

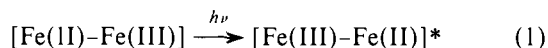
# Intervalence Transfer in Substituted Biferrocene Cations

Carole LeVanda,<sup>1a</sup> Klaus Bechgaard,<sup>1a</sup> D. O. Cowan,<sup>\*1a</sup> and Marvin D. Rausch<sup>1b</sup>

Contribution from the Departments of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, and University of Massachusetts, Amherst, Massachusetts 01002. Received July 27, 1976

**Abstract:** The visible and near-infrared spectra of electrochemically generated acetyl, methoxycarbonyl, and methylbiferrocene monocations were recorded. The monocations all exhibit visible transitions typical of ferrocenium ions and bands in the near-infrared similar to that observed for the biferrocene monocation. The near-infrared bands are assigned to intervalence transfer transitions. In unsymmetrically substituted cations, the bands are blue shifted relative to the symmetrically substituted ions. This is in accordance with predictions based on the Hush model. Band energies calculated from spectral and electrochemical data are in reasonable agreement with the observed values. The intensities of the intervalence transfer bands of cations with substituents in the 2- and/or 5-position are less than that observed for biferrocene due to a stereoelectronic effect.

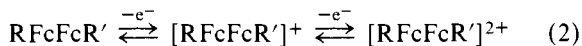
The mixed valence monocation of biferrocene (I) has been thoroughly characterized by a variety of physical measurements.<sup>2</sup> A low energy band observed in the near-infrared (1800–1900 nm) has been assigned to an intervalence transfer transition by which a vibrationally excited valence isomer is formed.



A simple model for intervalence transfer transitions has been proposed by Hush<sup>3a</sup> and expounded by Day.<sup>3b</sup> The model is one which correlates band energies of intervalence transfer transitions with rates of electron transfer. Based on this model, predictions of the relative energy and intensity of the bands as a function of structure can be made. The purpose of this study is to observe the effect of substituents on the near-infrared bands of biferrocene cations and to judge the usefulness of the Hush model in interpreting the results.<sup>4</sup>

Two general approaches have been employed in the synthesis of substituted biferrocenes: electrophilic substitution on biferrocene, and the coupling of suitably substituted ferrocenes. The following monosubstituted (II and III), and disubstituted (IV–VI) acetyl,<sup>5,6</sup> methoxycarbonyl,<sup>6</sup> and methyl biferrocenes<sup>7</sup> were synthesized by the literature procedures.

**Electrochemistry.** The neutral compounds (I–VI) all undergo two successive reversible one-electron oxidations to yield the mono- and dications, respectively (eq 2).

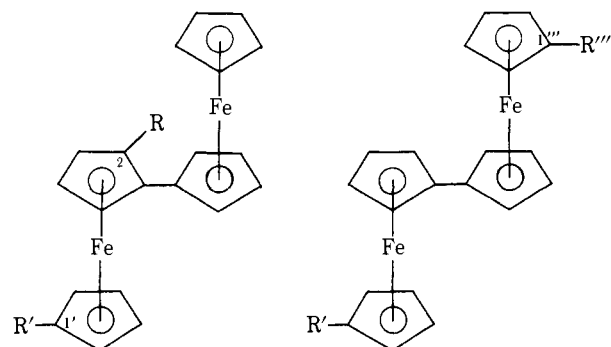


where Fc represents a ferrocenyl unit. Electrochemical reversibility was demonstrated by a 1:1 relationship of the anodic and cathodic peak currents,  $\Delta E_p$  values of 60 mV, and constancy of the current function,  $[i_p/(V^{1/2}C)]$  over a wide range of sweep rates (25–300 mV/s).<sup>8</sup> The half-wave potentials given in Table I were calculated from peak potentials.<sup>8</sup>

It has been demonstrated that the effect of substituents on the oxidation–reduction potential of ferrocene can be regarded as additive.<sup>9</sup> To a reasonable degree of accuracy, the reduction potential for a 1,1'-disubstituted ferrocene,  $\text{C}_5\text{H}_4\text{X-Fe-C}_5\text{H}_4\text{Y}$ , can be predicted by eq 3,

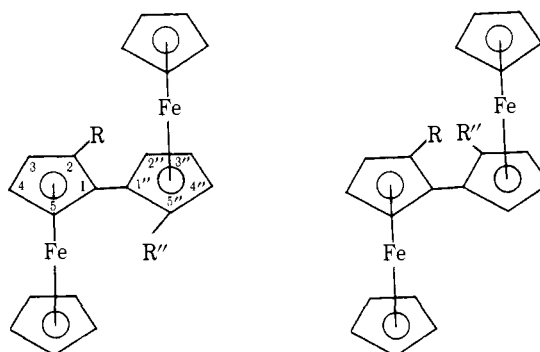
$$E_{\text{calcd}} = E_{(\text{Fc}^{+0})} + \delta_X + \delta_Y \quad (3)$$

where  $E_{(\text{Fc}^{+0})}$  is the potential for the  $\text{Fc}^{+0}$  couple and  $\delta_X$  and  $\delta_Y$  are the differences in the potential of the  $\text{Fc-X}^{+0}$  and  $\text{Fc-Y}^{+0}$  couples as compared to  $E_{(\text{Fc}^{+0})}$ . It is possible to extend this treatment to compounds where one of the substituents is a ferrocenyl or substituted ferrocenyl group.<sup>10</sup> We have used this formulism in calculations of the free energy difference between valence isomers of substituted biferrocene monocat-



I, R = R' = H  
 IIa, R = COCH<sub>3</sub>; R' = H  
 b, R = CO<sub>2</sub>CH<sub>3</sub>; R' = H  
 IIIa, R' = COCH<sub>3</sub>; R = H  
 b, R' = CO<sub>2</sub>CH<sub>3</sub>; R = H

IVa, R' = R''' = COCH<sub>3</sub>  
 b, R' = R''' = CO<sub>2</sub>CH<sub>3</sub>



Va, R = R'' = CH<sub>3</sub>  
 b, R = CH<sub>3</sub>; R'' = CH<sub>2</sub>OH

VI, R = R'' = CH<sub>3</sub>

ions (vide infra). Data derived in this manner are helpful in interpreting the electronic absorption results. The following example demonstrates that reasonable estimates (within 8%) of potentials for acetyl and methoxycarbonylbiferrocenes can be made by the addition of substituent effects.

In methylene chloride, a ferrocenyl group is electron donating and has a substituent effect,  $\delta_{\text{Fc}}$ , of  $-0.105$  V. From 1'-methoxycarbonylbiferrocene,  $\delta$  for a  $(-\text{FcCO}_2\text{CH}_3)$  substituent is  $-0.050$  V, reflecting the electron-withdrawing effect of methoxycarbonyl vs. hydrogen. With this latter number, the first reduction potential of 1',1'''-dimethoxycarbonylbiferrocene can be calculated (eq 4).

$$E_{\text{calcd}} = E_{(\text{Fc}^{+0})} + \delta_{\text{CO}_2\text{CH}_3} + \delta_{\text{FcCO}_2\text{CH}_3} = 0.730 \text{ V} \quad (4)$$

( $E_{\text{exptl}} = 0.690$  V). The agreement between the calculated and experimental results is slightly better if  $\delta_{\text{FcCO}_2\text{CH}_3}$  is determined

**Table I.** Half-Wave Potentials<sup>a</sup> for Substituted Ferrocenes and Biferrocenes

Compound	$E_{1/2}$ (1)	$E_{1/2}$ (2)
A. In CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>		
Biferrocene (I)	0.435	0.785
2-Acetylbiferrocene (IIa)	0.470	0.975
1'-Acetylbiferrocene (IIIa)	0.520	0.975
1',1'''-Diacetylbiferrocene (IVa)	0.715	1.025
2-Methoxycarbonylbiferrocene (IIb)	0.475	0.965
1'-Methoxycarbonylbiferrocene (IIIb)	0.490	0.960
1',1'''-Dimethoxycarbonylbiferrocene (IVb)	0.690	1.020
Ferrocene	0.540	—
Acetylferrocene	0.790	—
Methoxycarbonylferrocene	0.780	—
B. In CH <sub>3</sub> CN <sup>c</sup>		
Biferrocene (I)	0.285	0.600
2,5''-Dimethylbiferrocene (Va)	0.310	0.605
2,2''-Dimethylbiferrocene (VI)	0.370	0.630
2-Methyl-5''-hydroxymethylbiferrocene (Vb)	0.370	0.630
Ferrocene	0.355	—
Methylferrocene	0.305	—
Hydroxymethylferrocene	0.360	—

<sup>a</sup> Volts vs. SCE at 100 mV/s. <sup>b</sup> Containing *n*-Bu<sub>4</sub>NBF<sub>4</sub> (0.2 M). <sup>c</sup> Containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M).

from 2-methoxycarbonylbiferrocene, although the additivity of substituent effects for simple 1,2-disubstituted ferrocenes has not been demonstrated.

For the methyl substituted biferrocenes, attempts to predict potentials by the additivity of substituent effects fail completely. For example, both a methyl and a ferrocenyl group should serve to lower the first half-wave potential in 2,5''-dimethylbiferrocene ( $E_{\text{calcd}} \cong 0.235$  V) but the observed potential is higher than that of both methylferrocene and biferrocene.

In order to obtain absorption spectra, solutions of the monocations were electrochemically generated from the neutral compounds by passage of precisely 1 F/mol. Exhaustive Coulometric oxidation resulted in consumption of 2 F/mol and yielded the dications. Voltammetric and polarographic analyses of the resulting solutions indicated a current yield of 100%. Solutions of the monocations were stable for several days when protected from air and moisture. The dications of compounds I, V, and VI reverted to the monocations within a few hours.<sup>4</sup> The dications of II, III, and IV were too unstable under the experimental conditions to record their absorption spectra.

**Intervallence Transfer Transitions in Substituted Biferrocene Cations.** The low energy band observed in the absorption spectrum of the biferrocene monocation has been assigned to an intervalence transfer transition.<sup>1</sup> Several facts support this assignment: (1) the band is observed in the spectrum of the monocation, but not in the spectra of the dication or neutral species; (2) peaks due to the ferrocene and ferrocenium portions of the molecule can be detected in Mössbauer<sup>11</sup> and ESCA<sup>12</sup> experiments; (3) magnetic<sup>13</sup> properties can be reasonably well explained in terms of a perturbed ferrocenium ion. These observations are in compliance with the "weak interaction" criterion for the Hush model.<sup>2</sup>

As a consequence of the weak interaction between the donor and acceptor sites in the ground state, the electronic absorption spectra of mixed valence biferrocenes show transitions due to the ferrocene and ferrocenium portions of the molecule, in addition to the intervalence transfer band. A band in the 600-nm region is characteristic of a ferrocenium ion.<sup>14</sup> Based, in part, on substituent effects, the band at 617 nm for ferrocenium has been assigned to a ligand-to-metal transition.<sup>14</sup>

The visible spectra of biferrocene cations are more difficult to analyze than those of simple ferrocenium ions. For the biferrocene monocation, a band appears at 545 nm ( $\epsilon$  2160) with a shoulder at lower energy. It has been postulated that two separate ligand-to-metal transitions occur from the fulvalene and cyclopentadienyl ligands which give rise to the broad unsymmetrical band.<sup>4</sup>

The substituted biferrocene monocations (II–VI) all have visible transitions similar to the biferrocene cation (see Table II). The band maxima range in position from 515 to 570 nm; the extinction coefficients average about 2000, with the exception of the 2,2''-dimethyl derivative (Vb). The lower intensity in this case may be due to a conformational effect. The similarities in the visible spectra of the substituted and unsubstituted monocations serve as a monitor of the weak interaction prerequisite of the Hush model.

As shown in Table II, all the substituted biferrocene monocations have new transitions in the near-infrared, similar to that observed for the biferrocene monocation; they are assigned as intervalence transfer transitions. According to the model proposed by Hush,<sup>2</sup> the energy of an intervalence transfer transition ( $E_{\text{op}} = h\nu_{\text{max}}$ ) is greater than or equal to four times the activation energy for thermal electron transfer ( $E_{\text{th}}$ ). The energy of the band maximum is equal to the sum of the Frank–Condon energy ( $E_{\text{FC}}$ ) for a symmetrical one-electron transfer plus the difference in energy ( $E_0$ ) between the initial and final states at their equilibrium configurations, vis.,

$$\bar{\nu}_{\text{op}} = \bar{\nu}_{\text{FC}} + \bar{\nu}_0 \quad (5)$$

where  $\bar{\nu}$  values are in wavenumbers. This relationship is shown diagrammatically in Figure 1. The potential energy–configurational coordinate diagram A represents a one-electron transfer in a symmetrically substituted ion with  $E_0 = 0$  and  $E_{\text{op}} = E_{\text{FC}}$ . This pertains to the cations of the diacetyl (IVa), dimethoxycarbonyl (IVb), and dimethylbiferrocenes (Va, VI), as well as biferrocene (I).

Within experimental error, the absorption maxima are the same for all the symmetrically substituted ions.<sup>15</sup> This indicates that the rate of electron transfer is insensitive to both the position of substitution (cyclopentadienyl vs. fulvalene ligand) and to the nature of the substituents when they are symmetrically disposed. This result is not forecasted by the Hush model but is reasonable in terms of the small effect of substituents on the structure of ferrocene<sup>16a,b</sup> and ferrocenium ions.<sup>16c,d</sup> In comparing two different symmetrically substituted ions that have the same intervalence transfer band energy, if it is assumed that the oscillator frequency is the same in both cases, the distortion in transforming from one valence isomer to another must be the same in both cases. That is, the relative displacement of the curves along the horizontal axis in diagram A of Figure 1 is the same for both compounds.

For an unsymmetrically substituted mixed valence species, electron transfer will result in the formation of an energetically unfavorable valence isomer. The Hush model predicts that the IT band will be blue shifted relative to the symmetrical case. Diagram B reflects the situation for the unsymmetrical ions (II, III, and Vb).

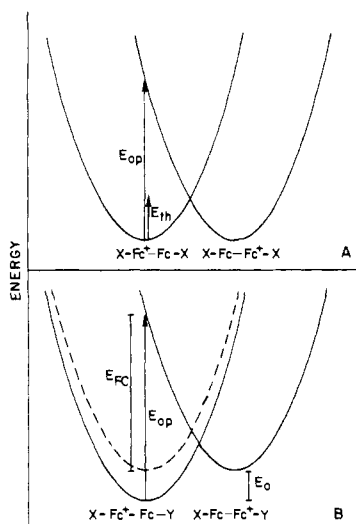
The results bear out the prediction. The unsymmetrically substituted biferrocene monocations have near-infrared bands at higher energy than the symmetrically substituted cations.

In going from diagram A to diagram B, the curve was displaced only along the vertical axis, with the assumption that the magnitude of the distortion is the same for both the symmetrically and unsymmetrically substituted ions and that any difference in band energy is due to the vertical displacement,  $E_0$ . In general this is not necessarily so; the right-hand curve representing the final state in an unsymmetrically substituted ion may be displaced on both axes relative to a symmetrically substituted ion.

**Table II.** Spectral Data for Substituted Biferrocene Monocations

Symmetrically substituted	$\lambda_{\max}$ , nm ( $\epsilon$ ) <sup>a</sup>			
	Solvent	Visible	Near-infrared	Calcd
Biferrocene (I)	<i>b, c</i>	545 (2160) <sup>d</sup>	1800 (750)	—
1',1'''-Diacetylbiferrocene (IVa)	<i>b</i>	570 (2120)	1780 (740)	—
1',1'''-Dimethoxycarbonylbiferrocene (IVb)	<i>b</i>	565 (2130)	1780 (770)	—
2,5''-Dimethylbiferrocene (Va)	<i>c</i>	560 (1850)	1800 (560)	—
2,2''-Dimethylbiferrocene (VI)	<i>c</i>	560 (1030)	1800 (340)	—
Unsymmetrically substituted				
2-Acetylbiferrocene (IIa)	<i>b</i>	515 (2300)	1400 (530)	1440
1'-Acetylbiferrocene (IIIa)	<i>b</i>	530 (2300)	1500 (570)	1360
2-Methoxycarbonylbiferrocene (IIb)	<i>b</i>	520 (2185)	1400 (500)	1380
1'-Methoxycarbonylbiferrocene (IIIb)	<i>b</i>	525 (2270)	1500 (600)	1400
2-Methyl-5''-hydroxymethylbiferrocene (Vb)	<i>c</i>	545 (2000)	1680 <sup>e</sup> (520)	1650

<sup>a</sup> Reproducible within 5%. <sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub> containing *n*-Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M). <sup>c</sup> CH<sub>3</sub>CN containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M). <sup>d</sup> All the monocations have shoulders at lower energy (650–700 nm). <sup>e</sup> Due to solvent absorption, values in 1660–1740-nm region are interpolated.

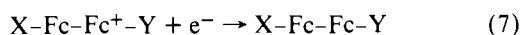
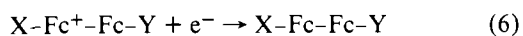


**Figure 1.** Potential energy-configuration coordinate diagrams: (A) for symmetrically substituted ions showing the transition  $X-Fc^+-Fc-X + h\nu \rightarrow [X-Fc-Fc^+-X]^*$ ; (B) for unsymmetrically substituted ions showing the transition  $X-Fc^+-Fc-Y + h\nu \rightarrow [X-Fc-Fc^+-Y]^*$ .

It is known that substituents on ferrocenium ions cause a large distortion in symmetry ( $Fc^+$  vs.  $Fc^+-X$ ).<sup>17</sup> In the case of the monoacetyl and methoxycarbonyl substituted ferrocenium ions, however, the comparison in going from diagram A to diagram B is  $X-Fc-Fc^+-X$  vs.  $X-Fc-Fc^+-H$ . Since little difference in energy was observed between  $X-Fc-Fc^+-X$  and  $H-Fc-Fc^+-H$ , we assume that displacement along the  $x$  axis is negligible compared to the energy difference,  $E_o$ . This permits us to approximate  $E_{FC}$  in the unsymmetrical case by  $E_{op}$  in the symmetrically substituted case.

If we assume that  $\Delta S$  is small in the electron transfer process, then  $E_o$  is approximately equal to the free energy difference between the valence isomers; this can be estimated from electrochemical data. We can then calculate band frequencies for the unsymmetrically substituted monocations by eq 5, since  $E_{FC}$  may be approximated from the band frequency of the symmetrically substituted ion ( $\bar{\nu}_{\max} = 5620 \text{ cm}^{-1} = \bar{\nu}_{FC}$ ).

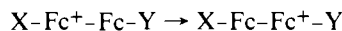
An estimate of the difference in free energy between valence isomers such as  $[X-Fc-Fc^+-Y]$  and  $[X-Fc^+-Fc-Y]$  is made from the following half reactions:



If  $X$  is electron donating relative to  $Y$ ,  $E_{1/2}$  for eq 6 is determined experimentally and  $E_{1/2}$  for eq 7 is calculated by:

$$E_{\text{calcd}} = E_{(FcY^{+0})} + \delta_{Fc-X} \quad (8)$$

Combining eq 6 and 7 yields:



$$\Delta E = E_{1/2}(\text{eq 6}) - E_{1/2}(\text{eq 7}) = \Delta G \quad (9)$$

Estimates of the free energy difference between the valence isomers of the monosubstituted acetyl and methoxycarbonylbiferrocene cations (II and III) were made by eq 9. The  $\Delta G$  values are on the order of 4–5 kcal/mol.<sup>18</sup> To make a very rough estimate of  $\Delta G$  for electron transfer between the valence isomers of 2-methyl-5''-hydroxymethylbiferrocene, we simply used the difference in potential between methylferrocene and hydroxymethylferrocene ( $\Delta E = -0.055 \text{ V}$ ;  $\Delta G \cong 1.27 \text{ kcal/mol}$ ).

The calculated values of the band energies of the intervalence transfer transitions for the unsymmetrically substituted biferrocene cations are given in Table II. Experimentally, no difference in energy is found for an acetyl and methoxycarbonyl substituent. The energy is slightly dependent on the position of substitution. The calculated energies are in reasonable agreement with the experimentally determined values, considering the approximations used in the calculation.

The solvent dependence of the intervalence transfer band maxima was not investigated for the substituted biferrocene cations. For the unsubstituted biferrocene cation, the absorption maximum was the same in solutions of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN that were 0.1 M in electrolyte. The bandwidth at half height, however, was solvent dependent. The bandwidths of ions generated in acetonitrile average  $4500 \text{ cm}^{-1}$ ; in methylene chloride, the symmetrical ions, I and IV, average  $3000 \text{ cm}^{-1}$  and the unsymmetrical ions, II and III, about  $4200 \text{ cm}^{-1}$ . The bandwidth in the high temperature limit is given by Hush as  $\Delta_{1/2} = (2310 \bar{\nu})^{1/2}$  for a symmetrical one-electron transfer (for  $\lambda_{\max} 1780 \text{ nm}$ ,  $\Delta_{1/2}(\text{calcd}) = 3600 \text{ cm}^{-1}$ ).<sup>19</sup>

The intensity of an intervalence transfer band is dependent on the extent of interaction of the donor and acceptor sites in the ground state.<sup>2,3</sup> Estimates of the interaction parameter,  $\alpha$ , can be made from eq 10,

$$\alpha^2 \cong \frac{(4.5 \times 10^{-4}) \Delta_{1/2} \epsilon_{\max}}{\bar{\nu} r^2} \quad (10)$$

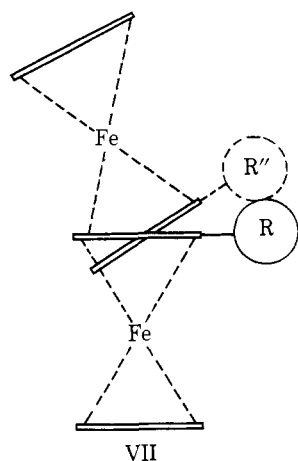
where  $\epsilon_{\max}$  is the extinction coefficient,  $r$  is the donor-acceptor distance,  $\alpha$  is the mixing coefficient,  $\Delta_{1/2}$  is the bandwidth, and  $\bar{\nu}$  is the frequency.<sup>1</sup> For the symmetrically substituted monocations, I, Va, and VI, the interaction parameter varies with

the intensity of the intervalence transfer band (assuming  $r$  is the same in all cases). A significant reduction in the intensity is noted in the 2,5''- and 2,2''-dimethyl derivatives as compared to the ferrocene monocation.

In the absence of direct metal-metal overlap, it is reasonable to assume that metal centers in mixed valence compounds interact via ligand  $\pi$  and  $\pi^*$  orbitals.<sup>20</sup> The extent of interaction can thus be reduced by distortions of the rings from coplanarity.

It has been shown that ring substituents in the 2- or 5-position effect the conformation of a ferrocene molecule.<sup>7,19</sup> From UV, NMR, and dipole moment measurements, a "nearly coplanar" trans conformation was deduced for a 2,5''-disubstituted ferrocene.<sup>21</sup> A model of 2,5''-dimethylbiferrocene, however, reveals some steric interaction between the 2-methyl and 2''-hydrogen and 5''-methyl and 5-hydrogen which leads to distortions from coplanarity.

The 2,2''-dimethyl derivative (VI) cannot adopt a trans or cis conformation without steric interaction of the substituents or the unsubstituted cyclopentadienyl rings. It presumably adopts a skewed conformation in which the rings are twisted from coplanarity (as in VII).<sup>7,21</sup> As a result, there is a reduced



$\pi$  interaction in the fulvalene ligand.

One measure of the extent of  $\pi$  overlap between the bonded cyclopentadienyl rings is the position and intensity of the absorption maximum of the  $\pi \rightarrow \pi^*$  transition in the neutral compound.<sup>7</sup> The 221-nm band ( $\log \epsilon$  4.76) in ferrocene corresponds to the  $\pi \rightarrow \pi^*$  transition of ferrocene ( $\lambda_{\max}$  201 nm,  $\log \epsilon$  4.70). Because of conjugation between the rings, the band for ferrocene is red shifted and of somewhat greater intensity than that of ferrocene. The UV data on the dimethyl derivatives are in support of a relatively planar conformation for 2,5''-dimethyl ( $\lambda_{\max}$  222 nm,  $\log \epsilon$  4.68) and a skewed conformation for 2,2''-dimethylbiferrocene ( $\lambda_{\max}$  215 nm,  $\log \epsilon$  4.55).<sup>7</sup>

The lower intensities of the intervalence transfer bands for the dimethylbiferrocene cations as compared to ferrocene are attributed to this stereoelectronic effect. For the unsymmetrically substituted acetyl and methoxycarbonyl cations, the 2-substituted isomers, which should experience the same steric interference to a coplanar geometry as Va, have smaller interaction parameters than do the 1'-substituted isomers.

## Conclusions

The present study has examined the usefulness of the Hush model in predicting the effects of symmetrical and unsymmetrical substitution on the energy and intensity of the intervalence transfer bands for nine substituted ferrocene cations. Using a simple formalism for calculating the energy differences of unsymmetrically substituted valence isomers from elec-

trochemical data, reasonable agreement between the predicted and experimental energies is obtained.

## Experimental Section

**Materials.** Ferrocene (I),<sup>22</sup> the methylbiferrocenes (V, VI),<sup>7</sup> acetylferrocenes (IIa,<sup>6a,b</sup> IIIa,<sup>5</sup> IVa<sup>5</sup>) and methoxycarbonylbiferrocenes (IIb,<sup>6a,b</sup> IIIb,<sup>6b</sup> IVb<sup>6a,b</sup>) were synthesized by literature procedures. Spectrograde  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  (Burdick and Jackson) were dried by passage through an alumina column (Woelm, Activity I basic for  $\text{CH}_2\text{Cl}_2$  and neutral for  $\text{CH}_3\text{CN}$ ), purged with argon, and stored in sealed siphon bottles until used. The electrolyte,  $n\text{-Bu}_4\text{NBF}_4$ , was prepared from  $n\text{-Bu}_4\text{NHSO}_4$  (Aldrich) and vacuum dried.<sup>23</sup> The electrolyte,  $\text{Et}_4\text{NClO}_4$ , was purchased (Eastman) and vacuum dried.

**Procedures.** Cyclic voltammograms were obtained using a PAR 175 Universal programmer and a PAR 173 potentiostat combined with a standard three-electrode configuration. The working electrode, a platinum button (Bechmann) and the reference, a saturated calomel electrode, were connected via a salt bridge containing either  $\text{Et}_4\text{NClO}_4$  in  $\text{CH}_3\text{CN}$  or  $n\text{-Bu}_4\text{NBF}_4$  in  $\text{CH}_2\text{Cl}_2$  (0.1 M). All electrochemical experiments were performed under argon.

In preparative runs, 0.05 mmol of substrate were oxidized on a platinum basket in a cell holding 50–100 mL of solvent (0.1 M in electrolyte). The monocations were generated by constant current oxidation. Samples for absorption spectra were transferred from the electrolysis cell through 2-mm Teflon tubing to a 1-cm quartz flow cell which was thoroughly rinsed with the electrolysis solution and then sealed by pinching the Teflon tubing. Visible and near-infrared spectra were recorded on a Cary 14 or Cary 17 spectrophotometer within 15 min of sample preparation. Extinction coefficients given in Table II are the average of three duplicate runs.

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values for electron transfer between valence isomers are: 1'-CO<sub>2</sub>CH<sub>3</sub>,  $\Delta E = -0.185$  V,  $\Delta G = 4.27$  kcal/mol; 2-CO<sub>2</sub>CH<sub>3</sub>,  $\Delta E = -0.200$  V,  $\Delta G = 4.61$  kcal/mol; 1'-COCH<sub>3</sub>,  $\Delta E = -0.165$  V,  $\Delta G = 3.81$  kcal/mol; 2-COCH<sub>3</sub>,  $\Delta E = -0.215$  V,  $\Delta G = 4.96$  kcal/mol.  
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## The Spectrochemical Properties of Tetragonal Complexes of High Spin Nickel(II) Containing Macrocyclic Ligands

Ludmila Y. Martin, C. Robert Sperati, and Daryle H. Busch\*

Contribution from The Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210. Received September 27, 1976

**Abstract:** A selected broad series of complexes with tetraaza macrocyclic ligands has been synthesized, characterized, and subjected to detailed electronic spectral studies. All complexes contain high spin, tetragonal nickel(II) and are of the general formula Ni(MAC)X<sub>2</sub>, where X = Br, Cl, N<sub>3</sub>, and NCS when possible. For macrocyclic ligands of greatest ligand field strengths only the NCS complexes are high spin. The saturated, unsubstituted tetraaza macrocycles [13]aneN<sub>4</sub>, [15]aneN<sub>4</sub>, and [16]aneN<sub>4</sub> and their Ni<sup>2+</sup> complexes were first synthesized during these studies. Combined with [14]aneN<sub>4</sub>, they comprise a unique series of ligands that is ideally suited for the study of ring-size effects among complexes with macrocyclic ligands. The smallest ring [13]aneN<sub>4</sub> gives no high spin complexes of the desired trans geometry—the other ligands do provide such species. A variety of additional, previously reported ligands was incorporated into these studies in order to cover a broad range of structural parameters. The effects due to varying extent and positions of unsaturation and those due to the presence of sterically demanding substituents have been considered. Electronic spectra were measured both in solution and in the solid state at room temperature and in the solid state at 77 K. The low temperature data were used in all calculations. Experimental curves were resolved into well-positioned absorption bands by Gaussian analysis. These input data were used in both weak and strong ligand field models, with complete configuration interaction, in order to calculate spectrochemical parameters. Observation of five or six bands permitted a tested best-fit calculation, while four bands allow analytical solution for the parameters in a closed calculation. The majority of the data was sufficient to facilitate extremely precise fitting to the model. Approximate techniques were developed for obtaining useful estimates of the maximum number of parameters from as few as two or three observed bands. A single crystal polarized spectrum eliminated <sup>3</sup>E<sub>g</sub> as a possible ground state for Ni([14]aneN<sub>4</sub>)Cl<sub>2</sub>. The precisely determined spectrochemical parameters reveal or confirm a number of significant relationships. The ligand field strength of the macrocycle,  $Dq^{xy}$ , varies systematically with ring size—[15]aneN<sub>4</sub> fits Ni<sup>2+</sup> well yielding a normal  $Dq^{xy}$  value; [14]aneN<sub>4</sub> is constrictive toward Ni<sup>2+</sup> and produces an unusually large value for  $Dq^{xy}$ ; [16]aneN<sub>4</sub> is dilative toward Ni<sup>2+</sup> and exerts a weak ligand field. Replacement of saturated amine linkages by imine groups increases  $Dq^{xy}$  but conjugation is unimportant as is the presence of axial CH<sub>3</sub> groups as substituents. The various structural contributions to  $Dq^{xy}$  can be quantitated and used in predictions.  $Dq^z$  reflects the normal spectrochemical series for axial ligands but the values depend on  $Dq^{xy}$  in a reciprocal fashion. Additional parameters are discussed.

Complexes of macrocyclic ligands having structure I are ideally suited to the study of the effects of tetragonal ligand fields on the electronic states of metal ions. Structure I is easily



obtained for many tetraaza macrocyclic ligands and the ligand structures available either as a result of earlier studies or as part of this work involve more highly systematic variations in structural parameters than are conveniently obtainable with noncyclic in-plane ligands. The macrocyclic ligands used are summarized in Figure 1, where their systematic abbreviations are given.<sup>1</sup> Ligands 1, 2, 8, and 9 provide the opportunity to study the effects of changing the ring size among the macrocyclic ligands; those numbered 5, 6, 7, 10, and 12 present different patterns and extents of unsaturation; while ligands 3 and 4 differ from 2 only in the extent of methyl substitution. Ligands 13 and 14 provide the additional complication of a

pyridine ring fused to the inner macrocyclic ring. The thorough assignments and interpretation of the electronic spectra of these tetragonal complexes are made possible by a progression of studies on more limited examples of such Ni<sup>2+</sup> complexes.

### Data Reduction and Interpretation of Spectra

Most octahedral and pseudo-octahedral complexes of Ni<sup>II</sup> yielded paramagnetism corresponding to two unpaired electrons and are green to violet in color. Their electronic spectra, that are traceable to the triplet term system, display three (in the case of octahedral) or more absorption bands with characteristically low extinction coefficients (ideally  $\epsilon = 1-10$  L<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup>). The theoretical energy level diagram<sup>2</sup> for a d<sup>8</sup> metal ion in O<sub>h</sub> and D<sub>4h</sub> symmetry is presented in Figure 2. The diagram indicates that as many as six triplet-triplet transitions may be observed in the electronic spectra of complexes with D<sub>4h</sub> symmetry. Observed spectra for such compounds rarely display more than five absorptions bands.<sup>3-5</sup> This often results from splittings that are small compared to bandwidths or to the overlap of more intense charge-transfer or ligand spectral bands. The spectra are also often complicated further by the occurrence of spin-forbidden transitions that may exhibit misleading apparent intensities because of their