Nonadiabatic, Short-Range, Intramolecular Electron Transfer from Ruthenium(II) to Cobalt(III) Complexes[†]

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The activation parameters reported for intramolecular electron-transfer between ruthenium(II) and cobalt(III) complexes have been corrected for the thermodynamic contributions of the entropy change for the reaction ΔS^0 to the entropy of activation ΔS^*, and it is concluded that these electron-transfers range from adiabatic (pyrazine bridge) to highly nonadiabatic. The electronic factors are about 20 times smaller than for diruthenium mixed-valence complexes. Spanning the metal−metal separation range of 7−14 Å over which $\beta = 0.7$ Å^{-1}, the electron-transfer rates are dominated by the electronic factors, which change three times more with separation than do the nuclear factors.

Introduction

The magnitude of the electronic-coupling element H_{da} between the donor and acceptor in an electron-transfer process can determine the rate of electron-transfer and is currently of great interest in a wide variety of research areas[1] including homogeneous processes involving inorganic[2] and organic[3,4] molecules, biological electron-transfer,[5] dye sensitization of semiconductors and interfacial charge-transfer in general,[6,7] and in single-molecule conductance studies.[8] In this work, there has been much emphasis on the distance dependence of the coupling and in the effectiveness of different electronic-coupling mechanisms depending upon the nature of the medium between donor and acceptor sites including molecular bridges and intervening medium (vacuum, solid, or solvent) and on the nature of the electronic structure of donor and acceptor. By the early 1980s, it was recognized that a number of outer-sphere electron self-exchange reactions of transition-metal complexes are nonadiabatic or only marginally adiabatic.[9−12] This was followed by a period during which inorganic researchers struggled to study metal-to-metal electron-transfer as a unimolecular process in bridged (B = bridge) complexes such as $(NH_3)_5Ru^{II}-B-Co^{III}-(NH_3)_5{}^{5+}$. A remarkable set of reactions involving the d^6/d^7 cobalt(III)/cobalt(II) couple attached to a reductant via a pyridyl-type bridge were studied by Isied,[13] Taube and colleagues,[14−16] and Haim and co-workers[17−20] with use of some ingenious chemical strategies. Those for which the reductant is a $(NH_3)_5Ru^{II}$ moiety are listed with their rate constants and activation parameters in Table 1 and form the subject of this paper. Also included in the table are metal−metal separations (d) and spectroscopic data for analogous diruthenium complexes.

Since the above data were first measured many long-range electron-transfer reactions have been studied in detail and the characteristics of various bridges have been established. There remains, however, some confusion about the interpretation of the earlier work with some authors favoring an interpretation in which all the reactions are adiabatic[20] and others less convinced.[16] Here, the data will be reanalyzed in an effort to better understand these systems.

Evaluation of Electronic Factors

The electron-transfer rate constant (k_{et}) may be expressed as the product of a nuclear frequency (ν_n) and the electronic (κ_{el}) and nuclear (κ_n) factors[21]

$$k_{et} = \kappa_{el}\nu_n\kappa_n = \kappa_{el}\nu_n \exp\left(-\frac{\Delta H^*}{RT}\right)\exp\left(\frac{\Delta S^*}{R}\right) \quad (1)$$

where R is the gas constant and T is temperature. Within the Landau−Zener treatment, the electronic factor is

$$\kappa_{el} = \frac{2\left[1 - \exp\left\{-\frac{H_{ad}^2}{h\nu_n}\left(\frac{\pi^3}{\lambda RT}\right)^{1/2}\right\}\right]}{2 - \exp\left[-\frac{H_{ad}^2}{h\nu_n}\left(\frac{\pi^3}{\lambda RT}\right)^{1/2}\right]} \quad (2a)$$

For an adiabatic reaction, $\kappa_{el} \sim 1$ (high probability of electron-transfer at the transition state), and $\kappa_{el} \ll 1$ for an electronically nonadiabatic reaction (small probability of electron-transfer at the transition state). When $\kappa_{el} \ll 1$, the electronic transmission coefficient is given by

$$\kappa_{el} = \frac{2H_{ad}^2}{h\nu_n}\left(\frac{\pi^3}{\lambda RT}\right)^{1/2} \quad (2b)$$

where λ is the nuclear reorganization energy. Thus when $\kappa_{el} \ll 1$,[22] κ_{el} is proportional to the square of the electronic-coupling element. If the electron-transfer is nonadiabatic but its entropy of activation is calculated from the experimental temperature dependence with the assumption that the reaction is adiabatic and $\nu_n = k_BT/h$, eq 3 holds.
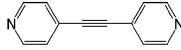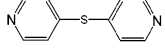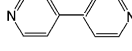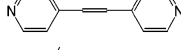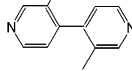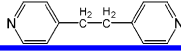
$$k_{et} = \frac{k_BT}{h} \exp\left(-\frac{\Delta H^\dagger}{RT}\right)\exp\left(\frac{\Delta S^\dagger}{R}\right) \quad (3)$$

Then, because $\Delta H^\dagger = \Delta H^*$, the "measured" activation entropy $\Delta S^\dagger$ is related to the activation entropy ΔS^* that is derived from the nuclear reorganization as eq 4.

$$\Delta S^\dagger = \Delta S^* + R \ln\kappa_{el} \quad (4)$$

[†] Part of the special issue "Norman Sutin Festschrift".

TABLE 1: Electron-Transfer Rate Parameters for B-Bridged Ru(II)−B−Co(III) and Intervalence Charge-Transfer Parameters for Ru(II)−B−Ru(III) Complexes at 25 °C

| Bridge, B | abbrev. | $(NH_3)_5Ru^{II}$-B-$Co^{III}(NH_3)_5^{5+\ a,b}$ | | | | $(NH_3)_5Ru^{II}$-B-$Ru^{III}(NH_3)_5^{5+a,c,d}$ | |
		d, Å	$10^3\ k$, s^{-1}	$\Delta H^\dagger$, kcal/mol	$\Delta S^\dagger$, e.u.	λ_{max}, nm (eV)	ε_{max}, M^{-1} cm^{-1}
PZ	PZ	6.8	128 (12800)[e]	22 (19.5)[e]	10.4	f	f
DPa	DPa	10.5	2.1[b]	18.4[g]	-9.0	810 (1.53)	30
DPS	DPS	~11	4.9[a]	20	-1.9	855 (1.45)	70
PBP	PBP	11.3	44[a]	20.1	+2.6	1030 (1.2)	920
DPEy	DPEy	13.8	18.7[a]	20.2	+1.2	960 (1.29)	760
DMPB	DMPB	11.3	5.5[a]	20.2	-1.1	890 (1.40)	165
DPEa	DPEa		1[a]	19.5	-6.5	g	<10

[a] Ref 14. See original reference for error limits. [b] Ref 15. See original reference for error limits. [c] Ref 32. See original reference for error limits. [d] Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1−73. [e] For the Ru(NH$_3$)$_4$(SO$_3$) complex. Ref 16. Corrected for driving force difference with respect to DBPa. [f] The mixed-valence species is not Class II. [g] No IVCT band is observed.

The standard entropy change for electron-transfer ΔS^0 is also reflected in measured $\Delta S^\dagger$ and ΔS^*. Neglecting any entropic contributions from nuclear tunneling and from vibrational, electronic, and solvation processes and provided that $\Delta G_{12}^0 \ll 4(\Delta G_{11}^* + \Delta G_{22}^*)$, where ΔG_{12}^0 is the net free-energy change for the electron-transfer and ΔG_{11}^* and ΔG_{22}^* are the free energies of activation for electron self-exchange for couples 1 and 2, respectively

$$\Delta S^* = \frac{\Delta S^0}{2} \tag{5a}$$

so that[12,21,23,24]

$$\Delta S^\dagger = \frac{\Delta S^0}{2} + R\ln(\kappa_{el}) \tag{5b}$$

Consequently, the electronic factor can be calculated from corrected entropy of activation

$$\kappa_{el} = \exp\frac{(\Delta S^\dagger - \Delta S^0/2)}{R} \tag{6a}$$

Recalling that $\nu_n = k_B T/h$, then

$$\exp\frac{(\Delta S^\dagger - \Delta S^0/2)}{R} = \left(\frac{2H_{ad}^2}{k_B T}\left(\frac{\pi^3}{\lambda RT}\right)^{1/2}\right) \tag{6b}$$

provided that $\kappa_{el} \ll 1$.

The magnitude of the electronic-coupling element for a nonadiabatic reaction may be estimated[11] from the temperature dependence of the rate constant (above, eqs 1−6), from the limiting rate constant at high-driving force, from cross-reaction data,[25] by computation,[26] from metal−ligand-coupling elements,[27] or from the distance dependence of the rate constant.[28] The intensity of electronic spectra of mixed-valence systems[29] may also be used to evaluate H_{da}. A Class II[30] mixed-valence complex may exhibit an intervalence charge-transfer absorption

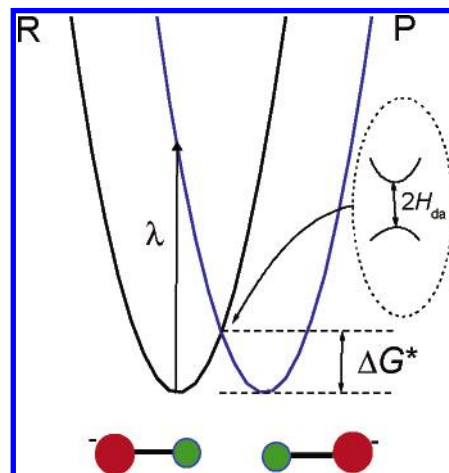**Figure 1.** Intervalence charge-transfer absorption from the minimum of the reactant (*R*) free-energy surface occurs at $E_{op} = \lambda$. At the intersection of the reactant and product (*P*) curves, the curves are split by 2 H_{da} (see inset).

band[31] (e.g., eq 7) for the B-bridged complex, $(NH_3)_5Ru^{II}$−B−$Ru^{III}(NH_3)_5^{5+}$.[32]

$$Ru^{II}-B-Ru^{III} \xrightarrow{h\nu=E_{op}} Ru^{III}-B-Ru^{II}* \tag{7}$$
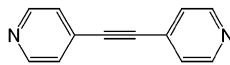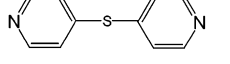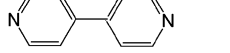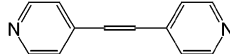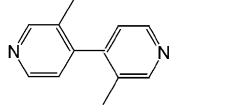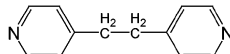
For a symmetric bridge, as depicted in Figure 1, the position of the absorption maximum is related to the classical reorganization energy λ (eq 8) where ΔG^* is the free energy of activation for the thermal electron self-exchange reaction, and the integrated intensity of the band is determined by the magnitude of the electronic-coupling H_{Ru}−Ru, between the two sites (eq 9)[29,33]

$$E_{op} = \lambda = 4\Delta G^* \tag{8}$$

$$H_{da}(cm^{-1}) = \frac{2.06 \times 10^{-2}}{d}[\epsilon_{max}\nu_{max}\Delta\nu_{1/2}]^{1/2} \tag{9}$$

where the units of H_{da}, ν_{max}, and $\Delta\nu_{1/2}$ are cm^{-1} and d is in Å.

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TABLE 2: Electronic Factors and Electronic-Coupling Elements for the Bridged Complexes at 25 °C[a]

| Bridge, B | d, Å | $\Delta S^\dagger - \Delta S^0/2$, e.u. | $(NH_3)_5Ru^{II}\text{-}B\text{-}Co^{III}(NH_3)_5{}^{5+}$ | | $(NH_3)_5Ru^{II}\text{-}B\text{-}Ru^{III}(NH_3)_5{}^5$ | |
			$\kappa_{el,CoRu}$	$H_{Co\text{-}Ru}$, cm^{-1}	$H_{Ru\text{-}Ru}$, cm^{-1}	κ_{RuRu}
(pyrazine)	6.8	~0.4	~1[a]	230		
(bis-pyridyl acetylene)	10.5	-19	7.0 x 10^{-5}	2	100	0.03
(dipyridyl sulfide)	~11	-11.9	2.5 x 10^{-3}	12	~150	0.07
(bipyridyl)	11.3	-7.4	2.4 x 10^{-2}	36	390	0.5
(bis-pyridyl ethyne)	13.8	-8.8	1.2 x 10^{-2}	26	305	0.32
(dimethyl bipyridyl)	11.3	-11.1	3.7 x 10^{-3}	14	195	0.1
(bis-pyridyl ethane)		-16.5	2.5 x 10^{-4}	4	(<30)	5.4 x 10^{-3}

[a] A linear fit of the data in Figure 2 gives slope 0.045, (intercept −0.001); thus the electronic factors for the Ru^{II}−Co^{III} reactions are ∼20 times smaller than for their Ru^{II}−Ru^{III} counterparts. The κ_{el} values range from 10−4 to 1.0 with corresponding H_{RuCo}-coupling elements of 4−200 cm^{-1}.

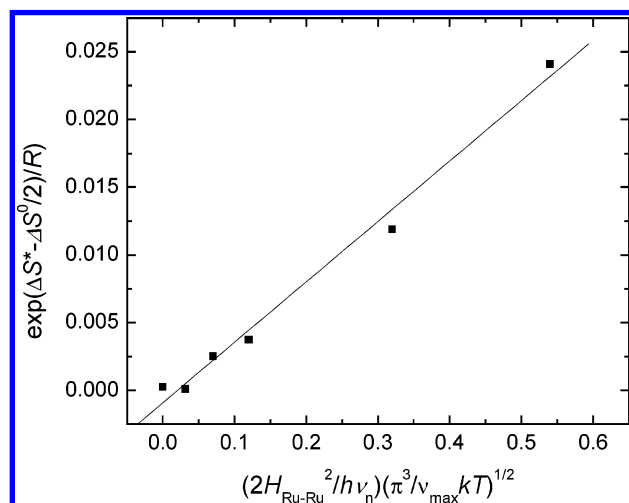**Figure 2.** Plot of κ_{el} values (Table 2) obtained from the corrected activation entropy values for Ru(II)−Co(III) reactions vs κ_{el} for diruthenium complexes (eqs 2b and 9, spectroscopic values in Table 1). The fit to the data gives slope 0.045, intercept −0.001.

Results

Yee et al. determined $\Delta S^0 = -13 \pm 0.5$ cal K^{-1} mol^{-1} and 37 ± 2 cal K^{-1} mol^{-1} for Ru(en)$_3{}^{3+/2+}$ and Co(en)$_3{}^{3+/2+}$, respectively.[34] From these values, ΔS^0 for the intramolecular Ru(II)−Co(III) reactions in Table 1 is estimated as +20 cal K^{-1}mol^{-1}. Values of $\Delta S^\dagger - \Delta S^0/2$ for the Ru(II)−Co(III) reactions and spectroscopic parameters for the diruthenium complexes are listed in Table 2. (The origins of these differences have been discussed in terms of the large changes in vibrational frequencies for the cobalt couples.[35,36]) Electronic factor κ_{el} values obtained from the corrected activation entropy (eq 5b) values for the Ru(II)−Co(III) reactions are also listed in Table 2 and plotted versus κ_{el} for diruthenium complexes (obtained from eq 9 and the spectroscopic values in Table 1) in Figure 2.

Discussion

Ammine complexes of cobalt(III) are low-spin (ls) d^6, while the cobalt(II) complexes are high-spin (hs) d^7. When $(\pi d)^6$ cobalt(III) accepts an electron, the equilibrium hs form cobalt-(II) $(\pi d)^5(\sigma d)^2$ may be formed directly via a spin-forbidden process[37] or the ls $(\pi d)^6(\sigma d)^1$ species could be formed as an intermediate[24] that is rapidly converted to the hs form. In either event, the hs form undergoes extremely rapid loss of NH$_3$, thereby rendering the redox reaction irreversible. Does reduction involve only hs Co^{II} product, or is the ls state an intermediate?[26] Newton[24] has simulated data for electron-transfer from bpy$^-$ to Co(III)[38] in Isied's polyproline-bridged systems[39] and provided evidence for involvement of the ls ligand-field excited-state of cobalt(II) as the electron-transfer primary product. Similarly, the ls cobalt(II) state has been studied in photoinduced, intramolecular electron-transfer to cobalt pyridyl complexes.[40−42] The reduction potential for Co(en)$_3{}^{3+}$/hs Co(en)$_3{}^{2+}$ is −0.22 V versus NHE[34] while that for Co(en)$_3{}^{3+}$/ls Co(en)$_3{}^{2+}$ is −0.68 V versus NHE.[43,44] Of the intramolecular reductants D studied so far, only D−B−Co^{III}(NH$_3$)$_5$ complexes in which D = (NH$_3$)$_5$Os^{II} ($E^0 \sim -0.2$ V versus NHE[39]) and D = bpy$^-$ attached to a Ru(II) ($E^0 \sim -1.1$ V vs NHE[38]) are sufficiently reducing to produce D$^+$−B−Co^{II}(NH$_3$)$_5$ hs and only bpy$^-$ attached to a Ru(II) is reducing enough to yield the ls species. In contrast, the reduction potentials of D = Ru(NH$_3$)$_5$ attached to a pyridyl-type bridge are typically +0.4 V versus NHE.[16] Evidently the (NH$_3$)$_5$Ru^{II}−B−Co^{III}(NH$_3$)$_5{}^{5+}$ electron-transfers are driven by irreversible ammonia loss.[45,46] Indeed, the rate constant recorded for bridging pyrazine (Table 1) requires ammonia loss to occur on a nanosecond time scale. Buhks et al. found κ_{el} for the Co-(NH$_3$)$_6{}^{2+}$/Co(NH$_3$)$_6{}^{3+}$ electron exchange via hs cobalt(II) to be 10^{-4} ($H_{CoCo} \sim 2$ cm^{-1}) with the ls excited-state pathway being significantly slower.[37,47] Newton obtained a similar value for rotationally averaged κ_{el}.[26,48] Both underestimate the actual self-exchange rate[49] by ca. 10^3, and experimental observations of Co^{III}(NH$_3$)$_5$L reductions suggest that the self-exchange reactions are close to adiabatic and do not involve a ls intermediate.[50,51]

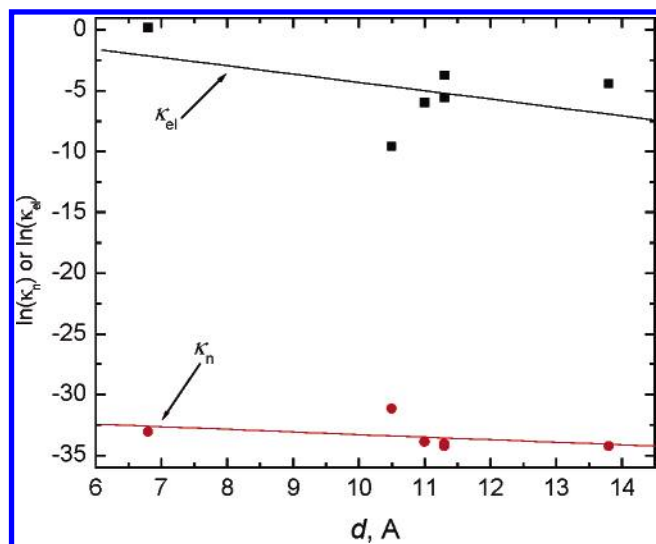**6716** *J. Phys. Chem. B, Vol. 111, No. 24, 2007*

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Figure 3. The natural logarithm of nuclear and electronic factors for the pyridyl-bridged Ru−Co systems as a function of Ru−Co separation. The plots yield $\beta_{el} = 0.7$ Å^{-1} and $\beta_n = 0.2$ Å^{-1}.

The strong correlation in Figure 2 suggests a common mechanism for the electronic coupling in Ru−Co and Ru−Ru systems. For the latter, a superexchange mechanism involving the metal-to-ligand charge transfer (MLCT) excited-states (e.g., Ru^{III}−(B$^-$)−Ru^{III}) in which B is the neutral bridge in Ru^{II}−(B)−Ru^{III} has proven successful.[27] For the present complexes, the analogous MLCT excited-state is Ru^{III}−(B$^-$)−Co^{III}. The overlap of the cobalt(III) e$_g$ acceptor orbital with the π*-centered B$^-$ orbital is expected to be poor compared to that with the t$_{2g}$ acceptor orbital of ruthenium(III), consistent with the 7 times smaller H_{da} values obtained in Figure 2. Further analysis of the system, however, would require detailed knowledge of energetic parameters useable in a superexchange treatment as given earlier for diruthenium complexes.[27]

Geselowitz has noted a correlation between the free energies of activation $\Delta G^{\dagger}$ for the Ru^{II}−B−Co^{III} reactions and the energy of the intervalence charge-transfer (IVCT) band for the corresponding ruthenium dimer (eq 7), attributing the correlation to the solvent reorganization for an adiabatic reaction.[52] The distance dependence of electron-transfer rate constants can arise from both the nuclear[53] and electronic factors. The magnitudes of κ_{el} and κ_n for the Ru(II)−Co(III) reactions are plotted as a function of metal−metal separation in Figure 3. The nuclear factors were obtained from the reported enthalpies of activation, that is, $\kappa_n = \exp(-\Delta H^{\dagger}/RT)$.

For these systems, the electronic factor is more than 3 times more sensitive to donor−acceptor separation than the nuclear factor in striking contrast to the polyproline-bridged Os^{II}−Ru^{III} system,[22] for which β_{el} and β_n are comparable in magnitude. (β is defined through the expression $\kappa_d = \kappa_0 \exp(-\beta d_{DA})$.) For the latter, $\beta_{el} = 0.65$ Å^{-1} and $\beta_n = 0.54$ Å^{-1} in the range 12−18 Å.[22,54] The slope in Figure 3 corresponds to a β_{el} value of 0.7 Å^{-1}.

Conclusion

The activation parameters reported for intramolecular electron-transfer between ruthenium(II) and cobalt(III) complexes have been corrected for the thermodynamic contributions of the entropy change for the reaction ΔS^0 to the entropy of activation $\Delta S^{\dagger}$, and it is concluded that these electron-transfers range from adiabatic (pyrazine bridge) to highly nonadiabatic. The electronic

factors for the ruthenium(II)−cobalt(III) electron-transfers are about 20 times smaller than for diruthenium mixed-valence complexes. Spanning the metal−metal separation range of 7−14 Å, the Ru^{II}−Co^{III} electron-transfer rates are dominated by the electronic factors, which change 3 times more with separation than do the nuclear factors.

References and Notes

(1) Adams, D.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B* **2003**, *107*, 6668−6697.

(2) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148−13168.

(3) Nelsen, S. F. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 1, pp 342−392.

(4) Rosokha, S. V.; Newton, M. D.; Head-Gordon, M.; Kochi, J. K. *Chem. Phys.* **2006**, *324*, 117−128.

(5) Gray, H. B.; Winkler, J. R. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 3534−3539.

(6) Creutz, C.; Brunschwig, B. S.; Sutin, N. *J. Phys. Chem. B* **2005**, *109*, 10251−10260.

(7) Creutz, C.; Brunschwig, B. S.; Sutin, N. *Chem. Phys.* **2006**, *324*, 244−258.

(8) Chen, F.; Li, X.; Hihath, J.; Huang, Z.; Tao, N. *J. Am Chem. Soc.* **2006**, *128*, 15874−15881.

(9) Newton, M. D. *Int. J. Quantum Chem.* **1980**, *17*, 363−391.

(10) Logan, J.; Newton, M. D. *J. Chem. Phys.* **1983**, *78*, 4086−4091.

(11) Newton, M. D.; Sutin, N. *Ann. Rev. Phys. Chem.* **1984**, *35*, 437−480.

(12) Sutin, N. In *Tunneling in Biological Systems*; Chance, B., Ed.; Academic Press: New York, 1979; pp 201−224.

(13) Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 8198−8200.

(14) Fischer, H.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 5512−5517.

(15) Rieder, K.; Taube, H. *J. Am. Chem. Soc.* **1977**, *99*, 7891−7894.

(16) Zawacky, S. K. S.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 3379−3387.

(17) Jwo, J. J.; Gaus, P. L.; Haim, A. *J. Am. Chem. Soc.* **1979**, *101*, 6189−6197.

(18) Lee, G. H.; Della, Ciana, L.; Haim, A. *J. Am. Chem. Soc.* **1989**, *111*, 2535−2541.

(19) de Oliveira, L. A. A.; Della, Ciana, L.; Haim, A. *Inorg. Chim. Acta* **1994**, *225*, 129−135.

(20) Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273−357.

(21) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265−322.

(22) Isied, S. S.; Vassilian, A.; Wishart, J. F.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 635−637.

(23) Marcus, R. A.; Sutin, N. *Comments Inorg. Chem.* **1986**, *5*, 119−133.

(24) Ungar, L. W.; Newton, M. D.; Voth, G. A. *J. Phys. Chem. B* **1999**, *103*, 7367−7382.

(25) Nelsen, S. F.; Weaver, M. N.; Pladziewicz, J. R.; Ausman, L. K.; Jentzsch, T. L.; O'Konek, J. J. *J. Phys. Chem. A* **2006**, *110*, 11665−11676.

(26) Newton, M. D. *Coord. Chem. Rev.* **2003**, *238*, 167−185.

(27) Creutz, C.; Newton, M. D.; Sutin, N. *J. Photochem. Photobiol., A.* **1994**, *82*, 47−59.

(28) Shin, Y.-g. K.; Newton, M. D.; Isied, S. S. *J. Am. Chem. Soc.* **2003**, *125*, 3722−3732.

(29) Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168−184.

(30) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(31) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357−339.

(32) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125−3134.

(33) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391−444.

(34) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131−1137.

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(35) Richardson, D. E.; Sharpe, P. *Inorg. Chem.* **1991**, *30*, 1412−1414.

(36) Richardson, D. E.; Sharpe, P. *Inorg. Chem.* **1993**, *32*, 1809−1812.

(37) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979**, *18*, 2014−2018.

(38) Ogawa, M. Y.; Wishart, J. F.; Young, Z. Y.; Miller, J. R.; Isied, S. S. *J. Phys. Chem.* **1993**, *97*, 11456−11463.

(39) Isied, S. S.; Vassilian, A.; Magnuson, R. H.; Schwarz, H. A. *J. Am. Chem. Soc.* **1985**, *107*, 7432−7438.

(40) Yoshimura, A.; Nozaki, K.; Ikeda, N.; Ohno, T. *J. Phys. Chem.* **1996**, *100*, 1630−1637.

(41) Song, X. Q.; Lei, Y. B.; Vanwallendal, S.; Perkovic, M. W.; Jackman, D. C.; Endicott, J. F.; Rillema, D. P. *J. Phys. Chem.* **1993**, *97*, 3225−3236.

(42) Torieda, H.; Nozaki, K.; Yoshimura, A.; Ohno, T. *J. Phys. Chem. A* **2004**, *108*, 4819−4829.

(43) Billing, R.; Vogler, A. *J. Photochem. Photobiol., A* **1997**, *103*, 239−247.

(44) Billing, R.; Benedix, R.; Stich, G.; Hennig, H. *Z. Anorg. Allg. Chem.* **1990**, *583*, 157−162.

(45) Lilie, J.; Shinohara, N.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6516−6520.

(46) Simic, M.; Lilie, J. *J. Am. Chem. Soc.* **1974**, *96*, 291−292.

(47) Newton, M. D. *J. Phys. Chem.* **1991**, *95*, 30−38.

(48) Newton, M. D. *J. Phys. Chem.* **1991**, *95*, 30.

(49) Hammershoi, A.; Geselowitz, D.; Taube, H. *Inorg. Chem.* **1984**, *23*, 979−982.

(50) Endicott, J. F.; Ramasami, T. *J. Phys. Chem.* **1986**, *90*, 3740−3747.

(51) Endicott, J. F. *Acc. Chem. Res.* **1988**, *21*, 59−66.

(52) Geselowitz, D. A. *Inorg. Chem.* **1987**, *26*, 4135−4137.

(53) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657−3668.

(54) Vassilian, A.; Wishart, J. F.; Vanhemelryck, B.; Schwarz, H.; Isied, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 7278−7286.