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Synthesis and Oxidation of Two Ferrocene-Capped Cobalt Clathrochelates in Methylene Chloride

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The synthesis and oxidation of two new ferrocene-capped cobalt clathrochelates are described. The compounds $Co(nox)_3(B(cp)Fe(cp))_2$ and $Co(dmg)_3(B(cp)Fe(cp))_2$ (nox is 1,2-cyclohexanedione dioximate(2−), dmg is dimethylglyoximate(2−), and cp is cyclopentadienide) can each proceed through a total of six species when a three-electron oxidation of the fully reduced forms occurs. A thermodynamic scheme has been developed to describe the oxidation process. The observed spectrophotometric behavior upon oxidation cannot be adequately explained by assigning one reduction potential to cobalt and one to the two iron centers. Instead, a minimum of three potentials is required. Reduction potentials for the six species, relative to ferrocene, are presented. These potentials show only slight temperature and added salt dependencies. Possible modes of interaction between the metal sites are discussed.

Introduction

There has been an increasing interest in characterizing the interaction between metal ion sites in polynuclear compounds,[1,2] mixed-valence compounds,[3,4] and metalloenzymes,[5] since systems which contain more than one redox-active metal site often exhibit properties that are dramatically different from those of the isolated sites.[6] This is primarily the result of the electronic interaction between the metal sites. In many systems the degree of interaction can be shown to correlate well with distance[7] and with the nature of the bonding of the ligands (σ or π) that bridge the metals.[8,9]

We have developed a synthesis for a new trimetallic complex, the components of which have been extensively studied by using electron-transfer kinetics, electrochemistry, and other physical methods. In the complex, the cobalt center is chelated by three dioxime ligands and capped by two ferrocenylborate groups as shown in Figure 1. It is a modification of the $Co(dmg)_3(BF)_2BF_4$ complex first synthesized by Rose and co-workers.[10]

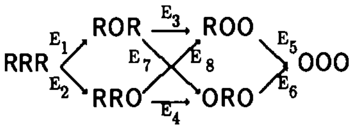
The $Co(nox)_3(B(cp)Fe(cp))_2$ and $Co(dmg)_3(B(cp)Fe(cp))_2$ complexes have the interesting feature of containing two different types of metal centers that are redox active. Oxidation of these compounds can proceed through a total of six different species as described by Scheme I. In the scheme R represents the reduced form and O represents the oxidized form of each metal center; the first and last positions represent iron centers, and the middle position represents cobalt. E_1 through E_8 are the reduction potentials relating the forms. The goal of this work is to determine the values of these potentials, as well as their temperature and salt dependencies. Further studies of these compounds will focus on their electron-transfer reactivity, especially the internal electron-transfer process.

Experimental Section

Materials. Starting materials and solvents were purchased from Aldrich Chemical Co., J. T. Baker Chemical Co., or Strem Chemical Co. The reagents $CoCl_2 \cdot 6H_2O$, dimethylglyoxime (H_2dmg), 1,2-cyclohexanedione dioxime (H_2nox), and BBr_3 were used as received. Ferrocene was sublimed prior to use. Solvents were reagent grade and were purified by drying over P_2O_5 (1 g for every 100 mL of solvent) for 24 h, followed by distillation under an argon atmosphere.[11] Elemental analyses were performed by Galbraith Laboratories, Inc.

$Co(nox)_3(B(cp)Fe(cp))_2$. Anhydrous cobalt chloride (1.76 g) and 1,2-cyclohexanedione dioxime (3.15 g) were combined in a sealed round-bottom flask, which was then evacuated and filled with argon. Deoxygenated methanol (125 mL) was then added by cannular transfer and the mixture allowed to stir overnight. Ferrocenylboronic acid (3.4 g), prepared from boron tribromide and ferrocene,[12] was also dissolved in deoxygenated methanol (50 mL) and then added by cannular transfer. The mixture was allowed to stir for 24 h, and the brown product was separated by filtration and washed with methanol. It was recrystallized by dissolving it in the minimum amount of methylene chloride followed by the addition of 25% methanol by volume. The more volatile methylene chloride was then removed by rotary evaporation. Following filtration, the brown solid was dissolved in methylene chloride and the resulting solution was passed through a silica gel column (4.5 cm × 30 cm) using methylene chloride as eluent at a flow of 2 mL/min. Only the major band was collected. The final product, a brown powder, was obtained by rotary evaporation of the solvent. The compound was characterized by comparison of infrared and visible spectra with those of analogous compounds. Anal. Calcd for $CoN_6O_6C_{38}H_{42}B_2Fe_2$: C, 52.39; H, 4.86; N, 9.65. Found: C, 51.80; H, 4.95; N, 9.39. For the fully reduced form, $\epsilon_{470nm} = 6050\ M^{-1}\ cm^{-1}$ and $\epsilon_{620nm} = 188\ M^{-1}\ cm^{-1}$. For the fully oxidized form, $\epsilon_{470nm} = 805\ M^{-1}\ cm^{-1}$ and $\epsilon_{620nm} = 840\ M^{-1}\ cm^{-1}$.

Scheme I



$Co(dmg)_3(B(cp)Fe(cp))_2$. This compound was prepared in the same manner as above except dimethylglyoxime replaces 1,2-cyclohexanedione dioxime. The visible absorption spectrum of the final product showed evidence for Co(III). The compound was therefore reduced to the Co(II) state by dissolving it in methylene chloride followed by the addition of a slight excess of anhydrous hydrazine prior to the recrystallization and purification as above. Anal. Calcd for $CoN_6O_6C_{32}H_{36}B_2Fe_2$: C, 48.47; H, 4.58; N, 10.60. Found: C, 48.63; H, 4.57; N, 10.68. For the fully reduced form, $\epsilon_{470nm} = 5200\ M^{-1}\ cm^{-1}$ and $\epsilon_{620nm} = 250\ M^{-1}\ cm^{-1}$, while, for its fully oxidized form, $\epsilon_{470nm} = 880\ M^{-1}\ cm^{-1}$ and $\epsilon_{620nm} = 1035\ M^{-1}\ cm^{-1}$.

$Mn(CNC_6H_4CH_3)_6(BF_4)_2$. The oxidant $Mn(CNC_6H_4CH_3)_6(BF_4)_2$ ($E° = 560$ mV vs ferrocene in CH_2Cl_2) was prepared from MnI_2, 0.065 mol, dissolved in 30 mL of anhydrous ethanol, to which 0.37 mol of *p*-tolylisocyanide was added with stirring. The solution was allowed to stir overnight and then evaporated to dryness. The solid was washed three times with ether. The dark brown solid was dissolved in a minimum amount of methylene chloride and the mixture shaken in a separatory funnel with a cold, aqueous solution of sodium dithionite. The yellow organic layer was evaporated to dryness, yielding a yellow powder. This

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† Original synthesis performed by D. Borchardt, Department of Chemistry, University of California Riverside, Riverside, CA 92521 (unpublished results).

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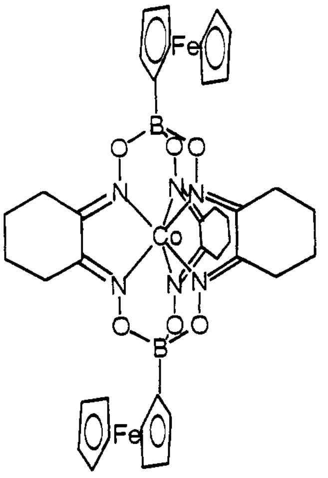

Figure 1. Pictorial representation of the compound Co(nox)$_3$(B(cp)Fe(cp))$_2$. For the compound Co(dmg)$_3$(B(cp)Fe(cp))$_2$ the doubly deprotonated dimethylglyoxime replaces doubly deprotonated 1,2-cyclohexanedione dioxime.

powder was dissolved in acetonitrile and passed over an ion-exchange column of Dowex 1-X8 anion-exchange beads in the BF_4^- form. The solvent was evaporated, and the compound was recrystallized from hot acetonitrile–water several times, yielding the Mn(I) product. This solid was then oxidized to the Mn(II) compound by dissolving it in acetonitrile and adding a slight excess of $NOBF_4$. The solvent was partially removed with a rotary evaporator, and ether was added to the solution, producing violet crystals.[13] In the Mn(II) oxidation state this compound is intensely colored with molar absorptivity coefficients of 5000 and 2800 M^{-1} cm^{-1} at 470 and 620 nm, respectively. The reduced form is essentially colorless, showing no absorbance in the visible region; therefore the presence of Mn(II) can easily be detected. All solutions were prepared just prior to use.

Absorption Spectra. The spectrophotometric titration was carried out on a Varian 219 spectrophotometer equipped with a thermostated cell holder. The solvent was methylene chloride, and 1.00-cm Spectrocell gastight cells were used. All solutions were prepared under argon and transferred by using Hamilton gastight syringes. An absorption spectrum of the cobalt compound in its fully reduced form was recorded; a known amount of oxidant was then added and the resulting spectrum recorded. Absorbance values at the wavelengths to be used in the data analysis, 620 and 470 nm, were read to four decimal places from the meter. This was repeated until the first excess of oxidant was detected. A titration typically required from 20 to 30 additions to reach the end point. For all titrations a 2-mL sample of the cobalt compound (see Table II for concentrations) was titrated, requiring from 0.38 to 0.68 mL of oxidant to reach the end point. The first excess of oxidant was detected by the addition of 0.010 mL of oxidant, which led to the appearance of absorbance due to the manganese(II) isocyanide complex; this represents less than 3% error in the determination of the end point. Approximately 5 min was allowed between additions of oxidant to ensure that the system had reached equilibrium.

Data Analysis. Absorbance values at 620 and 470 nm were corrected for dilution and for contributions from overlap between the absorbance bands of the cobalt and iron components (eqs 6 and 7). It was assumed that there was no intervalence band. The absorbance at any wavelength is described by eq 1. Substitution of $[Co^{3+}] = CT - [Co^{2+}]$, $[Fe^{3+}] =$

$$A_\lambda = \epsilon_\lambda{}^{Co^{2+}}[Co^{2+}] + \epsilon_\lambda{}^{Co^{3+}}[Co^{3+}] + \epsilon_\lambda{}^{Fe^{2+}}[Fe^{2+}] + \epsilon_\lambda{}^{Fe^{3+}}[Fe^{3+}] \qquad (1)$$

$FT - [Fe^{2+}] = 2(CT) - [Fe^{2+}]$, and $\Delta\epsilon^{M^{2+/3+}}$, where CT = total cobalt, FT = total iron, and $\Delta\epsilon_\lambda{}^{M^{2+/3+}}$ is the reduced minus oxidized extinction coefficient due to metal center M, into eq 1 yields

$$A_\lambda = \epsilon_\lambda{}^{Co^{3+}}(CT) + \epsilon_\lambda{}^{Fe^{3+}}(2(CT)) + \left(\Delta\epsilon_\lambda{}^{Co^{2+/3+}}\right)[Co^{2+}] + \left(\Delta\epsilon_\lambda{}^{Fe^{2+/3+}}\right)[Fe^{2+}] \qquad (2)$$

From the initial minus the final absorbance (eqs 3a and 3b), the values of $\Delta\epsilon_{470}{}^{Fe^{2+/3+}}$ and $\Delta\epsilon_{620}{}^{Co^{2+/3+}}$ can be determined (eqs 4a and 4b). Combining eqs 3b and 2 at 470 and 620 nm, respectively, yields eqs 5 and 6.

$$A_\lambda{}^{init} = \epsilon_\lambda{}^{Co^{2+}}(CT) + \epsilon_\lambda{}^{Fe^{2+}}(2(CT)) \qquad (3a)$$

$$A_\lambda{}^{final} = \epsilon_\lambda{}^{Co^{3+}}(CT) + \epsilon_\lambda{}^{Fe^{3+}}(2(CT)) \qquad (3b)$$

$$\Delta\epsilon_{470}{}^{Fe^{2+/3+}} = \left[\{A_{\lambda_{470}}{}^{init} - A_{\lambda_{470}}{}^{final}\} - (CT)\Delta\epsilon_{\lambda_{470}}{}^{Co^{2+/3+}}\right] \Big/ 2(CT) \qquad (4a)$$

$$\Delta\epsilon_{\lambda_{620}}{}^{Co^{2+/3+}} = \left[\{A_{\lambda_{620}}{}^{init} - A_{\lambda_{620}}{}^{final}\} - 2(CT)\Delta\epsilon_{\lambda_{620}}{}^{Fe^{2+/3+}}\right] \Big/ (CT) \qquad (4b)$$

$$[Co^{2+}] = \left\{(A_{470} - A_{470}{}^{final}) - \left(\Delta\epsilon_{470}{}^{Fe^{2+/3+}}\right)[Fe^{2+}]\right\} \Big/ \Delta\epsilon_{470}{}^{Co^{2+/3+}} \qquad (5)$$

$$[Fe^{2+}] = \left\{(A_{620} - A_{620}{}^{final}) - \left(\Delta\epsilon_{620}{}^{Co^{2+/3+}}\right)[Co^{2+}]\right\} \Big/ \Delta\epsilon_{620}{}^{Fe^{2+/3+}} \qquad (6)$$

Substitution of eq 6 into eq 5 leads to eq 7. At any point along the

$$[Co^{2+}] = \frac{(A_{470} - A_{470}{}^{final})\Delta\epsilon_{620}{}^{Fe^{2+/3+}} - (A_{620} - A_{620}{}^{final})\Delta\epsilon_{470}{}^{Co^{2+/3+}}}{\left(\Delta\epsilon_{470}{}^{Co^{2+/3+}}\right)\Delta\epsilon_{620}{}^{Fe^{2+/3+}} - \left(\Delta\epsilon_{620}{}^{Co^{2+/3+}}\right)\Delta\epsilon_{470}{}^{Fe^{2+/3+}}} \qquad (7)$$

titration, the total amount of Mn(II) that has been added (MT_{meas}) is related to the equilibrium concentrations of Co^{2+} and Fe^{2+} by eq 8.

$$MT = [CO^{3+}] + [Fe^{3+}] = ([CT] - [Co^{2+}]) + (2[CT] - [Fe^{2+}]) \qquad (8)$$

Initial guesses are made for the values of $\Delta\epsilon_{620}{}^{Fe^{2+/3+}}$ and $\Delta\epsilon_{470}{}^{Co^{2+/3+}}$ from the initial and final absorbances in a titration. Equations 4a and 4b are then used to calculate $\Delta\epsilon_{470}{}^{Fe^{2+/3+}}$ and $\Delta\epsilon_{620}{}^{Co^{2+/3+}}$. These values are used in eqs 6 and 7 to determine $[Co^{2+}]$ and $[Fe^{2+}]$, which are used to obtain MT. In a iterative procedure the values of $\Delta\epsilon_{620}{}^{Fe^{2+/3+}}$ and $\Delta\epsilon_{470}{}^{Co^{2+/3+}}$, which result in the smallest value of χ^2, based on eq 9, are retained. The

$$\chi^2 = \sum_{i=1}^{n}(MT_{meas} - MT_{calc})^2/N \qquad (9)$$

four $\Delta\epsilon_\lambda{}^{M^{2+/3+}}$ values are thus optimized. These optimized values are then used in eqs 6 and 7 to calculate values of $[Co^{2+}]$ and $[Fe^{2+}]$.

The values of $Co_{meas,i}{}^{2+}$ are then fit to eq 10. The values P1 through

$$\chi^2 = \sum_{i=1}^{n}(Co^{2+}{}_{calc,i} - Co^{2+}{}_{meas,i})^2/N \qquad (10)$$

$$Co^{2+}{}_{calc} = \frac{1 + P2 + P4}{1 + P1 + P2 + P3 + P4 + P5} \qquad (11)$$

P5 come from the Nernst equation as follows:

$$P1 = \frac{[ROR]}{[RRR]} = 10^{(E-E_1)/0.059} \qquad P2 = 2\frac{[RRO]}{[RRR]} = 10^{(E-E_2)/0.059}$$

$$P3 = 2\frac{[ROO]}{[RRR]} = 10^{(2E-E_1-E_3)/0.059} \qquad P4 = \frac{[ORO]}{[RRR]} = 10^{(2E-E_2-E_4)/0.059}$$

$$P5 = \frac{[OOO]}{[RRR]} = 10^{(3E-E_1-E_3-E_5)/0.059}$$

Here, E is the solution potential, n is the number of data points, N is the number of degrees of freedom (number of data points minus the number of parameters), $Co^{2+}{}_{meas,i}$ are the values of $[Co^{2+}]_i/[CT]$, and the rest of the parameters are shown in the scheme. From a nonlinear least-squares analysis of eq 10, using the program CURFIT described in Bevington[14] and converted to Microsoft Quick Basic, the values of the parameters E_1 through E_5 that result in the smallest value of χ^2 are determined. When E_1 is arbitrarily set to 0.0 and E_2 through E_5 are determined relative to E_1, the total number of parameters required to describe the system is reduced to 4. On the basis of the scheme, E_6, E_7, and E_8 can be calculated if E_1 through E_5 are known.

In a typical fit of the data, the value of E is initially set to a value substantially more negative than any of the initial guesses for the E_i's. The concentration of each of the six different species is calculated, and from these the fractions of cobalt (eq 11) and iron[15] in their reduced forms are calculated. The calculated moles of cobalt oxidized plus the iron oxidized is then compared to the experimental amount of oxidant that has been added at that particular point in the titration; if the two do not agree to within ±0.005 electron, the value of the solution potential (E) is changed in a stepwise manner until this criterion is met. The above is repeated for each point in the titration, with each point resulting in one value of $Co^{2+}{}_{calc,i}$. The value of χ^2 is then calculated as described in eq

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(15) $Fe^{2+}{}_{calc} = (2 + 2(P1) + P2 + P3)/(1 + P1 + P2 + P3 + P4 + P5)$.

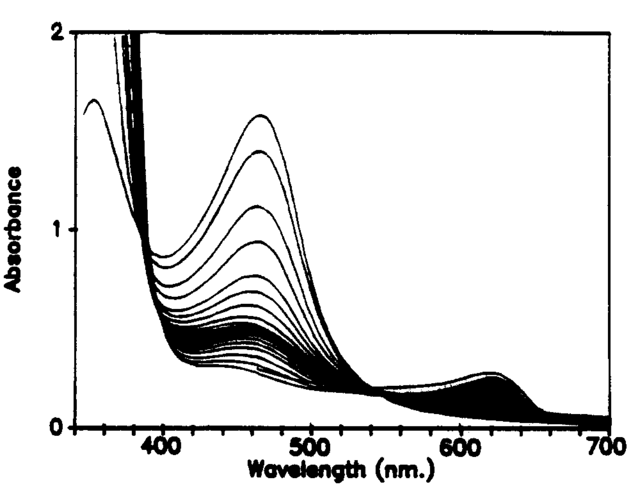

Figure 2. Absorption spectra for the titration of $Co(nox)_3(B(cp)Fe(cp))_2$ at 20 °C and 0.1 M salt. The curve that is highest at long wavelength and ends at shorter wavelength is the first excess of oxidant.

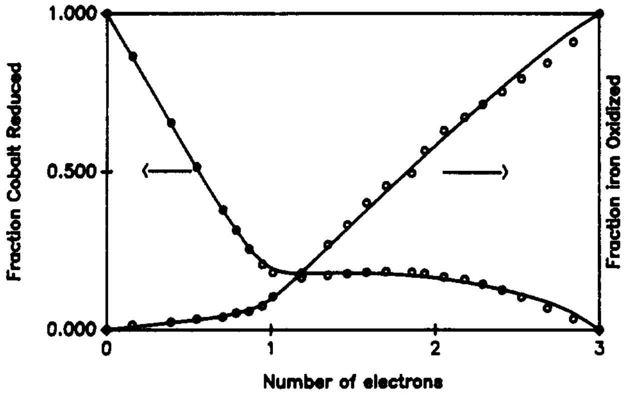

Figure 3. Plot of the fractions of Co^{2+} and Fe^{3+} as a function of number of electrons added from the titration data of Figure 2. Circles are experimental points. The solid line is the fit to the data based on the two-parameter model.

10. The values of E_2 through E_5 are next modified, and the above procedure is repeated. The reduction potentials that result in a minimum value of χ^2 are retained. Several fits were attempted, each with different initial guesses, as an attempt to eliminate obtaining a false minimum.

Electrochemistry. A potentiometric titration of the cage was performed in a manner analogous to the spectrophotometric titration under an inert atmosphere with a Princeton Applied Research Model 174A polarographic analyzer and a Model 303 cell. The solution potential was recorded after each addition of oxidant. A constant temperature of 20 ± 0.1 °C was maintained by surrounding the cell compartment in a thermostated jacket controlled by a circulating water bath. A three-electrode system employing platinum working and counter electrodes and an isolated silver reference electrode was used. The reduction potential of ferrocene was determined from a titration of sublimed ferrocene with $Mn(CNR)_6(BF_4)_2$ oxidant at the same temperature and with the same reference electrode. The supporting electrolyte was $(n\text{-}Bu)_4NBF_4$.

Results

The resultant electronic absorption spectra for a typical titration of $Co(nox)_3(B(cp)Fe(cp))_2$, "cage", with $Mn(CNR)_6(BF_4)_2$ is shown in Figure 2. The cage has major absorbances in the visible region at 360 and 470 nm. Upon addition of oxidant, the absorbance at 360 nm increases while the absorbance at 470 nm begins to decrease in intensity. These changes are consistent with the loss of an electron from Co(II) to form Co(III). In addition, a new absorption peak begins to appear at 620 nm, which is consistent with the loss of an electron from Fe(II) to form Fe(III). The titration was found to require 3 equiv of oxidant, within the precision of the solution preparation, at which point the presence of the excess oxidant is detected by its absorption over the range 420–700 nm. Therefore the net reaction is taken to be

$$Co(nox)_3(cap)_2 + 3Mn(CNR)_6^{2+} \rightarrow [Co(nox)_3(cap)_2]^{3+} + 3Mn(CNR)_6^{+}$$

Table I. Results of the Four-Parameter Fit to Scheme I (mV)[a]

	T, °C	E_2	E_3	E_4	E_5	E_6[b]	E_7[b]	E_8[b]
A	5	75^{+1}_{-3}	154^{+2}_{-1}	78^{+8}_{-7}	124^{+23}_{-2}	125	153	79
	10	70^{+1}_{-1}	154^{+4}_{-4}	80^{+3}_{-7}	120^{+13}_{-8}	124	150	74
	15	70^{+4}_{-3}	134^{+3}_{-10}	64^{+20}_{-15}	117^{+27}_{-4}	117	134	64
	20	64^{+5}_{-2}	147^{+8}_{-10}	74^{+15}_{-11}	107^{+26}_{-5}	116	138	83
	25	58^{+3}_{-2}	137^{+4}_{-5}	73^{+12}_{-8}	115^{+15}_{-6}	121	131	79
B	20	83^{+2}_{-3}	163^{+25}_{-15}	35^{+15}_{-35}	38^{+14}_{-35}	89	128	89

[a] A: $[Co(nox)_3(B(cp)Fe(cp))_2]$ = 0.23 mM, $[Mn(CNR)_6(BF_4)_2]$ = 2.3 mM. B: $[Co(dmg)_3(B(cp)Fe(cp))_2]$ = 0.24 mM, $[Mn(CNR)_6(BF_4)_2]$ = 2.1 mM. [b] Calculated from Scheme I. $E_1 = 0.0$.

Table II. Results of the Two-Parameter Fit to Scheme I (mV)[a]

	T, °C	$E_2 = E_4 = E_5$	E_3	$E_6 = E_8$[b]	E_7[b]
A	5	75^{+2}_{-1}	175^{+7}_{-1}	100	150
	10	72^{+2}_{-1}	170^{+6}_{-1}	98	144
	15	69^{+2}_{-2}	162^{+5}_{-2}	93	140
	20	65^{+3}_{-1}	159^{+10}_{-4}	94	130
	20[c]	72^{+2}_{-2}	161^{+5}_{-2}	89	144
	25	62^{+2}_{-2}	150^{+6}_{-4}	88	124
B	20	71^{+3}_{-1}	174^{+8}_{-4}	100	142

[a] A: $[Co(nox)_3(B(cp)Fe(cp))_2]$ = 0.23 mM, $[Mn(CNR)_6(BF_4)_2]$ = 2.3 mM. B: $[Co(dmg)_3(B(cp)Fe(cp))_2]$ = 0.2j mM, $[Mn(CNR)_6(BF_4)_2]$ = 2.1 mM. [b] Calculated from Scheme I. [c] In 0.10 M $(n\text{-}Bu)_4NBF_4$; $[Co(nox)_3(B(cp)Fe(cp))_2]$ = 0.27 mM, $[Mn(CNR)_6(BF_4)_2]$ = 1.5 mM. $E_1 = 0.0$.

Table III. Potentials (mV) Related to Ferrocene at 20 °C[a]

	E_1[b]	$E_2 = E_4 = E_5$[c]	E_3[c]	$E_6 = E_8$[d]	E_7[d]
A	-176^{+6}_{-6}	-111^{+8}_{-7}	-17^{+14}_{-9}	−82	−46
B	-165^{+9}_{-9}	-94^{+11}_{-10}	$+9^{+15}_{-11}$	−76	−21

[a] A: $Co(nox)_3(B(cp)Fe(cp))_2$; B: $Co(dmg)_3(B(cp)Fe(cp))_2$. [b] Calculated from potentiometric titration. [c] Values from Table II adjusted relative to E_1. [d] Calculated from Scheme I.

In the calculations, the volume of oxidant necessary to complete the titration was taken as representing exactly three electrons. From this volume the number of reducing equivalents that had been added at each point in the titration was determined. This was considered more accurate than the concentrations obtained from sample weights. Figure 3 shows the fraction Co^{2+} and Fe^{3+} (see data analysis) as a function of number of electrons added for the data in Figure 2.

The results of the fit of eq 11 at five temperatures for $Co(nox)_3(B(cp)Fe(cp))_2$ and at 20 °C for $Co(dmg)_3(B(cp)Fe(cp))_2$ with no added salt are presented in Table I. These results are based on a four-parameter model, relative to E_1, which is set equal to 0.0. The results of the fit based on a two-parameter model, with $E_2 = E_4 = E_5$ and $E_1 = 0.0$, are presented in Table II. The titration was also performed in the presence of 0.1 M salt. The results of the fits to these data, based on the two-parameter model, are also presented in Table II.

A comparison of the measured and calculated values is shown in Figure 3 for the two-parameter model. Only the data at 470 nm are fit on the basis of on (11). The parameters generated from this fit were then used to produce the line for fraction of iron oxidized. It was decided to fit the data at 470 nm and not at 620 nm for two reasons. First, the absorbance changes were much larger at 470 nm, and second, there was considerably less interference from absorbance due to the Fe center at this wavelength than due to the Co center at 620 nm.

The results of the potentiometric titration are presented in Figure 4. The value of E_1 is obtained as the difference between the measured solution potential and the value obtained from the fitting program. A value of E_1 was determined for each point in the titration, and the average value reported. With the value of E_1 determined, the values of E_2 through E_8 can now be adjusted accordingly and are reported in Table III. The values of E_1, as determined from the potentiometric titration relative to ferrocene

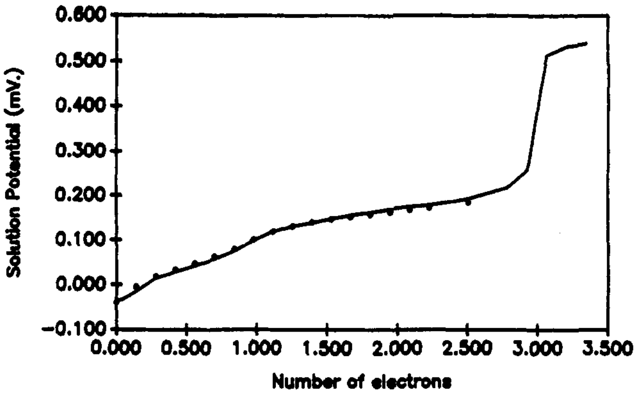

Figure 4. Potentiometric titration of $Co(nox)_3(B(cp)Fe(cp))_2$ at 20 °C and 0.1 M $(n\text{-}Bu)_4NBF_4$. The solid line is the measured solution potential. Points are calculated solution potentials from the two-parameter model.

at 20 °C, are −176 and −165 mV for $Co(nox)_3(B(cp)Fe(cp))_2$ and $Co(dmg)_3(B(cp)Fe(cp))_2$, respectively. The presence of the $Co(dioxime)_3(B-)_2$ structure thus makes the Fe(II) (E_2) easier to oxidize than ferrocene. This shift in potential can be attributed to the presence of boron, as the reduction potential of $(cp)Fe(cp)B(OH)_2$ is −76 mV relative to ferrocene. The presence of $Fe(cp)_2$ makes the Co(II) (E_1 and E_6) more difficult to oxidize. The magnitude of this effect can be estimated by comparison with the $Co(nox)_3(BC_6H_5)_2$ and $Co(dmg)_3(BC_6H_5)_2$ systems ($E^{1/2}$ = −200 mV and $E^{1/2}$ = −212 mV, respectively). These potentials have been shown to be independent of added salt over the range 0.05–0.5 M BF_4^- in several different solvents.[16,17]

Using E_1 determined from the potentiometric titration and the other potentials determined relative to E_1 in the spectrophotometric titration, it is possible to determine a calculated solution potential of each point of titration from eq 11. As can be seen, there is excellent agreement between measured and calculated solution potentials.

Cyclic voltammetry of the compound in methylene chloride shows quasireversible waves, one at −243 mV and another with a greater peak current at −85 mV relative to ferrocene. The wave at −243 mV can be associated with the Co(II/III) couple, while the Fe(II/III) couple corresponds to the wave at −85 mV. In $Co(dmg)_3(B(cp)Fe(cp))_2$ the wave associated with the Co(II/III) couple is found at −258 mV while the Fe(II/III) signal is at −70 mV relative to ferrocene. Assignments are consistent with measurements on ferrocenylboronic acid and $Co(dmg)_3(BC_6H_5)_2$ or $Co(nox)_3(BC_6H_5)_2$. The results of the cyclic voltammetry experiments differ from those of the potentiometric titration in the number of reversible potentials, the value of these potentials, and the separation between the potentials. This occurs because, in the case of the potentiometric titration, we are dealing with a system that is allowed to reach equilibrium, while, in the cyclic voltammetry experiments, the system is not at equilibrium and results are in fact controlled by the electrode kinetics. Evidence that other electron-transfer processes, either intramolecular or intermolecular, are also contributing has been found from analysis of the scan rate dependence of the peak currents.[23] These results cannot be analyzed as simple reversible processes. The cyclic voltammetry results most closely resemble E_1 and E_5, which are the potentials for the formation of ROR and OOO, respectively. These are the predominant intermediate species throughout the titration, on the basis of the fit parameter results (Figure 5).

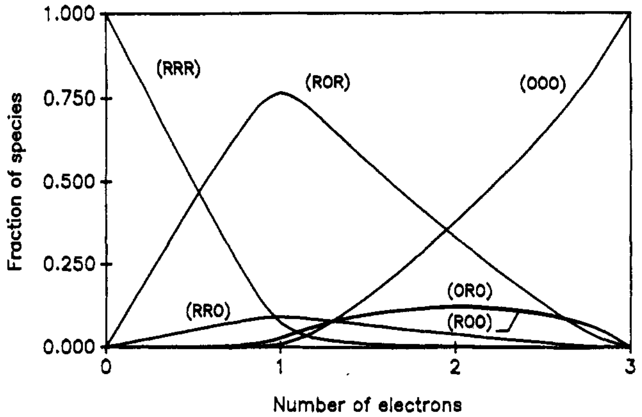

Figure 5. Distribution of species as a function of number of electrons added for the compound $Co(nox)_3(B(cp)Fe(cp))_2$ at 20 °C in 0.1 M salt, based on the two-parameter model. All curves are labeled above the line except ROO.

Discussion

Initial fits to the data of Figure 3 were done by assuming that all potentials relating the various species of the scheme were different from each other (four-parameter model). Upon inspection of the best fit parameters based on this model, it was clear the value of E_3 was significantly larger than the other potentials at all temperatures. However, the remaining three potentials were not as clearly distinguished. Therefore attempts were made to fit the data with a smaller number of parameters.

Three parameter fits were performed for all six possible combinations of setting any two parameters equal, with the two remaining parameters being left independent. χ^2 values less than 1.05 times larger than the four-parameter fits were obtained for the condition $E_5 = E_2$, $E_5 = E_4$, or $E_2 = E_4$. The condition $E_3 = E_2$, $E_3 = E_4$, or $E_3 = E_5$ increased χ^2 by as much as 1.3 times. However, visual inspection of plots showed the three-parameter fits to be indistinguishable from the four-parameter fits.

Fits based on the four possible two-parameter models with three parameters equal to each other and the remaining parameter independent were also performed. Of these, the condition $E_2 = E_4 = E_5$, with E_3 still independent (two-parameter model), resulted in the smallest χ^2, as may have been suggested by the three-parameter fits above. χ^2 values were an average of only 1.60 times larger than those from the four-parameter fits. The other three possible conditions gave χ^2 values as much as 120 times the four-parameter model. As can be seen in Figure 3, there is excellent agreement between the calculated and measured fractions of Co^{2+} and Fe^{3+} when the data are fit with the two-parameter model.

Attempts to reduce the number of parameters further by setting $E_2 = E_3 = E_4 = E_5$, a model with one potential for the oxidation of cobalt and one potential for the oxidation of iron, both of which are then independent of the oxidation state of the other metal, failed to produce adequate fits to the data, giving average χ^2 values 100 times those obtained with the four-parameter fits.

Errors for the parameters were determined by the method of support planes.[18] From Table I, it can be seen that E_2 and E_3 are well defined with errors of 10% or less with only one exception. The errors for E_4 and E_5 are significantly larger. During the error analysis the following observations were made. The parameter E_2 determines the slope of the line for the fraction of cobalt present up to one electron having been added. E_3 and to a lesser extent E_4 and E_5 determine the fraction of cobalt present in the two- to three-electron range. A change in E_3 is compensated by a change in the opposite direction of E_5 and vice versa, whereas a change in E_2 or E_5 is compensated by all the remaining parameters.

From the results of the two-parameter fits, the principal oxidation path taken can be described. First, RRR is oxidized to ROR. The next thermodynamically favored product is ORO, which results in the two oxidized metal centers having the greatest separation possible. The final oxidation is the formation of the totally oxidized product OOO. The species RRO and ROO are

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only present at low concentration, as shown in Figure 5.

From Table III we see that the potential necessary to oxidize cobalt when both of the irons are in their reduced state (E_1) is different from the potential necessary when either one or both are in their oxidized state (E_6 and E_8). In addition the potentials necessary to oxidize each of the iron sites are the same when cobalt is in its reduced form ($E_2 = E_4$) but not when cobalt is in its oxidized form ($E_3 \neq E_5$). It is interesting that, within our precision, E_5 is not different from E_2 or E_4, and E_3 is greater than E_5, while both reflect Fe oxidation in the presence of an oxidized Co.

The potentials E_2 through E_5 (two-parameter model), relative to E_1, decrease with increasing temperature. Substitution of dmg for nox in the cage shifts the potential of cobalt (E_1 in Table III) to a more positive value, which is consistent in magnitude but opposite in direction compared with the cyclic voltammetry results for the related cobalt clathrochelate compounds $Co(nox)_3(BF)_2$ and $Co(dmg)_3(BF)_2$.

Determination of E_1 required using an ionic strength of 0.1 M. In order to determine if the ionic strength requirement has an effect on the various potentials, a spectrophotometric titration was carried out at this ionic strength and best fit parameters were determined. The resultant potentials (Table II) showed that ionic strength over the range 0–0.1 M has little effect on the potentials.

On the basis of these results, we can conclude that the metal sites do interact with each other and that a minimum of three different potentials are necessary to describe the system (E_1, $E_{2,4,5}$, and E_3). In addition, these potentials are independent of added salt and only slightly dependent on temperature.

It is of interest to consider how the interaction between sites occurs. The apparent lack of a salt dependence of the potentials may suggest that the observed interaction is more likely of a "through bonds" nature than through space. Ion-pair formation would be likely to stabilize the formation of species ROO and OOO, in which two or more charges are next to each other. This, however, assumes that the salt (BF_4^-) is able to get into a position that might promote or hinder any interaction. It also assumes that, at the concentrations used in the experiments where no salt was added, no ion-pair formation is occurring. For a low dielectric solvent such as methylene chloride, ion-pair formation may occur even at the low concentration of BF_4^- present from the oxidant. Thus the through space alternative cannot be ruled out. From crystallographic studies of $Co(dmg)_3(BF)_2$[19] and $Fe(cp)_2$[20] a through space Co–Fe distance of approximately 6.3 Å can be calculated (from a Co–B distance of 3.6 Å in conjunction with a Fe–B distance of 2.0 Å for Fe–C plus a 1.5 Å for C–B with the appropriate angle). A "through bonds" mechanism of interaction requires that five bonds (8.4 Å), including a coordinatively saturated boron atom, be traversed. In bridged ferrocenes coordinatively saturated molecules such as Se[21] and B[22] have been shown to allow some inductive communication to occur. In this instance neither of the two mechanisms can be ruled out although the through space interaction seems to be the more plausible alternative.

Various attempts have been made to observe the internal electron transfer between the Co and Fe centers.[23] Stopped-flow studies of the titration reaction, including any internal electron transfer, have shown it to be complete within ca. 5 ms. Initial temperature-jump experiments, in which equal concentrations of $Co(nox)_3(B(cp)Fe(cp))_2$ and oxidant are intially present, show evidence of a relaxation process in the 100-μs time scale.[24] These studies are being pursued further.

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Supplementary Material Available: Tables of all absorbance data (7 pages). Ordering information is given on any current masthead page.

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Bimetallic μ-Oxo Complexes Formed by Coordination of the Oxo Ligands of $Cp_2Mo{=}O$ and $Cp_2W{=}O$ to Rhodium(I) and Iridium(I) Centers

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The μ-oxo complexes $[Cp_2M{=}O{-}M'(PPh_3)_2(CO)]^+$ (M = Mo, W; M′ = Rh, Ir) have been prepared by solvent displacement from $[M'(CO)(PPh_3)_2(CH_3CN)]^+$ by the oxo ligand of $Cp_2M{=}O$. Crystallographic analysis of the salt $[Cp_2Mo{=}O{-}Rh(PPh_3)_2(CO)][BF_4]\cdot{}^1/_2C_3H_6O\cdot{}^1/_2C_5H_{12}$ [$P2_1/c$, $a = 17.288$ (4) Å, $b = 13.729$ (3) Å, $c = 23.168$ Å, $\beta = 110.49$ (2)°, $V = 5151$ (2) Å^3, $Z = 4$, $R(F) = 6.85\%$, $R_w(F) = 7.42\%$ for 5095 reflections with $F_o \geq 4\sigma(F_o)$] has shown the complex to consist of a square-planar Rh center ligated by the CO, two PPh_3 ligands, and the μ-oxo ligand of the $Cp_2Mo{=}O$ moiety. The Mo—O—Rh linkage is nearly linear (Mo—O—Rh = 167.1 (4)°), and the complex appears best described as having a dative interaction of the oxo ligand with the unsaturated Rh center. Spectroscopic data imply similar structures for the other complexes in this series. ^1H NMR studies show that the $Cp_2M{=}O$ units of these complexes rapidly exchange with CD_3CN solvent and with excess $Cp_2M{=}O$ on the ^1H NMR time scale.

Introduction

A large number of organometallic oxo-bridged complexes are known,[1] but relatively few are heterometallic and fewer yet have oxo bridges between metals widely separated in the periodic table. Particularly important are complexes with oxo bridges between transition metals in groups 4–6 and those in groups 8–10,[2] in part because such compounds can provide insight into the chemistry that occurs at the interface between a metal and its oxide support during catalytic reactions of the later transition metals supported on oxides of the earlier metal (e.g., TiO_2, MoO_3). We have sought the preparation of such oxo-bridged complexes using the

Table I. Crystallographic Data for $[Cp_2Mo{=}O{-}Rh(PPh_3)_2(CO)][BF_4]\cdot{}^1/_2C_3H_6O\cdot{}^1/_2C_5H_{12}$ (**3**)

formula	$C_{47}H_{40}BF_4O_2P_2RhW\cdot{}^1/_2C_3H_6O\cdot{}^1/_2C_5H_{12}$	Z	4
		D(calc), g/cm^{-3}	1.221
fw	946.59	T, K	293
space group	$P2_1/c$	μ, cm^{-1}	6.62
a, Å	17.288 (4)	radiation λ, Å	0.71073
b, Å	13.729 (3)	$R(F)$, %	6.85
c, Å	23.168 (5)	$R_w(F)$, %	7.42
β, deg	110.49 (2)		
V, Å^3	5151 (2)		

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