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

Electron-Transfer Studies on a Series of Cobalt Clathrochelates in Acetonitrile[1]

Dan Borchardt and Scot Wherland*

Received June 18, 1985

The outer-sphere electron-transfer reactivity of a series of cobalt clathrochelates of the type $Co(L)_3(BX)_2^+$ (L = doubly deprotonated dimethylglyoxime (dmg), nioxime (nox), and diphenylglyoxime (dpg) and X = F, C_6H_5, and C_4H_9) has been studied through cross reactions with ferrocene ($Fe(Cp)_2$), 1,1′-dimethylferrocene ($Fe(CpCH_3)_2$), or decamethylferrocene ($Fe(Cp(CH_3)_5)_2$) in CH_3CN. The reactions have been studied as a function of ferrocene concentration, temperature, and added electrolyte. The equilibrium constants and their temperature dependences have been determined through electrochemical measurements. The reactions are first order in each reactant, and second-order rate constants at 0.1 M n-Bu_4NBF_4 range from 3.92×10^3 M^{-1} s^{-1} for the $Co(dmg)_3(BC_6H_5)_2^+$–$Fe(CpCH_3)_2$ reaction to 3.86×10^6 M^{-1} s^{-1} for the $Co(nox)_3(BC_4H_9)_2^+$–$Fe(Cp(CH_3)_5)_2$ reaction. However, when the rate constants are corrected for variations in the thermodynamic driving force with use of Marcus theory, the range becomes less than 1 order of magnitude. Analysis within Marcus theory gave apparent self-exchange rate constants for the clathrochelates that vary from 45 M^{-1} s^{-1} for $Co(dmg)_3(BF)_2^{+/0}$ to 643 M^{-1} s^{-1} for $Co(dpg)_3(BC_6H_5)_2^{+/0}$. Temperature dependences of the cross reactions with 0.1 M n-Bu_4NBF_4 gave activation enthalpies that ranged from 4.0 to 9.0 kcal mol^{-1}, while ΔS_{12}^* values varied little, from −15.7 to −10.4 cal mol^{-1} deg^{-1}. Calculated self-exchange activation parameters for the cobalt complexes showed much more variation with ΔH_{11}^* values running from 3.9 to 9.4 kcal mol^{-1} and ΔS_{11}^* values ranging from −39 to −14 cal mol^{-1} deg^{-1}; however, the variations showed pronounced enthalpy–entropy compensation. Addition of n-Bu_4NBF_4 up to 0.5 M lowered the second-order rate constants by about a factor of 2 for all reactions studied. Similar behavior was observed for n-Bu_4NPF_6, n-Bu_4NBr, and n-Bu_4NI. Fits of these data to a rate law employing ion pairing gave association constants that were less than 15 M^{-1}, except for the n-Bu_4NI case, which gave an association constant of 126 M^{-1}. Since iodide can reduce the clathrochelate complexes, it was possible to measure its association constant in the absence of ferrocene; for this case the association constant was found to be 25 M^{-1}. This discrepancy in the association constants may indicate some ferrocene–iodide interaction. It is concluded that increasing bulk of the clathrochelates accounts for the observed increase in the self-exchange rate constants by lowering the outer-sphere reorganization energy.

Introduction

The study of electron-transfer reactions is inherently of interest because these reactions are so common and because they are involved in energy transduction and transfer. As a topic in basic research these reactions are receiving a great deal of attention from theoreticians and from experimentalists.[2-8] Currently there is a need for studies of well-defined systems that are amenable to theoretical interpretation. In our laboratory we are especially interested in extending experimental work, previously done on aqueous solutions, to nonaqueous solvents, both to probe the influence of the solvent and to work with systems that are not stable in aqueous media.

The systems studied here are outer-sphere electron-transfer reactions between substitution-inert complexes and are thus the easiest to analyze within existing theory. This work is an attempt to characterize the effect of structural variations in the ligand on electron-transfer rates for a class of cobalt complexes called clathrochelates or cage complexes. The first of these complexes, $Co(dmg)_3(BF)_2BF_4$ (dmg is the doubly deprotonated dimethylglyoxime ligand), was synthesized by Rose and co-workers.[9] It shows reversible redox behavior and quite a large increase in molar absorptivity upon reduction of the Co(III) complex to the Co(II) complex. The rigid cage structure (see Figure 1) forces substitution-inert behavior for both cobalt oxidation states. The Co(III) complex has an approximately octahedral coordination environment while the Co(II) complex is more nearly trigonal prismatic and low spin. The low overall charge of +1 for the Co(III) complex makes the compounds especially amenable to study in a variety of solvents,[10] and the structure of the cages can be altered quite easily by using different dioxime ligands and boron capping agents. These structural changes do alter the physical properties, most notably the reduction potential (see Table IV). The complexes do not lend themselves to direct study of their electron self-exchange properties. It is therefore necessary to study them through cross reactions with some well-defined system. The series of ferrocenes $Fe(Cp)_2$, $Fe(CpCH_3)_2$, and $Fe(Cp(CH_3)_5)_2$ are appropriate, since their redox potentials span the proper range so that only low-driving-force reactions are studied and their electron self-exchange behavior in acetonitrile has been studied in depth by Wahl and co-workers.[4]

The reactions studied as a function of ferrocene concentration, temperature, and added electrolyte are as follows: (I) $Co(dmg)_3(BF)_2^+ + Fe(Cp)_2$; (II) $Co(dmg)_3(BF)_2^+ + Fe(CpCH_3)_2$; (III) $Co(dmg)_3(BC_6H_5)_2^+ + Fe(CpCH_3)_2$; (IV) $Co(dmg)_3(BC_4H_9)_2^+ + Fe(Cp(CH_3)_5)_2$; (V) $Co(nox)_3(BF)_2^+ + Fe(Cp)_2$; (VI) $Co(nox)_3(BF)_2^+ + Fe(CpCH_3)_2$; (VII) $Co(nox)_3(BC_6H_5)_2^+ + Fe(CpCH_3)_2$; (VIII) $Co(nox)_3(BC_4H_9)_2^+ + Fe(Cp(CH_3)_5)_2$; (IX) $Co(dpg)_3(BC_6H_5)_2^+ + Fe(Cp)_2$; (X) $Co(dpg)_3(BC_6H_5)_2^+ + Fe(CpCH_3)_2$. nox and dpg are the doubly deprotonated nioxime (1,2-cyclohexanedione dioxime) and diphenylglyoxime ligands. The general cross reaction can be represented by eq 1. This is a continuation of previously reported work.[10,11]

$$Co(L)_3(BX)_2^+ + Fe(CpR')_2 \overset{K_{eq}}{\rightleftharpoons} Co(L)_3(BX)_2 + Fe(CpR')_2^+ \qquad (1)$$

Experimental Section

Dimethylglyoxime, $CoCl_2 \cdot 6H_2O$, acetonitrile, methanol, anhydrous diethyl ether, and methylene chloride were reagent grade from Baker Chemicals. 1,1′-Dimethylferrocene and decamethylferrocene were purchased from Strem Chemicals. n-Bu_4NBr, n-Bu_4NI, nioxime, ferrocene, $C_6H_5BCl_2$, $C_6H_5B(OH)_2$, $NOBF_4$, and $BF_3 \cdot O(C_2H_5)_2$ were purchased from Aldrich Chemical Co. Diphenylglyoxime, n-$C_4H_9BCl_2$, n-Bu_4NBF_4, n-Bu_4NPF_6, and n-$Bu_4NB(C_6H_5)_4$ were prepared and purified according to literature methods.[12-15] Acetonitrile for kinetic and electrochemical measurements was distilled under argon from P_2O_5 and used within 24 h of distillation. $Fe(Cp)_2$ was sublimed at ambient pressure, $Fe(CpCH_3)_2$ was recrystallized two times from methanol/water solution, and $Fe(Cp(CH_3)_5)_2$ was sublimed at reduced pressure before use.

$Co(dmg)_3(BF)_2BF_4$ and $Co(nox)_3(BF)_2BF_4$. The synthesis of the dmg complex has been reported in the literature.[9] The nox complex was

---

(1) Paper presented in part at the 39th Northwest Regional American Chemical Society Meeting, Moscow, ID, June 14, 1984.
(2) Reynolds, W. L.; Lumry, R. W. "Mechanisms of Electron Transfer"; Ronald Press: New York, 1966.
(3) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.
(4) Yang, E. S.; Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094.
(5) Cannon, R. D. "Electron Transfer Reactions"; Butterworths: London, 1980.
(6) Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1982**, *86*, 126.
(7) Li, T. T. T.; Weaver, M. J.; Brubaker, C. H., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 2381.
(8) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.
(9) Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 4163.
(10) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 2537.
(11) Borchardt, D.; Pool, K.; Wherland, S. *Inorg. Chem.* **1982**, *21*, 93.
(12) Boyer, J. H.; Reinisch, R. F.; Danzig, M. J.; Stoner, G. A.; Sahhar, F. *J. Am. Chem. Soc.* **1955**, *77*, 5688.
(13) Gerrard, W.; Mooney, E. F.; Rees, R. G. *J. Chem. Soc.* **1964**, 740.
(14) House, H. O.; Feng, E.; Peet, N. P. *J. Org. Chem.* **1971**, *36*, 2371.
(15) Accascina, F.; Petrucci, S.; Fuoss, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 1301.

0020-1669/86/1325-0901$01.50/0

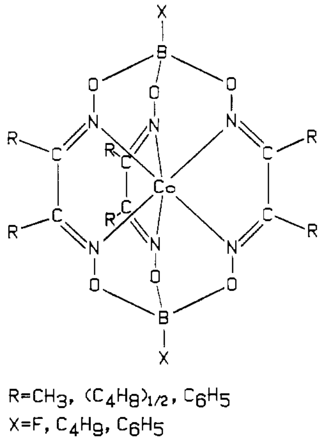

Figure 1. Structural representation of the cobalt clathrochelates.

prepared in the same manner, with H_2nox substituted for H_2dmg. Anal. Calcd for $Co(dmg)_3(BF)_2BF_4$: C, 26.32; H, 3.31; N, 15.35. Found: C, 26.44; H, 3.13; N, 15.12. Anal. Calcd for $Co(nox)_3(BF)_2BF_4$: C, 34.55; H, 3.87; N, 13.43. Found: C, 34.25; H, 3.71; N, 13.28.

$Co(dmg)_3(BC_6H_5)_2BF_4$. A 1.0-g (2-mmol) sample of $K_3Co(dmg)_3$[16] was placed in a 50-mL Schlenk flask evacuated and purged with argon. The solid was then suspended in 25 mL of methylene chloride with stirring. The suspension was allowed to stir for 5 min, and then 0.6 mL (4.3 mmol) of $C_6H_5BCl_2$ was syringed into the flask, causing most of the solid to dissolve. The solution was then gravity-filtered open to the air, and the chloride salt was crystallized from solution by the addition of anhydrous diethyl ether. An acetonitrile solution of the chloride salt was passed over an ion-exchange column (Dowex IX-8 100–200 mesh) in the BF_4^- form. The volume of the recovered solution was reduced by rotary evaporation and the BF_4^- salt recrystallized by addition of anhydrous diethyl ether. Anal. Calcd: C, 43.42; H, 4.25; N, 12.66. Found: C, 43.33; H, 4.07; N, 12.91.

$Co(dmg)_3(BC_4H_9)_2BF_4$. This compound was prepared in the same manner as above except n-$C_4H_9BCl_2$ was used in place of $C_6H_5BCl_2$. Anal. Calcd: C, 38.5; H, 5.82; N, 13.47. Found: C, 38.25; H, 5.68; N, 13.13.

$Co(nox)_3(BC_6H_5)_2BF_4$ and $Co(nox)_3(BC_4H_9)_2BF_4$. These compounds were prepared in the same manner as the analogous dmg compounds except $K_3Co(nox)_3$ was used as the starting complex. Anal. Calcd for $Co(nox)_3(BC_6H_5)_2BF_4$: C, 48.56; H, 4.62; N, 11.33. Found: C, 48.40; H, 4.67; N, 11.57. Anal. Calcd for $Co(nox)_3(BC_4H_9)_2BF_4$: C, 44.48; H, 6.03; N, 11.97. Found: C, 44.16; H, 6.07; N, 11.90.

$Co(dpg)_3(BC_6H_5)_2BF_4$. A 1.19-g (5-mmol) sample of $CoCl_2 \cdot 6H_2O$ was dissolved in 75 mL of deoxygenated methanol along with 3.60 g (15 mmol) of H_2dpg and 1.22 g (10 mmol) of $C_6H_5B(OH)_2$. The solution was then refluxed overnight under argon. The product was vacuum-filtered open to the air and washed with methanol then anhydrous diethyl ether. The solid was taken and product separated from unreacted ligand by dissolving it in methylene chloride. The insoluble ligand was filtered off and the product crystallized by adding enough methanol to make the solution 20% v/v methanol and then rotary evaporating off the more volatile methylene chloride. The product obtained is the Co(II) complex and was oxidized to the Co(III) form by dissolving a weighed amount of Co(II) in methylene chloride, adding a 10% excess of $NOBF_4$, stirring the mixture for 10 min, filtering, and recrystallizing the product by the addition of anhydrous diethyl ether. Anal. Calcd: C, 62.59; H, 3.89; N, 8.11. Found: C, 62.15; H, 3.92; N, 8.06.

Yields for all the cobalt clathrochelates were >50% except for the $Co(dpg)_3(BC_6H_5)_2BF_4$ complex, which, due to the low solubility of the ligand (H_2dpg), gave a yield of 10%. It should also be noted that the procedure used to prepare the $Co(dpg)_3(BC_6H_5)_2$ complex can also be used to prepare some of the other clathrochelates (X = C_6H_5, C_4H_9) with yields in excess of 70%.[17]

Electrochemistry. Measurements were performed with use of cyclic voltammetry as previously described[10,11] except for modification of the apparatus to allow computer data acquisition and fitting. Potentials were measured in triplicate over a range of 0–30 °C for each clathrochelate complex and ferrocene.

Table I. Spectrophotometric Data for the Co(II) Clathrochelates in Acetonitrile

complex	λ_{1max}, nm	ϵ_{1max}, $M^{-1}\ cm^{-1}$	λ_{2max}, nm	ϵ_{2max}, $M^{-1}\ cm^{-1}$
$Co(dmg)_3(BF)_2$[a]	348	5774	460	5450
$Co(dmg)_3(BC_6H_5)_2$[b]	354	6051	465	5551
$Co(dmg)_3(BC_4H_9)_2$	353	5460	464	5114
$Co(nox)_3(BF)_2$	355	6713	467	6328
$Co(nox)_3(BC_6H_5)_2$	358	6512	472	5935
$Co(nox)_3(BC_4H_9)_2$	359	6853	471	6399
$Co(dpg)_3(BC_6H_5)_2$	383	11505	494	9472

[a] Taken from: Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 4163. [b] The solvent was methylene chloride.

Table II. Summary of Electrochemical Data for the Clathrochelate–Ferrocene Cross Reactions

reacn	$\Delta H°$,[a] kcal mol^{-1}	$\Delta S°$,[b] cal mol^{-1} deg^{-1}	K_{eq}^{298}
I	5.0	15	0.33 ± 0.03
II	3.6	19	28 ± 2
III	6.9	15	0.018 ± 0.002
IV	-1.4	5	152 ± 12
V	3.9	12	0.60 ± 0.03
VI	2.5	16	50 ± 4
VII	2.8	2	0.029 ± 0.002
VIII	-3.1	7	5765 ± 467
IX	5.3	10	0.022 ± 0.002
X	2.5	9	1.59 ± 0.13

[a] All values ±1.0 kcal mol^{-1}. [b] All values ±4 cal mol^{-1} deg^{-1}.

Table III. Second-Order Rate Constants and Activation Parameters for the Clathrochelate–Ferrocene Cross Reactions

reacn	$10^{-3}k_{12}$, $M^{-1}\ s^{-1}$	$10^{-3}k_{12}/K_{eq}^{1/2}$, $M^{-1}\ s^{-1}$	ΔH_{12}^{*}, kcal mol^{-1}	ΔS_{12}^{*}, cal mol^{-1} deg^{-1}
I	12.2	21.2	8.5 ± 0.8	−11.5 ± 3.5
II	98.0	18.5	6.4 ± 0.7	−14.5 ± 2.3
III	3.92	29.2	9.0 ± 0.6	−12.3 ± 2.1
IV	1580	128	5.9 ± 0.6	−10.4 ± 2.2
V	25.2	32.5	7.1 ± 0.7	−14.9 ± 2.3
VI	204	28.8	6.4 ± 0.8	−13.1 ± 2.6
VII	7.67	45.0	7.6 ± 0.6	−15.6 ± 2.1
VIII	3860	50.8	4.0 ± 0.8	−15.0 ± 2.7
IX	8.07	54.8	7.9 ± 0.6	−14.4 ± 2.2
X	67.8	53.8	6.2 ± 0.6	−15.7 ± 2.2

Kinetic Measurements. Rate constants were determined as previously described[10] by using the stopped-flow method and following the signal log (I_{450}/I_{600}) as the reduced cobalt complex was formed. Exceptions to this were the reactions involving the $Co(dpg)_3(BC_6H_5)_2^+$ complex, for which the signal followed was log (I_{500}/I_{600}) due to a shift in the absorption spectrum of the Co(II) complex (see Table I). The dual-detector method improves the signal-to-noise ratio and eliminates some artifacts. Data were fit to a pseudo-first-order rate law or an approach to equilibrium rate law, pseudo first order in the forward direction and second order with equal concentrations in the reverse direction, depending on the magnitude of the equilibrium constant. All kinetic runs were done in triplicate on one filling of the stopped-flow syringes. For each reaction the cobalt complex was typically 0.03 mM and the ferrocene concentration was 0.3–6.0 mM. All ferrocene concentration dependences were performed at 0.1 M n-Bu_4NBF_4. Temperature dependences for each reaction were also done at 0.1 M n-Bu_4NBF_4 over a temperature range of 0–30 °C. Added electrolyte dependences were measured over the range 0–0.5 M electrolyte. 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 $\Delta E_{1/2}$ ($E_{1/2}$(Co(cage)) − $E_{1/2}$(ferrocene)) vs. temperature with use of eq 2a to derive values for $\Delta H°$ and $\Delta S°$. Equation 2b was used

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

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

---

(16) Drago, R. S.; Elias, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 6570.

(17) Robbins, M. K.; Naser, D. W.; Heiland, J. L.; Grzybowski, J. *Inorg. Chem.* **1985**, *24*, 3381.

Table IV. Calculated Self-Exchange Rate Constants, Activation Parameters, and Reduction Potentials for the Cobalt Clathrochelates[a]

couple	k_{11}, M^{-1} s^{-1}	ΔH_{11}^{*}, kcal mol^{-1}	ΔS_{11}^{*}, cal mol^{-1} deg^{-1}	$E_{1/2}$,[c] mV
$Co(dmg)_3(BF)_2^{+/0}$ [b]	86 ± 22	6.5 ± 2.4	−28.5 ± 8.1	−28
	45 ± 10	3.9 ± 1.9	−38.8 ± 6.8	
$Co(dmg)_3(BC_6H_5)_2^{+/0}$	118 ± 25	5.2 ± 1.8	−31.9 ± 6.6	−212
$Co(dmg)_3(BC_4H_9)_2^{+/0}$	546 ± 103	9.4 ± 1.7	−14.4 ± 6.4	−374
$Co(nox)_3(BF)_2^{+/0}$ [b]	200 ± 51	4.9 ± 2.2	−32.2 ± 7.8	−13
	114 ± 23	5.0 ± 2.1	−33.0 ± 7.3	
$Co(nox)_3(BC_6H_5)_2^{+/0}$	272 ± 57	6.8 ± 1.8	−24.8 ± 6.6	−200
$Co(nox)_3(BC_4H_9)_2^{+/0}$	132 ± 16	7.1 ± 2.0	−25.4 ± 7.1	−282
$Co(dpg)_3(BC_6H_5)_2^{+/0}$ [b]	634 ± 149	4.9 ± 2.1	−29.7 ± 7.7	−99
	349 ± 83	4.4 ± 1.8	−31.8 ± 6.7	

[a] Ferrocene self-exchange parameters taken from ref 4 are as follows: $Fe(Cp)_2$, $k_{22} = 5.3 \times 10^6$ M^{-1} s^{-1}, $\Delta H_{22}^{*} = 4.4$ kcal mol^{-1}, $\Delta S_{22}^{*} = -13$ cal mol^{-1} deg^{-1}; $Fe(CpCH_3)_2$, $k_{22} = 8.3 \times 10^6$ M^{-1} s^{-1}, $\Delta H_{22}^{*} = 5.6$ kcal mol^{-1}, $\Delta S_{22}^{*} = -8$ cal mol^{-1} deg^{-1}; $Fe(Cp(CH_3)_5$, $k_{22} = 3.8 \times 10^7$ M^{-1} s^{-1}, $\Delta H_{22}^{*} = 3.8$ kcal mol^{-1}, $\Delta S_{22}^{*} = -11$ cal mol^{-1} deg^{-1}. [b] The two values shown are derived from the cobalt complex cross reaction with $Fe(Cp)_2$ and $Fe(CpCH_3)_2$, respectively. [c] Values reported are vs. $Fe(Cp)_2$ in 0.1 M *n*-Bu_4NBF_4 at 25 °C. A value for the $Fe(Cp)_2$ $E_{1/2}$ vs. the aqueous saturated calomel electrode is +309 mV (Sahami, S.; Weaver, M. J. *J. Solution Chem.* **1981**, *10*, 199).

to calculate K_{eq} at the temperature 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} are shown in Table II. The reduction potentials of the cobalt complexes vs. $Fe(Cp)_2$ are shown in Table IV.

The second-order rate constants (k_{12}) derived from the ferrocene concentration dependence data are shown in Table III. The temperature-dependence data were fit to the Eyring equation,[18] and the activation parameters calculated from these fits are shown in Table III.

The effects of added electrolyte are depicted in Figure 2 as plots of rate constant vs. electrolyte concentration. 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 deviations of the multiple determinations performed.

Errors for the second-order rate constants were estimated as ±10%. The errors shown for the cross-reaction activation parameters were determined on the basis of this assumption. Errors for the values derived from electrochemical measurements were based on a reproducibility in $E_{1/2}$ of ±2 mV. All fit parameters from plots of $E_{1/2}$ vs. T were given the error of the data set with the worst fit. Other values reported here were derived from those mentioned above and from results in ref 10; their errors were determined through a propagation of error analysis on the equations used.

Discussion

Table III shows that the measured cross-reaction rate constants cover 3 orders of magnitude. Since these reactions necessarily involve an outer-sphere mechanism and the electron self-exchange behavior of the ferrocene partners is known,[4] the Marcus theory cross-reaction formalism can be applied in order to interpret the variation. The Marcus equations (eq 3a–c)[19,20] involve separation

$$k_{12} = (K_{eq}k_{11}k_{22}f)^{1/2} \tag{3a}$$

$$\ln f = \frac{(\ln K_{eq})^2}{4 \ln ((k_{11}k_{22})/A_{12}^2)} \tag{3b}$$

$$A_{12} = (A_{11}A_{22})^{1/2} \tag{3c}$$

of the individual contributions from the two reagents and the dependence on the thermodynamic driving force of the reaction. The end result is the calculation of an apparent self-exchange rate constant for the cobalt clathrochelate complexes. In the equations k_{12}, k_{11}, k_{22}, K_{eq}, and f are the cross-reaction rate constant, the cobalt self-exchange rate constant, the ferrocene self-exchange rate constant, the equilibrium constant for the cross reaction, and a driving force correction, respectively. The "A" term is the product of several factors, including a nuclear and an electronic part. These have been discussed extensively most recently by Sutin.[8] However, since they are not easily derived for our situation, an estimate of 10^{11} M^{-1} s^{-1} has been used in the calculations.

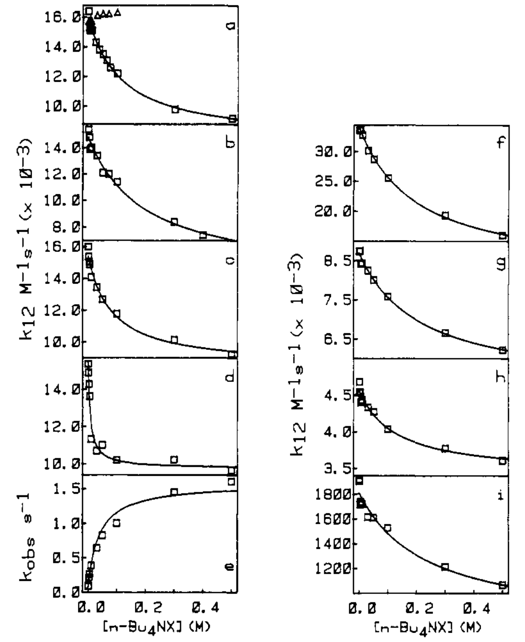

Figure 2. (a–d) Dependence of k_{12} on added electrolyte at 25 °C: (a) reaction I, counterion BF_4^- (□), $B(C_6H_5)_4^-$ (△); (b) reaction I, counterion PF_6^-; (c) reaction I, counterion Br^-; (d) reaction I, counterion I^-. (e) Dependence of k_{obsd} for the $Co(dmg)_3(BF)_4^+$–*n*-Bu_4NI reaction on *n*-Bu_4NI concentration at 25 °C. (f–i) Dependence of k_{12} on added electrolyte at 25 °C (counterion BF_4^-): (f) reaction V; (g) reaction VII; (h) reaction III; (i) reaction IV.

Within Marcus theory, the contribution of K_{eq}, the driving force, can be separated from the contribution of k_{22}. If k_{12} is divided by the square root of K_{eq}, we have a rate constant that is a pseudo self-exchange containing only contributions from k_{11}, k_{22}, and f. For these reactions f is near unity and does not contribute significantly. Upon making this thermodynamic driving force correction, as shown in Table III, we see that the variation in K_{eq} was the main cause for the observed variation in the k_{12} values. What was a range of 3 orders of magnitude has been reduced to less than 1 order of magnitude.

Next we calculate the apparent k_{11}'s of the cobalt clathrochelates (see Table IV) and find that there is still some variation of rate constants with cage structure.[21] The general trend in the data, an increase in rate with the size of the complex, is the pattern most often observed in self-exchange systems, including the ferrocenes and a series of ruthenium ammines.[3,4] The opposite trend, a decrease in self-exchange rate with ligand bulk, has been observed recently for a series of Mn(I,II) hexakis(isocyanide) complexes.[22]

---

(18) Glasstone, S.; Laidler, K. J.; Eyring, H. "Theory of Rate Processes"; McGraw-Hill: New York, 1940.

(19) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(20) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 2654.

(21) In these calculations k_{22}'s used for the ferrocenes were measured at 0.6–12 mM PF_6^- for $Fe(Cp)_2$, 4 mM for $Fe(CpCH_3)_2$, and 0.1 mM for $Fe(Cp(CH_3)_5)_2$. The k_{12} values used were measured at 0.1 M *n*-Bu_4NBF_4. This was done for consistency in the comparison of our calculated k_{11}'s since only k_{22} for $Fe(Cp)_2$ has been measured as a function of added electrolyte. In a previous paper[10] we used the k_{22} value for $Fe(Cp)_2$ at 0.1 M *n*-Bu_4NBF_4 to calculate an apparent k_{11} for the $Co(dmg)_3(BF)_2^{+/0}$ self-exchange, thus causing what appears to be a discrepancy between reported values here and in ref 10 and 11. The same is true for the activation parameters.

(22) Nielson, R. M.; Wherland, S. *J. Am. Chem. Soc.* **1985**, *107*, 1506.

Again using the Marcus theory approach in the classical limit, the rate constant for a self-exchange reaction can be considered as the product of several terms (eq 4a–e). Here ΔG^* is the

$$\Delta G^* = \Delta G_{\text{out}} + \Delta G_{\text{in}} + w_r \quad (4a)$$

$$k = K_p k_e \quad (4b)$$

$$K_p = [4\pi N r^3/3000] \exp(w_r/RT) \quad (4c)$$

$$k_e = A \exp(-\Delta G^*/RT) \quad (4d)$$

$$A = \nu_{\text{n,eff}} \kappa_{\text{el}} [S(r,\theta)] \quad (4e)$$

Marcus theory free energy of activation, ΔG_{in} is the reorganization energy of the complex on going to the compromise geometry between the oxidized and reduced forms, ΔG_{out} is the analogous solvent reorganization term, w_r is the electrostatic work required to bring the two complexes together to form the precursor complex, K_p is the precursor formation constant, k_e is the electron-transfer rate constant within the precursor complex, $\nu_{\text{n,eff}}$ is an effective nuclear frequency associated with the inner-sphere reorganization, κ_{el} is the electronic transmission coefficient, and $S(r,\theta)$ is a steric factor. These factors are now considered in turn. The value for ΔG_{in} should not vary extensively, but it is difficult to estimate because of the complicated variation in bond lengths and angles involved. If it does vary, it is not likely to correlate with the bulk of the complex but with the electronic factors. The solvent reorganization, ΔG_{out}, generally decreases as the size increases, due to the change in the charge density of the transition state. This would predict a variation in rate constant in the direction we observe. In making our calculation, we have assumed that the A factor is a constant and have no basis for changing that assumption here. The effective nuclear frequency is difficult to evaluate for the same reason that ΔG_{in} is difficult to evaluate, but the constancy of the structural type involved in this comparison should make it reasonably constant. The electronic transmission coefficient will decrease from 1 once a critical electron-transfer distance is exceeded, but for the interaction of the small ferrocene complexes with the rather open clathrochelate structure, on which our estimates are based, such a decrease is not necessarily expected. The steric factor should also be rather constant because of the constancy of the structural type involved. The added ligand bulk is always at the periphery of the ligand and leaves the space between the dioxime moieties open.

Thus we conclude that the variation in the apparent self-exchange rate constants calculated for the cobalt clathrochelates is most likely to be a solvation effect. The number of other contributions that might be involved and cannot be well estimated and the smallness of the observed effect leave open the possibility that a variety of compensating factors are involved.

For three of the cages it was possible to study their reaction with two different ferrocenes. The result is that the self-exchange rate constants calculated from the $Fe(Cp)_2$ cross reaction are approximately 2 times greater than those calculated from the $Fe(CpCH_3)_2$ cross reaction. This difference might arise from variations in reactant–reactant interaction between the measured ferrocene self-exchange reactions and the cross reactions measured here. Such factors are not considered in Marcus theory. Alternatively, if the k_{22} value is assumed to be the same for the two ferrocenes, then there is excellent agreement between the calculated k_{11} values for the cobalt complexes. In any case, a factor of 2 is barely resolved, due to the propagation of errors in the calculation procedure, and should not be interpreted extensively.

The activation parameters, in Table III, for the cross reactions show that all of the entropies of activation ($\Delta S_{12}^{\ddagger}$) are fairly constant while the enthalpies of activation ($\Delta H_{12}^{\ddagger}$) vary significantly. One interpretation of this would be that the contribution from the A factor is similar for all the cross reactions while reorganization energies are varying. This interpretation assumes that the reorganization energies are primarily enthalpic. However, as with the discussion of the cross-reaction rate constants, it is preferable to interpret the apparent $\Delta H_{11}^{\ddagger}$ and $\Delta S_{11}^{\ddagger}$ values instead of the cross-reaction parameters. It is especially important to compensate for $\Delta H°$ and $\Delta S°$, since these values vary extensively. The activation enthalpies and entropies are calculated within Marcus theory by eq 5a–f. The symbols not already

$$\Delta H_{12}^* = \frac{\Delta H_{11} + \Delta H_{22}}{2}(1 - 4(\alpha^*)^2) + \frac{\Delta H°}{2}(1 + 2\alpha^*) \quad (5a)$$

$$\Delta S_{12} = \frac{\Delta S_{11}^* + \Delta S_{22}^*}{2}(1 - 4(\alpha^*)^2) + \frac{\Delta S°}{2}(1 + 2\alpha^*) \quad (5b)$$

$$\alpha^* = \frac{\Delta G°}{4(\Delta G_{11}^* + \Delta G_{22}^*)} \quad (5c)$$

$$\Delta S^* = \Delta S^{\ddagger} - R \ln\left(\frac{hA}{k_B T}\right) + \frac{R}{2} \quad (5d)$$

$$\Delta H^* = \Delta H^{\ddagger} + \frac{RT}{2} \quad (5e)$$

$$\Delta G^* = \Delta G^{\ddagger} + RT \ln\left(\frac{hA}{k_B T}\right) \quad (5f)$$

defined are Planck's constant h, and Boltzmann's constant k_B. The "$*$" indicates Marcus-theory activation parameters, and the "$\ddagger$" indicates transition-state-theory activation parameters. The calculated values of $\Delta H_{11}^{\ddagger}$ and $\Delta S_{11}^{\ddagger}$ are shown in Table IV. These values give a much different picture than the cross-reaction activation parameters presented. The apparent self-exchange parameters have considerable scatter in both the enthalpy and the entropy. The enthalpy changes by approximately 5 kcal mol^{-1} and the entropy by approximately 25 cal mol^{-1}/deg^{-1}. These values tend to compensate, giving values of $\Delta G_{11}^{\ddagger}$ that vary by less than 2 kcal mol^{-1}. This compensation behavior, as so often happens,[23] obscures any trend that might allow any mechanistic interpretation, except to note that it probably arises from solvation effects.

We again want to look at the activation parameters for reactions in which a single cage complex was reacted with two ferrocenes. What we see this time is that for two of the three cages, $Co(dpg)_3(BC_6H_5)_2$ and $Co(nox)_3(BF)_2$, the activation parameters are very similar.[24] The calculated values for the $Co(dmg)_3(BF)_2$ complex do not agree as well, but all are within the error limits we have estimated.

Figure 2 shows the effect of added n-Bu_4NBF_4 on k_{12} for five of the cages and the effect of varying the counterion for reaction I. For all cases, except for the addition of n-$Bu_4NB(C_6H_5)_4$, a decrease in k_{12} with added electrolyte is seen. As noted previously,[10,11] we ascribe this effect to ion pairing of the cobalt complex with the ion pair reacting more slowly than the free cobalt cage ion. We have also stated[11] that the observed decrease in k_{12} with added electrolyte may be due to changes in activity coefficients. In a subsequent study[10] we used calculated activity coefficients in the fitting equations and demonstrated that the effect was still observed. In the case of added n-$Bu_4NB(C_6H_5)_4$ there is no change in k_{12} (see Figure 2a) while a significant change in activity coefficient is predicted. This result gives us further evidence that the decrease in k_{12} with added electrolyte is due to ion pairing and not to changes in the activity coefficients. With this assumption, a rate law employing ion pairing was derived and used for fitting the data. The solid lines in Figure 2 are a result of these fits to eq 6. The parameters k_0, k_{IP}, K_{assoc}, and $[X^-]$ are

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

the rate constant for the free-ion path, the rate constant for the ion-paired path, the association constant for the cobalt cage with

---

[23] (a) Leffler, J.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963. (b) Ives, D. I. G.; Marsden, P. D. *J. Chem. Soc.* **1965**, 649. (c) Laidler, K. J. *Trans. Faraday Soc.* **1959**, *55*, 1725. (d) Larson, J. W.; Hepler, L. G. In "Solvent-Solute Interactions"; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969. (e) Ritchie, C. D.; Sager, W. *Prog. Phys. Org. Chem.* **1964**, *2*, 323. (f) Lumry, R.; Rajendar, S. *Biopolymers* **1970**, *9*, 1125.

[24] This is the expected result since a factor of 2 in k_{11} makes only a 0.4 kcal mol^{-1} difference in $\Delta G_{11}^{\ddagger}$.

Table V. Fit Parameters Obtained from the Cross-Reaction Dependence on Added Electrolyte[a]

reacn	electrolyte	$10^{-3}k_0$, M^{-1} s^{-1}	$10^{-3}k_{IP}$, M^{-1} s^{-1}	K_{assoc}
I	n-Bu_4NBF_4	15.9 (+0.14, −0.18)	7.7 (+0.34, −0.56)	9 (+1.2, −1.5)
III	n-Bu_4NBF_4	4.6 (±0.04)	3.4 (+0.11, −0.19)	8 (±2.8)
IV	n-Bu_4NBF_4	1810 (+45, −34)	720 (+267, −298)	4 (+4.8, −1.8)
V	n-Bu_4NBF_4	33.9 (±0.20)	9.3 (+0.70, −0.80)	5 (+0.5, −0.4)
VII	n-Bu_4NBF_4	8.7 (±0.05)	5.2 (±0.30)	5 (+1.2, −0.9)
I	n-Bu_4NPF_6	14.8 (+0.26, −0.22)	4.1 (+1.20, −1.40)	5 (+1.9, −1.3)
I	n-Bu_4NBr	15.4 (+0.40, −0.15)	8.4 (+0.72, −0.35)	12 (+6.5, −1.7)
I	n-Bu_4NI	15.5 (+0.52, −0.30)	9.8 (+0.36, −0.23)	126 (+66, −22)
				25[b] (+4.2, −4.1)

[a] Errors calculated from the method of support planes: Duggleby, R. G. *Eur. J. Biochem.* **1980**, *109*, 93. [b] Derived from the $Co(dmg)_3(BF)_2^+$–n-Bu_4NI reaction in the absence of ferrocene (see Figure 2e).

the counterion, and the total counterion concentration, respectively. Fit parameters are shown in Table V. Before the data are discussed, it should be mentioned that the data fitting did not take into account variation of activity coefficients with ionic strength. Equations employing activity coefficients calculated from the extended Debye–Hückel equation have been used previously[10] with good success, but for some of the data sets in this study, no fit with reasonable parameters was obtained. This occurred for those data sets that gave K_{assoc} of 5 M^{-1} or less (when fit with $\gamma = 1$). This arises due to the failure of the Debye–Hückel equation to predict activity coefficients correctly at high ionic strength. Attempts to use the Davies equation were no more successful. The inability of the fitting procedure to produce realistic association constants in some cases of especially weak apparent ion association does not alter the conclusion that all reactions studied, except for the reaction in the presence of n-$Bu_4NB(C_6H_5)_4$, have shown inhibition by added electrolyte. We have presented the fit parameters assuming activity coefficients of 1 for consistency. By doing this we can only assign the k_{IP}'s as upper limits and the K_{assoc}'s as lower limits (the k_0's do not change significantly from one model to the other). We still note that the cage complexes behave as relatively strong electrolytes in acetonitrile.[25]

The effect of different counterions on k_{12} for reaction I was studied by addition of different tetra-n-butylammonium salts. The salts used were n-Bu_4NBF_4, n-$Bu_4NB(C_6H_5)_4$, n-Bu_4NPF_6, n-Bu_4NBr, and n-Bu_4NI. Our interest in this aspect arose from publications by Endicott et al.,[26,27] in which they observed an increase in electron-transfer rate between two cations, by more than the electrostatic factor, when ion pairing occurred. Their results were interpreted as indicating participation of the anion in a superexchange mechanism, whereby the anion orbitals provide an electron-transfer path but the anion is never present as a reduced species. Furthermore, they found that as the reduction potential for the process $X\cdot + e^- = X^-$ (X^- being the ion-pairing anion) became closer to that of the oxidized reactant, the rate enhancement increased. The result in Figure 2 is that there is no effect or the rate decreases even though the reduction potentials of $Br\cdot$ and $I\cdot$ are close to that of the cobalt cage; in fact, I^- can reduce the cobalt cage. The interpretation in our case is that there is no electronic advantage in the use of the superexchange pathway, whereas the Endicott systems are of a significantly nonadiabatic nature without the anion and thus find a preferred path through use of the anion bridge. As we have discussed before,[10,11] the inhibition by the anion probably arises from a decrease in electron-transfer precursor complex stability, from a change in solvent reorganization, or possibly from an increase in electron-transfer distance that cannot be offset by a superexchange mechanism. Data for the ion-pairing behavior of two of the clathrochelates with BF_4^-, PF_6^-, and $B(C_6H_5)_4^-$ in other solvents have been reported elsewhere.[10,28]

An interesting point remains in the data for the iodide reduction of the $Co(dmg)_3(BF)_2^+$ complex and the iodide inhibition of the ferrocene reduction. As presented in Table V and Figure 2d,e, the apparent association constant of the clathrochelate with I^- is significantly higher in the presence of ferrocene than in its absence. This is independent of whether the I^- reduction is run at constant ionic strength, with use of n-Bu_4NBF_4, or with only n-Bu_4NI as the electrolyte. The difference in the association constants indicates that there is some type of interaction between I^- and $Fe(Cp)_2$ but is difficult to interpret further.

Conclusion

In conclusion, we have prepared several cobalt clathrochelates by varying the dioxime ligand and the boron cap. We have studied the electron-transfer behavior of these complexes through cross reactions with one or two of three different ferrocenes. We see wide variation in these measured k_{12}'s but can attribute most of this to changes in the thermodynamic driving force. Calculated self-exchange rate constants show little variation, indicating that structural changes have not affected their reactivity to any great extent. Simple Marcus theory seems to predict the behavior of these systems quite well, and in general the k_{11}'s are about the same as that of $Co(phen)_3^{3+}$ when work terms are included.[29,30] The activation parameters show some interesting behavior but have not yet been especially interpretable. Ion pairing decreases electron-transfer reactivity, and no evidence for a superexchange mechanism was found in our counterion studies; however, in the presence of $Fe(Cp)_2$, I^- shows a much higher affinity for the cobalt cage than would be predicted from studies in the absence of ferrocene.

This study is the basis for further work in which reactions between two clathrochelates will be studied in an attempt to determine how reactant interaction contributes to the electron-transfer reactivity and in which the behavior of the activation parameters will be further investigated.

Acknowledgment. We are pleased to acknowledge the financial assistance of the National Science Foundation through Grant CHE 8204101.

Registry No. $Co(dmg)_3(BF)_2^+$, 47596-93-0; $Co(dmg)_3(BC_6H_5)_2^+$, 100113-28-8; $Co(dmg)_3(BC_6H_5)_2BF_4$, 100113-33-5; $Co(dmg)_3(BC_4H_9)_2^+$, 100113-29-9; $Co(dmg)_3(BC_4H_9)_2BF_4$, 100113-34-6; $Co(nox)_3(BF)_2^+$, 100165-34-2; $Co(nox)_3(BC_6H_5)_2^+$, 100113-30-2; $Co(nox)_3(BC_6H_5)_2BF_4$, 100113-35-7; $Co(nox)_3(BC_4H_9)_2^+$, 100113-31-3; $Co(nox)_3(BC_4H_9)_2BF_4$, 100113-36-8; $Co(dpg)_3(BC_6H_5)_2^+$, 100113-32-4; $Co(dpg)_3(BC_6H_5)_2BF_4$, 100113-37-9; $Fe(Cp)_2$, 102-54-5; $Fe(CpCH_3)_2$, 1291-47-0; $Fe(Cp(CH_3)_5)_2$, 12126-50-0; Bu_4NBF_4, 429-42-5; Bu_4NPF_6, 3109-63-5; Bu_4NBr, 1643-19-2; Bu_4NI, 311-28-4.

Supplementary Material Available: Tables of $E_{1/2}$ vs. temperature, second-order rate constant dependence on added electrolyte, concentration-dependence, and temperature-dependence data (36 pages). Ordering information is given on any current masthead page.

---

(25) Insertion of activity coefficients for those cases that gave good fits raised K_{assoc} by less than a factor of 2.

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

(27) Ramasami, T.; Endicott, J. F. *Inorg. Chem.* **1984**, *23*, 3324.

(28) Borchardt, D. Ph.D. Thesis, Washington State University, 1985.

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

(30) Pelizzetti, E. *Inorg. Chem.* **1979**, *18*, 1386.