reexamined in view of the evident lack of a Bpm bridge in the (Fe, Cu) or (Fe, Zn) heterobinuclears. The binuclear adducts have a half-wave potential for the Fe(II)/Fe(II) couple E = 0.60 V, 700 mV less than that for the mononuclear precursor, which is good evidence that the adducts are discrete entities in solution. The difference in half-wave potentials was attributed to the electronic substituent effect caused by the presence of the M(acac)$_2$.[13] However, this substituent effect is perhaps larger than we could reasonably expect from a Cu(acac)$_2$ weakly linked through Bpm, remote from the iron. On the other hand, adduction to a mac N atom adjacent to the Fe–N bond can and should lead to a greater substituent effect and is therefore more consistent with the electrochemistry.

Acknowledgment. We are grateful to Dr. Lon J. Wilson for making complex I available and to the Research Corp. and the NSF (Grant CHE83-00516) for support.

Supplementary Material Available: Listings of thermal parameters, interatomic distances and angles, least-squares planes, and observed and calculated structure factors and a packing diagram (12 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164-4630

Solvent, Temperature, and Electrolyte Studies on the Electron-Transfer Reaction between Ferrocene and a Cobalt Clathrochelate[1]

DAN BORCHARDT and SCOT WHERLAND*

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The kinetics of the outer-sphere electron-transfer reaction between the clathrochelate Co(dmg)$_3$(BF)$_2^+$ (dmg is the doubly deprotonated ion of dimethylglyoxime) and ferrocene (Fe(Cp)$_2$) have been studied as a function of the Fe(Cp)$_2$ concentration, added electrolyte, and temperature in acetonitrile, acetone, nitrobenzene, and ethylene dichloride. The equilibrium constants and their temperature dependences have been determined through electrochemical measurements. The reaction is first order in each reactant, and the second-order rate constants with no added electrolyte are 1.6×10^4, 8.3×10^3, 3.8×10^4, and 1.8×10^5 M^{-1} s^{-1} in the solvents as listed above. Analysis within the Marcus theory gave self-exchange rate constants for the Co clathrochelate that ranged from 100 M^{-1} s^{-1} in acetone to 2.2×10^4 M^{-1} s^{-1} in ethylene dichloride. The self-exchange and cross-reaction rate constants corrected for the equilibrium constant varied with the dielectric term $(1/D_{op} - 1/D_s)$ but did not agree well with the prediction of the Marcus theory. Addition of n-Bu$_4$NBF$_4$ up to 0.5 M lowered the second-order rate constant by a factor of 5 in acetonitrile and acetone, 19 in nitrobenzene, and 27 in ethylene dichloride. A fit to a rate law employing ion-pairing and activity coefficients gave association constants of 17, 200, 53, and 2.9×10^4 in acetonitrile, acetone, nitrobenzene, and ethylene dichloride, respectively. Temperature dependences with no added electrolyte and with 0.1 M n-Bu$_4$NBF$_4$ gave similar activation parameters for a given solvent. Values of $\Delta H_{12}^{\ddagger}$ fell within the range 6–9 kcal mol^{-1}, and $\Delta S_{12}^{\ddagger}$ values were −13 to −7 cal mol^{-1} deg^{-1}. Calculated self-exchange activation parameters for the cobalt complex varied considerably from solvent to solvent, with $\Delta H_{11}^{\ddagger}$ ranging from 7.3 to 14.1 kcal mol^{-1} and $\Delta S_{11}^{\ddagger}$ ranging from −26 to 3 cal mol^{-1} deg^{-1}, but the $\Delta G_{11}^{\ddagger}$ value varied only 2 kcal mol^{-1}, indicating some compensation. It is concluded that ion pairing decreases electron-transfer reactivity by increasing the electron-transfer distance and by decreasing precursor complex stability, with BF$_4^-$ between the reactants. The transition-state structure is apparently sensitive to the identity of the solvent.

Introduction

The study of the electron-transfer mechanisms employed by transition-metal complexes has been a major field in inorganic chemistry for several decades, but most research has been done on aqueous systems.[2–5] Recently, several investigators[6–8] have reported the effects of varying the solvent on the rates of certain electron-transfer reactions. These studies can be expected to reflect the influence of the solvent on the interaction between the reactants, the actual electron-transfer process, and properties of the reactants such as electrochemical potential and the extent of ion-pair formation. Furthermore, in the case of outer-sphere electron-transfer reactions, reactions in which no bonds are made or broken within the complexes during the reaction, theoretical models are available that make testable predictions about solvent dependences. Within the Marcus theory, one of the more successful and easily applied theories, solvent-dependence data can be used to separate contributions to the total activation energy from the inner-sphere reorganization of the complexes themselves and the outer-sphere reorganization of the solvent.[4,5,9,10] Previous studies have shown that the predictions of the Marcus theory are sometimes obeyed quite precisely, while other cases are not so well modeled.[6–8] Since the model treats the solvent as a dielectric continuum, specific solvent effects and dielectric saturation are possible contributors to the observed deviations.

The system presented here is especially appropriate for detailed solvent-dependence studies. The reaction between

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$Co(dmg)_3(BF)_2BF_4$ (dmg is the doubly deprotonated dimethylglyoxime ion) and ferrocene ($Fe(Cp)_2$) (eq 1) is nec-

$$Fe(Cp)_2 + Co(dmg)_3(BF)_2^+ \overset{K_{eq}}{\rightleftharpoons} Fe(Cp)_2^+ + Co(dmg)_3(BF)_2 \quad (1)$$

essarily outer sphere since both reactants are substitution inert in both oxidation states. Equilibrium constants can be determined from electrochemical measurements since both complexes react reversibly at a platinum electrode. The problem of calculating the charge–charge electrostatic work terms involved in the association of the reactants or products is eliminated since a neutral species is involved in both cases. There is only a small driving force for the reaction in all solvents used, and both reactants are soluble in a variety of media. Also, the solvent effect on the electron self-exchange of $Fe(Cp)_2^{+/0}$ has been measured by Wahl and co-workers,[6] and these data are useful in the Marcus theory analysis.

Four solvents, acetonitrile, acetone, nitrobenzene, and ethylene dichloride, were studied, which cover a range in dielectric constant of 10–37. Temperature and concentration dependences of the rate constants were investigated, and ion-association effects were studied through the addition of tetra-*n*-butylammonium tetrafluoroborate (n-Bu_4NBF_4). This study is a continuation of the work presented in ref 11.

Experimental Section

The cage complex $Co(dmg)_3(BF)_2BF_4$, ferrocene, and the electrolyte n-Bu_4NBF_4 were prepared and purified as previously described.[11] The Co(II) form of the cobalt complex was prepared and recrystallized according to literature procedures.[12] $Fe(Cp(CH_3)_5)_2$ was purchased from Strem and purified by vacuum sublimation.

All solvents were obtained as technical grade and purified.[13] Acetonitrile and ethylene dichloride were distilled from P_2O_5. Acetone was distilled from Drierite. Nitrobenzene was passed over a 0.5-m column of chromatographic alumina and then distilled at less than 1 torr from P_2O_5. The nitrobenzene collected was then fractionally crystallized. All distillations were through a 470-mm Vigreux column, and the solvents were used within 1 day of purification.

Potentials for the ferrocene and $Co(dmg)_3(BF)_2^{+/0}$ couples were measured as described before[11] except for the use of cyclic voltammetry. In some cases the reduced form of the cobalt complex was studied, and the Ag/Ag^+ ion reference electrode was used along with an internal standard, $Fe(Cp(CH_3)_5)_2$. The variation of the reference between solvents was immaterial since the difference in potential of the two couples, $\Delta E_{1/2}$, was the only parameter of interest (eq 2).

$$\Delta E_{1/2} = E_{1/2}(Co) - E_{1/2}(Fe) \quad (2)$$

Potentials were measured in triplicate over a range of 3–30 °C for each solvent.

Rate constants were determined as previously described[11] by using the stopped-flow method and following the signal log (I_{450}/I_{600}) as the reduced form of the cobalt complex ($\epsilon = 5450$ M^{-1} cm^{-1} at 450 nm) was formed. All data were fit to an approach-to-equilibrium rate law, pseudo first order in the forward direction and second order with equal concentrations in the reverse direction, by using the nonlinear least-squares program CURFIT of Bevington[14] and assuming the equilibrium constant calculated from the electrochemical data. All kinetic runs were done in triplicate on one filling of the stopped-flow syringes. For each solvent, the cobalt complex concentration was typically 0.03 mM and the ferrocene concentration was 0.3–6.0 mM. The dependence on ferrocene concentration was performed at 0.1 M n-Bu_4NBF_4 for all solvents except acetonitrile for which it was done with no added electrolyte. Temperature dependences at 0.1 M n-Bu_4NBF_4 (0.5 M n-Bu_4NBF_4 for acetonitrile) and with no added electrolyte were performed over a temperature range of typically 3–30 °C. The dependence on added electrolyte was measured over the range 0–0.5 M n-Bu_4NBF_4.

Table I. Summary of Electrochemical Data for the $Co(dmg)_3(BF)_2BF_4$, $Fe(Cp)_2$ Cross-Reaction in Each Solvent (25 °C)

solvent	$[E_{1/2}(Co) - E_{1/2}(Fe)]$,[a] mV	$\Delta H°$,[b] kcal mol^{-1}	$\Delta S°$,[c] cal mol^{-1} deg^{-1}	K_{eq}
CH_3CN	−28	5.0	15	0.33 ± 0.03
$(CH_3)_2CO$	−49	3.2	7	0.15 ± 0.02
$C_6H_5NO_2$	−45	2.6	5	0.17 ± 0.02
$(CH_2Cl)_2$	−26	1.7	4	0.36 ± 0.03

[a] All values ±2 mV. [b] All values ±0.1 kcal mol^{-1}. [c] All values ±1 cal mol^{-1} deg^{-1}.

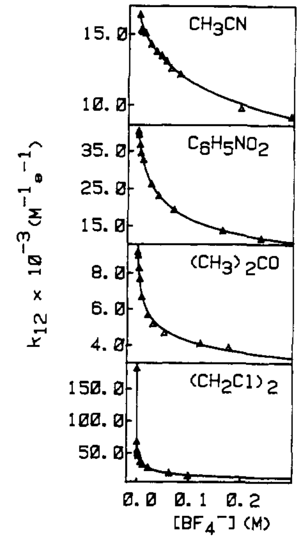

Figure 1. Dependence of k_{12} on added n-Bu_4NBF_4 at 25 °C. Solid lines are results of fits to eq 6 or 8. Table III lists the fit parameters.

All data fitting was done by weighted least-squares techniques with appropriate standard deviations of the measured parameters estimated, or taken from the multiple determinations if these were larger.

Results

The electrochemical data were analyzed as plots of $\Delta E_{1/2}$ vs. temperature using eq 3 to derive values for $\Delta H°$ and $\Delta S°$.

$$\Delta E_{1/2} = -\frac{\Delta H°}{nF} + \frac{T\Delta S°}{nF} \quad (3)$$

$$\Delta E_{1/2} = \frac{RT}{nF} \ln K_{eq} \quad (4)$$

Equation 4 was used to calculate K_{eq} at the temperatures of the kinetic measurements. In the equations, n is the number of electrons transferred, F is the Faraday constant, T is the absolute temperature, and R is the gas constant. The values of $\Delta H°$, $\Delta S°$, and K_{eq} (298 K) for reaction 1 are shown in Table I.

The second-order rate constants derived from the ferrocene concentration dependence data are shown in Table II. The data for the two temperature dependences done in each solvent were fit to the Eyring equation, and the activation parameters calculated from these fits are shown in Table II.

The effects of added electrolyte are depicted in Figure 1 as plots of rate constant vs. concentration of BF_4^-. The fit lines are discussed below.

All rate data, electrochemical data, and reaction conditions are listed in the supplementary material, with the mean and standard deviation of the multiple determinations performed.

Discussion

There is a significant variation of the observed second-order rate constant with solvent especially in the absence of added

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Table II. Second-Order Rate Constants and Activation Parameters for the $Fe(Cp)_2$, $Co(dmg)_3(BF)_2BF_4$ Cross-Reaction and the $Co(dmg)_3(BF)_2^{+/0}$ Self-Exchange Reaction

	k_{12}, M^{-1} s^{-1} ($\times 10^{-3}$)			$\Delta H_{12}^{\ddagger}$, kcal mol^{-1}			$\Delta S_{12}^{\ddagger}$, cal mol^{-1} deg^{-1}			
solvent	no electrolyte	0.1 M n-Bu_4NBF_4	k_{11},[a] M^{-1} s^{-1}	no electrolyte	0.1 M n-Bu_4NBF_4	$\Delta H_{11}^{\ddagger}$,[a] kcal mol^{-1}	no electrolyte	0.1 M n-Bu_4NBF_4	$\Delta S_{11}^{\ddagger}$,[a] cal mol^{-1} deg^{-1}	$((1/D_{op}) - (1/D_s))$[b]
CH_3CN	16.4 ± 1	12.2 ± 1	146	8.4	8.2	7.3	−11.1	−13.4	−26	0.5289
$(CH_3)_2CO$	8.3 ± 1	4.8 ± 1	104	8.7	9.1	9.8	−11.2	−11.4	−28	0.4956
$C_6H_5NO_2$	37.8 ± 1	20.3 ± 1	3700	9.2	9.0	14.1	−6.7	−8.8	3	0.3875
$(CH_2Cl)_2$	182 ± 10	27.4 ± 1	22 000	6.4	7.6	9.7	−13.0	−12.8	−8	0.3843

[a] Calculated from no added electrolyte values. [b] Values of D_{op} and D_s taken from ref 7.

electrolyte. The accompanying change in the activation parameters is generally for the enthalpy of activation to decrease with increasing rate constant and the entropy to remain constant, except for the case of nitrobenzene, which has a more positive enthalpy and entropy of activation and thus compensate. The rather negative entropies of activation cannot arise from charge concentration in the transition state, as may be the case for reactions between +3 and +2 ions,[15,16] and thus probably arise from reactant orientation requirements, solvent binding, or solvent orientation from nonelectrostatic interaction or low electron-transfer probability.

In all solvents there is a decrease in the rate upon addition of the electrolyte n-Bu_4NBF_4. Since there is no electrostatic work involved in bringing the reactants or products together, this effect cannot be attributed to the ionic strength dependence of the Coulombic interaction. As discussed previously,[11] however, other effects are likely to be involved and will predominate in the absence of electrostatic interaction. These include changes in the activity of the reactants and changes in the identity of the reactants through the formation of ion pairs. Within the ion-pairing formalism eq 5a–c could apply.

$$Co(dmg)_3(BF)_2^+ + BF_4^- \underset{}{\overset{K_{1assoc}}{\rightleftharpoons}} Co(dmg)_3(BF)_2BF_4 \quad (5a)$$

$$Co(dmg)_3(BF)_2^+ + Fe(Cp)_2 \overset{k_0}{\rightleftharpoons} Co(dmg)_3(BF)_2 + Fe(Cp)_2^+ \quad (5b)$$

$$Co(dmg)_3(BF)_2BF_4 + Fe(Cp)_2 \overset{k_{1IP}}{\rightleftharpoons} Co(dmg)_3(BF)_2 + Fe(Cp)_2BF_4 \quad (5c)$$

The rate law derived from this mechanism, and the assumption that the $Co(dmg)_3(BF)_2^+$ is always in equilibrium with its ion-paired form, is given in eq 6. It was assumed that all

$$\frac{d[Co(III)]_{tot}}{dt} = \left[\frac{k_0 + k_{1IP}K_{1assoc}[BF_4^-]\gamma^2}{1 + K_{1assoc}[BF_4^-]\gamma^2}\right][Fe(Cp)_2][Co(III)]_{tot} \quad (6)$$

singly charged species, including the transition state for the k_0 path, have the same activity coefficient. The activity coefficients were calculated by an iterative procedure using the ion-pair association constants for the electrolyte, n-Bu_4NBF_4,[17,18] and the extended Debye–Hückel equation. The cobalt complex does not contribute significantly to the ionic strength.

The data for the solvents acetonitrile, acetone, and nitrobenzene were fit well by eq 6 and gave the solid lines in Figure 1. The constants k_0, k_{1IP}, and K_{1assoc} are given in Table III.

Table III. Fit Parameters Obtained from the Dependence of the Cross-Reaction on Ionic Strength in Each Solvent

solvent	k_0,[a] M^{-1} s^{-1} ($\times 10^{-3}$)	k_{1IP},[c] M^{-1} s^{-1} ($\times 10^{-3}$)	K_{1assoc}[c]	k_0/k_{1IP}
CH_3CN[b]	16.3 (0.1)	3.1 (1.0)	17 (3)	5.3
$(CH_3)_2CO$[b]	9.5 (0.2)	1.7 (0.3)	200 (24)	5.6
$C_6H_5NO_2$[b]	40.5 (0.2)	2.1 (0.6)	53 (3)	19.3
$(CH_2Cl)_2$[c]	271 (10)	30 (2)	29 000 (3000)	9.0

[a] Errors calculated from the method of support planes: Duggleby, R. G. *Eur. J. Biochem.* **1980**, *109*, 93. [b] Kinetic data fit to eq 6. [c] Kinetic data fit to eq 8, $k_{2IP}(M^{-1}\ s^{-1}) = 9.9 \times 10^3$, $K_{2assoc} = 50$.

The ethylene dichloride data were fit poorly by this rate law. The low dielectric, 10.36, of this solvent and the high concentration of added electrolyte involved suggested the possibility of ion triples,[19] or association between $Co(dmg)_3(BF)_2BF_4$ and n-Bu_4NBF_4. Adding eq 7a and 7b to the

$$Co(dmg)_3(BF)_2BF_4 + BF_4^- \overset{K_{2assoc}}{\rightleftharpoons} Co(dmg)_3(BF)_2(BF_4)_2^- \quad (7a)$$

$$Co(dmg)_3(BF)_2(BF_4)_2^- + Fe(Cp)_2 \overset{k_{2IP}}{\rightleftharpoons} Co(dmg)_3(BF)_2 + Fe(Cp)_2(BF_4)_2^- \quad (7b)$$

$$d[Co(III)]_{tot}/dt = [(k_0 + k_{1IP}K_{1assoc}[BF_4^-]\gamma^2 + k_{2IP}K_{1assoc}K_{2assoc}[BF_4^-]^2\gamma^2)/(1 + K_{1assoc}[BF_4^-]\gamma^2 + K_{1assoc}K_{2assoc}[BF_4^-]^2\gamma^2)][Fe(Cp)_2][Co(III)]_{tot} \quad (8)$$

previous mechanism gives the rate law (8). The result of the fit of the ethylene dichloride data to this equation was quite satisfactory as shown by the solid line in Figure 1. The constants, including k_{2IP} and K_{2assoc}, are given in Table III. Support for the ion-pairing mechanism was previously found from conductivity data on the cobalt complex in acetonitrile.[11]

The data were also fit well, with different parameters, by the same rate law without the activity coefficients included. The activity terms have been retained because they do vary significantly and in order to demonstrate that a consistent pattern of inhibition by added electrolyte is observed even when they are included. It is likely that the extended Debye–Hückel equation is not a precise representation of the activity coefficients, but any further corrections to the activity calculations are not expected to be significant to the arguments presented. The calculated values for the activity coefficients are included in the supplementary material.

It has been shown[11] that the electrochemical potential of the cobalt complex does not vary with ion pairing in acetonitrile; thus, the rate variation with added electrolyte is not related to a change in the electron-transfer equilibrium constant. Another possibility is that the bound BF_4^- ion blocks one of the preferred sites for electron transfer and thus leaves

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reaction to take place by the remaining equivalent sites. This model would predict a lowering of the rate constant with ion pairing and a uniform ratio of $k_0/k_{1\text{IP}}$. This ratio should be less than 2 because of the high symmetry of the reactants and the small size of the BF_4^- ion. The observed effect, shown in Table III, is that the ion-paired form does react more slowly in all of these cases, as well as for the ferrocene/ferrocenium self-exchange,[6] but the $k_0/k_{1\text{IP}}$ ratio is often greater than 5 and is not constant. This could be explained if the BF_4^- ion is required to be equidistant from the metal complexes in the transition state, and thus in a position to stabilize the incipient ferrocenium ion. Assuming that association between the reactants in both the ion-free and ion-paired forms is equally probable and that all geometries are equally likely, the fraction of associated reactants with the proper orientation for electron transfer should be much lower for the case that has the anion included than for the more symmetric case without the anion. This effect will significantly lower the precursor complex formation constant. The efficiency of electron transfer and other factors may also be involved, as is discussed below. The system studied here may be compared with the anthracene/anthracene radical anion electron self-exchange, in which various tetraalkylammonium cations were used to prove the effects of ion pairing on electron-transfer rates.[20] In this latter system, it was also found that ion pairing slowed the reaction rate and that the rate decreased with increasing alkyl substituent chain length. It has also been shown that in reactions of this type the cation is transferred with the electron, even in the case of ion triples.[21,22] These results support our assumption about the geometry of the transition state and suggest that the BF_4^- ion is transferred in the opposite direction as the electron; that is, it stays associated with the cation and in the transition state is between the two complexes that each carry a partial positive charge. Recently, Endicott and Ramasami have reported systems in which ion pairing increases the rate of electron transfer between two cations by more than the electrostatic factor. The dependence on the identity of the anion is interpreted as indicating catalysis via a superexchange mechanism in certain cases.[23] The BF_4^- ion should not support a superexchange path, but the viability of such a pathway in the system being considered here is being pursued through the use of other anions.

The activation parameters shown in Table II vary in no regular manner with increasing $n\text{-Bu}_4NBF_4$. For acetonitrile and nitrobenzene, the rate decreases primarily because of a more negative entropy of activation despite a slightly smaller enthalpy of activation. For acetone and ethylene dichloride, the entropy of activation is unchanged and the rate decreases because of the increased activation enthalpy. The change in rate on going from no added electrolyte to 0.1 M $n\text{-Bu}_4NBF_4$ is largest for ethylene dichloride and results from an activation enthalpy contribution. The contribution from the lower probability of attaining the transition-state nuclear arrangements in the ion-paired case should have lowered the activation entropy. Entropy–enthalpy compensation could mask this, and there could be small differences in the enthalpy of formation of the precursor complex between the ion-paired and ion-free paths.

Further discussion will involve analysis within the Marcus theory. To the extent that the Marcus theory describes the reactions being considered here, it allows separation of the individual contributions from the two reagents and their solvation from the dependence on the driving force of the reaction and thus the calculation of the actual self-exchange behavior of the cobalt complex, which has not been measured directly. Equations [4] 9–11 involve the related rate constants

$$k = K_p k_e = K_p A \exp(-\Delta G^*/RT) \qquad (9)$$

$$k_{12} = K_{12p}k_{12e} = (K_{eq}K_{11p}k_{11e}K_{22p}k_{22e}f)^{1/2} \qquad (10a)$$

$$\ln f = (\ln K_{eq})^2/(4 \ln (K_{11p}k_{11e}K_{22p}k_{22e})/(A_{11}A_{22})) \qquad (10b)$$

$$A_{12} = (A_{11}A_{22})^{1/2} \qquad (11)$$

and their activation parameters, where $K_{11p}k_{11e}$ and $K_{22p}k_{22e}$ are the self-exchange rate constants for the cobalt complex and ferrocene, respectively, K_{eq} is the equilibrium constant for the cross-reaction, and $K_{12p}k_{12e}$ is the rate constant in the forward direction. The precursor complex formation constants (K_{11p}, K_{22p}, K_{12p}) have been included explicitly with the unimolecular rate constants for electron transfer (k_{11e}, k_{22e}, k_{12e}) to emphasize their importance in the discussion. However, only their product is used in the calculations. The "A" term is the product of several factors, including a nuclear factor and an electronic factor. These have been discussed extensively, most recently by Sutin.[24] Values for the transition-state theory activation parameters are indicated by a "$\ddagger$" and are calculated from the equations for the Marcus theory activation parameters which carry a "$*$" (eq 12 and 13). The symbols not

$$\Delta H_{12}^* = \left(\frac{\Delta H_{11}^* + \Delta H_{22}^*}{2}\right)(1 - 4\alpha^2) + \frac{\Delta H^\circ}{2}(1 + 2\alpha) \qquad (12a)$$

$$\Delta S_{12}^* = \left(\frac{\Delta S_{11}^* + \Delta S_{22}^*}{2}\right)(1 - 4\alpha^2) + \frac{\Delta S^\circ}{2}(1 + 2\alpha) \qquad (12b)$$

$$\alpha = \frac{\Delta G^\circ}{4(\Delta G_{11}^* + \Delta G_{22}^*)} \qquad (12c)$$

$$\Delta S^* = \Delta S^\ddagger - R \ln \frac{hA}{k_B T} + \frac{R}{2} \qquad (13a)$$

$$\Delta H^* = \Delta H^\ddagger + \frac{RT}{2} \qquad (13b)$$

$$\Delta G^* = \Delta G^\ddagger + RT \ln \frac{hA}{k_B T} \qquad (13c)$$

already defined are Planck's constant, h, and Boltzmann's constant, k_B. The data for the cross-reactions were taken from this work and ref 11, and the data on the self-exchange of ferrocene were taken from ref 6. The results of the calculations of k_{11}, $\Delta S_{11}^\ddagger$, and $\Delta H_{11}^\ddagger$ are given in Table II. Different A terms should be used as indicated in eq 9–11. However, since values cannot be easily derived, a typical value of 10^{11} M^{-1} s^{-1} is used for all calculations.

The calculated k_{11}, $\Delta H_{11}^\ddagger$, and $\Delta S_{11}^\ddagger$ values vary more with solvent than do the k_{12} values and their activation parameters. This arises partly from the equilibrium constant terms but mostly from the contribution of the ferrocene exchange and its relative lack of a solvent dependence. Some trends observed for the cross-reaction are thus more pronounced in the cobalt complex self-exchange parameters. Nitrobenzene shows much different behavior, with $\Delta H_{11}^\ddagger$ and $\Delta S_{11}^\ddagger$ compensating by both being more positive than for any of the other solvents.

Through the Marcus theory there is a further prediction about the dependence of electron-transfer rate constants on the solvent. The activation energy is separated into two terms, the inner-sphere reorganization of the complexes, also called

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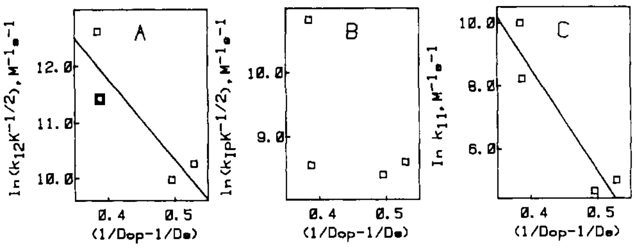

Figure 2. Dependence of second-order rate constants on the dielectric term for the three cases considered: (A) $Fe(Cp)_2$, $Co(dmg)_3(BF)_2^+$ cross-reaction (fit line slope = −14.5, intercept = 17.6); (B) $Fe(Cp)_2$, $Co(dmg)_3(BF)_2BF_4$ ion-pair cross-reaction; (C) $Co(dmg)_3(BF)_2^{+/0}$ self-exchange reaction (fit line slope = −32.6, intercept = 21.6).

the Frank–Condon barrier, and the outer-sphere reorganization of the solvent. The precursor complex association constant is estimated from the electrostatic work required to bring two charged species together and a probability factor. The pertinent equations for an outer-sphere electron transfer reaction are given in eq 14a–d. In these equations ΔG_{out}, ΔG_{in}, w_r,

$$K_p = \left(\frac{4\pi N r^3}{3000}\right) \exp\left(-\frac{w_r}{RT}\right) \tag{14a}$$

$$\Delta G^* = \Delta G_{\text{out}} + \Delta G_{\text{in}} \tag{14b}$$

$$\Delta G_{\text{out}} = \left(\frac{e^2}{4}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s}\right) \tag{14c}$$

$$\Delta G_{\text{in}} = \sum_i \left[\frac{n_{1i}f_{1i}}{2}(d_r^0 - d_o^0)_i^2 + \frac{n_{2i}f_{2i}}{2}(d_r^0 - d_o^0)_i^2\right] \tag{14d}$$

N, a_1 (a_2), r, n_{1i} (n_{2i}), f_{1i} (f_{2i}), $(d_r^0 - d_o^0)_i$, D_s, and D_{op} are the outer-sphere component of the activation energy, the inner-sphere component of the activation energy, the work to bring the reactants together, Avogadro's number, the radius of the reactants, the distance between the reactant centers in the transition state, the number of bonds per complex, the force constant of the motion required to convert the reactants to the activated state, the difference in the equilibrium bond distance in the two oxidation states, the static dielectric of the solvent, and the optical frequency dielectric constant equal to the square of the index of refraction, respectively. The subscript i refers to the various bonds that change on going from the reactants to the transition state. Since one of the reactants is neutral and the work is primarily due to charge–charge electrostatic interactions, w_r is assumed to be zero. The precursor complex formation constant is estimated on the basis of a dielectric continuum model and spherical reactants.[4,5] A plot as in Figure 2 of ln k vs. $((1/D_{\text{op}}) - (1/D_s))$ should have a slope of -1.4×10^6 $((1/2a_1) + (1/2a_2) - (1/r))$ and an intercept of ln $(K_pA) - \Delta G_{\text{in}}/RT$. The A term is often taken as about 10^{11} M^{-1} s^{-1}; however, the uncertainty about the value of the precursor complex formation constant and the electron-transfer probability in the different solvents and between the ion-free and ion-paired paths makes it difficult to estimate a value with any precision. The difference in metal–ligand bond lengths for the Co(II) and Co(III) complexes is known to be rather small, 0.08 Å, and other changes are even smaller.[25] However, without information on the force constants for the complex motion that converts the nearly octahedral Co(III) complex into the approximately trigonal prismatic Co(II) form, the inner-sphere reorganization energy cannot be calculated and the two terms in the intercept cannot be separated.

Three cases were considered in testing the solvent-dependence prediction. The first two are the ion-free and ion-paired paths of the cross-reaction. These rate constants were corrected to zero driving force by dividing k_{12} by $K_{\text{eq}}^{1/2}$, as suggested by eq 10, with the slight approximation that f is 1. The third case is the calculated apparent self-exchange rate constant (k_{11} or $K_{11p}k_{11e}$) of the cobalt complex. The value of A was taken as 10^{11} M^{-1} s^{-1}, as discussed previously. Equations 14a–d could be written with the contributions from the two self-exchange terms and the equilibrium constant resolved, but there is little change in the relative contributions from the cobalt complex and ferrocene with solvent variation, since this depends on the equilibrium constant, which is near one and nearly constant. Consistency with the Marcus model was tested by plotting log k vs. $((1/D_{\text{op}}) - (1/D_s))$.

In all three cases presented in Figure 2 there is a consistent and rather large deviation from a linear relationship. Acetonitrile gives a higher rate than acetone, which is the opposite of the prediction, and there is a large difference in rate between nitrobenzene and ethylene dichloride when the dielectric parameters predict that there should be no difference. The degree of scatter is more extensive than is observed in the cases of $Ru(hfacac)_3^{0/-}$ [17] (hfacac is hexafluoroacetylacetonate) and $Cr(arene)_2^{+/0}$,[8] but more like the theoretical relationship than the $Fe(Cp)_2^{+/0}$ [6] self-exchange reaction. In studies of the solvent dependence of the optical electron-transfer process in type 2 intervalence compounds, the analogous treatment consistently gives a linear dependence on the solvent function, but the slope is not always predicted with precision.[26]

In Figure 2A, the data do have roughly the slope predicted when the radii are taken as the full size of the complexes and no interpenetration of the coordination spheres is allowed. In Figure 2B, however, the data from the ion-paired path show no correlation with the solvent parameter. The rate constants in acetontirile, acetone, and nitrobenzene are approximately equal while that for ethylene dichloride is over 1 order of magnitude higher. Several factors could contribute to the much larger deviations observed for the ion-paired path compared to that of the reaction of the free ions. The precursor complex formation constant, besides being lower for the ion-paired path, could vary with solvent, or the structure of the precursor complex could vary with solvent. The former possibility is less likely since the overall stability of the precursor complex should be most strongly influenced by the bulk dielectric constant, and the data do not correlate with this parameter. The latter possibility could change the electron-transfer distance and the effective size of the transition state and thus the radius terms in the outer-sphere reorganization term. The molecular nature of the solvent, which is ignored in the dielectric continuum equations for the outer-sphere reorganization, is likely to influence the specifics of the transition-state conformation. This contribution is more likely to change the transition-state structure for the ion-paired path than for the free-ion path because there are more similar but not quite equivalent structures possible in the more complex transition state. Figure 2C shows the data for the calculated self-exchange of the cobalt complex. The scatter about a linear relationship is more extreme than in Figure 2A, and the logarithmic scale is thus compressed. The slope of the line through the points is much steeper than would be predicted without extreme interpenetration of the ligands in the transition state. Calculations employing other models for the transition state such as the ellipsoidal form suggested by German and Kuznetsov[27] did not improve the fit. The ferrocene–ferrocenium self-exchange data used to make these calculations show an extremely poor correlation with the solvent parameter. To

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the extent that the outer-sphere reorganization energy is separable into contributions from the two reactants, as is assumed in the Marcus theory, the self-exchange of the cobalt complex should not be required to fit poorly just because it is calculated from a ferrocene cross-reaction. However, the assumption that the reorganization processes are separable is much less likely to hold for the outer-sphere than for the inner-sphere term, since the reactants must significantly influence each other's solvation in the transition state, and the optimal conformation of the transition state is by definition a function of both partners as well as the solvent.

A pattern is emerging in the solvent-dependence studies that relates the linearity of the solvent-dependence plot and the activation parameters. The best behaved systems, in terms of the linearity of the ln k vs. $((1/D_{op}) - (1/D_s))$ plot, show much less variation in the entropy of activation, while those systems that are poorly behaved show erratic and highly negative activation entropies. This pattern is consistent with the deviations from theory originating in variation in precursor complex stability and structure and changes in electron-transfer probability.

In conclusion, we have shown that electron-transfer reactivity for a system with no charge–charge interactions required in forming the precursor complex is sensitive to ion pairing and the solvent. The solvent dependence is not well predicted by the Marcus theory, which assumes a dielectric continuum model for the solvent, and a solvent-invariant precursor complex structure. Important factors that contribute to the rate variation probably include changes in transition-state structure, electron-transfer distance, and the particulate nature of the solvent. The dielectric continuum model may be adequate for those cases in which the transition-state structure is not changed by solvation effects, as in intervalence compounds, but when more structural flexibility is available, the transition-state conformation is clearly sensitive to solvation factors.

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Registry No. $Fe(Cp)_2$, 102-54-5; $Co(dmg)_3(BF)_2^+$, 34248-47-0; CH_3CN, 75-05-8; $(CH_3)_2CO$, 67-64-1; $C_6H_5NO_2$, 98-95-3; $(CH_2Cl)_2$, 107-06-2.

Supplementary Material Available: Tables of concentration dependence, temperature dependence, second-order rate constant dependence on added electrolyte, and $\Delta E_{1/2}$ vs. temperature data (16 pages). Ordering information is given on any current masthead page.

Contribution from the Dipartimento di Chimica and Istituto di Mineralogia e Cristallografia,
Università di Perugia, 06100 Perugia, Italy

Exchange Interaction in Multinuclear Transition-Metal Complexes. 5.[1] Through-Bond Exchange Coupling in $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$ (A^{2-} = Anion of *N*,*N*′-Bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)piperazine)

B. CHIARI, O. PIOVESANA,* T. TARANTELLI, and P. F. ZANAZZI

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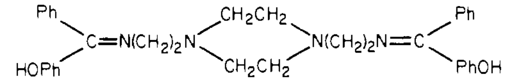
The synthesis, crystal structure, and magnetic properties are reported for the novel compound $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$, where A^{2-} is the hexadentate anion of *N*,*N*′-bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)piperazine:



$$\mathrm{(Ph)(HOPh)C{=}N(CH_2)_2N(CH_2CH_2)_2N(CH_2)_2N{=}C(Ph)(PhOH)}$$

The complex crystallizes in the triclinic space group $P\bar{1}$. Cell dimensions are a = 10.034 (3) Å, b = 14.057 (3) Å, c = 6.897 (2) Å, α = 92.93 (2)°, β = 97.47 (2)°, and γ = 89.64 (2)°. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques to a conventional R value of 0.062. The unit cell comprises one $Cu_2A(CH_3COO)_2$ dinuclear molecule and two uncoordinated methanol molecules of solvation. There are no short intermolecular contacts between the dinuclear units. The coordination sphere of each copper atom is distorted square planar and contains two cis nitrogens and one phenolic oxygen of hexadentate A^{2-} and one oxygen atom of an acetate anion. The second oxygen of each carboxylate ligand is at a very weakly linking distance (2.795 (9) Å) of only one copper atom. The two copper atoms are bridged by a "chair"-shaped piperazine fragment of A^{2-}. The Cu–Cu separation is 6.881 (5) Å. The ESR spectrum of the compound indicates a predominantly $d_{x^2-y^2}$ ground state for the copper(II) ion. The angle formed by the Cu–N(piperazine) bonds with the C–C bonds of piperazine is only 1.9°. The Cu_2(piperazine) bridging unit, therefore, has an almost ideal symmetry for propagating magnetic exchange between the copper atoms through a dominant through-bond mechanism. The magnetic susceptibility of the compound has been examined in the liquid helium to ~100 K range. A maximum in the susceptibility at ~18 K is indicative of an antiferromagnetic exchange interaction. The best fit to the Van Vleck equation derived from the $H = -2J(\hat{S}_A \cdot \hat{S}_B)$ Hamiltonian yielded $J = -10.42$ cm^{-1}. The efficiency of the piperazine bridge in propagating magnetic exchange between the copper(II) ions is discussed.

Introduction

Rapidly increasing efforts have been directed toward obtaining an adequate understanding of the viability of extended polyatomic bridging units to support magnetic exchange interactions between paramagnetic metal centers.[2] This problem has important implications to topics such as the nature of orbital interactions,[3] electron transfer in redox reaction precursors,[4] and biological electron-transport chains.[5] The ex-

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*To whom correspondence should be addressed at the Dipartimento di Chimica.

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