data are a measure of electron density at an atom.

A kinetic comparison between methylsulfonium ion reactivities and those of palladium(II) methyl thioether complexes is possible. The second-order rate constant for methyl transfer from p-$O_2NC_6H_4SMe_2^+$ to benzylamine in acetonitrile solvent at 25 °,c is 4.36×10^{-3} M^{-1} s^{-1}.[7] Comparative respective rate constants for $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ and $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ are 2.5 (7) $\times 10^{-3}$ M^{-1} s^{-1} at 29.5 °C, and 3.0 (6) $\times 10^{-5}$ M^{-1} s^{-1} at 45 °C. It is apparent that the rate constants for the reaction of benzylamine with p-$O_2NC_6H_4SMe_2^+$ and $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2]^{2+}$ are closely similar but that the reaction with $PdCl_2(Ph_2PC_6H_4SMe)$ is much slower.

The creation of a carbonium ion center at the methyl carbon is not discernible by comparison between methyl carbon–sulfur distances as found by X-ray crystallography. From single-crystal structure data the measured carbon (methyl)–sulfur distances in the carbonium ion of $[PhSMe_2]^+ClO_4^-$ and in the complex $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ are 1.81 (2), 1.83 (2), and 1.815 (11) Å.[28,29] These carbon–sulfur distances are identical with the accepted value (1.82 Å) found in divalent dialkyl sulfides.[30] Structural arguments have, nevertheless, been used to try to propose a direction of attack at an alkyl caron atom of an alkylsulfonium ion compound; nevertheless, the authors conclude that there is no general tendency for nucleophilic centers to approach the α-carbon atoms in any particular direction.[31] The analogous chelate complexes of o-(diphenylphopshino)thioanisole with both nickel and platinum can be prepared. The complex $PtI_2(o\text{-}Ph_2PC_6H_4SMe)$ has been prepared from treating K_2PtCl_4 with excess iodide and 1 mol of o-$Ph_2PC_6H_4SMe$ (eq 8). The ^1H NMR spectrum

$$K_2PtCl_4 + o\text{-}Ph_2PC_6H_4SMe \xrightarrow{2KI} PtI_2(o\text{-}Ph_2PC_6H_4SMe) + 4KCl \quad (8)$$

shows a downfield-shifted methyl resonance at δ 3.62 (^3J(PtH) = 34 Hz) and the ^{31}P NMR spectrum a resonance at δ 43.6 (^1J(PtP) = 1660 Hz). No reactions with this compound have been attempted, but preliminary work on the compound $NiCl_2(o\text{-}Ph_2C_6H_4SMe)$ shows that it will transfer the methyl group to an amine.

Acknowledgment. We thank D. Appel for collecting the FTNMR data.

Registry No. $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$, 91741-05-8; $PtI_2(o\text{-}Ph_2PC_6H_4SMe)$, 91686-91-8; $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$, 14876-85-8; $[Pd(\mu\text{-}SC_6H_4PPh_2\text{-}o)Cl]_2$, 91686-92-9; *trans*-$Pd(o\text{-}Ph_2PC_6H_4S)_2$, 91741-06-9; benzylamine, 100-46-9.

Supplementary Material Available: Tables of final atomic positional parameters, bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom coordinates, and structure factors (12 pages). Ordering information is given on any current masthead page.

---

(28) Lopez-Castro, A.; Truter, M. R. *Acta Crystallogr., Sect. B* **1964**, *B17*, 465–471.

(29) Clark, G. R.; Orbell, J. D. *J. Organomet. Chem.* **1981**, *215*, 121–129.

(30) Abrahams, S. C. *Q. Rev., Chem. Soc.* **1956**, *10*, 407–436.

(31) Britton, D.; Dunitz, J. D. *Helv. Chim. Acta* **1980**, *63*, 1068–1073.

Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Nonadiabatic Effects in Outer-Sphere Electron-Transfer Reactions of Cobalt(III) Complexes: Experimental Probes of Charge-Transfer Perturbations of the Rates of Several Cross-Reactions[1]

T. RAMASAMI and JOHN F. ENDICOTT*

Received August 24, 1983

Whereas Franck–Condon models such as the one proposed by Marcus have been successful in treating the electron-transfer reactions of several metal ions, there have been some persistent issues in the reactivity of Co(III) complexes, which are not easily analyzed in terms of Franck–Condon-only models. Herein is presented the evidence for nonadiabatic effects that cause deviations from the Franck–Condon-only models in the reactions of $Co(H_2O)_6^{3+}$–$Fe(phen)_3^{2+}$, $Co((bzo)_3\text{-}[12]hexaeneN_3)_2^{3+}$–$Co(sep)^{2+}$, and $Co(phen)_3^{3+}$–$Co([9]aneN_3)_2^{2+}$. The presence of an electronic constraint to reactions in the above systems is inferred on the basis that those bimolecular reactions may be perturbed by medium effects when the medium can participate in low-energy charge-transfer interactions. For example, several cross-reactions involving $Co(H_2O)_6^{3+,2+}$ would suggest a self-exchange rate of 10^{-12} M^{-1} s^{-1} for the couple, which differs from the experimentally measured value of 5 M^{-1} s^{-1} as well as that calculated from ground-state structural parameters, on the assumption of Franck–Condon-only models, viz. 7.5×10^{-6} M^{-1} s^{-1}. Such deviations are often the result of "electronic" or nonadiabatic effects. It has been found that those reactions in which an electronic barrier persists are sensitive to both the nature and the concentration of anions in the medium and the observed anion effects are over and above the electrostatic factors. A proposal is made that charge-transfer interactions between the anions and the collision complex may increase the radial parameters within the collision complex to permit better donor–acceptor overlaps, thereby decreasing the electronic constraints. In this work, an experimental means to assess nonadiabatic effects in electron-transfer reactions using three distinctly different sets of reaction partners is presented.

Introduction

Electron-transfer reactions not only are the simplest of oxidation–reduction processes but are also of central importance in many chemical and biological reaction systems.[2–13] At least in limiting cases, these reactions are simple enough that they have attracted a great deal of theoretical atten-

---

[1] Partial support of this research by the National Institutes of Health (Grant AM 143211) and the National Science Foundation (Grant CHE 80-05497) is gratefully acknowledged.

(2) Cannon, R. D. "Electron Transfer Reactions"; Butterworths: New York, 1980.

(3) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(4) (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) *Acc. Chem. Res.* **1982**, *15*, 275. (c) Sutin, N.; Brunschwig, B. S. *ACS Symp. Ser.* **1982**, *No. 198*, 105. (d) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(5) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. *Prog. Inorg. Chem.* **1983**, *30*, 141.

(6) Pennington, D. *ACS Monogr.* **1978**, *No. 174*, 476.

(7) Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273.

(8) Moore, G. R.; Williams, R. J. P. *Coord. Chem. Rev.* **1976**, *18*, 125.

0020-1669/84/1323-3324$01.50/0

tion.[2,4,9,10,14-20] In a general way, the electron-transfer process is treated as a nonradiative electronic transition in a collision complex made up of the reactant molecules. The electronic and nuclear contributions to the transition probability are usually treated separately, by assuming the Born–Oppenheimer approximation holds. A semiclassical formulation

$$k = K_0\kappa_{\mathrm{el}}\nu_{\mathrm{nu}}\Gamma \exp(-\Delta G^*(\mathrm{FC})/RT) \qquad (1)$$

for the electron-transfer rate constant is often conceptually useful,[4,19,20] where the nuclear contributions give rise to an effective nuclear frequency term appropriate to the reaction coordinate (ν_{nu}), a nuclear tunneling factor (Γ), and a Franck–Condon factor, $\exp(-\Delta G^*(\mathrm{FC})/RT)$; any electronic contributions then appear in the electronic transmission coefficient, κ_{el} (K_0 is the equilibrium constant describing association of the reactants).

Franck–Condon factors dominate most of the observed outer-sphere electron-transfer reactivity patterns,[2,4-6,20-23] and the role of contributions from electronic factors has remained equivocal. Several theoretical treatments have indicated that κ_{el} could be small for some kinds of systems,[4,10,18-20,24] but these theories have not provided a great deal of insight into the factors that are responsible for variations in the electronic contributions to electron-transfer reactions. Many experimental studies have indicated that there are deviations from the reactivity patterns predicted by simple Franck–Condon models, especially in some solvated electron reactions,[25] in electron transport between widely separated reactants,[9-11,18,24,25] and in reactions accompanied by large changes in bond lengths at the reactant centers (e.g., as in Co(III)–Co(II) couples).[5,22,26]

In principle, one might seek to evaluate transmission coefficients, κ_{el}, by comparing observed rate constants, k(obsd), to those calculated on the basis of ground-state structural and vibrational parameters and some theoretical expression for the Franck–Condon factor. For reactions involving large changes in first coordination sphere bond lengths, ΔX, ΔG^*(FC) contains a very large first coordination sphere reorganizational contribution that varies as $(\Delta X)^2$. Unfortunately, the uncertainties in estimates of the bond lengths of the solvated reactants are sufficiently large (typically at least 1 pm where typical values of ΔX are 10–20 pm) that uncertainty in these calculated values of the rate constants tends to be as large as the expected magnitude of κ_{el}.[5,22c,27]

Over the past few years we have been seeking alternative experimental approaches to the evaluation of factors contributing to κ_{el}.[5,10,28] We have been able to demonstrate that the introduction of charge-transfer perturbations can increase the rates of certain transition-metal energy-transfer and electron-transfer reactions without significantly altering the Franck–Condon factors. More specifically, we have reported on the systematic increase in rates of $\mathrm{Co(sep)^{2+}}$ (where sep = (*S*)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane)[29] reductions of $(\mathrm{Co(phen)_3}^{3+},\mathrm{X^-})$ ion pairs with decreases in the energy of the $\mathrm{X^-} \rightarrow \mathrm{Co(III)}$ ion-pair charge-transfer absorption.[28b,c] A significant sensitivity of the reaction rate to the nature of the ion pair was found for the $\mathrm{Co(sep)^{3+,2+}}$ couple but not for the $\mathrm{Ru(NH_3)_6}^{3+,2+}$ couple, the latter being presumed to be relatively adiabatic (i.e., $\kappa_{\mathrm{el}} \rightarrow 1$, probably owing to the small difference in bond lengths found for the ruthenium couple (ΔX = 4 pm)[30] and/or greater overlap expected for 4d compared to 3d orbitals). Naturally, we have been concerned about the generality of these effects, and the present report describes our studies of the ion-pair perturbations of the rates of several additional simple electron-transfer reaction systems.

It is useful to formulate the electronic transmission coefficient, based on an application of the Landau–Zener model,[31] as[4,19,20]

$$\kappa_{\mathrm{el}} = 2[1 - \exp(-\nu_{\mathrm{el}}/2\nu_{\mathrm{nu}})]/[2 - \exp(-\nu_{\mathrm{el}}/2\nu_{\mathrm{nu}})] \qquad (2)$$

For reasonably large values of ΔX one expects high-frequency nuclear modes ($\nu_{\mathrm{nu}} \sim 10^{12}$–$10^{13}\ \mathrm{s^{-1}}$) to be dominant over solvent modes ($\nu_{\mathrm{nu}} \sim 10^{11}\ \mathrm{s^{-1}}$). This is expected to give rise to smaller values of κ_{el} even for comparable values of the frequency of electronic motion at the surface crossing (ν_{el}). This consideration has largely restricted our studies to Co(III)–Co(II) couples, since these couples nearly always involve large values of ΔX. The electronic frequency may be approximately represented[4,9,10,12,18,19,24,25,28,32] as

$$\nu_{\mathrm{el}} \sim A \exp(-2\alpha r_{\mathrm{DA}}) \qquad (3)$$

where A can be interpreted as a coupling constant containing all the reactant–product interaction terms and the exponential

---

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

(10) Buhks, E.; Wilkins, R. G.; Isied, S. C.; Endicott, J. F. *ACS Symp. Ser.* **1982**, *No. 198*, 213.

(11) Winkler, J. R.; Nocera, D. G.; Yocum, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 5798.

(12) Chang, A. M.; Austin, R. H. *J. Chem. Phys.* **1982**, *77*, 5272.

(13) Isied, S. S.; Worsila, G.; Atherton, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 7659.

(14) (a) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21. (b) *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (c) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 748. (d) Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622. (e) *ACS Symp. Ser.* **1982**, *No. 198*, 235. (f) Marcus, R. A. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7.

(15) (a) Hush, N. S. *Electrochim. Acta* **1958**, *13*, 1005. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (c) Hush, N. S. *ACS Symp. Ser.* **1982**, *No. 198*, 301.

(16) Levich, V. G. *Adv. Electrochem. Electrochem. Eng.* **1966**, *4*, 249.

(17) (a) Dogonadze, R. R.; Kuznetsov, A. M.; Levich, V. G. *Electrochim. Acta* **1968**, *13*, 1025. (b) Dogonadze, R. R. In "Reactions of Molecules at Electrodes"; Hush, N. S., Ed.; Wiley-Interscience: New York, 1971; Chapter 3, p 135.

(18) (a) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148. (b) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (c) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979**, *18*, 2014. (d) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860. (e) Buhks, E.; Jortner, J. *J. Phys. Chem.* **1980**, *84*, 3370. (f) Buhks, E.; Jortner, J. *Chem. Phys.* **1981**, *55*, 41. (g) Bixon, M.; Jortner, J. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 17.

(19) (a) Newton, M. D. *Int. J. Quantum Chem.*, *Quantum Chem. Symp.* **1980**, *14*, 363. (b) *ACS Symp. Ser.* **1982**, *No. 198*, 255. (c) Tembe, B. L.; Friedman, H. L.; Newton, M. D. *J. Chem. Phys.* **1982**, *76*, 1490.

(20) Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798.

(21) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

(22) (a) Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 429. (b) Endicott, J. F.; Durham, B.; Kumar, K. *Inorg. Chem.* **1982**, *21*, 2437. (c) Endicott, J. F.; Brubaker, G. R.; Ramasami, T.; Kumar, K.; Dwarakanath, K.; Cassel, J.; Johnson, D. *Inorg. Chem.* **1983**, *22*, 3754.

(23) Taube, H.; Geselowitz, D. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 391.

(24) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640.

(25) (a) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579. (b) Miller, J. R.; Beitz, J. V. *Ibid.* **1981**, *74*, 6746. (c) Miller, J. R.; Hartman, K. W.; Abrash, S. *J. Am. Chem. Soc.* **1982**, *104*, 4296.

(26) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

(27) Bernhard, P.; Buergi, H. B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936.

(28) (a) Endicott, J. F.; Heeg, M. J.; Gaswick, D. C.; Pyke, S. C. *J. Phys. Chem.* **1981**, *85*, 1777. (b) Endicott, J. F.; Ramasami, T. *J. Am. Chem. Soc.* **1982**, *104*, 5252. (c) Endicott, J. F.; Ramasami, T.; Gaswick, D. L.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301.

(29) (a) Creaser, I. I.; Harrowfield, J. MacB.; Herit, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181. (b) Sargeson, A. M. *Chem. Ber.* **1979**, *15*, 23. (c) Creaser, I. I.; Geue, R. J.; Harrowfield, J. MacB.; Herit, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

(30) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304.

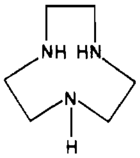
(31) Thorson, W. R.; Delos, J. B.; Boorstein, S. A. *Phys. Rev. A* **1971**, *4*, 1052.

(32) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

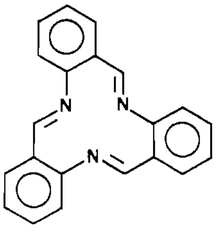
may be interpreted as a donor–acceptor overlap integral (spherical wave approximation, with r_{DA} being the distance of separation of orbital centers and α^{-1} a parameter dependent on the orbitals involved). Thus, one expects ν_{el} to decrease as the reactants become progressively more bulky (for α approximately constant). The ion-pair CT perturbations mentioned above have been interpreted in terms of contributions to the electron-exchange integral (i.e., by means of an anion-mediated superexchange interaction).[28b,c] Experimental study of a variety of systems is needed to evaluate the importance of electronic effects and the various factors that may contribute to them.

Experimental Section

Materials. The complexes $Fe(phen)_3(ClO_4)_2$,[33] $Co(sep)Cl_3\cdot H_2O$,[22c,34,35] and $Co(phen)_3(ClO_4)_3$[36] were prepared according to standard procedures and characterized by means of elemental analysis, electronic spectra, and in the case of the latter two complexes by electrochemical measurements. The solutions of $Co(H_2O)_6^{3+}$ in 3 M $HClO_4$ and $Co(sep)^{2+}$ in 0.1 M $NaCF_3SO_3$ were obtained by means of electrochemical oxidation of Co^{2+} and Zn reduction of $Co(sep)Cl_3$, respectively. The samples of $Co([9]aneN_3)_2Cl_3$[37] were kindly supplied to us by Prof. Karl Wieghardt and the solutions of $Co([9]aneN_3)_2^{2+}$ in 0.1 M $NaCF_3SO_3$ were obtained by Zn-dust reduction followed by air-free filtration. The concentrations of Co(II) were analyzed by oxidizing with $Fe(phen)_3^{3+}$ and monitoring Fe(II) using spectrophotometric methods. Ascorbic acid was freshly recrystallized after decolorization by activated charcoal in the absence of oxygen and light, and the solutions were used within 3–4 h. Doubly distilled trifluoromethanesulfonic acid (HTFMS) and triply recrystallized samples of sodium salts prepared from distilled acid and Na_2CO_3 were used. Other reagents used were reagent grade or better.



$[9]aneN_3$



$(bzo)_3[12]hexaeneN_3$

Preparation and Further Characterization of $Co((bzo)_3[12]hexaeneN_3)_2^{3+,2+}$ Complexes.[37] Samples of *o*-aminobenzaldehyde, the trimeric ligand $(bzo)_3[12]hexaeneN_3$, and its Co(III) complexes may be conveniently prepared by the slight adaptations of the procedures already described in the literature.[38–40] There are indeed two series of isomers of Co(III) complexes denoted by Busch and co-workers as "A" and "B" that are assigned to meso and racemic configurations, respectively.[39] The fractional crystallization procedures described by Cummings and Busch[39] for the separation of the nitrate salts of the A and B isomers using aqueous acidic propanol mixtures had limited success in our hands. Further purification using chromatographic procedures was essential for the quantitative studies made in the present work.

Purification of isomers A and B was carried out on a Sephadex LH 20 column. A concentrated methanolic solution of $Co((bzo)_3[12]hexaeneN_3)_2(NO_3)_3$ (obtained after crystallization from aqueous acidic propanol) was adsorbed on a Sephadex LH 20 (25 cm × 1.2 cm) column to a height of ~1.5 cm and was eluted with either neat methanol or methanol–water (4:1) mixture acidified slightly with HNO_3. Two distinct bands, orange and yellow, were separated. Rotary evaporation of the methanolic fractions followed by the addition of ethyl ether gave shining orange crystals of the isomer A and yellow needles of isomer B, identified by means of their characteristic UV spectra. The B isomer has a well-resolved absorption maximum at 285 nm (8.0 ± 0.1) × 10^4 M^{-1} cm^{-1}. The visible spectrum was, however, sensitive to the nature of the medium as described in a later section. Anal. Calcd for $Co((bzo)_3[12]hexaeneN_3)_2(NO_3)_3\cdot H_2O$ (isomer A): C, 57.21; H, 3.63; N, 14.30. Found: C, 57.20; H, 3.64; N, 14.09. Anal. Calcd for $Co((bzo)_3[12]hexaeneN_3)_2(NO_3)_3\cdot 3H_2O$ (isomer B): C, 54.96; H, 3.92; N, 13.74. Found: C, 54.36; H, 3.95; N, 13.24. The electrochemical investigations of the $Co((bzo)_3[12]hexaeneN_3)_2^{3+,2+}$ couples were made by using differential-pulse polarographic methods, which permitted the use of [Co(III)] ~ 10^{-5} M, a limit imposed by the poor solubilities of the Co(II) compounds. The direct procedures starting from Co^{2+} and the free ligand gave a mixture of Co(II) products, which could not be purified well by means of crystallization procedures. Therefore, the Co(II) salts were prepared by Zn (or Cr^{2+}) reduction of the corresponding Co(III) salts in deaerated aqueous methanol, and solid products were obtained either by the addition of deaerated water or by evaporation under air-free conditions. The reduction of the meso isomer of Co(III) gave a green Co(II) product while that of the racemic isomer gave a maroon Co(II) derivative. Further purification was best done by using an air-free Sephadex LH 20 column (20 cm in length × 1.2 cm i.d.) and deaerated methanol as the solvent for elution. The evaporation of methanol under an argon atmosphere gave the desired products. These had broad absorption maxima in the visible region: at 540 nm (5 × 10^3 M^{-1} cm^{-1}) for the maroon Co(II) isomer; at 570 nm for the green Co(II) product. These were further characterized by means of magnetic susceptibility and electron spin resonance measurements.

Magnetic Susceptibility and ESR Measurements. The magnetic measurements for the $Co((bzo)_3[12]hexaeneN_3)_2^{2+}$ compounds were made on powder samples by using the Guoy method and a Cahn Rh electrobalance and a Varian electromagnet with the magnet current set at 4 A. Generally, quadriplicate measurements were made, and the system was calibrated with $HgCo(NCS)_4$ as the standard at a temperature of 26 °C. The diamagnetic correction was made by using Pascal's constants.[41]

The ESR measurements were carried out only on the maroon isomer either as a powder (at room or liquid-nitrogen temperature) or as a glass in 2,4,6-trimethylpyridine (or methanol) at liquid-nitrogen temperature on a Varian E-4 electron spin resonance spectrometer and microwave powers in the range of 5–200 mW and DPPH as the external standard.

Charge-Transfer Spectral Measurements. The charge-transfer spectra for the couples $\{M(III),X^-\} \xrightarrow{h\nu} {}^*\{M(II),X\cdot\}$, where $X^- = I^-$, NO_2^-, and NCS^- and M(III) = $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$, $Ru(NH_3)_6^{3+}$, or $Co(phen)_3^{3+}$, were recorded at 25 °C and 0.5 M ($NaCF_3SO_3$) ionic strength. These were obtained from difference spectra in which the reference beam was passed through separate cuvettes containing the unmixed Co(III) and X^- species; the concentrations of these species were identical with those mixed in the sample cell of a Cary 14 spectrophotometer (ensuring that the solutions in the reference beam had absorbance <1.0). The spectra were generally recorded in the region of 650–350 nm (except the NO_2^- systems for which the useful spectral range was only up to 390 nm).

Outer-Sphere Equilibrium Constant Determinations. The outer-sphere association constants for the complexation

$$Co((bzo)_3[12]hexaeneN_3)_2^{3+} + X^- \overset{K_{os}}{\rightleftharpoons} \{Co((bzo)_3[12]hexaeneN_3)_2^{3+},X^-\}$$

were measured for $X^- = NCS^-$, NO_2^-, and I^- by using spectrophotometric methods. The ready reaction of ascorbate with $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ prevented any attempt to measure charge-transfer spectra. The equilibrium measurements were made at 400 nm with a Benesi–Hildebrand type[42] treatment (eq 4), where

$$\epsilon_{obsd} - \epsilon_0 = \frac{(\epsilon_1 - \epsilon_0)K_{os}[X^-]}{1 + K_{os}[X^-]} \qquad (4)$$

---

(33) Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.

(34) Harrowfield, J. MacB.; Herit, A. J.; Sargeson, A. M. *Inorg. Synth.*, **1980**, *20*, 85.

(35) Ferraudi, G. J.; Endicott, J. F. *Inorg. Chim. Acta* **1979**, *37*, 219.

(36) Baker, B. R.; Basolo, F.; Neumann, H. M. *J. Phys. Chem.* **1959**, *63*, 371.

(37) Abbreviations: $[9]aneN_3$ = 1,4,7-triazacyclononane; $(bzo)_3[12]hexaeneN_3$ = 3,4:7,8:11,12-tribenzo-1,3,9-triazadodeca-1,3,5,7,9,11-hexaene; sep = (*S*)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane.

(38) Smith, I. I.; Opie, J. W. *Org. Synth.* **1948**, *28*, 11.

(39) Cummings, S. C.; Busch, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 1924.

(40) Wing, R. M.; Eiss, R. *J. Am. Chem. Soc.* **1970**, *92*, 1929.

(41) Mabbs, F. E.; Macher, D. J. "Magnetism and Transition Metal Complexes"; Wiley: New York, 1973.

ϵ_0, ϵ_1, and ϵ_{obsd} represent the molar absorptivities of unassociated, completely associated, and a mixture of the two forms of the Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{3+}$ complexes, respectively. Although with X = NO_2 or NCS, 1:1 complexation behavior is supported by the precise fit of the optional changes data to (4), for I^- deviations from eq 4 at high concentrations (complications characteristic of some minor formation of 1:2 complexes) were also observed. Therefore, for X = I optical changes at lower concentrations of I^- were weighted more. In any case, the value of K_{os} obtained even for I^- is accurate to ±40%. Similar determinations of the K_{os} values for the {Co(phen)$_3^{3}$,X^-} systems have already been reported in our previous studies.[28b,c] The values of K_{os} appropriate to the kinetic conditions were also determined by the analysis of kinetic data as described in a later section.

Kinetic Studies. The kinetic investigations for the reactions (5)–(7)

$$\mathrm{Co(phen)_3^{3+} + Co([9]aneN_3)_2^{2+} \xrightarrow{X^-} products} \qquad (5)$$

$$\mathrm{X = I,\ NO_2,\ ascorbate}$$

$$\mathrm{Co(H_2O)_6^{3+} + Fe(phen)_3^{2+} \xrightarrow{X^-} products} \qquad (6)$$

$$\mathrm{X = Cl,\ Br,\ NCS}$$

$$\mathrm{Co((bzo)_3[12]hexaeneN_3)_2^{3+} + M(II) \xrightarrow{X^-} products} \qquad (7)$$

$$\mathrm{X = I,\ NO_2,\ ascorbate;\ M(II) = Co(sep)^{2+},\ Ru(NH_3)_6^{2+}}$$

were at different ionic strength conditions due to the experimental difficulties associated with each system. The ionic strength conditions for (5)–(7) were 0.1 M ($NaCF_3SO_3$), 2.0 M ($NaClO_4$ + $NaCF_3SO_3$), and 0.5 M ($NaCF_3SO_3$), respectively. The reactions were generally initiated by mixing the oxidant solution with a mixture of the reductants and anions in the stopped-flow mixing chamber. In the case of the reaction (6), it was necessary to take into proper account the reaction

$$\mathrm{Co(H_2O)_6^{3+} + X^- \rightarrow Co^{2+} + {}^1/_2X_2} \qquad (8)$$

When [X^-] and [Fe(phen)$_3^{2+}$] were in large excess over [Co(H$_2$O)$_6^{3+}$], the observed pseudo-first-order rate constants would be the sums of the first-order decay of Co(III) by the reactions (6) and (8). In view of the stoichiometry or reaction 8 one might expect a higher order dependence on [X^-] (e.g., through mediation of the reaction by {Co(H$_2$O)$_6^{3+}$,X^-} ion pairs). However, previous studies[43,44] have shown that for a pseudo-first-order excess of [X^-] over [Co(III)], the observed rate constants exhibit a first-order dependence on [X^-] for the anions investigated in this study. Similarly, anion-unassisted bimolecular rate constants for (6) have also been reported previously.[45] However, the kinetics of the reactions (6) and (8) were reinvestigated under our experimental conditions for 1:1 mixtures of $HClO_4$ and $NaCF_3SO_3$ at 2.0 M ionic strength. The need to use large concentrations of X^- in studies of reaction 6 (large [X^-] was required to increase the percentage of ion pairs for X = Cl, Br, or NCS) limited the range of concentrations of Fe(phen)$_3^{2+}$ that could be used to investigate (6) on the stopped-flow time scale. Further, to obviate the problems arising from the formation of hydroxo species of Co(III) and the decomposition of Co(H$_2$O)$_6^{3+}$, Co(III) was preserved at high [H^+] and the reactions were investigated at a [H^+] of 1.0 M. Under our experimental conditions, pseudo-first-order plots were linear to 3 half-lives and the rates were reproducible to ±10%.

The kinetics of reaction 7 were carried out in 20% aqueous methanol due to the poor solubility of Co^{II}((bzo)$_3$[12]hexaeneN$_3$) salts. The [H^+] for (7) was 10^{-5} M and the wavelengths were chosen such that both the Co(II) formation and the Co(III) decay could be monitored. The redox stoichiometry was separately determined for the Co((bzo)$_3$[12]hexaeneN$_3$)$^{3+,2+}$ couples, utilizing the Cr^{2+} reductions of the Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{3+}$ complexes and the Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{2+}$ reductions of Co(phen)$_3^{3+}$. In solutions at pH 5, the stoichiometric ratios were 1:(1.0 ± 0.1) and 1:(0.9 ± 0.1), respectively, for the two kinds of redox titration, thus confirming the one-electron stoichiometry.

The procedures and precautions taken for monitoring (5) are the same as described for the corresponding reactions of Co(sep)$^{2+}$ already described.[28b,c] All the reactions reported in this study were monitored on an Aminco stopped-flow spectrophotometer thermostated at 25 °C.

Results

Preparation and Further Characterization of Co((bzo)$_3$-[12]hexaeneN$_3$)$_2^{3+,2+}$ Complexes. Although the synthetic procedures described by earlier workers[39,40] were successful, chromatographic separations using gel filtration procedures were found essential for the kinetic studies since the meso and racemic isomers had different reactivities. Similar purification procedures aided also the separation of the green and maroon isomers of Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{2+}$. The formal potentials (vs. NHE) measured for the Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{3+,2+}$ couples are 0.055 V (for the racemic isomer) and 0.035 V (for the meso isomer) in 0.1 M $NaCF_3SO_3$ and with [H^+] = 10^{-4}–10^{-6} M. Both isomers exhibited quasi-reversibility, and at 0.5 M $NaCF_3SO_3$ in a water–methanol (4:1) mixture (i.e., conditions under which kinetic experiments had to be carried out), the potentials of both isomers were shifted toward the postive side by 15 mV compared to those at 0.1 M ionic strength in water. Reproducible electrochemical results were obtained regardless of whether the Co(III) or Co(II) forms were used. The stoichiometric titrations of Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{2+}$ with Co(phen)$_3^{3+}$ and of Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{3+}$ with Cr^{2+} gave 1:(0.9 ± 0.1) and 1:(1.0 ± 0.1), respectively, confirming metal-centered one-electron redox stoichiometry.

The magnetic measurements on the powder samples revealed that both green and maroon isomers of Co(II) were low spin, i.e. with doublet ground states. The magnetic moment obtained for the maroon isomer (from racemic Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{3+}$ of 1.7 ± 0.1 μ_B may be lower than that expected because of an underestimate of the diamagnetic correction for the free ((bzo)$_3$[12]hexaeneN$_3$) ligands. Measurements on Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{3+}$ salts using a residual paramagentism of 0.5 μ_B indicated that the diamagnetic correction for the Co(II) products using Pascal's constants may underestimate the susceptibility of Co(II) by as much as 0.2 μ_B. Nevertheless, both the maroon and the green isomers of Co(II) were found to be low spin, accounting for one unpaired electron. It is of interest that species such as (hexanitrito)cobaltate(II) have susceptibilities comparable[46,47] to that observed for the maroon isomer of Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{2+}$. The susceptibility observed for the green isomer (from *meso*-Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{3+}$) had a value of 2.1 ± 0.1 μ_B, which is typical of many related low-spin Co(II) complexes.[48-50] The temperature dependence of the magnetic moment was not analyzed. The low-spin configuration of Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{2+}$ is further corroborated by the ESR studies. At room temperature, the isotropic "g" value observed for powder samples, viz. 2.0 ± 0.1, is in keeping with a low-spin hexacoordinated structure having a doublet ground state; however, a rhombic pattern, with $g_x \neq g_y \neq g_z$, is observed. The low-temperature, viz. −100 °C, or liquid-nitrogen temperature spectra in 2,4,6-trimethylpyridine lattices also gave a rhombic pattern with hyperfine structure (Figure 1). The complexity of the observed ESR behavior of Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{2+}$ suggests that the energy gap for the low-spin–high-spin conversion is not very large and the high-spin excited states mix with the doublet ground state, similar to the behavior of some

---

(42) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1948**, *70*, 2832.

(43) McAuley, A.; Malik, M. N.; Hill, J. *J. Chem. Soc. A* **1970**, 2461.

(44) Davies, G.; Watkins, O. *Inorg. Chem.* **1970**, *9*, 273.

(45) Campion, R. J.; Purdie, N.; Sutin, N. *Inorg. Chem.* **1964**, *3*, 1091.

(46) Nishida, Y.; Kida, S. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 325.

(47) Gerlock, M.; Questeet, P. N.; Slade, R. C. *J. Chem. Soc. A* **1971**, 3741.

(48) Endicott, J. F.; Lilie, J.; Kuszaj, J. M.; Ramaswamy, B. S.; Schmonsees, W. G.; Simic, M. G.; Rillema, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 429.

(49) Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 4163.

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

Table I. Estimates of Charge-Transfer Energies and Formation Constants for Ion Pairs

cation	anion	K_{os}, M^{-1} kinetic[a]	K_{os}, M^{-1} spectrophotometric[b]	$^*E_{CT}$(obsd), eV	$^*E_{CT}$(calcd),[c] eV
$Ru(NH_3)_6^{3+}$	Cl^-			4.23[d]	4.26[e]
	Br^-			3.85[d]	3.70[e]
	NCS^-			3.32	3.30[e]
	I^-			3.10[d]	3.04[f]
$Co(H_2O)_6^{3+}$	Cl^-				3.35[g]
	Br^-				2.87[g]
	NCS^-				2.48[g]
rac-$Co((bzo)_3[12]hexaeneN_3)_2^{3+}$	I^-	(0.5)	2.5 ± 0.6	3.13	3.04[h]
	NO_2^-	0.8 ± 0.4	1.7 ± 0.6	2.70	2.74[h]
	NCS^-		3.3 ± 3	3.43[i]	3.30[h]
	ascorbate	1.7 ± 0.3			2.43[h]
$Co(phen)_3^{3+}$	I^-	30 ± 6	40 ± 5	3.39	3.13
	NO_2^-	7 ± 2	10	2.74	2.74
	Cl^-				4.26
	NCS^-	(35)	37 ± 3	3.43[i]	3.35
	ascorbate	20 ± 4	35 ± 5		2.43

[a] Based on eq 9. [b] Based on eq 4. [c] Calculated on the basis that $^*E_{CT}(\text{calcd}) = {}^*E_{CT}\{Ru(NH_3)_6^{3+}, X^-\} - \Delta G^\circ\{Ru(NH_3)_6^{3+},X^-\} - 2\Delta G_{ex}^{\ddagger}(Ru(NH_3)_6^{3+,2+}) + \Delta G^\circ\{M^{3+},X^-\} + 2\Delta G_{ex}^{\ddagger}(M^{3+,2+})$, where $\Delta G^\circ\{^{3+},X^-\}$ is the standard free energy change for the $M^{3+} + X^- \rightarrow M^{2+} + X\cdot$) reaction and $\Delta G_{ex}^{\ddagger}(M^{3+,2+})$ is the activation free energy for the $M^{3+,2+}$ self-exchange electron-transfer reaction. See ref 2 and: Endicott, J. F.; Ferraudi, G. J.; Barber, J. R. *J. Phys. Chem.* 1975, *79*, 630. [d] Waysbort, D.; Evenor, M.; Navon, G. *Inorg. Chem.* 1975, *14*, 514. [e] Based on $^*E_{CT}(\text{calcd}) = \Delta G^\circ\{Ru(NH_3)_6,X^-\} + 2\Delta G_{ex}^{\ddagger}(Ru(NH_3)_6^{3+,2+})$. [f] Referenced to the $\{Co(en)_3^{3+},I^-\}$ ion-pair absorption. [g] Assuming $k_{ex} = 8 \times 10^{-6}$ M^{-1} s^{-1} for $Co(H_2O)_6^{3+,2+}$. [h] Assuming $\Delta G_{ex}^{\ddagger}(Ru(NH_3)_6^{3+,2+}) = \Delta G_{ex}^{\ddagger}(Co((bzo)_3[12]hexaeneN_3)_2^{3+,2+})$. [i] A very weak transition at ~2.4 eV was also observed.

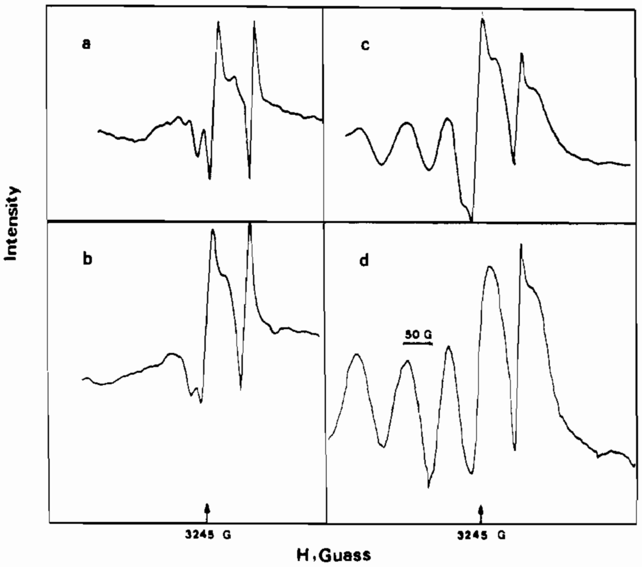


Figure 1. ESR spectra of *meso*-$Co((bzo)_3[12]hexaeneN_3)_2^{2+}$: (a) powder at room temperature; (b) methanolic solution containing 2,4,6-trimethylpyridine at room temperature; (c) methanolic glass with 2,4,6-trimethylpyridine at ~170 K; (d) same medium as (c) at ~77 K.

of the related Co(II) complexes investigated by McGarvey and co-workers.[51]

Charge-Transfer Spectra and Outer-Sphere Association Constant Determinations. The association of anions with *rac*-$Co((bzo)_3[12]hexaeneN_3)_2^{3+}$, $Co(phen)_3^{3+}$, and $Ru(NH_3)_6^{3+}$ was accompanied by the appearance of new absorption bands in the region of 360–500 nm. A typical difference spectrum for the association of I^- with $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$, $Co(phen)_3^{3+}$, and $Ru(NH_3)_6^{3+}$ is given in Figure 2. The new bands observed were broad, and the energies of the major (new) bands for other systems are included in Table I, along with the association constants estimated from spectrophotometric methods. The charge-transfer energies estimated also on the basis of other related systems such as $Co(en)_3^{3+}$ and $Ru(NH_3)_6^{3+}$ (from half-wave potentials and self-exchange parameters) are also included in Table I. Since the *rac*-$Co((bzo)_3[12]hexaeneN_3)_2^{3+,2+}$ couple has a half-wave potential very similar to that of the $Ru(NH_3)_6^{3+,2+}$ couple, the strong similarities in the charge-transfer spectra of $\{Ru(NH_3)_6^{3+},X^-\}$ and $\{$*rac*-$Co(bzo_3[12]hexaeneN_3)_2^{3+},X^-\}$ systems indicate that they have similar intrinsic electron-exchange barriers. The observed spectra further support the contention[28b,c] that the ion-pair charge-transfer energy gaps for some $\{Co((bzo)_3[12]hexaeneN_3)_2^{3+},X^-\}$, $\{Ru(NH_3)_6^{3+},X^-\}$, and $\{Co(phen)_3^{3+},X^-\}$ species are sufficiently low that these charge-transfer states could influence to some extent the observed electron-transfer rates.

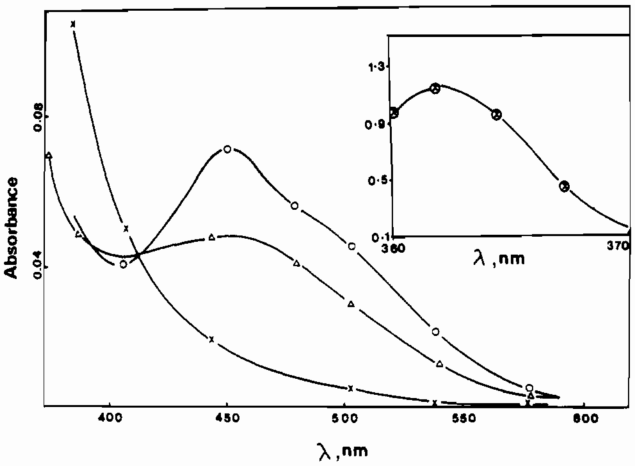


Figure 2. Illustration of charge-transfer (difference) spectra for various ion pairs at 0.5 M ionic strength ($NaCF_3SO_3$): $\{Ru(NH_3)_6^{3+},I^-\}$, △; $\{$*rac*-$Co((bzo)_3[12]hexaeneN_3)_2^{3+},I^-\}$, ○; $\{Co(phen)_3^{3+},I^-\}$, × and ⊗ (inset).

Whereas the energies of the charge-transfer absorption are calculable by using some experimental parameters,[52] the intensities of such absorptions are not easily assessed for the systems reported in this study. Similarly, the outer-sphere association constants are also generally estimated from Col-

---

(51) (a) Reuveni, A.; Malatesta, V.; McGarvey, B. R. *Can. J. Chem.* **1977**, *55*, 70. (b) McGarvey, B. R. *Can. J. Chem.* **1975**, *53*, 2498.

(52) Endicott, J. F. In "Concepts in Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; p 81.

Table II. Anion Dependencies of Bimolecular Rate Constants for Co(III) Electron-Transfer Reactions (25 °C)

anion (X^-)	$[X^-]$, M	$10^{-4}k_{sec}$,[a] $M^{-1}\,s^{-1}$	anion (X^-)	$[X^-]$, M	$10^{-4}k_{sec}$,[a] $M^{-1}\,s^{-1}$
A. $Co(OH_2)_6^{3+} + Fe(phen)_3^{2+}$					
$CF_3SO_3^-$		1.1 ± 0.1	Br^-	0.15	9.8 ± 0.6[b]
Cl^-	0.10	2.5 ± 0.2[b]		0.20	13.8 ± 1[b]
	0.15	3.8 ± 0.3[b]		0.25	15.8 ± 1[b]
	0.20	4.9 ± 0.4[b]		0.30	17.8 ± 1[b]
	0.25	6.2 ± 0.5[b]	NCS^-	0.0125	5 ± 0.3[b]
	0.30	7.7 ± 0.6[b]		0.025	12.5 ± 0.8[b]
Br^-	0.10	7.4 ± 0.4[b]		0.050	23 ± 1[b]
B. *rac*-$Co((bzo)_3[12]hexaeneN_3)_2^{3+} + Co(sep)^{2+}$					
$CF_3SO_3^-$		0.051 ± 0.002	NO_2^-	0.25	1.1 ± 0.1
I^-	0.13	0.10 ± 0.01	ascorbate	0.05	0.62 ± 0.07
	0.25	0.17 ± 0.015		0.08	0.80 ± 0.05
	0.40	0.28 ± 0.02		0.10	1.1 ± 0.1
NO_2^-	0.05	0.26 ± 0.02		0.15	1.4 ± 0.1
	0.13	0.70 ± 0.08			
C. *rac*-$Co((bzo)_3[12]hexaeneN_3)_2^{3+} + Ru(NH_3)_6^{2+}$					
$CF_3SO_3^-$		0.14 ± 0.01	NO_2^-	0.25	0.17 ± 0.02
I^-	0.10	0.15 ± 0.02	ascorbate	0.05	0.18 ± 0.03
	0.25	0.16 ± 0.01		0.10	0.22 ± 0.03
NO_2^-	0.05	0.16 ± 0.01		0.15	0.26 ± 0.03
D. $Co(phen)_3^{3+} + Co([9]aneN_3)_2^{2+}$					
$CF_3SO_3^-$		5.2 ± 2	I^-	0.10	13 ± 1
I^-	0.01	6.8 ± 0.2	ascorbate	0.005	15 ± 1
	0.05	11 ± 1		0.010	27 ± 1
	0.08	12 ± 1			

[a] See eq 9. [b] In the absence of $Fe(phen)_3^{2+}$, k_3 = 28 ± 2, 30 ± 2, and 250 ± 10 $M^{-1}\,s^{-1}$, respectively, for X = Cl, Br, and NCS NCS.

oumbic models,[53,54] and for the 3+,1− couples investigated, one would expect similar values of K_{os} after allowing for the differences in the sizes of the Co(III) reagents. However, the values estimated in this study for $\{Co(phen)_3^{3+},X^-\}$ (37 (NCS), 40 (I), 35 (ascorbate), and 10 (NO_2) M^{-1} in 0.1 M $NaCF_3SO_3$) are 1 order of magnitude larger than those observed for $\{Co((bzo)_3[12]hexaeneN_3)_2^{3+},X^-\}$ (3.3 ± 0.3 (NCS), 2.5 ± 0.6 (I), and 1.7 ± 0.6 (NO_2) M^{-1} at 0.5 M $NaCF_3SO_3$ in 20% methanol). The larger cation size and more concentrated ionic strength conditions for the $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ systems would favor smaller magnitudes of K_{os} compared to those for $\{Co(phen)_3^{3+},X^-\}$ while the smaller mean dielectric constant arising from the methanolic composition of the solvent medium would be expected to increase the magnitude of K_{os} for the $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ systems, on the basis of Coloumbic models.[53,54] However, certain specific interactions resulting from forces such as hydrogen and/or hydrophobic bonding, extents of solvation of counterions, etc., often cause deviations from Coloumbic models.[55] Therefore, in the present study, the association constants, K_{os}, estimated were used only to obtain the relative rate constants, referred to $\{Co^{III},CF_3SO_3^-\}$ ion pairs. The estimated values of K_{os} for both $\{Co(phen)_3^{3+},X^-\}$ and $\{Co((bzo)_3[12]hexaeneN_3)_2^{3+},X^-\}$ systems indicate that ion-pair saturation is effective in both systems to 30–90% for the concentrations of X^- used. On the other hand, the experimental difficulties arising from relatively rapid reactions of $\{Co(H_2O)_6^{3+},X^-\}$ (X = NCS, Br, Cl) precluded direct measurements of the ion-pair association constants using spectrophotometric methods. The values of K_{os} relevant to the kinetic conditions may also be estimated by analyzing the variations of bimolecular rate constants, k_{sec}, given in Table II for (5)–(7) according to

$$k_{sec} = \frac{k_2 + k_1 K_{os}[X^-]}{1 + K_{os}[X^-]} \tag{9}$$

where k_1 and k_2 are obtained from

$$\{Co^{III},X^-\} + R \xrightarrow{k_1} Co(II) + X^- + P$$

$$Co(III) + R \xrightarrow{k_2} Co(II) + P$$

and where

$$K_{os} = [\{Co^{III},X^-\}]/[Co(III)][X^-]$$

The rate coefficients labeled as k_{II} in Table III have been obtained by dividing the observed pseudo-first-order rate constants by [reductant]. The values obtained for K_{os} by using kinetic and spectrophotometric methods agreed to within 50% for $\{Co(phen)_3^{3+},X^-\}$ systems and within a factor of 5.0 for the $\{Co((bzo)_3[12]hexaeneN_3)_2^{3+},X^-\}$ systems. The proportion of the kinetically relevant species may well be different from that detected by spectrophotometric methods, so the agreement between the methods is reasonable.[56] For the $\{Co(H_2O)_6^{3+},X^-\}$ couples, however, no reliable estimate of the outer-sphere association constant may be obtained by either optical or kinetic methods since $(1 + K_{os}[X^-]) \sim 1$ for those systems. Only an upper limit of 0.5–0.7 M^{-1} may be estimated under the experimental conditions employed in the present study judging from the lack of curvature in the plots of rate constant data described in the later section.

Kinetic Studies. (a) $Co(H_2O)_6^{3+}$–$Fe(phen)_3^{2+}$ Systems. Bimolecular rate laws have already been established for the reaction of $Co(H_2O)_6^{3+}$ with $Fe(phen)_3^{2+}$ in perchlorate media.[45] Similarly, the reactions of $Co(H_2O)_6^{3+}$ with the anions Cl^-, Br^-, and NCS^- have also been investigated and bimolecular rate constants reported.[43,44] Our results, obtained in 2.0 M ($HClO_4$ + $NaCF_3SO_3$) media (Table II; Table S-I[57]), viz. (1.1 ± 0.1) × 10^4, 28 ± 2, 30 ± 2, and 250 ± 10 $M^{-1}\,s^{-1}$, respectively, for the $Co(H_2O)_6^{3+}$ oxidations of $Fe(phen)_3^{2+}$, Cl^-, Br^-, and NCS^-, are in satisfactory agreement with rate laws and bimolecular rate constants previously reported.[43-45] Since the $Co(H_2O)_6^{3+}$–X^- reactions are known to occur by a mechanism in which X^- initially forms an inner-sphere complex with Co(III), our investigations of the outer-sphere effects of X^- on the $Co(H_2O)_6^{3+}$–$Fe(phen)_3^{2+}$ reaction required the lifetime for the Co(III)–Fe(II) reaction to be much smaller than that for the inner-sphere complexation of X^- with Co(III). Therefore, the range of the concentrations of X^- and $Fe(phen)_3^{2+}$ over which the anion effects could be investigated was necessarily limited (see Table S-I[57]). It was, however, evident that the experimental data gave a satisfactory fit to the rate law

$$k_{obsd} = k_3[X^-] + (k_4 + k_5[X^-])[Fe(phen)_3^{2+}]$$

Values of k_3 and k_4 were determined for $[Fe(phen)_3^{2+}] = 0$ and $[X^-] = 0$, respectively. Typical plots of $(k_{obsd} - k_3[X^-])[Fe(phen)_3^{2+}]^{-1}$ against $[X^-]$ are shown in Figure 3, for X = NCS, Cl, or Br. It is evident from Figure 3 that (a) the bimolecular rate constants for this reaction are sensitive to the

---

(53) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

(54) Margerum, D. W.; Cayley, G. R.; Weaterburn, D. C.; Pasenkopf, G. K. *ACS Monogr.* **1978**, *No. 174*, 1.

(55) Rorabacher, D. B. *ACS Symp. Ser.* **1982**, *No. 175*, 34.

(56) Even for spherical ions the necessary compromise between maximum direct donor–acceptor overlap (α^0 in eq 10) and the maximum CT perturbation (the second-order term in eq 10) will tend to favor some ion-pair geometries over others. A wide distribution of geometries (including variations in ion–ion distances) will contribute to the CT spectrum, and from these considerations alone one expects somewhat different values of K_{os} from the two kinds of determinations. However, $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ is more nearly cylindrical than spherical, and one expects distinctly different "contact sites", axial and equatorial, for ion association. It seems very likely that one of these (e.g., equatorial association) has a much larger kinetic effect than the other, while the spectroscopic discrimination is likely to be small.

(57) Supplementary material.

Table III. Rate Parameters and Charge-Transfer Energy Gaps for Anion-Assisted Reductions of Cobalt(III) Complexes

reaction system	X	ionic strength, M	$10^{-4}k_{III}$,[a] $M^{-2}\,s^{-1}$	$10^{-4}k_{II}$, $M^{-1}\,s^{-1}$	$1/\Delta E_{CT}^{\ddagger}$,[b] eV^{-1}	$-\ln(k_{II}/k_{ad}$ (calcd))
$\{Co(OH_2)_6^{3+},X^-\} + Fe(phen)_3^{2+}$	Cl	2.0	22 ± 6	73[c]	0.65[d]	2.62
	Br	2.0	59 ± 12	197[c]	1.01[d]	1.62
	NCS	2.0	430 ± 80	430[c]	1.61[d]	0.84
$\{Co(phen)_3^{3+},X^-\} + Co([9]aneN_3)_2^{2+}$	I	0.10	300 ± 20	10 ± 1[e]	0.64[d]	4.4
	ascorbate	0.10	2250 ± 200	113 ± 10[e]	1.13[d]	2.02
$\{Co((bzo)_3[12]hexaeneN_3)_2^{3+},X^-\} + Co(sep)^{2+}$	I	0.50	0.50 ± 0.05	0.25[f]	0.66[g]	3.44
	NO_2	0.50	4.7 ± 0.5	2.35[f]	0.89[g]	1.20
	ascorbate	0.50	10 ± 1	5.0[e]	1.22[d]	0.43

[a] $k_{III} = k_1K_{os}$ in eq 9; all measurements at 25 °C. [b] Based on eq 12. [c] With $K_{os} = 0.3\ M^{-1}$ for the Cl^- and Br^- ion pairs and $K_{os} = 1.0\ M^{-1}$ for NCS^-; based on $Cr(OH_2)_6^{3+}$ and $Cr(NH_3)_5OH_2^{3+}$ ion-pair constants. [d] Calculated from estimated values of $^*E_{CT}$ from Table I. [e] Based on the kinetically determined value of K_{os} from Table I. [f] From $K_{os} = 2\ M^{-1}$ based on the spectrophotometric determination (Table I). [g] Calculated with the observed values of $^*E_{CT}$ from Table I.

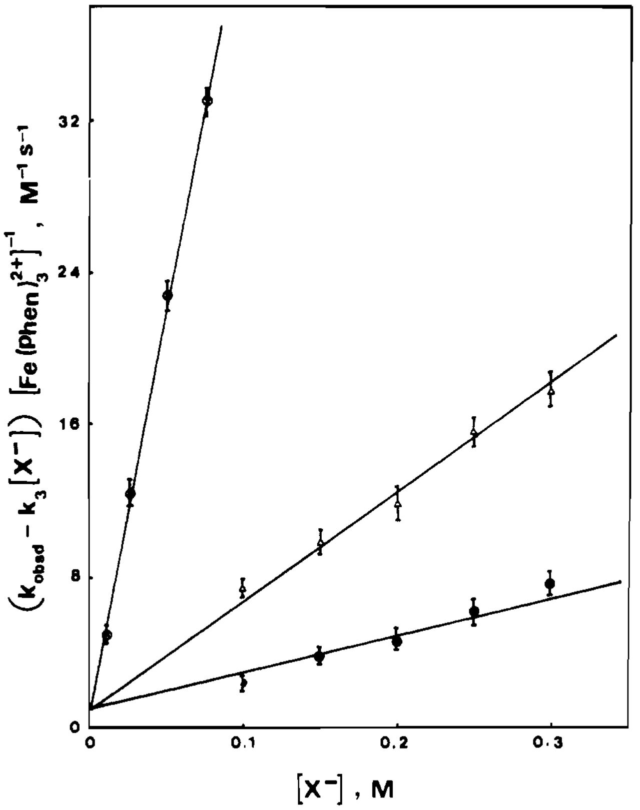


Figure 3. Plot of bimolecular rate constants for the reaction of $Co(H_2O)_6^{3+}$ with $Fe(phen)_3^{2+}$ in the presence of Cl^- (●), Br^- (▲), and NCS^- (○) as functions of $[X^-]$ (2.0 M ionic strength ($HClO_4 + NaCF_3SO_3$); $[H^+] = 1.0$ M).

nature of the medium, (b) ion-pair saturation is not achieved for $\{Co(H_2O)_6^{3+},X^-\}$ under experimentally accessible $[X^-]$, and (c) the value of the ion-pair association constants appropriate to $\{Co(H_2O)_6^{3+},X^-\}$ systems is $<1.0\ M^{-1}$ (as seen from the lack of curvature in Figure 3). Therefore, the third-order rate coefficients k_5, observed for the $Co(H_2O)_6^{3+}$–$Fe(phen)_3^{2+}$ reaction in NCS^-, Cl^-, and Br^- media, are listed in Table III, along with similar parameters denoted as k_{III}, for the other systems investigated in this study. The dependence of the bimolecular rate constants, $(k_{obsd} - k_3[X^-])[Fe(phen)_3^{2+}]^{-1}$, for the $Co(H_2O)_6^{3+}$–Fe(II) reaction on the nature and the concentration of anions in the medium demonstrates qualitatively similar effects to those we already reported for $Co(phen)_3^{3+} + Co(sep)^{2+}$ systems.[28b,c]

(b) $Co(phen)_3^{3+}$–$Co([9]aneN_3)_2^{2+}$ Systems. Precise pseudo-first-order behavior was observed for the reaction of $Co(phen)_3^{3+}$ with $Co([9]aneN_3)_2^{2+}$ in the various media. The pseudo-first-order rate constants observed, k_{obsd}, are listed in Table S-II.[57] The bimolecular rate constants, $k_{obsd}[Co([9]aneN_3)_2^{2+}]^{-1}$ in Table II show a dependence on the nature and the concentrations of the anions in the medium. The values of $k_5'K_{os}$, K_{os}, and k_4' were obtained from the dependence of $k_{obsd}[Co(II)]^{-1}$ on $[X^-]$, from

$$k_{obsd}[Co(II)]^{-1} = \frac{k_4' + k_5'K_{os}[X^-]}{1 + K_{os}[X^-]}$$

where the rate and equilibrium parameters have been defined above. The value of k_4' may be obtained from independent measurements with $[X^-] = 0$. From the values of K_{os} listed in Table I, k_5' may be evaluated, which are 5.2×10^4 (TFMS), 10×10^4 (I^-), and $113 \times 10^4\ M^{-1}\ s^{-1}$ (ascorbate). Under identical conditions, the $Ru(NH_3)_6^{2+}$ reactions with $Co(phen)_3^{3+}$ were relatively insensitive to the nature and concentration of anions X^- in the medium.[28b,c] This indicates that the $Co(phen)_3^{3+}$–$Co([9]aneN_3)_2^{2+}$ reaction is relatively nonadiabatic and that charge-transfer interactions with environmental species can increase the reaction rate.

(c) *rac*-$Co((bzo)_3[12]hexaeneN_3)_2^{3+}$–$Co(sep)^{2+}$ and –$Ru(NH_3)_6^{2+}$ Reactions. The pseudo-first-order rate constants for the reductions of $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ (both meso and racemic isomers) are listed in Table S-III[57] as functions of both [reductant] and $[X^-]$, when X = I, NO_2, and ascorbate and reductant = $Co(sep)^{2+}$ or $Ru(NH_3)_6^{2+}$. Due to the limited solubility of the reduction products from the *meso*-$Co((bzo)_3[12]hexaneN_3)_2^{3+}$ isomer, only a limited amount of work was carried out on that system. The bimolecular rate constants, k_{sec}, obtained from $k_{obsd}[reductant]^{-1}$ for the racemic isomer showed a much stronger dependence on the nature and the concentration of X^- for the reaction with $Co(sep)^{2+}$ than with $Ru(NH_3)_6^{2+}$ (see Table II). Consistent with the small values of the ion-pair association constant, K_{os}, reported in Table I and obtained by spectrophotometric means, the kinetic data also failed to reveal appreciable ion-pair saturation for the concentrations of X^- investigated. Therefore, only the third-order rate coefficients for the reaction of *rac*-$Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ are listed in Table III. In the absence of reliable estimates of K_{os}, quantitative interpretation is difficult. Qualitatively, the ratios of third-order rate coefficients listed in Table III, viz. $k_3[X]/k_3[I^-]$ of 9.4 and 20.0 when X = NO_2 and ascorbate, respectively, for the $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ system are comparable to the rate ratios observed for the better characterized $Co(phen)_3^{3+}$–$Co(sep)^{2+}$ reaction; viz. 1.2 and 14 for NO_2^- and ascorbate, respectively.

Discussion

In earlier work[28b,c] it was reported that the $Co(polypyridyl)_3^{3+}$–$Co(sep)^{2+}$ reactions were exceptionally sensitive to the anionic composition of the reaction medium, and this sensitivity was attributed to the ion-pair charge-transfer perturbations of donor–acceptor mixing in reactions that are relatively nonadiabatic ($\kappa_{el} \ll 1$). In the present study qualitatively comparable effects of ion-pair perturbations have been found for three additional reactant combinations: (a) $Co(phen)_3^{3+}$–$Co([9]aneN_3)_2^{2+}$; (b) $Co(H_2O)_6^{3+}$–$Fe(phen)_3^{2+}$; (c) $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$–$Co(sep)^{2+}$. For the $Co(phen)_3^{3+}$ and $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ oxidants it has been demonstrated that the anion effects are a characteristic of the use of a cobalt(II) reductant and that no comparable variation in the rate constant with the nature of X^- is observed when the $Ru(NH_3)_6^{2+}$ reductant is used. The electrochemical studies on $Co((bzo)_3[12]hexaeneN_3)_2^{3+,2+}$ systems revealed that the Co(III)–Co(II) couple is isoenergetic with the $Ru(NH_3)_6^{2+,3+}$ couple. Therefore, assuming Marcus behavior[14] for the $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$–$Ru(NH_3)_6^{2+}$ reaction, we obtain a self-exchange rate constant of $10^{3.5 \pm 0.5}$ M^{-1} s^{-1} for the $Co((bzo)_3[12]hexaeneN_3)_2^{3+,2+}$ couple. It is of interest that a self-exchange rate constant of $\sim 10^2$ M^{-1} s^{-1} has been estimated for $Co([9]aneN_3)_2^{3+,2+}$ couple by Wieghardt and co-workers,[58] although Co(II) is high spin. The relatively similar magnitudes of self-exchanges for $Co((bzo)_3[12]hexaeneN_3)_2^{3+,2+}$ and $Co([9]aneN_3)_2^{3+,2+}$ systems suggest that spin multiplicity changes do not make the major contributions to the self-exchange processes in these systems. However, there does seem to be an electronic constraint for the cross-reactions involving $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ and $Co(sep)^{2+}$ as inferred from the sensitivity of bimolecular rates to the nature and concentrations of anions in the medium. The new results add support to our hypotheses[28b,c] that (a) simple electron-transfer cross-reactions with large ΔX and ν_{nu} are frequently nonadiabatic and (b) the rates of nonadiabatic electron-transfer reactions should be very sensitive to perturbation by polarizable constituents of the reaction medium.

It must be observed that we have used deviations from classical Marcus behavior as an operational criterion for nonadiabaticity. Since the classical Marcus–Hush equations can be interpreted as a direct consequence of the intersection of zero order, nuclear potential energy surfaces, deviations from such expectation could be the result of coupled nuclear and electronic motion in the intersection region. This view will be explored elsewhere.[59]

The present level of theoretical treatment and experimental resolution of these phenomena does not permit quantitative comparisons between the systems studied. However, the qualitative differences from system to system are remarkably consistent with expectation based on eq 2 and 3. Since these systems are providing new clues about the nature of the donor–acceptor electronic coupling (e.g., as in ν_{el} or κ_{el}), the issues are developed with some care below.

An analysis of the rate constant in terms of eq 1, or its equivalent, is based on the separation of electronic and nuclear coordinates (Born–Oppenheimer approximation) and evaluation of the Franck–Condon and tunneling factors on the basis of the zero-order potential energy surfaces. Coupling of these zero-order surfaces in the neighborhood of their nominal crossing point can be formulated in terms of an electron-exchange perturbation.[18,32,60] The electronic matrix element describing the coupling of zero-order surfaces is most simply written in the form CS_{ij}.[32,61-64] In the asymptotic, or spherical, wave limit the overlap integral, S_{ij}, takes the form of the exponential term in eq 3. It is conceptually attractive to represent the electronic frequency as a product of separate orbital overlap and Hamiltonian coupling terms, as in eq 3. However, such a separation of contributions to the electronic matrix element is a limiting, simple form since the overlap and coupling terms are not entirely separable in the integrations over configuration coordinates. Nevertheless, eq 3 is a useful starting place in a perturbation approach to treating contributions to the electronic matrix element, but it is not always convenient to treat the coupling and overlap terms separately when simple perturbations are introduced. Thus, we have found it convenient to treat the ion-pair, charge-transfer enhancements of outer-sphere electron-transfer rates in terms of a Mulliken-type induced dipole moment that increases the effective donor–acceptor orbital radii. This treatment of the effect of environmental species is roughly analogous to Newton's inference that the electrons of the coordinated ligands influence values of α for different approaches of donor and acceptor.[65] In a more general way, our approach is analogous to the second-order perturbations of the zero-order potential energy surfaces by high-energy intermediate states, as treated by Kuznetsov and Ulstrup.[60] However, for reasons of convenience in discussing the observations, we have in effect treated all deviations from behavior predicted by the zero-order functions, as manifested in the classical Marcus equations, as contributions to κ_{el}.

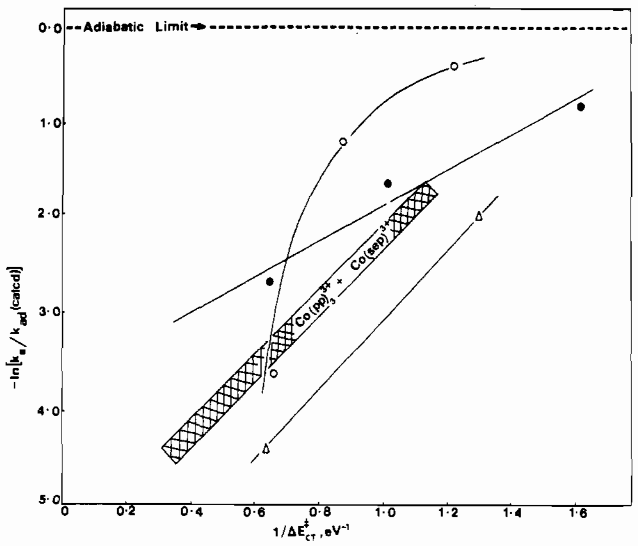


Figure 4. Effect of ion-pair charge-transfer perturbations on bimolecular rate constants. Rate constants, k_{II}, and $1/\Delta E_{CT}^*$ are from Table III; "adiabatic rate constants", k_{ad}, are calculated from the Marcus square root relation and self-exchange parameters. Reactions: $Co(H_2O)_6^{3+}$ + $Fe(phen)_3^{2+}$, ●; *rac*-$Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ + $Co(sep)^{2+}$, ○; $Co(phen)_3^{3+}$ + $Co([9]aneN_3)_2^{2+}$, △. A representation of the similar correlation for $Co(polypyridyl)_3^{3+}$ + $Co(sep)^{2+}$ reactions (from ref 28c) is included for comparison.

The effect of ionizable anions can be treated as a first-order perturbation of α^{-1} in eq 3, such that

$$\alpha = \alpha^0 - (\alpha^0)^2 \sum_i \frac{C_i F_i(\alpha^0)}{\Delta E_{CT}(i)} + \dots \qquad (10)$$

where $(\alpha^0)^{-1}$ is the unperturbed radial parameter, ΔE_{CT} is the charge-transfer excited state–ground state energy gap, $F(\alpha^0)$ is the zero-order redox field intensity, C is a constant of proportionality, and the summation is over all the charge-transfer interactions. (Note that for electronic charge e, an induced dipole moment, $eC_iF_i(\alpha^0)/\Delta E_{CT}(i)$ can be associated with each CT(i) interaction). For electron-transfer reactions one must consider the effect of the CT perturbation on the

---

(58) Weighardt, K., personal communication.
(59) Ramasami, T.; Endicott, J. F., work in progress.
(60) Kuznetsov, A. M.; Ulstrup, J. *J. Chem. Phys.* **1981**, *75*, 20.
(61) For our purposes, C can be treated as a constant characteristic of the system; i.e., $C \simeq k_{WH}(E_R^* + E_P^*)/2$, where E_R^* and E_P^* are the energies of the reactants and products evaluated at the crossing of zero-order surfaces and k_{WH} is the Wolfsberg–Helmholtz constant.[62-64]
(62) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 295.
(63) Wolfsberg, M.; Helmholtz, L. *J. Chem. Phys.* **1952**, *20*, 837.
(64) Larsson, S. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1375.
(65) Newton, M. D. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 110.

reactants with nuclear coordinates appropriate to the crossing point of the simple Born–Oppenheimer surfaces. The vertical energy gap, ΔE_{CT}^*, between the Franck–Condon transition state and the charge-transfer excited state may be expressed[28c] as

$$\Delta E_{CT}^* = E_{CT}^* - \Delta G^*(FC) + \left[\frac{\Delta G^*(FC)}{\lambda} - 2\left(\frac{\Delta G^*(FC)}{\lambda}\right)^{1/2}\right][E_{CT}^* - \Delta G^\circ\{Co,X\}] \qquad (11)$$

on the assumption of parabolic surfaces and similar ground-state and excited-state force constants (and other assumptions noted previously),[28c] where $\Delta G^*(FC)$ is the free energy difference between the ground state and the crossing point, E_{CT}^* is the vertical energy gap between the CT excited state and the ground state, λ is the usual Marcus[14] reorganizational parameter, and $\Delta G^\circ\{Co,X\}$ is the standard free energy difference of the Co(III)–Co(II) and $X^{-,0}$ couples. For a single, low-energy CT perturbation, α varies inversely with ΔE_{CT}^*.

To facilitate the representation of our results in Figure 4, we have used the rate constant ratios, k_1/k_{ad}, where k_{ad} is our estimate of adiabatic cross reaction rate constant (i.e., k/κ_{el} from eq 1). These values of k_{ad} are based on the Marcus cross-relation, thermodynamic parameters, and rate constants either known (5 and 20 $M^{-1}\ s^{-1}$, respectively, for $Co(sep)^{3+,2+}$ [29] and $Co(phen)_3^{3+,2+}$ [66]), estimated (75 ± 25 $M^{-1}\ s^{-1}$ for $Co([9]aneN_3)_2^{3+,2+}$ from cross-reactions determined by us or by Wieghardt and co-workers[58]), or calculated from ground-state structural parameters ($8 \times 10^{-6}\ M^{-1}\ s^{-1}$ [22b] for $Co(H_2O)_6^{3+,2+}$). Values of K_1 have been corrected to unit activity of the appropriate ion pair either by using the spectroscopically determined K_{os}, by fit of the kinetic data for $Co(phen)_3^{3+}$ and $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ reactions, or by applying values of the ion-pair association constants determined for $Cr(H_2O)_6^{3+}$ or $Cr(NH_3)_5OH_2^{3+}$ [67,68] to the $\{Co(H_2O)_6^{3+},X^-\}$ ion pairs.

Given the uncertainties in parameters for the present systems, it is gratifying that the effect of charge-transfer perturbations on the $Co(OH_2)_6^{3+}$–$Fe(phen)_3^{2+}$, $Co(phen)_3^{3+}$–$Co([9]aneN_3)_2^{3+}$, and $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$–$Co(sep)^{2+}$ reactions are similar in kind to those found earlier[28c] for the $Co(polypyridyl)_3^{3+}$–$Co(sep)^{2+}$ reactions. The differences between the systems as indicated in Figure 4, are conveniently discussed in terms of the "sensitivity" to CT perturbation (or the approximate slopes) and the apparent intercepts (for $1/\Delta E_{CT}^* \rightarrow 0$). In this approach, the intercept varies as the magnitude of the transmission coefficient in the absence of any charge-transfer perturbation in α. The limited data suggest that the approximate intercepts decrease in the order ($Co(OH_2)_6^{3+}$ + $Fe(phen)_3^{2+}$) > ($Co(phen)_3^{3+}$ + $Co(sep)^{2+}$) > ($Co(phen)_3^{3+}$ + $Co([9]aneN_3)_2^{2+}$) ≥ ($Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ + $Co(sep)^{2+}$). The ligands $[9]aneN_3$ and $(bzo)_3[12]hexaeneN_3$ are relatively bulky, and the cobalt complexes we have used increase in mean (van der Waals contact) diameter in the order $Co(OH_2)_6^{3+} < Co(sep)^{3+,2+} < Co([9]aneN_3)_2^{3+,2+} \leq Co(phen)_3^{3+,2+} < Co((bzo)_3[12]hexaeneN_3)_2^{3+,2+}$. The ordering of apparent intercepts, $\ln (k_{II}(obsd\ (X^-))/k_{ad}(calcd))_0$ for $1/\Delta E_{CT}^* \rightarrow 0$, in Figure 4 follows the order expected variations in r_{DA} (see eq 2 and 3), but some additional factors may contribute to the $Co(OH_2)_6^{3+}$–$Fe(phen)_3^{2+}$ reaction. There is very little difference in bond length between $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$, resulting a relatively small effective value of ν_{nu}. Furthermore, the low-energy metal to ligand charge-transfer states of $Fe(phen)_3^{2+}$ would, in our analysis, contribute to a relatively large value of α^{-1}. The combination of these factors should make the $Co(OH_2)6^{3+}$–$Fe(phen)_3^{2+}$ reaction relatively more adiabatic than the other reactions considered here. The sensitivity of the variations in $\ln k_1$ to E_{CT}^{-1} should, in principle, be functionally dependent on the transition moment of the $X^- \rightarrow$ Co(III) CT transition (i.e., through C_i in eq 11). For a reducing agent R, our very simple model treats the perturbation in terms of increases in electron density along the Co(III)–R internuclear axis. The strong distance dependence of eq 3 will tend to force rather intimate contact of oxidant and reductant (as at van der Waals radii). For the three-center, Co(III)–R–X^-, interactions, eq 3, 11, and 12 should be averaged over all arrangements of the reaction partners. For weak CT perturbations, the first term will dominate eq 11, dictating close Co(III)–R contact; thus, it is likely that the effective induced $X^- \rightarrow$ Co(III) dipole moment vectors will subtend acute angles with respect to the Co(III)–R axis. The slopes of the correlations of $\ln k_1$ with E_{CT}^{-1} can then be expected to depend on the magnitude of the projection of the induced dipole moment along the Co(III)–R axis. If everything else were held constant (e.g., C_i, $F_i(\alpha^0)$, α^0) and in the simplest of models, the larger the Co(III) oxidant the larger should be the projection of the induced dipole along the Co(III)–R axis and the greater sensitivity to CT perturbations one would expect, more or less as observed in Figure 4. The similar changes in $k_{11}/k_{ad}(calcd)$ found for similar values of ΔE_{CT}^* in the $Co(phen)_3^{3+}$–$Co(sep)^{2+}$ and $Co(phen)_3^{3+}$–$Co([9]aneN_3)_2^{2+}$ reactions are supportive of our argument that the principle perturbation introduced in these systems is the variation in energy of the $\{Co(phen)_3^{3+},X^-\} \rightarrow \{Co(phen)_3^{2+},X\cdot\}$ charge-transfer transition. The weaker dependence on CT perturbations found for the ($Co(OH_2)_6^{3+}$ + $Fe(phen)_3^{2+}$) reaction and the very dramatic dependence found for the ($Co((bzo)_3[12]hexaeneN_3)_2^{3+}$ + $Co(sep)^{2+}$) reaction are consistent with smaller and larger ground-state charge separations respectively, in the Co(III) ion pairs (compared to $\{Co(phen)_3^{3+},X^-\}$).

Conclusions

In this study we have reported on the factors affecting the electronic matrix element in three apparently nonadiabatic electron-transfer reactions. On the basis of our studies to date of such classes of reactions, the following points are emerging as general features:

1. Two criteria seem to be important for the observation of nonadiabaticity in simple electron-transfer reactions: (a) The effective frequencies of nuclear motion along the critical configuration coordinate must be reasonably large ($\nu_{nu} > 10^{12}$ s^{-1}), and this nearly always requires large differences in reactant and product bond lengths. (b) Donor–acceptor overlap must be poor ($r_{DA} > 2\alpha$).

2. Even when these criteria are met, the reaction rates may be more adiabatic than expected owing to enhancements of donor–acceptor overlap promoted by the mixing of low-energy charge-transfer states with the zero-order ground state wave functions.

3. The charge-transfer perturbations of nonadiabatic reaction rates are conveniently discussed in terms of a "super-exchange" like contribution to the electron-exchange integral. The quantum-mechanical exchange interaction may dominate the mixing of donor and acceptor wave functions in the electron-transfer transition state. Since the effects have been formulated in terms of deviations from classical Marcus behavior, the observed nonadiabaticities may actually originate from the coupling of nuclear and electronic motion in the region of crossing from the reactant to the product potential energy surfaces. However, the perturbations investigated are electronic and do significantly alter reaction patterns. At this

---

(66) Farina, R.; Wilkins, R. G. *Inorg. Chem.* **1968**, *7*, 514.
(67) Postmus, C.; King, E. L. *J. Phys. Chem.* **1955**, *59*, 1208; 1216.
(68) Duffy, N. V.; Earley, J. *J. Am. Chem. Soc.* **1967**, *89*, 272.

stage of study of such systems, the exchange formulation of the perturbations has been very useful.

Registry No. $Ru(NH_3)_6^{3+}Cl^-$, 53293-35-9; $Ru(NH_3)_6^{3+}Br^-$, 53293-36-0; $Ru(NH_3)_6^{3+}NCS^-$, 91760-60-0; $Ru(NH_3)_6^{3+}I^-$, 53293-37-1; $Co(H_2O)_6^{3+}$, 15275-05-5; $Co(H_2O)_6^{3+}Cl^-$, 91760-61-1; $Co(H_2O)_6^{3+}Br^-$, 91760-62-2; $Co(H_2O)_6^{3+}NCS^-$, 91760-63-3; $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$, 47872-01-5; $Co((bzo)_3[12]hexaeneN_3)_2^{3+}I^-$, 91839-93-9; $Co((bzo)_3[12]hexaeneN_3)_2^{3+}NO_2^-$, 91839-94-0; $Co((bzo)_3[12]hexaeneN_3)_2^{3+}NCS^-$, 91839-95-1; $Co((bzo)_3[12]hexaeneN_3)_2^{3+}X^-$ (X^- = ascorbate), 91839-96-2; $Co(phen)_3^{3+}$, 18581-79-8; $Co(phen)_3^{3+}I^-$, 31415-56-2; $Co(phen)_3^{3+}NO_2^-$, 86176-93-4; $Co(phen)_3^{3+}Cl^-$, 86163-76-0; $Co(phen)_3^{3+}NCS^-$, 68369-95-9; $Co(phen)_3^{3+}NCS^-$, 68369-95-9; $Co(phen)_3^{3+}X^-$ (X^- = ascorbate), 86163-74-8; $Fe(phen)_3^{2+}$, 14708-99-7; $Co(sep)^{2+}$, 63218-22-4; $Co([9]aneN_3)_2^{2+}$, 91760-59-7.

Supplementary Material Available: Tables of pseudo-first-order rate constants (7 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry and Physics, Karl Marx University, DDR-7010 Leipzig, GDR, and
Department of Molecular Spectroscopy, University of Nijmegen, 6525 ED Nijmegen, The Netherlands

Single-Crystal ^{13}C ENDOR and TRIPLE Resonance Studies on Tetra-*n*-butylammonium Bis(*cis*-1,2-dicyanoethenedithiolato)cuprate(II), $(n\text{-}Bu_4N)_2[Cu(mnt)_2]$

R. KIRMSE,[*†] J. STACH,[†] U. ABRAM,[†] W. DIETZSCH,[†] R. BÖTTCHER,[‡] M. C. M. GRIBNAU,[§]
and C. P. KEIJZERS[*§]

Received February 23, 1984

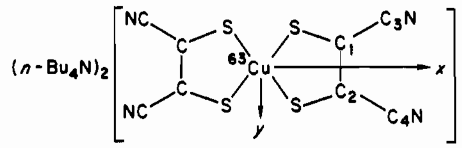
A single-crystal ENDOR study of tetra-*n*-butylammonium bis(*cis*-1,2-dicyanoethenedithiolato)cuprate(II), $(n\text{-}Bu_4N)_2[Cu(mnt)_2]$, is reported. The hyperfine tensors of all ^{13}C nuclei of the complex anion were evaluated. With TRIPLE resonance experiments the signs of the hyperfine couplings could be determined. The coupling constants could be understood with the aid of spin densities, which were obtained from extended Hückel molecular orbital calculations. Especially the inclusion of two- and three-center contributions to these ligand hyperfine couplings but also the TRIPLE experiments are shown to be essential in order to be able to draw conclusions about the electronic structure and the symmetry of the "highly covalent" $[Cu(mnt)_2]^{2-}$ anion.

Introduction

Transition-metal dithiolene complexes have attracted the interest of EPR spectroscopists already for many years because of (i) the high covalency of the metal–sulfur bonds, which is the cause of a large delocalization of the unpaired spin density, (ii) the different metal oxidation states that are stabilized by these ligands and result in various electronic configurations, (iii) the interesting behavior with respect to ligand-exchange reactions, and (iv) the ability to form one-dimensional systems and π-donor–acceptor complexes. Apart from the numerous EPR studies of dithiolene complexes in liquid or frozen solutions, to our knowledge more than 20 single-crystal EPR studies were reported, most of them[1–15] on homoligand complexes, some on donor–acceptor complexes,[16–18] and some on mixed-ligand systems with one dithiolene ligand.[19–23]

In order to characterize the bonding in detail, ligand hyperfine data are needed because they provide direct information about the nature of the electronic ground state and about the extent of electron-spin delocalization over the ligand orbitals. For dithiolene complexes it is very difficult to measure ligand hyperfine interactions with EPR because the only sulfur isotope with nonzero nuclear spin, ^{33}S, has a natural abundance of only 0.74%. Only in a few dithiolene complexes could ^{33}S hyperfine couplings (hfc's) be observed and analyzed.[2,9,11–13,21] The magnetic interactions of the other ligand nuclei–^{13}C, ^{14}N–are too weak to be resolved in the EPR spectra even if ^{13}C-enriched ligands are used.

In this paper we report a single-crystal ^{13}C ENDOR study on tetra-*n*-butylammonium bis(*cis*-1,2-dicyanoethenedithiolato)cuprate(II) (*cis*-1,2-dicyanoethenedithiolato is often called maleonitriledithiolato, mnt^{2-}), $(n\text{-}Bu_4N)_2[^{63}Cu(mnt)_2]$ (I), diamagnetically diluted by the corresponding nickel(II) complex, $(n\text{-}Bu_4N)_2[Ni(mnt)_2]$. The investigation of the ^{13}C hfc's was stimulated by the successful ^{13}C experiments that were recently carried out by us on the complex bis(diethyl-



I

[†] Department of Chemistry, Karl Marx University.

[‡] Department of Physics, Karl Marx University.

[§] University of Nijmegen.

(1) Maki, A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580.

(2) Schmitt, R. D.; Maki, A. H. *J. Am. Chem. Soc.* **1968**, *90*, 2288.

(3) Van Rens, J. G. M.; de Boer, E. *Mol. Phys.* **1970**, *19*, 745.

(4) Kwik, W.; Stiefel, E. I. *Inorg. Chem.* **1973**, *12*, 2337.

(5) Atherton, N. M.; Winscom, C. J. *Inorg. Chem.* **1973**, *12*, 383.

(6) Schlupp, R. L.; Maki, A. H. *Inorg. Chem.* **1974**, *13*, 44.

(7) Van Rens, J. G. M.; Viegers, M. P. A.; de Boer, E. *Chem. Phys. Lett.* **1974**, *28*, 104.

(8) Plumlee, K. W.; Hoffman, B. M.; Ibers, J. A.; Soos, Z. G. *J. Chem. Phys.* **1975**, *63*, 1926.

(9) Kirmse, R.; Dietzsch, W. *J. Inorg. Nucl. Chem.* **1976**, *38*, 255.

(10) White, L. K.; Belford, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 4428.

(11) Kirmse, R.; Dietzsch, W.; Solovev, B. V. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1157.

(12) Kirmse, R.; Stach, J.; Dietzsch, W.; Hoyer, E. *Inorg. Chim. Acta* **1978**, *26*, L53.

(13) Kirmse, R.; Stach, J.; Dietzsch, W.; Steimecke, G.; Hoyer, E. *Inorg. Chem.* **1980**, *19*, 2679.

(14) Duliba, E.; Seebauer, E. G.; Belford, R. L. *J. Magn. Reson.* **1982**, *49*, 507.

(15) Snaathorst, D.; Doesburg, H. M.; Perenboom, J. A. A. J.; Keijzers, C. P. *Inorg. Chem.* **1981**, *20*, 2526.

(16) Schmitt, R. D.; Wing, R. M.; Maki, A. H. *J. Am. Chem. Soc.* **1969**, *91*, 4391.

(17) Wing, R. M.; Schlupp, R. L. *Inorg. Chem.* **1970**, *9*, 471.

(18) Manoharan, P. T.; Noordik, J. H.; de Boer, E.; Keijzers, C. P. *J. Chem. Phys.* **1981**, *74*, 1980.

(19) Dietzsch, W.; Stach, J.; Kirmse, R. *Z. Chem.* **1977**, *17*, 191.

(20) Stach, J.; Kirmse, R.; Dietzsch, W.; Hoyer, E. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 143.

(21) Stach, J.; Kirmse, R.; Dietzsch, W. *Inorg. Chim. Acta* **1979**, *36*, L395.

(22) Kirmse, R.; Böttcher, R.; Keijzers, C. P. *Chem. Phys. Lett.* **1982**, *87*, 467.

0020-1669/84/1323-3333$01.50/0 © 1984 American Chemical Society