INTERVALENCE ELECTRON TRANSFER IN BICOBALTOCENE CATIONS: COMPARISON WITH BIFERROCENES(U) PURDUE UNIV LAFAYETTE IN DEPT OF CHEMISTRY G E MCHANIS ET AL.
Intervalence Electron Transfer in Bicobaltocene Cations:
Comparison with Biferrocenes

by

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Abstract

The near-infrared absorption parameters for bicobaltocene monocation, \((\text{Cp}_2\text{Co})_2^+\), evaluated in several solvents, are compared with corresponding data for biferrocene cation, \((\text{Cp}_2\text{Fe})_2^+\), in order to ascertain the consequence of metal substitution upon the degree of redox-site electronic coupling. From the markedly (ca. 5 fold) larger intervalence band intensities, narrower bandwidths, and milder solvent dependence of the band energy observed for the former system, the degree of Co(III)-Co(II) electronic coupling is deduced to be substantially greater than for Fe(III)-Fe(II). A similar conclusion is reached from a comparison of near-infrared spectra for bis(fulvalene)-dicobalt and -diiron monocations. These differences are also reflected in more negative comproportionation free energies for the cobalt mixed-valence analogs, as derived from electrochemical data. These findings are consistent with orbital symmetry considerations, since electron transfer for the Co(III)-Co(II) system is expected to involve a ligand-centered 4e_{1g} orbital, as compared with strongly metal-localized 4e_2 or 8a_{1g} orbitals that are apparently utilized in the Fe(III)-Fe(II) metalloocene case. The results provide support to a recent interpretation of the markedly faster self-exchange kinetics for the cobaltocenium-cobaltocene versus the ferrocenium-ferrocene redox couples in terms of differences in donor-acceptor orbital overlap.
As part of a detailed exploration of solvent dynamical effects in electron-transfer reactions, we have recently examined solvent-dependent rate parameters for the self exchange of cobaltocenium-cobaltocene (Cp₂Co⁺/₀, where Cp = cyclopentadiene) and for the decamethyl derivative (Cp-Me₅)₂Co⁺/₀ (where Cp-Me₅ = pentamethylcyclopentadiene).¹ A surprising finding from these studies is that the self-exchange rate constant, kₑₓ, in a given solvent is markedly (ca. tenfold) larger for Cp₂Co⁺/₀ and (Cp-Me₅)₂Co⁺/₀ relative to that for the ferrocene analogs, Cp₂Fe⁺/₀ and (Cp-Me₅)₂Fe⁺/₀, respectively. Since the nuclear reorganization parameters can be deduced to be essentially identical for the corresponding cobalt and iron systems, these rate differences were traced to dissimilarities in the nature and extent of donor-acceptor orbital overlap. This interpretation is consistent with the spatial properties of the orbitals involved; thus Cp₂Fe⁺/₀ electron exchange appears to employ either an 4e₂ or 8a₁g orbital which are both strongly metal centered, whereas Cp₂Co⁺/₀ exchange apparently utilizes a markedly more ligand-centered 4e₁g orbital.¹ The greater facility with which electron exchange occurs for the cobaltocene versus ferrocene systems is attributed to a greater electronic transmission coefficient κₑ₁ (i.e., higher electron-tunneling probability within the nuclear transition state) and/or to a correspondingly larger probability of forming reactive precursor complexes with the former reactions.¹

Even though this apparent manifestation of donor-acceptor orbital coupling effects in thermal electron transfer is relatively unambiguous, it is desirable to obtain more direct experimental evidence. Such information is readily obtained in suitable cases from the characteristics of optical charge-transfer transitions within mixed-valence complexes.² Among the
systems of this type that have received detailed experimental scrutiny are biferrocene cations linked by a variety of bridging groups.\textsuperscript{3,4} Although the extent of mixed-valence electronic coupling is very sensitive to the structure of the groups linking the metallocene rings, the majority of these systems display near-infrared bands in solution at room temperature that are consistent with so-called "Class II" behavior, whereby the optical transition involves electron transfer between valence-trapped metal sites.\textsuperscript{3} In this case the extent of donor-acceptor coupling can be quantified by means of Hush theory.\textsuperscript{2-6}

Given this favorable picture, we decided to examine the optical properties of analogous mixed-valence bicobaltocene species in order to ascertain if, and to what extent, greater donor-acceptor electronic coupling is indeed engendered in comparison with that for the corresponding biferrocene systems. We selected initially the bicobaltocene cation 1 in view of its simple structure, the availability of a synthetic procedure,\textsuperscript{7} and the solvent-dependent intervalence characterization afforded to the biferrocene cation, 2.\textsuperscript{5} The results of this study are presented here. We also compare briefly the optical properties of the corresponding bis-(fulvalene)-dicobalt and -diiron cations 3 and 4.

**Experimental**

Acetonitrile, propylene carbonate, dimethylformamide, and methylene chloride were obtained from Burdick and Jackson ("high purity") and benzonitrile from Fluka Chemicals. Acetonitrile and methylene chloride were distilled over P\textsubscript{2}O\textsubscript{5}; the other solvents were used as received. n-Tetrabutylammonium hexafluorophosphate (TBAH) was prepared by mixing
tetrabutylammonium iodide (Eastman Kodak) and ammonium hexafluorophosphate (Ozark-Mahoning) in acetone, and adding water to precipitate the TBAH. It was recrystallized from ethanol.

A solid mixture containing bicobaltocenium(III,III) hexafluorophosphate \([(\text{CP}_2\text{Co})_2(\text{PF}_6)_2]\), bis(fulvalene)-dicobalt(III,III) hexafluorophosphate, cobaltocenium hexafluorophosphate \([\text{CP}_2\text{Co}^+\text{PF}_6]\), and higher order oligomers was prepared using the procedure of Davison and Smart.\(^\text{7b}\) We isolated a sample of \((\text{CP}_2\text{Co})_2(\text{PF}_6)_2\) by dissolving 1.0 g of the solid mixture in a minimum amount of acetonitrile and passing the solution over a 1.0 x 50 cm column of activated alumina. Elution with acetonitrile yielded four distinct bands; isolation and recrystallization (acetonitrile/ethyl ether) of the material from the second band gave a green powder, determined to be \((\text{CP}_2\text{Co})_2(\text{PF}_6)_2\) from the cyclic voltammetry (vide infra) and the proton NMR spectrum.

After dissolving \((\text{CP}_2\text{Co})_2(\text{PF}_6)_2\) in the desired solvent, it was reduced to \((\text{CP}_2\text{Co})_2^+\) by adding an appropriate quantity of cobaltocene in a nitrogen-atmosphere dry box. The solution was sealed into a 1 cm near-infrared quartz cuvette and the spectrum obtained immediately so as to minimize the extent of oxidation by trace oxygen and other impurities. These spectra were recorded on a Cary Model 17D spectrophotometer, typically scanned from 1700-800 nm. The bicobaltocene concentration was about 0.3-0.7 mM, adjusted so to yield a maximum absorbance of the intense near-infrared feature (vide infra) around 0.5. Although these solutions inevitably contained \(\text{Cp}_2\text{Co}^+\) as well as small amounts of bis(fulvalene)dicobalt monocation, separate solutions of the latter species displayed no detectable absorbance in the wavelength region
(ca. 1300-1800 nm) over which the bicobaltocene near-infrared band was analyzed.

Cyclic voltammetric characterization was performed using a PAR Model 173/179 potentiostat driven by a PAR Model 175 Potential Programmer. All measurements were made at room temperature, 23 ± 1°C.

Results and Discussion

Cathodic-anodic cyclic voltammograms for 1 mM (Cp₂Co)₂⁺ at a gold electrode in acetonitrile containing 0.1 M TBAH consisted of a pair of reversible one-electron waves, yielding formal potentials, E₁ and E₂, of -0.650 and -1.045 V versus a saturated calomel electrode (SCE). Bis(fulvalene)dicobalt dication, (BFD-Co)₂⁺, exhibited similar voltammetric characteristics, with E₁ and E₂ equalling -0.10 and -1.03 V vs. SCE, respectively. This behavior is consistent with that reported previously for these species.⁷

The potential difference, E₁ - E₂ = ΔE, provides a measure of the stability of the mixed-valence species with respect to the corresponding fully oxidized and reduced states (i.e., the comproportionation equilibrium⁸). These values are larger than observed with the corresponding diiron species; thus ΔE is 0.315 V for the biferrocene system, (Cp₂Fe)₂⁺/⁺/⁺/⁺, (acetonitrile, 0.1 M TBAH³) and 0.59 V for bis(fulvalene)diiron, (BFD-Fe)₂⁺/⁺/⁺, (acetonitrile, 0.1 M tetraethylammonium perchlorate⁹), as compared with 0.395 V and 0.93 V, respectively, for the corresponding dicobalt systems. The free energy of the comproportionation reaction, ΔG°, is related to ΔE by⁸

\[ ΔG° = -0.5(FΔE - RT \ln 4) \]
This relation yields values of $\Delta G^*_C$ equal to -4.15 and -3.2 kcal mol$^{-1}$ for the bicobaltocene and biferrocene systems, and -10.3 kcal mol$^{-1}$ and -6.4 kcal mol$^{-1}$ for bis(fulvalene)dicobalt and bis(fulvalene)diiron, respectively. The relatively greater stabilization afforded to the mixed-valence cobalt analogs is clearly evident in both cases.

Table I summarizes near-infrared spectral data for bicobaltocene cation, $(\text{Cp}_2\text{Co})^+$, in several solvents in comparison with some corresponding data for biferrocene cation, $(\text{Cp}_2\text{Fe})^+$, the latter taken from ref. 5. The solvents were selected so to yield a significant variation in the "solvent polarity" parameter, $(D_{\text{op}} - D_{\text{s}}^{-1})$, where $D_{\text{op}}$ and $D_{\text{s}}$ are the optical and static dielectric constants, respectively. Two notable differences are seen in the form of the intervalence bands for this pair of systems, in that the band intensity, $\epsilon_{\text{max}}$, for $(\text{Cp}_2\text{Co})^+_2$ is considerably (ca. 5 fold) greater and the band energy at maximum intensity, $\nu_{\text{max}}$, is markedly less solvent dependent than that for $(\text{Cp}_2\text{Fe})^+_2$. In addition, the bandwidth, $\Delta \nu_{1/2}$, is about 20% narrower for the former system. The variation of $\nu_{\text{max}}$ with solvent in both cases is nonetheless qualitatively in accordance with the solvent continuum model in that a rough correlation with $(D_{\text{op}} - D_{\text{s}}^{-1})$ is observed (Table I).

Previous discussions of the biferrocene mixed-valence system have concluded that while it can be considered to be valence trapped (i.e. Class II in the Robin-Day classification$^{12}$), there is nonetheless substantial interaction between the Fe(III) and Fe(II) sites.$^{3a,b,5}$ A useful parameter for estimating the extent of this coupling is the "electronic mixing coefficient" $\alpha$, given by$^{2,3a,6}$

$$\alpha^2 = (4.2 \times 10^{-4}) \epsilon_{\text{max}} \frac{\Delta \nu_{1/2}}{\nu_{\text{max}}} a^2$$  \hspace{1cm} (2)
where \( d \) (Å) is the redox-site separation. Table II contains \( \alpha \) values, along with \( \epsilon_{\text{max}}^\prime \), \( \nu_{\text{max}}^\prime \), and \( \Delta \tilde{\nu}_H \), for \((\text{Cp}_2\text{Co})_2^+\) in acetonitrile in comparison with the corresponding parameters for \((\text{Cp}_2\text{Fe})_2^+\) and a pair of related systems, bis(fulvalene) dicobalt \((\text{BFD-Co})^+\) and the corresponding iron dimer, \((\text{BFD-Fe})^+\) (Fig. 1). (See footnotes to Table II for literature sources.) Also listed for each system in Table II are calculated bandwidths, \( \Delta \tilde{\nu}_H(\text{calcd}) \), where

\[
\Delta \tilde{\nu}_H(\text{calcd}) = (2310 \nu_{\text{max}}^\prime)^{1/2} \text{cm}^{-1}
\]

This relation results from the Hush model for Class II systems.\(^2,\)\(^6a\)

Inspection of these comparative data in Tables I and II provide a consistent picture attesting to the substantially greater metal-metal electronic coupling for the cobalt relative to the iron mixed-valence compounds. Thus, both the \((\text{Cp}_2\text{Co})_2^+\) and the \((\text{BFD-Co})^+\) systems display substantially larger \( \alpha \) values and narrower bandwidths than the diiron analogs. While the observation that \( \Delta \tilde{\nu}_H > \Delta \tilde{\nu}_H(\text{calcd}) \) for \((\text{Cp}_2\text{Fe})_2^+\) is consistent with Class II behavior,\(^6b\) the opposite finding for \((\text{Cp}_2\text{Co})_2^+\) (Table II) suggests that there is sufficient electronic coupling with the latter system to place it on the Class II/III borderline. The relatively small solvent dependence of \( \nu_{\text{max}}^\prime \) observed for \((\text{Cp}_2\text{Co})_2^+\) is also indicative of stronger donor-acceptor coupling than can be accommodated strictly in terms of Class II behavior.\(^2\)

Especially since both \((\text{BFD-Co})^+\) and \((\text{BFD-Fe})^+\) also display essentially solvent-independent band energies,\(^4a,b,11\) comparison of \( \alpha \) values for such delocalized systems\(^4d\) can be misleading since conventional interpretation of this parameter for intervalence transitions is linked to the Hush
Nevertheless, discussion of the overall trends in this and related quantities is likely to be qualitatively valid. The markedly larger $\alpha$ value, as well as the narrower bandwidth, observed for (BFD-Co)$^+$ versus (BFD-Fe)$^+$ (Table II) indicates that the additional metal-metal coupling provided by cobalt also applies to this strong-overlap, doubly-linked, structure (Fig. 1).

It is also interesting to compare the intervalence band parameters for $(\text{Cp}_2\text{Co})^2$ and (BFD-Fe)$^+$. In spite of the additional electronic coupling engendered by the doubly-linked ring structure of the latter, the former system nonetheless appears to involve a greater extent of electron delocalization as signaled by substantially larger $\alpha$ value (Table II). These variations in the extent of electronic coupling brought about by metal substitution, as gauged by differences in $\alpha$, are at least as large as those engendered by significant or even substantial alterations in the structure of the ring linkages.3-5

Estimates of the contribution of electronic delocalization, $\Delta G_{\text{del}}^0$, to $\Delta G^0$ can also be readily made, at least for Class II systems, from

$$-\Delta G_{\text{del}}^0 = \alpha^2 \nu_{\text{max}}$$

This yields $\Delta G_{\text{del}}^0$ values of -0.55 and -0.2 kcal mol$^{-1}$ for $(\text{Cp}_2\text{Co})^2$ and $(\text{Cp}_2\text{Fe})^2$, respectively, in acetonitrile. An additional electrostatic contribution to $\Delta G^0$, $\Delta G_{\text{el}}^0$, can be estimated approximately to be -1.0 kcal mol$^{-1}$ under these conditions (acetonitrile, ionic strength 0.1 M).13 The substantial remaining components of the overall $\Delta G^0$ values, ca. -3.5 and -2 kcal mol$^{-1}$ for $(\text{Cp}_2\text{Co})^2$ and $(\text{Cp}_2\text{Fe})^2$, respectively, are presumably due to further stabilization of the mixed-valence species by inductive effects.
via the bridging ligand (cf. bipyridyl diruthenium systems\textsuperscript{8}).

These findings are therefore qualitatively consistent with the aforementioned interpretation of the larger rate constants for \( \text{CP}_2\text{Co}^{+/-} \) versus \( \text{CP}_2\text{Fe}^{+/-} \) self exchange in terms of electronic coupling effects. More quantitative comparisons between the bimolecular kinetic and intervalence optical systems, however, are precluded since the latter undoubtedly feature much stronger electronic interactions as a result of a direct linkage between the redox sites. Thus from the usual expression\textsuperscript{2,6} \( H_{AB} = \alpha \tilde{V}_{\text{max}} \), the electronic matrix coupling element \( H_{AB} \) is estimated to be roughly 3.2 and 1.7 kcal mol\(^{-1}\) for \( \text{(CP}_2\text{Co})^{+/-} \) and \( \text{(CP}_2\text{Fe})^{+/-} \), respectively.\textsuperscript{16} Much smaller \( H_{AB} \) values, leading to weakly adiabatic or nonadiabatic electron transfer, are expected for thermally activated outer-sphere processes.\textsuperscript{17} Nevertheless, the present results do point clearly to the importance of the orbital symmetry in electron transfer via its influence on the extent of electronic coupling.

**Acknowledgments**

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References and Notes


2. For a review, see Creutz, C., Prog. Inorg. Chem. 1983, 30, 1.


13. This estimate is obtained by using the expression \(-\Delta C_e = e^2/4\pi\kappa d(1 + \kappa d)\), where \(e\) is the electronic charge, \(\kappa\) is the reciprocal Debye length, and \(d\) is the distance between the metal centers in the mixed-valence compound (see footnote e to Table II).
This relation is the Debye-Huckel expression\textsuperscript{14} for the work required to form a bimetallocone dication from two unipositive metallocene fragments. This represents the sole contribution to $\Delta G_e^\circ$ since the corresponding electrostatic work for forming the neutral and monocation (i.e., mixed-valence) bimetallocone species are zero. Although Taube and coworkers have used a rather different $\Delta G_e^\circ$ expression for various bipyridine-bridged diruthenium systems,\textsuperscript{15} the above relation is considered to be adequate for the present bimetallocone systems.


16. This relationship will probably underestimate $H_{AB}'$, at least for (Cp\textsubscript{2}Co)$^\ddagger$, since this system lies on the Class II/III borderline; for Class III systems, $H_{AB} = \bar{\nu}_{\text{max}}/2$.

17. For example, Newton, M. D., J. Phys. Chem. 1986, 90, 3734.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>(D_{\text{op}} - D_s)</th>
<th>((\text{Bicobaltocene})^+)</th>
<th>((\text{Biferrocene})^+)</th>
</tr>
</thead>
</table>
|                |                           | \(\epsilon_{\text{max}}^{c,f}\) | \(\nu_{\text{max}}^{d}\) | \(\Delta
u_h^{e,g}\) | \(\epsilon_{\text{max}}^{c,h}\) | \(\nu_{\text{max}}^{d,h}\) | \(\Delta
u_h^{e,h}\) |
| Acetonitrile   | 0.528                    | 6.58                          | 3.28                          | -750 9650 |
| Propylene      | 0.480                    | 6.58                          | -3.7                          | 650 5570 |
| Carbonate      | 0.463                    | 6.54                          | 6.40                          | 723 5230 |
| DMF            | 0.390                    | 3900                          | 5.88                          | 919 5000 |
| Benzonitrile   | 0.390                    | 3900                          | 6.40                          | 723 5230 |
| Nitrobenzene   | 0.390                    | 4500                          | 5.88                          | 919 5000 |
| \(\text{CH}_2\text{Cl}_2\) | 0.380                    | 4500                          | 5.88                          | 919 5000 |

\(a\) DMF = N,N-dimethylformamide; \(\text{CH}_2\text{Cl}_2 = \) dichloromethane.

\(b\) \(D_{\text{op}}\) = optical dielectric constant; \(D_s\) = static (i.e., zero frequency) dielectric constant; values obtained from ref. 10.

\(c\) Molar absorptivity at the band maximum.

\(d\) Energy of band maximum.

\(e\) Bandwidth at half height, obtained from high-wavelength portion as described in ref. 5.

\(f\) Values reproducible to ca. 20-30%.

\(g\) Values not given for several solvents due to solvent interference band wings and spectral instability.

\(h\) Values extracted from ref. 5, unless otherwise noted.

\(i\) From ref. 3b.
TABLE II  Intervalence Band and Related Parameters for some Dicobalt and Diiron Monocations in Acetonitrile

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\epsilon_{\text{max}}$</th>
<th>$\bar{\nu}_{\text{max}}$</th>
<th>$\Delta\bar{\nu}_H^c$</th>
<th>$\Delta\bar{\nu}_H$ (calcd)$d$</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M$^{-1}$ cm$^{-1}$</td>
<td>10$^3$ cm$^{-1}$</td>
<td>10$^3$ cm$^{-1}$</td>
<td>10$^3$ cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(Cp$_2$Co)$_2$</td>
<td>3500</td>
<td>6.58</td>
<td>3.28</td>
<td>3.90</td>
<td>0.17 f</td>
</tr>
<tr>
<td>(Cp$_2$Fe)$_2$</td>
<td>750</td>
<td>5.68</td>
<td>3.90</td>
<td>3.62</td>
<td>0.09 g</td>
</tr>
<tr>
<td>(BFD-Co)$^+$</td>
<td>7300</td>
<td>10.65</td>
<td>1.88</td>
<td>4.96</td>
<td>0.19 h</td>
</tr>
<tr>
<td>(BFD-Fe)$^+$</td>
<td>1800</td>
<td>6.67</td>
<td>3.25</td>
<td>3.92</td>
<td>0.09 i</td>
</tr>
</tbody>
</table>

$a$ Molar absorptivity at band maximum.

$b$ Energy of band maximum.

$c$ Observed bandwidth at half height.

$d$ Bandwidth at half height, calculated from Eq. (3).

$e$ Electronic mixing coefficient, estimated using Eq. (2); d (metal-metal distance) values taken as 5 Å for bicobaltocene and biferrocene, and 4 Å for (BFD-Co)$^+$ and (BFD-Fe)$^+$ (after ref. 5).

$f$ This work.

$g$ Ref. 5 ($\epsilon_{\text{max}}$ from ref. 3b).

$h$ From Fig. 3 of ref. 11.

$i$ Ref. 4a ($\Delta\bar{\nu}_H$ from ref. 5).
FIGURE I

1. Bicobaltocene$^+$

2. Biferrocene$^+$

3. Bisfulvalene dicobalt$^+$

4. Bisfulvalene diiron$^+$
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