+ reactants: $r = 11$ Å; $\mu = 0.12$ M) as described in the Appendix. The correlation coefficients of the straight lines are in all cases higher than 0.90.

Gafney and Adamson,[25] who first reported the quenching of $^*Ru(bpy)_3^{2+}$ by some $Co(NH_3)_5X^{2+}$ complexes, proposed an electron-transfer mechanism (eq 2). After some controversy,[35,36] the electron-transfer mechanism has been clearly demonstrated by Navon and Sutin[27] and is now generally accepted.[24,37] Gafney et al. have also shown that the quenching of $^*Ru(bpy)_3^{2+}$ by $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$ [38] and of $^*Os(bpy)_3^{2+}$ by several $Co(NH_3)_5X^{2+}$ complexes[26] occurs by electron transfer. By analogy, it seems reasonable to assume that electron transfer is the mechanism responsible for quenching results reported in this paper (Table I).

Confirmation for an electron-transfer quenching mechanism comes from Figure 2, where the rate constants for the quenching of $^*Ru(bpy)_3^{2+}$ and $^*Os(phen)_3^{2+}$ by the Co(III)

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(25) Gafney, H. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1972**, *94*, 8238.

(26) Finkenberg, E.; Fischer, P.; Huang, S. Y.; Gafney, H. D. *J. Phys. Chem.* **1978**, *82*, 526.

(27) Navon, G.; Sutin, N. *Inorg. Chem.* **1974**, *13*, 2159.

(28) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321.

(29) Wilkinson, F. *Pure Appl. Chem.* **1975**, *41*, 661.

(30) Ermolaev, V. L.; Sveshnikova, E. G.; Shakhverdov, T. A. *Russ. Chem. Rev.* (*Engl. Transl.*) **1975**, *44*, 26.

(31) The standard redox potentials of some Co(III)–Co(II) couples are known[32] (Table I). The $Co(NH_3)_5X^{2+}$ [33] and the $Co(en)_2X_2^{+}$ [34] complexes undergo reduction at >−0.5 V vs. SCE.

(32) Maki, N.; Tanaka, N. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Marcel Dekker: New York, 1973; Vol. III, p 43.

(33) Yamaoka, H. *Collect. Czech. Chem. Commun.* **1977**, *42*, 2845; Guyer, K. L.; Barr, S. W.; Cave, R. J.; Weaver, M. J. *Proc.—Electrochem. Soc.* **1979**, *80*, 390.

(34) Maki, N.; Shimura, Y.; Tsuchida, R. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 150. Yamada, A.; Yoshikuni, T.; Kato, Y.; Tanaka, N. *Ibid.* **1980**, *53*, 942.

(35) Natarajan, P.; Endicott, J. F. *J. Phys. Chem.* **1973**, *77*, 971.

(36) Natarajan, P.; Endicott, J. F. *J. Phys. Chem.* **1973**, *77*, 1823.

(37) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

(38) Berkoff, R.; Krist, K.; Gafney, H. D. *Inorg. Chem.* **1980**, *19*, 1.

complexes are plotted against the rate constants for oxidation of $Ru(NH_3)_6^{2+}$[39] by the same complexes. As expected for an electron-transfer quenching mechanism, the rates of both quenching processes increase linearly with increasing rate of the outer-sphere electron-transfer reaction between $Ru(NH_3)_6^{2+}$ and the Co(III) complexes. In Figure 2, the available data for the reduction of Co(III) complexes by $Cr(bpy)_3^{2+}$[40] vs. $Ru(NH_3)_6^{2+}$[39] are also plotted for comparison purposes. In this figure, some common trends in the scattering of the points can be observed. While it cannot be excluded that this is due to experimental errors, it is also possible that departure from linearity reflects some intimate factor affecting the electron-transfer rate constants.

In a previous paper[18] we reported the rate constants for the energy-transfer quenching (eq 3) of $^*Cr(bpy)_3^{3+}$ by the same Co(III) complexes that have now been used to quench $^*Ru(bpy)_3^{2+}$, $^*Os(phen)_3^{2+}$, and the other $^*M(LL)_3^{2+}$ complexes listed in Table I. It was shown that the energy-transfer process

$$^*Cr(bpy)_3^{3+} + (^1A_{1g})Co(III) \rightarrow Cr(bpy)_3^{3+} + (^3T_{1g} \text{ or } ^5T_{2g})Co(III) \quad (3)$$

(eq 3) is always sufficiently exergonic to cancel out the effect of the intrinsic barrier so that its rate constant is controlled by electronic factors which depend on the ability of the ligands to delocalize the metal orbitals and on those parameters (size, electric charge, geometrical configuration) that affect orbital overlap in the encounter process. Energy transfer from $^*Ru(bpy)_3^{2+}$ or $^*Os(phen)_3^{2+}$ to the Co(III) complexes (eq 1) would be a process even more exergonic than that involving $^*Cr(bpy)_3^{3+}$ as an energy donor (eq 3). Thus, if the quenching of $^*Ru(bpy)_3^{2+}$ and $^*Os(phen)_3^{2+}$ occurred by energy transfer, it would also be controlled by electronic factors and one would expect to observe some correlation between the quenching constants of $^*Ru(bpy)_3^{2+}$ or $^*Os(phen)_3^{2+}$ and $^*Cr(bpy)_3^{3+}$. However, comparison between the quenching constants reported in Table I and those reported in Table I of ref 18 shows that no such correlation exists, again suggesting that the quenching takes place via different mechanisms. In particular, the rate constants for the quenching of $^*Ru(bpy)_3^{2+}$ and $^*Os(bpy)_3^{2+}$ by the $Co(NH_3)_5X^{2+}$ and *cis*- and *trans*-$Co(en)_2X_2^+$ complexes do not follow the same trend observed for the quenching of $^*Cr(bpy)_3^{3+}$. For example, the rate constant for the quenching of $^*Cr(bpy)_3^{3+}$ by $Co(NH_3)_5NCS^{2+}$ is more than 4 times larger than that for quenching by $Co(NH_3)_5Cl^{2+}$, whereas $^*Ru(bpy)_3^{2+}$ and $^*Os(phen)_3^{2+}$ are more rapidly quenched by $Co(NH_3)_5Cl^{2+}$ than by $Co(NH_3)_5NCS^{2+}$. Also, the rate constant for the quenching of $^*Cr(bpy)_3^{3+}$ by *cis*-$Co(en)_2Cl_2^+$ is 18 times larger than that for the trans isomer, which, in contrast, is a better quencher than the cis isomer toward $^*Ru(bpy)_3^{2+}$ and $^*Os(phen)_3^{2+}$. Lacking knowledge of the standard reduction potentials of the Co(III) complexes, it is difficult to say whether such a different behavior reflects energetics or, as it might be, different electronic requirements for energy- or electron-transfer quenching.

Role of Nuclear and Electronic Factors. As discussed in more detail elsewhere,[9,21,22,41] the experimental rate constant k_{exptl} of an electron-transfer process

$$D + A \xrightarrow{k_{exptl}} D^+ + A^- \quad (4)$$

is given by

$$k_{exptl} = \frac{k_d}{1 + \dfrac{k_{-d}}{k_e} + \dfrac{k_{-d}}{k'_{-d}}\dfrac{k_{-e}}{k_e}} \quad (5)$$

where k_d is the diffusion rate constant, k_{-d} and k'_{-d} are the rate constants for dissociation of the precursor and successor complex, and k_e and k_{-e} are unimolecular rate constants for electron transfer. With use of a classical approach,[42] k_{-e}/k_e is given by $\exp(\Delta G/RT)$, where ΔG is the free energy change of the electron-transfer step, and the rate constant of the electron-transfer step is given by eq 6, where k_e^0 is the

$$k_e = k_e^0 e^{-\Delta G^\ddagger/RT} = \mathbf{k}\frac{kT}{h}e^{-\Delta G^\ddagger/RT} \quad (6)$$

preexponential factor, **k** is the electronic transmission coefficient, kT/h is the universal frequency of the absolute reaction rate theory, and $\Delta G^\ddagger$ is the free activation energy that can be expressed by the free energy relationship given by eq 7.[43] In

$$\Delta G^\ddagger = \Delta G + \frac{\Delta G^\ddagger(0)}{\ln 2}\ln\left(1 + \exp\left(-\frac{\Delta G \ln 2}{\Delta G^\ddagger(0)}\right)\right) \quad (7)$$

this equation, ΔG is the previously seen free energy change and $\Delta G^\ddagger(0)$ is the so-called intrinsic barrier, a parameter related to the amount of distortion of both the inner coordination spheres and the outer solvation shells accompanying electron transfer. As far as k_e^0 and $\Delta G^\ddagger(0)$ are concerned, it is convenient to split those parameters of the cross-reaction (eq 4) into intrinsic parameters of the two exchange processes (eq 8 and 9). This can be done by using the basic assumptions[10] given by eq 10 and 11.

$$D + D^+ \rightarrow D^+ + D \quad (8)$$

$$A^- + A \rightarrow A + A^- \quad (9)$$

$$\Delta G^\ddagger(0) = \frac{\Delta G_D^\ddagger + \Delta G_A^\ddagger}{2} \quad (10)$$

$$k_e^0 = \frac{kT}{h}(\mathbf{k}_D\mathbf{k}_A)^{1/2} \quad (11)$$

In conclusion, according to the classical treatment the rate constant of an electron-transfer reaction is expressed by a product of an electronic term associated with **k** and a nuclear term associated with $\exp(-\Delta G^\ddagger/RT)$. In the current terminology, a reaction is said to be adiabatic when the electronic interaction is sufficiently strong so as to make $\mathbf{k} \simeq 1$ and nonadiabatic when the electronic interaction is small and thus $\mathbf{k} < 1$.

If we consider a series of homogeneous electron-transfer reactions[9,21,22] such as those between the same reductant and a series of structurally related oxidants that have variable redox potential but the same size, shape, electronic structure, and electric charge, we may assume that throughout the series the reaction parameters k_d, k_{-d}, and k'_{-d} in eq 5, **k** in eq 6, and $\Delta G^\ddagger(0)$ in eq 7 are constant. (Procedures are also available[22] to account for a small degree of nonhomogeneity of some of the above parameters; see Appendix.) Under these assumptions, k_{exptl} (eq 5) is only a function of the free energy change, i.e. of the redox potentials of the reaction partners. For such homogeneous series of reactions eq 5–7 predict that a plot of

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(39) Endicott, J. F.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1688. Patel, R. C.; Endicott, J. F. *Ibid.* **1968**, *90*, 6364. Guenther, P. R.; Linck, R. G. *Ibid.* **1969**, *91*, 3769. Adegite, A.; Dosumu, M.; Ojo, J. F. *J. Chem. Soc., Dalton Trans.* **1977**, 630.

(40) Candlin, J. P.; Halpern, J.; Trimm, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 1019.

(41) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834; *Isr. J. Chem.* **1970**, *8*, 259.

(42) For a comparison between the classical and quantum-mechanical models, see ref 7.

(43) Equation 7 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.

Table II. Rate Constants for the Redox Reactions of Some Cobalt Complexes

Co complex	redox partner	k_{exptl}, M^{-1} s^{-1} [a]	μ, M (anion)	ref	ΔG, eV[b]	k_{cor}, M^{-1} s^{-1} [c]
$Co(NH_3)_6{}^{3+}$	$Ru(NH_3)_6{}^{2+}$[d]	0.011	0.2 (Cl^-)	*e*	−0.03	3.9×10^1
	$Cr(bpy)_3{}^{2+}$	6.9×10^2	0.1 ($ClO_4{}^-$)	40	−0.35	4.2×10^3
	$^*Ru(bpy)_3{}^{2+}$	4×10^7	0.12 ($SO_4{}^{2-}$)	*f*	−0.96	1.2×10^8 [g]
	$^*Ru(phen)_3{}^{2+}$	1.2×10^7	0.12 ($SO_4{}^{2-}$)	*f*	−1.02	6.7×10^7
	$^*Ru(DM\text{-}bpy)_3{}^{2+}$	8.7×10^6	0.12 ($SO_4{}^{2-}$)	*f*	−1.04	4.9×10^7
	$^*Os(phen)_3{}^{2+}$	1.0×10^8	0.12 ($SO_4{}^{2-}$)	*f*	−1.06	5.1×10^8
	$^*Ru(DM\text{-}phen)_3{}^{2+}$	2.3×10^7	0.12 ($SO_4{}^{2-}$)	*f*	−1.13	1.3×10^8
	$Ru(bpy)_3{}^+$	3.5×10^8	1×10^{-3} (OH^-)	*h*	−1.38	1.4×10^9
$Co(NH_3)_5H_2O^{3+}$	$Ru(NH_3)_6{}^{2+}$	3	0.2 (Cl^-)	*e*	−0.30	9.8×10^3
	$Cr(bpy)_3{}^{2+}$	5×10^4	0.1 ($ClO_4{}^-$)	40	−0.62	3.1×10^5
	$^*Ru(bpy)_3{}^{2+}$	7.5×10^7	0.12 ($SO_4{}^{2-}$)	*f*	−1.23	3.9×10^8
	$^*Os(phen)_3{}^{2+}$	3.7×10^8	0.12 ($SO_4{}^{2-}$)	*f*	−1.33	1.5×10^9
	$^*Os(bpy)_3{}^{2+}$	2.1×10^8	0.5 ($SO_4{}^{2-}$)	26	−1.39	5.3×10^8
$Co(phen)_3{}^{3+}$	$Ru(NH_3)_5py^{2+}$[i]	1.9×10^3	0.5 (Cl^-)	*j*	−0.09	4.2×10^4
	$Ru(NH_3)_6{}^{2+}$	1.5×10^4	0.1 (Cl^-)	11	−0.33	3.3×10^6
	$^*Ru(bpy)_3{}^{2+}$	1.9×10^9	0.12 ($SO_4{}^{2-}$)	*f*	−1.26	1.9×10^9
	$^*Os(bpy)_3{}^{2+}$	5.7×10^9	0.5 (Cl^-)	*k*	−1.42	4.5×10^9
$Co(phen)_3{}^{2+}$	$Ru(bpy)_3{}^{3+}$	1.4×10^8	1 ($SO_4{}^{2-}$)	38	−0.84	7.2×10^7
$Co(bpy)_3{}^{3+}$	$Ru(NH_3)_6{}^{2+}$	1.1×10^4	0.1 (Cl^-)	11	−0.27	2.6×10^6
	$^*Ru(bpy)_3{}^{2+}$	2.3×10^9	1 ($SO_4{}^{2-}$)	38	−1.20	1.3×10^9
	$Ru(bpy)_3{}^+$	1.6×10^9	1×10^{-3} (OH^-)	*h*	−1.62	1.8×10^9
$Co(bpy)_3{}^{2+}$	$Ru(bpy)_3{}^{3+}$	2.4×10^8	1 ($SO_4{}^{2-}$)	38	−0.90	1.3×10^8
$Co(en)_3{}^{3+}$	$Cr(bpy)_3{}^{2+}$	1.8×10^2	0.1 ($ClO_4{}^-$)	40	−0.07	6.0×10^2
	$^*Ru(bpy)_3{}^{2+}$	2×10^7	0.12 ($SO_4{}^{2-}$)	*f*	−0.68	6.1×10^7
	$^*Os(phen)_3{}^{2+}$	1.0×10^8	0.12 ($SO_4{}^{2-}$)	*f*	−0.78	2.9×10^8
	$Ru(bpy)_3{}^+$	3.2×10^8	1×10^{-3} (OH^-)	*h*	−1.10	8.9×10^8
	MV^+[l]	5×10^4	1 ($ClO_4{}^-$)	*m*	−0.51	1.3×10^6

[a] Conditions: aqueous solution, 22 or 25 °C (see reference). [b] Free energy change of the electron-transfer step calculated from the standard redox potentials of the reaction partners, with neglect of the work term (~3×10^{-2} eV). For the redox potentials of the cobalt complexes, see Table I. The redox potentials of the $M(LL)_3{}^{z+}$ complexes have been taken from ref 24 unless otherwise noted. [c] Homogenized to 3+, 2+ reactants, $r = 14$ Å, and $\mu = 0.12$ M according to the Appendix. [d] $E° = +0.067$ V, from: Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374. [e] Endicott, J. F.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1688. [f] This paper. [g] Average between our experimental value and that reported in ref 27. [h] Mulazzani, Q. G., unpublished results. [i] $E° = +0.31$ V, from: Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460. [j] McArdle, J. V.; Yokom, K.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 4141. [k] Lin, C.-T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97. [l] $E° = -0.51$ V, from: Fanchiang, Y.-T.; Gould, E. S. *J. Am. Chem. Soc.* **1977**, *99*, 5226. [m] Fanchiang, Y.-T.; Gould, E. S. *Ibid.* **1977**, *99*, 5226.

log k_{exptl} vs. ΔG consists of (i) a plateau region for sufficiently exoergonic reactions, (ii) an Arrhenius type linear region (slope $1/(2.3RT)$) for sufficiently endoergonic reactions, and (iii) a more or less wide (depending on $\Delta G^*(0)$) intermediate region in which k_{exptl} increases in a complex but monotonous way as ΔG decreases. The intermediate region is centered at $\Delta G = 0$, where the slope of the curve is $0.5[1/(2.3RT)]$. The plateau value of k_{exptl}, $k_{\text{exptl}}{}^{\text{P}}$, is given by eq 12 and is equal to k_{d} or

$$k_{\text{exptl}}{}^{\text{P}} = \frac{k_{\text{d}}k_{\text{e}}{}^0}{k_{\text{e}}{}^0 + k_{-\text{d}}} \qquad (12)$$

$k_{\text{e}}{}^0(k_{\text{d}}/k_{-\text{d}})$ depending on whether $k_{\text{e}}{}^0$ is much larger or much smaller than $k_{-\text{d}}$. It follows that a very low value of the frequency factor (i.e., $\mathbf{k} < k_{-\text{d}}h/kT$) is reflected in a lower than diffusion value of $k_{\text{exptl}}{}^{\text{P}}$. On the other hand, the value of the intrinsic barrier $\Delta G^*(0)$ does not affect $k_{\text{exptl}}{}^{\text{P}}$ but strongly influences the values of the rate constant in the intermediate nonlinear region. This type of approach, which in favorable cases allows the disentanglement of the effects of nonadiabaticity and intrinsic barrier on the rate constant, has been successfully applied to interpret the results of several electron-[22,41,45-57] and energy-transfer[21,58-61] processes. We have

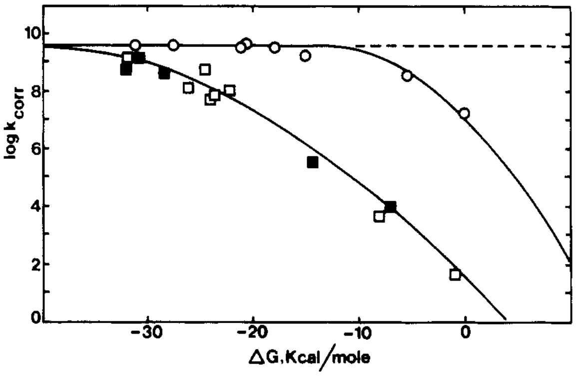

Figure 3. Plot of log k_{cor} vs. ΔG for the electron-transfer reactions of $Co(NH_3)_6{}^{3+}$ (□) and $Co(NH_3)_5H_2O^{3+}$ (■). For comparison purposes, the data for $Ru(NH_3)_6{}^{3+/2+}$ [33] (○) are also reported.

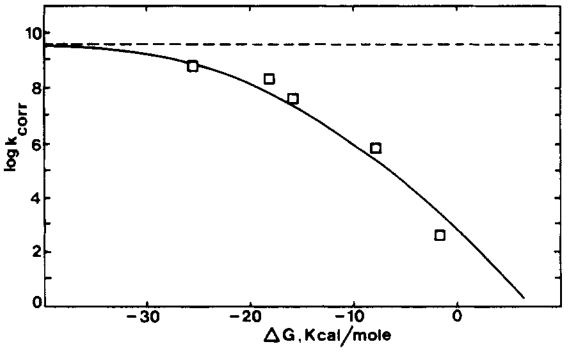

Figure 4. Plot of log k_{cor} vs. ΔG for the electron-transfer reactions of $Co(en)_3{}^{3+}$.

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(45) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710.
(46) Vogelman, E.; Schreiner, S.; Rausher, W.; Kramer, H. E. A. *Z. Phys. Chem. (Wiesbaden)* **1976**, *101*, 321.
(47) Kikuchi, K.; Tamura, S. I.; Iwenege, C.; Kokubun, K.; Usui, Y. *Z. Phys. Chem. (Wiesbaden)* **1977**, *106*, 17.
(48) Breyman, V.; Dreeskamp, H.; Koch, E.; Zander, M. *Chem. Phys. Lett.* **1978**, *59*, 63.
(49) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219.

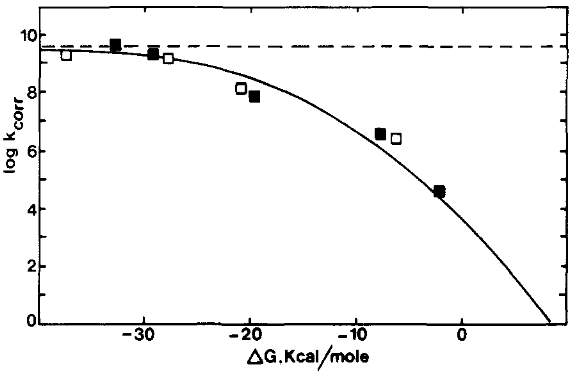

Figure 5. Plot of log k_{cor} vs. ΔG for the electron-transfer reactions of $Co(bpy)_3^{3+/2+}$ (□) and $Co(phen)_3^{3+/2+}$ (■).

now used this approach in an attempt to elucidate the role played by electronic and nuclear factors in the electron-transfer processes of Co(III) complexes.

The available data on the rate constants for the reduction of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$, $Co(en)_3^{3+}$, $Co(bpy)_3^{3+}$, and $Co(phen)_3^{3+}$ (or $Co(bpy)_3^{2+}$ and $Co(phen)_3^{2+}$ oxidation) by a homogeneous series of reaction partners are reported in Table II. After further homogenization to 3+, 2+ reactants, r = 14 Å, and μ = 0.12 M (Appendix), the logarithms of the rate constants have been plotted against the free energy change (Figures 3–5). For comparison purposes, the data concerning the $Ru(NH_3)_6^{3+}$ reduction (or $Ru(NH_3)_6^{2+}$ oxidation) are also reported in Figure 3.[62] Figures 3–5 also show the best fitting curves that have been obtained with use of eq 5–7, leaving **k** and $\Delta G^*(0)$ free to change, and with use of the following values for the other parameters (see Appendix): $k_d = 3.8 \times 10^9$ M^{-1} s^{-1}, $k_{-d} = k'_{-d} = 1.8 \times 10^9$ s^{-1}. If **k** = 1^5 and $\Delta G^*(0) = 6$ kcal/mol[22] are taken for the self-exchange reactions of the homogenized reaction partners, the best fitting curves correspond to the following values for **k** and ΔG^* of the self-exchange reactions: $Co(NH_3)_6^{3+/2+}$ and $Co(NH_3)_5H_2O^{3+/2+}$ (Figure 3), **k** = 10^{-1}, ΔG^* = 24 kcal/mol; $Co(en)_3^{3+/2+}$ (Figure 4), **k** = 10^{-3}, ΔG^* = 17 kcal/mol; $Co(bpy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ (Figure 5), **k** = 10^{-5} and ΔG^* = 13 kcal/mol; $Ru(NH_3)_6^{3+/2+}$ (Figure 3), **k** = 1 and ΔG^* = 10.6 kcal/mol.[63] Comparison among curves obtained with use of different **k** and ΔG^* couples allows us to estimate a maximum uncertainty of $10^{\pm 1}$ on **k** and ±2 kcal/mol on ΔG^*.

The value obtained from our analysis for the intrinsic barrier of the $Co(NH_3)_6^{3+/2+}$ self-exchange (24 ± 2 kcal/mol) is slightly higher than that calculated by Endicott et al.[8] (18.9 or 20.6 kcal/mol, depending on whether a quantum-mechanical or classical formulation was used). The intrinsic barrier obtained for the $Co(en)_3^{3+/2+}$ reaction (17 ± 2 kcal/mol) is in fair agreement with the values calculated by Sutin[5] (19.3 kcal/mol) and by Endicott et al.[8] (17.2 or 19.6 kcal/mol). A further decrease in ΔG^* as one passes to $Co(bpy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ is qualitatively justified by the decrease in the contribution of ΔG_{out}^* owing to the increased size of the complexes.

Table III. Comparison between Experimental[a] Electron-Transfer Rate Constants and Calculated Diffusion Rate Constants[b]

			$10^{-9}k_d$(calcd), M^{-1} s^{-1}	
reaction	μ, M	$10^{-9}k_{exptl}$, M^{-1} s^{-1}	eq A5	eq A4
$*Ru(bpy)_3^{2+} + Ru(NH_3)_6^{3+}$	0.5	3.1[c]	3.8	9.6
$*Ru(bpy)_3^{2+} + Ru(NH_3)_6^{2+}$	0.2	2.4[c]	4.1	7.6
$*Ru(bpy)_3^{2+} + Ru(NH_3)_5Cl^{2+}$	0.5	2.7[d]	5.0	10.4
$*Ru(bpy)_3^{2+} + Os(bpy)_3^{3+}$	0.5	3.8[e]	5.0	11.8
$*Ru(bpy)_3^{2+} + Cr(bpy)_3^{3+}$	0.2	3.3[f]	4.3	8.9
$*Os(bpy)_3^{2+} + Ru(NH_3)_6^{3+}$	0.5	4.8[e]	3.8	9.6
$Ru(NH_3)_6^{3+} + Ru(bpy)_3^{+}$	0.5	4.7[c]	5.4	9.8
$Ru(NH_3)_6^{2+} + Ru(bpy)_3^{3+}$	1	3.7[c]	4.5	12.5
$Ru(bpy)_3^{3+} + Cr(bpy)_3^{2+}$	0.2	2.6[f]	4.3	8.9

[a] In all cases the experimental values have been taken in the literature as diffusion controlled. [b] Conditions: aqueous solution, 25 °C. [c] Reference 22. [d] Reference 27. [e] Lin, C.-T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97. [f] Ballardini, R.; Varani, G.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1976**, *98*, 7432.

The results of the above analysis show that the electron-transfer reactions of cobalt complexes are intrinsically nonadiabatic, in agreement with evaluations made by other authors. On the basis of the spin-forbidden character of the low-spin Co(III)–high-spin Co(II) reactions, Buhks et al.[12] have estimated a **k** value of $\sim 10^{-4}$ for the $Co(NH_3)_6^{3+/2+}$ self-exchange and Sutin[5] has estimated a **k** value of 10^{-2}–10^{-3} for the analogous $Co(en)_3^{3+/2+}$ reaction. Endicott et al.[8,13,17b] did not find any outstanding effect that can be associated with spin forbiddenness and attributed the estimated nonadiabatic factor (**k** = 10^{-1}–10^{-5} for Co(III)–Co(II) complexes in general, 10^{-3} for $Co(NH_3)_6^{3+/2+}$) to poor donor–acceptor orbital overlap. A retarding effect of nonadiabaticity on the reactions between $Co(bpy)_3^{2+}$ or $Co(phen)_3^{2+}$ and $Ru(bpy)_3^{3+}$ has been indicated by Berkoff et al.[38] The decrease in the electronic transmission coefficient found in passing from $Co(NH_3)_6^{3+/2+}$ (or $Co(NH_3)_5H_2O^{3+/2+}$) to $Co(en)_3^{3+/2+}$ and to $Co(bpy)_3^{3+/2+}$ (or $Co(phen)_3^{3+/2+}$) can be accounted for by considering that (i) the electron-transfer reaction involves a $\sigma^*(e_g)$ cobalt orbital and (ii) as the ligand size increases, the overlap between the $\sigma^*(e_g)$ orbitals and the relevant orbitals of the reaction partner is expected to decrease. A similar effect of the increasing ligand size is well documented for energy-transfer processes involving metal-centered excited states.[15,60,61] The low value of the transmission coefficient found for $Co(bpy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ is also in qualitative agreement with the results of recent calculations,[64] which have shown that the $Ru(bpy)_3^{3+/2+}$ self-exchange would be highly nonadiabatic (**k** < 10^{-6}) if it had to occur on the basis of direct 4d–4d overlap. The strong nonadiabaticity of the $Co(phen)_3^{3+/2+}$ self-exchange is also consistent with the large negative activation entropy ($\Delta S^*(0)$ = −34 kcal/(mol deg)),[65] which cannot be due to a contribution from the work term.[20]

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(50) Martens, F. M.; Verhoeven, J. W.; Gase, R. A.; Pandit, N. K.; de Boer, T. J. *Tetrahedron* **1978**, *34*, 44.

(51) Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 7568.

(52) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.

(53) Nagle, J. K.; Dressick, W. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3993.

(54) Amouyal, E.; Zidler, B.; Keller, P.; Moradpour, A. *Chem. Phys. Lett.* **1980**, *74*, 314.

(55) Rillema, D. P.; Nagle, J. K.; Barringer, L. F., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 56.

(56) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, *104*, 3618.

(57) Indelli, M. T.; Ballardini, R.; Scandola, F. *J. Phys. Chem.*, in press.

(58) Balzani, V.; Indelli, M. T.; Maestri, M.; Sandrini, D.; Scandola, F. *J. Phys. Chem.* **1980**, *84*, 852.

(59) Maestri, M.; Sandrini, D. *J. Phys. Chem.* **1981**, *85*, 2050.

(60) Wilkinson, F.; Tsiamis, C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1681.

(61) Wilkinson, F.; Tsiamis, C. *J. Phys. Chem.* **1981**, *85*, 4153.

(62) The data for $Ru(NH_3)_6^{3+/2+}$ have been homogenized here to the same parameters used for the cobalt complexes (Table II).

(63) Note that the **k** values obtained from our analysis rely on the validity of eq 11. This equation might not be a good approximation because of the different nature of the orbitals involved in the cross- and self-exchange reactions.[10] The observed trend of the **k** values, however, would remain valid.

(64) Sutin, N.; Brunschwig, B. S. In ref 6, p 105.

(65) Neumann, H. M., quoted in: Farina, R.; Wilkins, R. G. *Inorg. Chem.* **1968**, *7*, 514.

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Appendix

Generally, the diffusion and dissociation rate constants k_d and k_{-d} are obtained from the Debye[66] and Eigen[67] equations

$$k_d(\mu = 0) = \frac{8RT}{3000\eta}\,\frac{b/r}{e^{b/r} - 1} \qquad \text{(A1)}$$

$$k_{-d} = \frac{2kT}{\pi r^3 \eta}\,\frac{b/r}{1 - e^{-b/r}} \qquad \text{(A2)}$$

$$b = \frac{Z_D Z_A e^2}{\epsilon kT} \qquad \text{(A3)}$$

$$\log k_d(\mu) = \log k_d(\mu = 0) + \frac{1.02 Z_D Z_A \mu^{1/2}}{1 + Ar\mu^{1/2}} \qquad \text{(A4)}$$

where η is the viscosity, r is the encounter distance, e is the electron charge, ϵ is the dielectric constant, $Z_D Z_A$ is the electric charges of the two reactants, and A is $(8\pi Ne^2/1000\epsilon kT)^{1/2}$. Equation A4 is usually valid for $r < 5$ Å and $\mu < 0.1$ M.[68-70]

It should be noted, however, that the values predicted by eq A1, A3, and A4 for larger ions and higher values of ionic strength are always much higher than the values experimentally measured for processes that are believed to be diffusion controlled (Table III). An empirical equation that gives better agreement with the "experimental" values (see Table III) is eq A5, which was previously used in ref 22

$$k_d = \frac{8RT}{3000\eta}\,\frac{W_r/RT}{e^{W_r/RT} - 1} \qquad \text{(A5)}$$

where

$$W_r = \frac{Z_D Z_A N e^2}{\epsilon r(1 + Ar\mu^{1/2})} \qquad \text{(A6)}$$

From the equilibrium constant[71]

$$K_0 = \frac{4\pi N r^3}{3000} e^{-W_r/RT} \qquad \text{(A7)}$$

and eq A5, one gets eq A8 for the dissociation rate constant,[22]

$$k_{-d} = \frac{2kT}{\pi r^3 \eta}\,\frac{W_r/RT}{1 - e^{-W_r/RT}} \qquad \text{(A8)}$$

which thus is also dependent on the ionic strength. Equations A5 and A8 have been used to evaluate the k_d and k_{-d} values under different experimental conditions. The encounter distance r in the above equations is obtained as the sum of the individual radii of the reactants. The following values have been used for the radii: $M(LL)_3^{n+}$, 7 Å; $Ru(NH_3)_6^{n+}$, 3.5 Å; $Ru(NH_3)py^{n+}$, 4.5 Å; *c*- and *t*-$Co(en)_2Cl_2^{n+}$, *c*-$Co(en)_2(H_2O)Cl^{n+}$, and *c*-$Co(en)_2(NH_3)Cl^{n+}$, 3.9 Å; *c*- and *t*-$Co(en)_2(NCS)Cl^{n+}$, 4.4 Å; *c*- and *t*-$Co(en)_2(NCS)_2^{n+}$, 5.0 Å; $Co(en)_3^{n+}$, 4.3 Å; $Co(NH_3)_5(NCS)^{n+}$, 3.6 Å; other Co complexes, 3.2 Å.

Equation 3a of ref 22 was used to homogenize bimolecular electron-transfer rate constants which differ in encounter distance (r), charge product ($Z_D Z_A$), and ionic strength (μ). The method for homogenizing for the different ΔG^* values of the self-exchange reactions of the reaction partners has been given in Appendix I of ref 22.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(phen)_3^{2+}$, 22873-66-1; $Ru(DM\text{-}phen)_3^{2+}$, 24414-00-4; $Ru(DM\text{-}bpy)_3^{2+}$, 32881-03-1; $Os(phen)_3^{2+}$, 31067-98-8; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(en)_3^{3+}$, 14878-41-2; $Co(phen)_3^{3+}$, 18581-79-8; $Co(NH_3)_5H_2O^{3+}$, 14403-82-8; $Co(NH_3)_5F^{2+}$, 15392-06-0; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5NCS^{2+}$, 14970-18-4; $Co(NH_3)_5(O_2CH)^{2+}$, 19173-64-9; $Co(NH_3)_5(NO_2)^{2+}$, 14482-68-9; *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.

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(66) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.
(67) Eigen, M. *Z. Phys. Chem. (Wiesbaden)* **1954**, *1*, 176.
(68) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions"; Butterworths: London, 1959.
(69) Bockris, J. O.; Reddy, A. K. N. "Modern Electrochemistry"; Plenum Press: New York, 1970; Vol. 1.
(70) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.
(71) If eq 7a is replaced by the alternative expression

$$K_0 = \frac{4\pi N r^2(\delta r)}{1000} e^{-W_r/RT}$$

with $\delta r = 0.8$ A,[7] one obtains for k and ΔG^* values that are within the uncertainty given in the text.

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The Boric Acid/Lactic Acid System. Equilibria and Reaction Mechanism[1]

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Boric acid, $B(OH)_3$, reacts with lactic acid, $CH_3CH(OH)COOH$, to produce anionic complexes of both 1:1 and 1:2 stoichiometries. The boron atom is four-coordinate in the complex ions. The equilibria can be formulated as follows, where H_2L is fully protonated lactic acid: $B(OH)_3 + H_2L \rightleftarrows 1{:}1^- + H_3O^+$, $K_1 = 1.8 \times 10^{-3}$; $1{:}1^- + H_2L \rightleftarrows 1{:}2^- + 2H_2O$, $K_2 = 6.6 \times 10\ M^{-1}$. The formation of 1:2 complex is strongly favored at low pH. Kinetic studies were carried out by temperature-jump and stopped-flow methods. The forward rate constant for the reaction of the 1:1 complex with lactic acid is 3 orders of magnitude greater than the rate constant for the reaction of trigonal $B(OH)_3$ with lactic acid. This result is consistent with the previously observed substitution lability of four-coordinate borates.

Bidentate ligands such as polyols,[2-5] 1,2-benzenediols,[2,3,6,7] and α-hydroxy carboxylic acids[8,9] form complexes with boric acid according to eq 1 and 2. The formation of the 1:1 complex is both an addition reaction and a substitution re-

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(2) Roy, G. L.; Laferriere, A. L.; Edwards, J. O. *J. Inorg. Nucl. Chem.* **1957**, *4*, 106 and earlier references therein.
(3) Lorand, J. P.; Edwards, J. O. *J. Org. Chem.* **1959**, *24*, 769.
(4) Knoeck, J.; Taylor, J. *Anal. Chem.* **1969**, *41*, 1730.
(5) Oertel, R. P. *Inorg. Chem.* **1972**, *11*, 544.
(6) Antikainen, P. J.; Pitkanen, I. P. *Suom. Kemistil. B* **1968**, *41*, 65.