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free energy that is responsible for this residual peak in the specific heat cannot be obtained from the transition $\gamma(x,T)$ curve.

The fact that the residual peak is just in the transition region where $\partial\gamma/\partial T$ is maximal hints at a small γ-dependent term in the free enthalpy of the compound, which does not influence the shape of the transition $\gamma(x,T)$ curves. We conclude that the missing part of the free energy results from a change in the lattice of the compound that is triggered by the HS ↔ LS transition. The coupling that would be formally given by a weak γ dependence of $C(x,T,\gamma)$ must be so small that an influence of the HS ↔ LS transition cannot be observed but large enough to trigger an independent transition in the lattice. The nondeuteriated compound $[Fe(2\text{-pic})_3]Cl_2{\cdot}EtOH$ shows a pronounced anomaly, i.e. a two-step behavior, in the transition $\gamma(T)$ curve. This case may be an example where the coupling to the inner degrees of freedom of the lattice is strong enough to be observed in the HS ↔ LS transition.

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Notes

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Intervalence Electron Transfer in Bicobaltocene Cations: Comparison with Biferrocenes

George E. McManis, Roger M. Nielson,
and Michael J. Weaver*

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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 ($Cp_2Co^{+/0}$ where Cp = cyclopentadiene) and for the decamethyl derivative $(Cp\text{-}Me_5)_2Co^{+/0}$ (where $Cp\text{-}Me_5$ = pentamethylcyclopentadiene).[1] A surprising finding from these studies is that the self-exchange rate constant, k_{ex}, in a given solvent is markedly (ca. 10-fold) larger for $Cp_2Co^{+/0}$ and $(Cp\text{-}Me_5)_2Co^{+/0}$ relative to that for the ferrocene analogs, $Cp_2Fe^{+/0}$ and $(Cp\text{-}Me_5)_2Fe^{+/0}$, respectively. Since the nuclear reorganization parameters can be deduced from bond length and vibrational data to be almost 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.[1b] This interpretation is consistent with the spatial properties of the orbitals involved; thus $Cp_2Fe^{+/0}$ electron exchange appears to employ either an $4e_2$ or $8a_{1g}$ orbital, both of which are strongly metal centered, whereas $Cp_2Co^{+/0}$ exchange apparently utilizes a markedly more ligand-centered $4e_{1g}$ orbital.[1b] The greater facility with which electron exchange occurs for the cobaltocene versus ferrocene systems is attributed to a greater electronic transmission coefficient κ_{el} (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.[1b]

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.[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 roughly consistent with so-called "class II" behavior, whereby the optical transition involves electron transfer between valence-trapped metal sites.[3] In this case the extent of donor–acceptor coupling can be treated, at least approximately, by means of Hush theory.[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,[7] and the solvent-dependent intervalence characterization afforded to the biferrocene cation, **2**.[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 Section

Acetonitrile, propylene carbonate, dimethylformamide, and methylene chloride were obtained from Burdick and Jackson ("high purity"), and benzonitrile was obtained from Fluka Chemicals. Acetonitrile and methylene chloride were distilled over P_2O_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 $[(Cp_2Co)_2(PF_6)_2]$, bis(fulvalene)dicobalt(III,III) hexafluorophosphate, cobaltocenium hexafluorophosphate $[Cp_2CoPF_6]$, and higher order oligomers was prepared using the procedure of Davison and Smart.[7b] We isolated a sample of $(Cp_2Co)_2(PF_6)_2$ by dissolving 1.0 g of the solid mixture in a minimum amount of acetonitrile and passing the solution over a 1.0 × 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 $(Cp_2Co)_2(PF_6)_2$ from the cyclic voltammetry (vide infra) and the proton NMR spectrum.

After $(Cp_2Co)_2(PF_6)_2$ was dissolved in the desired solvent, it was reduced to $(Cp_2Co)_2^+$ by adding an appropriate quantity of cobaltocene

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Table I. Comparison of Intervalence Transfer Bands for Bicobaltocene and Biferrocene Monocations in Selected Solvents

		$(Cp_2Co)_2^+$			$(Cp_2Fe)_2^+$		
solvent[a]	$(D_{op}^{-1} - D_s^{-1})$[b]	ϵ_{max},[c,f] $M^{-1}\ cm^{-1}$	$\bar{\nu}_{max}$,[d] $10^3\ cm^{-1}$	$\Delta\bar{\nu}_{1/2}$,[e,g] $10^3\ cm^{-1}$	ϵ_{max},[c,h] $M^{-1}\ cm^{-1}$	$\bar{\nu}_{max}$,[d,h] $10^3\ cm^{-1}$	$\Delta\bar{\nu}_{1/2}$,[e,h] $10^3\ cm^{-1}$
acetonitrile	0.528	3500	6.58	3.28	~750[i]	5.68	3.90
propylene carbonate	0.480		6.58	~3.3	650	5.57	4.12
DMF	0.463	3100	6.54				
benzonitrile	0.390	3900	6.40				
nitrobenzene	0.390				723	5.23	3.74
CH_2Cl_2	0.380	4500	5.88		919	5.00	3.70

[a] DMF = *N,N*-dimethylformamide; CH_2Cl_2 = dichloromethane. [b] D_{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 Dicobalt and Diiron Monocations in Acetonitrile

compd	ϵ_{max},[a] $M^{-1}\ cm^{-1}$	$\bar{\nu}_{max}$,[b] $10^3\ cm^{-1}$	$\Delta\bar{\nu}_{1/2}$,[c] $10^3\ cm^{-1}$	$\Delta\bar{\nu}_{1/2}$(calcd),[d] $10^3\ cm^{-1}$	α[e]	data source
$(Cp_2Co)_2^+$	3500	6.58	3.28	3.90	0.17	*f*
$(Cp_2Fe)_2^+$	750	5.68	3.90	3.62	0.09	*g*
$(BFD\text{-}Co)^+$	7300	10.65	1.88	4.96	0.19	*h*
$(BFD\text{-}Fe)^+$	1800	6.67	3.25	3.92	0.09	*i*

[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 by using eq 2; *d* (metal–metal distance) values taken as 5 Å for bicobaltocene and biferrocene and 4 Å for $(BFD\text{-}Co)^+$ and $(BFD\text{-}Fe)^+$ (after ref 5). [f] This work. [g] Reference 5 (ϵ_{max} from ref 3b). [h] From Figure 3 of ref 11. [i] Reference 4a ($\Delta\bar{\nu}_{1/2}$ from ref 5).

in a nitrogen-atmosphere drybox. The solution was sealed in 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 2000 to 800 nm. The bicobaltocene concentration was about 0.1–0.5 mM, adjusted so to yield a maximum absorbance of the intense near-infrared feature (vide infra) around 0.5. Although these solutions inevitably contained Cp_2Co^+ 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 by 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 $(Cp_2Co)_2^{2+}$ at a gold electrode in acetonitrile containing 0.1 M TBAH consisted of a pair of reversible one-electron waves, yielding formal potentials, E_1^f and E_2^f, of –0.650 and –1.045 V versus a saturated calomel electrode (SCE). Bis(fulvalene)dicobalt dication, $(BFD\text{-}Co)^{2+}$, exhibited similar voltammetric characteristics, with E_1^f and E_2^f equaling –0.10 and –1.03 V versus SCE, respectively. This behavior is consistent with that reported previously for these species.[7]

The potential difference, $E_1^f - E_2^f = \Delta E_f$, 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 equilibrium[8]). These values are larger than observed with the corresponding diiron species; thus ΔE_f is 0.315 V for the biferrocene system, $(Cp_2Fe)_2^{2+/+/0}$ (acetonitrile, 0.1 M TBAH[3d]), and 0.59 V for the bis(fulvalene)diiron system, $(BFD\text{-}Fe)^{2+/+/0}$ (acetonitrile, 0.1 *M* tetraethylammonium perchlorate[9]), as compared with 0.395 and 0.93 V, respectively, for the corresponding dicobalt systems. The free energy of the comproportionation reaction, $\Delta G_c°$, is related to ΔE_f by[8]

$$\Delta G_c° = -0.5(F\Delta E_f - RT \ln 4) \qquad (1)$$

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 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 analogues is clearly evident in both cases.

Table I summarizes near-infrared spectral data for bicobaltocene cation, $(Cp_2Co)_2^+$, in several solvents in comparison with some corresponding data for biferrocene cation, $(Cp_2Fe)_2^+$; the latter are taken from ref 5. The solvents were selected so to yield a significant variation in the "solvent polarity" parameter, $(D_{op}^{-1} - D_s^{-1})$, where D_{op} and D_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, ϵ_{max}, for $(Cp_2Co)_2^+$ is considerably (ca. 5-fold) greater and the band energy at maximum intensity, $\bar{\nu}_{max}$, is markedly less solvent dependent than those for $(Cp_2Fe)_2^+$. In addition, the bandwidth, $\Delta\bar{\nu}_{1/2}$, is about 20% narrower for the former system. The variation of $\bar{\nu}_{max}$ with solvent in both cases is nonetheless qualitatively in accordance with the solvent continuum model in that a rough correlation with $(D_{op}^{-1} - D_s^{-1})$ is observed (Table I).

Previous discussions of the biferrocene mixed-valence system have concluded that while it might be considered to be valence trapped (i.e. class II in the Robin-Day classification[2]), there is nonetheless substantial interaction between the Fe(III) and Fe(II) sites.[3a,b,e,5] A useful parameter for estimating the extent of this coupling is the "electronic mixing coefficient" α, given on the basis of the Hush model by[2,3a,6]

$$\alpha^2 = (4.2 \times 10^{-4})\epsilon_{max}(\Delta\bar{\nu}_{1/2}/\bar{\nu}_{max})d^2 \qquad (2)$$

where *d* (Å) is the redox-site separation. Table II contains α values, along with ϵ_{max}, $\bar{\nu}_{max}$, and $\Delta\bar{\nu}_{1/2}$, for $(Cp_2Co)_2^+$ in acetonitrile in comparison with the corresponding parameters for $(Cp_2Fe)_2^+$ and a pair of related systems, bis(fulvalene) dicobalt, $(BFD\text{-}Co)^+$, and the corresponding iron dimer, $(BFD\text{-}Fe)^+$ (Figure 1). (See footnotes to Table II for literature sources.) Also listed for each system in Table II are calculated bandwidths, $\Delta\bar{\nu}_{1/2}$(calcd), where

$$\Delta\bar{\nu}_{1/2}(\text{calcd}) = (2310\bar{\nu}_{max})^{1/2}\ \text{cm}^{-1} \qquad (3)$$

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 mix-

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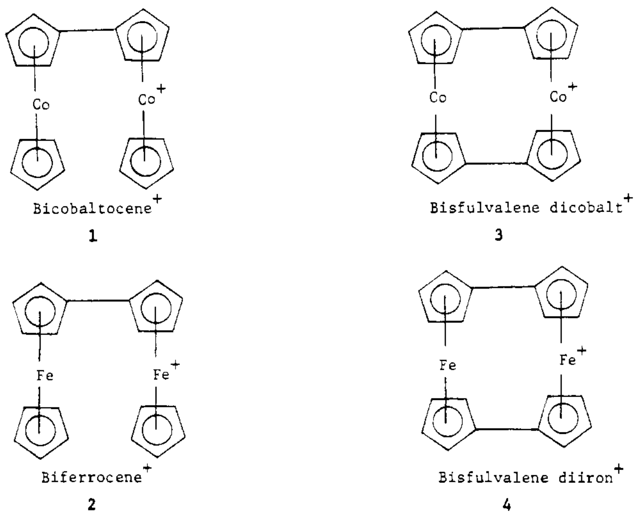

Bicobaltocene$^+$ 1

Bisfulvalene dicobalt$^+$ 3

Biferrocene$^+$ 2

Bisfulvalene diiron$^+$ 4

Figure 1.

ed-valence compounds. Thus, both the $(Cp_2Co)_2^+$ and the $(BFD\text{-}Co)^+$ sytems display substantially larger α values and narrower bandwidths than the diiron analogues. While the observation that $\Delta\bar{\nu}_{1/2} > \Delta\bar{\nu}_{1/2}$(calcd) for $(Cp_2Fe)_2^+$ is consistent with class II behavior,[6b] the opposite finding for $(Cp_2Co)_2^+$ (Table II) suggests that there is sufficient electronic coupling with the latter system to place it at least on the class II/III borderline. The relatively small solvent dependence of $\bar{\nu}_{\max}$ observed for $(Cp_2Co)_2^+$ is also indicative of stronger donor–acceptor coupling than can be accomodated strictly in terms of class II behavior.[2]

In particular, since both $(BFD\text{-}Co)^+$ and $(BFD\text{-}Fe)^+$ also display essentially solvent-independent band energies,[4a,b,11] comparison of α values for such extensively delocalized systems[4d] can be misleading given that (2) is obtained from the Hush model.[2,6] Nevertheless, discussion of the overall trends in this and related quantities is likely to remain qualitatively valid.[12] The markedly larger α value, as well as the narrower bandwidth, observed for $(BFD\text{-}Co)^+$ versus $(BFD\text{-}Fe)^+$ (Table II) indicates that the additional metal–metal coupling provided by cobalt also applies to this strong-overlap, doubly linked, structure (Figure 1).

It is also interesting to compare the intervalence band parameters for $(Cp_2Co)_2^+$ and $(BFD\text{-}Fe)^+$. 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 a substantially larger α value (Table II). These variations in the extent of electronic coupling brought about by metal substitution, as gauged by differences in α, 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, $\Delta G_{\text{del}}^\circ$, to ΔG_c° can also be readily made, at least for class II systems, from[8]

$$-\Delta G_{\text{del}}^\circ = \alpha^2\bar{\nu}_{\max} \qquad (4)$$

This yields $\Delta G_{\text{del}}^\circ$ values of −0.55 and −0.2 kcal mol^{-1} for $(Cp_2Co)_2^+$ and $(Cp_2Fe)_2^+$, respectively, in acetonitrile. An additional electrostatic contribution to ΔG_c°, ΔG_e°, can be estimated approximately to be −1.0 kcal mol^{-1} under these conditions (acetonitrile, ionic strength 0.1 M).[15] The substantial remaining components of the overall ΔG_c° values, ca. −3.5 and −2 kcal mol^{-1} for $(Cp_2Co)_2^+$ and $(Cp_2Fe)_2^+$, respectively, are presumably due to further stabilization of the mixed-valence species by inductive effects via the bridging ligand (cf. (bipyridyl)diruthenium systems[8]).

These findings are therefore qualitatively consistent with the aforementioned interpretation of the larger rate constants for $Cp_2Co^{+/0}$ versus $Cp_2Fe^{+/0}$ 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[2,6] $H_{AB} = \alpha\bar{\nu}_{\max}$, the electronic matrix coupling element H_{AB} is estimated to be roughly 3.2 and 1.7 kcal mol^{-1} for $(Cp_2Co)_2^+$ and $(Cp_2Fe)_2^+$, respectively.[18] Much smaller H_{ab} values, leading to weakly adiabatic or nonadiabatic electron transfer, are expected for thermally activated outer-sphere processes.[19] 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.

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Registry No. **1**, 114031-48-0; **2**, 51263-10-6; **3**, 69365-58-8; **4**, 51140-52-4; **4**·PF_6, 52732-79-3; Cp_2Co, 1277-43-6.

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[12] Strictly speaking, the Hush model and hence eq 2 are only valid for weak coupling between the redox sites. Application of a more sophisticated vibronic coupling model, specifically the PKS treatment,[13] indicates that the Hush theory may significantly underestimate the extent of valence delocalization, even for $(Cp_2Fe)_2^+$.[3e] On the other hand, the PKS treatment itself may not provide an entirely satisfactory description of systems on the class II/III borderline.[14] However, despite these complications, the Hush model remains adequate for the largely qualitative purposes of the present study.

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[15] This estimate is obtained by using the expression $-\Delta G_e^\circ = e^2/D_s d(1 + \kappa d)$, where e is the electronic charge, κ 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-Hückel expression[16] for the work required to form a bimetallocene dication from two unipositive metallocene fragments. It represents the sole contribution to ΔG_e° since the corresponding electrostatic work for forming the neutral and monocation (i.e., mixed-valence) bimetallocene species are zero. Although Taube and co-workers have used a rather different ΔG_e° expression for various bipyridine-bridged diruthenium systems,[17] the above relation is considered to be adequate for the present bimetallocene systems.

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[18] This relationship will probably underestimate H_{AB}, at least for $(Cp_2Co)_2^+$, since this system lies at least on the class II/III borderline; for Class III systems, $H_{AB} = \bar{\nu}_{\max}/2$.

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Contribution from the School of Science,
Griffith University, Brisbane, Australia 4111,
and Department of Physical and Inorganic Chemistry,
University of Western Australia, Perth, Australia 6009

Conformational Isomerism in Mixed-Ligand Complexes of 2,2′-Bipyridine and Triphenylphosphine with Copper(I) Halides[†]

Peter F. Barron,[‡] Lutz M. Engelhardt,[§] Peter C. Healy,*[‡]
John D. Kildea,[§] and Allan H. White[§]

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Our recent studies on the CP-MAS solid-state ^{31}P NMR spectroscopy of triphenylphosphine (PPh_3) adducts with copper(I)

[†] Lewis-Base Adducts of Group 11 Metal(I) Compounds. 38.

[‡] Griffith University.

[§] University of Western Australia.

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