

## Mixed-Valence Ferrocene Chemistry<sup>1</sup>

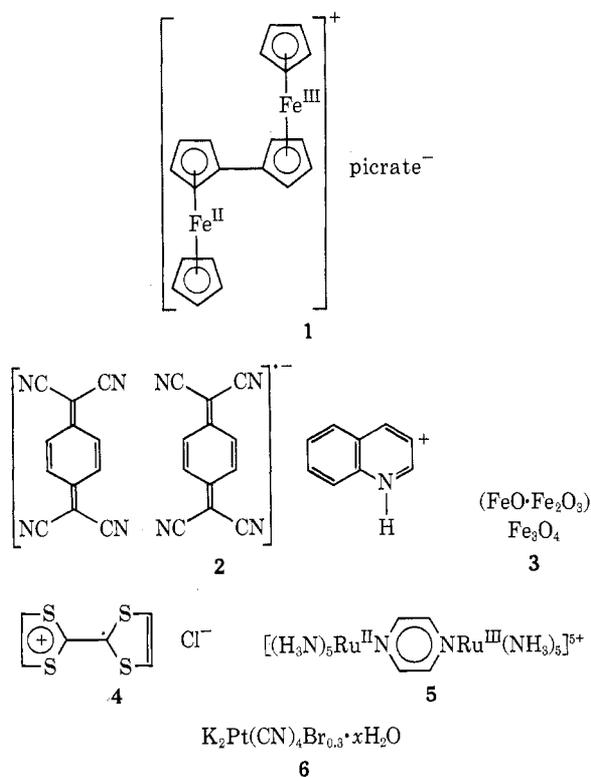
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Mixed-valence compounds contain at least two atoms or two identical molecular moieties in different oxidation states.<sup>2</sup> Compounds 1-6 are examples



of intra- and intermolecular mixed-valence compounds.<sup>2-7</sup> These and other related mixed-valence compounds are of great interest because they form an important link in the study of inorganic, organic, and biological oxidation-reduction reactions. More-

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over, data derived from the study of inorganic mixed-valence molecules suggest that the properties of mixed-valence compounds will rarely be just the sum of the properties of the component parts taken separately. For example, most Fe(II) and Fe(III) salts are colorless to pale green, while most Fe(II)-Fe(III) mixed-valence salts are deep blue to black. Likewise, the electrical conductivity of Fe<sub>3</sub>O<sub>4</sub>, a mixed-valence Fe(II)Fe(III) oxide, is 10<sup>6</sup> times larger than the trivalent Fe<sub>2</sub>O<sub>3</sub>.

The properties of these mixed-valence compounds will depend upon the amount of delocalization or the extent of interaction ( $\alpha$ ) between the two moieties. A classification now in common usage is<sup>2a</sup>

Class I	Little or no interaction Interaction parameter $\alpha \approx 0$ Properties = sum of components	} Integral oxidation states, $\alpha > 0.25$
Class II	Interaction parameter $0.707 > \alpha > 0$ New optical and electronic properties + properties of constituent components	
Class III	Interaction parameter $\alpha = 0.707$ New optical and electronic properties	} Fractional oxidation states, $\alpha > 0.25$

where  $\alpha$  is defined for the ground state of the complex as

$$\psi_G = (1 - \alpha^2)^{1/2} \Phi_i + \alpha \Phi_j \quad (1)$$

$\Phi_i$  and  $\Phi_j$  are wave functions for the donor-acceptor components of the mixed-valence system.

(1) Paper VIII, The Organic Solid State. Paper VII: D. O. Cowan, J. Park, C. U. Pittman, Jr., Y. Sasaki, T. K. Mukhejee, and N. A. Diamond, *J. Amer. Chem. Soc.*, **94**, 5110 (1972).

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(5) F. Wudl, D. Wobschall, and E. J. Hufnagel, *J. Amer. Chem. Soc.*, **94**, 672 (1972).

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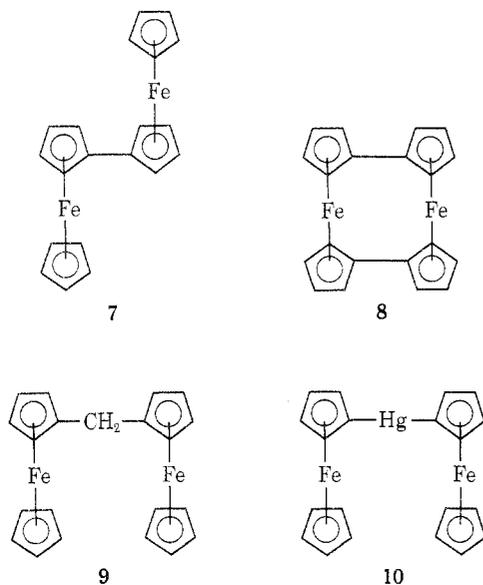
The optical and electronic properties of compounds 1,<sup>3</sup> 3,<sup>2a</sup> and 5<sup>6</sup> suggest that they belong in class II, while compounds 2,<sup>4</sup> 4,<sup>5</sup> and 6<sup>7</sup> exhibit greater delocalization and probably belong in class III. While the preparation and properties of mixed-valence inorganic compounds have been explored in some depth, relatively little work has been published regarding mixed-valence organic and organometallic compounds. This situation should rapidly change inasmuch as the following statement made by Robin and Day with specific reference to inorganic compounds is equally applicable to organic and organometallic compounds:

"For those interested in the interrelationships between electronic structure, molecular structure, electronic spectra, electronic conduction, and molecular magnetism, the mixed-valence systems offer a class of compounds unique in chemistry."<sup>2a</sup>

Furthermore it is our prejudice that mixed-valence organometallic compounds are more amenable to architectural tinkering than are their inorganic counterparts and thus provide the means with which to probe the variety and complexity of mixed-valence interactions.

### Molecular and Electronic Structure of Ferrocene and Ferricenium Ion

The ferrocenyl unit is an attractive component in the study of mixed-valence compounds due to the ease with which it may be oxidized. A variety of ferrocene compounds<sup>8</sup> have been prepared (7-10). It



should be possible to convert these and similar compounds into mixed-valence compounds *via* chemical and electrochemical means. Compound 1 was readily prepared by oxidation of 7, with an excess of benzoquinone in the presence of picric acid.<sup>3,9</sup> In the conformation shown, 1 has less opportunity for both through-bond and through-space interaction than the oxidized form of 8, while compounds 9 and 10 when oxidized should exhibit less delocalization than 1. Biferrocene [Fe(II)Fe(III)] picrate (1) and related

(8) (a) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Wiley, New York, N. Y., 1965; (b) D. E. Bublitz and K. L. Rinehart, Jr., *Org. React.*, 17, 1 (1969).

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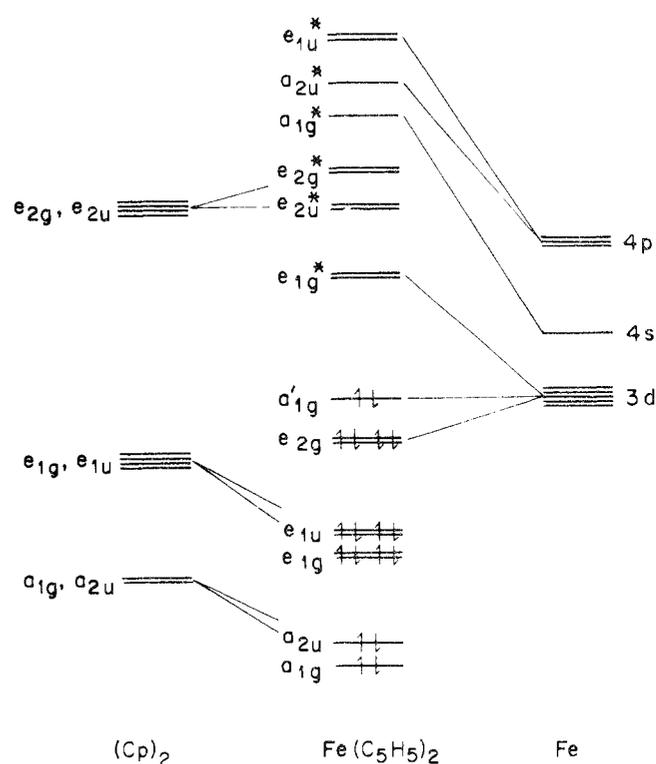


Figure 1. Molecular orbital energy level diagram of ferrocene (re-drawn from R. Prins, *Mol. Phys.*, 19, 603 (1970)).

mixed-valence organometallic compounds possess a number of interesting properties that will be considered after a short review of the current ideas regarding the electronic structure of ferrocene and ferrocenium cation.

Most semiempirical molecular orbital theory calculations for ferrocene<sup>10</sup> give a molecular orbital energy level scheme similar to the one shown in Figure 1. While there are some level-ordering differences among the various calculations, it is now generally accepted that the LUMO and the two HOMO are primarily metal d orbital in character, as shown by Mossbauer, optical, esr, and photoelectron spectroscopic studies.

Ferrocenium ion ( $\text{Fc}^+$ ) has been assigned the orbitally degenerate  ${}^2E_g [(e_{2g})^3(a_{1g})^2]$  configuration based on magnetic susceptibility<sup>10a,11,12</sup> and esr<sup>10a,11a,12,13</sup> studies which indicate that the  $e_{2g}$  orbital is not completely filled. For example, the magnetic moment of  $\text{Fc}^+\text{BF}_4^-$  at room temperature is  $2.49 \mu_B$ ; this value is much larger than the spin only moment of  $1.73 \mu_B$ . However, the  $e_{2g}$  and  $a_{1g}$  orbitals are close in energy, and it is difficult to decide which is the HOMO,  $(e_{2g})^3(a_{1g})^2$  or  $(a_{1g})^2(e_{2g})^3$ .

The blind application of photoelectron spectroscopy and Koopmans' theorem ( $\epsilon_{\text{ionization}} = -\epsilon_{\text{orbital}}^{\text{SCF}}$ ) to the study of ferrocene would suggest that the HOMO is the  $e_{2g}$  level since the intensity of the signal corresponding to the first ionization is

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twice as great as that of the second ionization. However, since the first two ionizations differ by only 0.35 eV (2800  $\text{cm}^{-1}$ ), all that can safely be concluded is that the two levels are close in energy.<sup>10a,12,13,14</sup> The success of Koopmans' theorem depends upon the approximate cancelation of (a) the reorganizational energy required by the ion after the electron has been ejected and (b) the electron-electron correlation energy difference between the neutral molecule and ion. It is therefore not surprising that, in contrast to PES, the optical spectrum of ferrocene is best interpreted in terms of a highest occupied  $a_{1g}$  orbital.<sup>10c</sup>

The 617-nm (1600- $\text{cm}^{-1}$ ) absorption of the ferrocenium ion was originally attributed to the  ${}^2E_{2g} \rightarrow {}^2A_{1g}$  transition in which an electron is excited from the  $a_{1g}(3d)$  to the  $e_{2g}(3d)$  orbital.<sup>15</sup> Prins<sup>10a,16</sup> and Gray<sup>11</sup> have argued that this assignment is improbable since the molar absorptivity ( $\epsilon = 340$ ) is larger than that observed for similar 3d-3d transitions in the absorption spectra of other metallocenes. They assign this band to the symmetry-allowed  ${}^2E_{2g} \rightarrow {}^2E_{2u}$  transition, in which an electron is excited from the  $e_{1u}$  ligand orbital to the partly filled  $e_{2g}$  ion orbital. In favor of this assignment are the observations that substitution of an electron-donating methyl group on the ferrocenium ion produces a red shift of 700  $\text{cm}^{-1}$ , while an electron-withdrawing acetyl group produces a blue shift of 2700  $\text{cm}^{-1}$ .

### Electronic Absorption Spectroscopy of Mixed-Valence Compounds

In order to discuss the electronic spectra of biferrrocene [Fe(II)Fe(III)] picrate and related compounds, it is desirable to know more about the extent of delocalization ( $\alpha$ ) in these compounds. X-Ray photoelectron spectra (PES) of the following six ferrocene compounds were measured<sup>17</sup> in order to evaluate the extent of interaction between the two ferrocenyl units: ferrocene, biferrrocene, ferrocene [Fe(III)] picrate, ferrocene [Fe(III)] fluoroborate, biferrrocene [Fe(II)Fe(III)] picrate, and biferrrocene [2Fe(III)] fluoroborate.

If there is only weak interaction between the two ferrocene units in biferrrocene, then upon formation of biferrrocene [Fe(II)Fe(III)] picrate the charge should be relatively localized on one ferrocene unit. In the closely related series of ferrocene compounds described, the binding energies of a specific iron core level are expected to vary approximately linearly with the charge on these atoms. If our postulate that biferrrocene [Fe(II)Fe(III)] picrate can be described as a class II ( $\alpha = 0-0.1$ ) mixed-valence compound is correct, then we should observe two transitions for each Fe core level. This is in fact what was observed for biferrrocene [Fe(II)Fe(III)] picrate. The transition at a binding energy of 707.7 eV corresponds in shape and position to Fe  $2p_{3/2}$  bands found in ferrocene and biferrrocene, while the transition at a binding energy of 711.1 eV corresponds in position and shape to the Fe  $2p_{3/2}$  bands observed in ferrocene [Fe(III)]

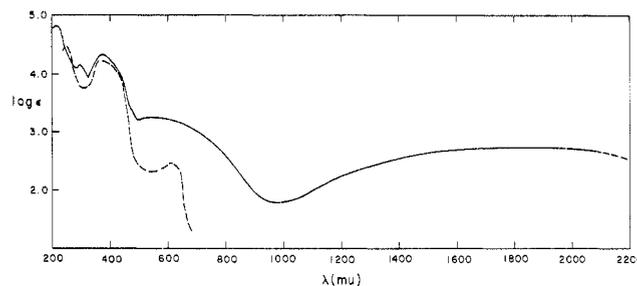


Figure 2. Visible-ultraviolet-near infrared spectrum of biferrrocene [Fe(II)Fe(III)] picrate (1), solid line; spectrum of ferrocene [Fe(III)] picrate, broken line.

picrate, ferrocene [Fe(III)] fluoroborate, and biferrrocene [2Fe(III)] fluoroborate. This latter ionization band is broadened by exchange interaction of the core electrons and unpaired valence electrons.

The X-ray PES results indicate that there is at best weak interaction between the two ferrocenyl rings in biferrrocene [Fe(II)Fe(III)] picrate. This conclusion is confirmed by the Mossbauer spectrum of this compound.<sup>18</sup> Here again the Mossbauer spectrum appears to be a composite of the spectra obtained for ferrocene and ferrocene [Fe(III)] picrate.

There are several factors that could account for the weak interaction between the ferrocene and ferrocenium portions of biferrrocene [Fe(II)Fe(III)] picrate. The most important is probably the fact that the HOMO is nonbonding in character.

Since  $\alpha$  is small for biferrrocene [Fe(II)Fe(III)] picrate, we expect to observe electronic transitions similar to those observed for ferrocene and ferrocenium picrate. The electronic spectrum of biferrrocene [Fe(II)Fe(III)] picrate is shown in Figure 2 along with the spectrum of ferrocene [Fe(III)] picrate.<sup>9</sup> The presence of the ferrocene-ferrocenium transitions is consistent with the suggested weak interaction between the two portions of the molecule. There are, however, at least two important differences. The 600-nm ( ${}^2E_{2g} \rightarrow {}^2E_{2u}$ ) band is broadened and shifted to higher energy, and a new near-infrared transition is observed at 1900 nm ( $\epsilon = 550$ , acetonitrile) which is assigned to a mixed-valence electron-transfer transition.

A simple substitution effect cannot explain the broadening and change in energy of the 600-nm transition since ferrocene, like an alkyl group, is electron donating relative to the ferrocenium ion and should give rise to a red shift. The determination of the Hammett  $\sigma_p$  for the ferrocenyl group as a substituent on benzene shows it to be a stronger electron-donating ligand than the methyl group.<sup>19</sup>

It is possible that the broad 600-nm band is composed of two transitions (see Figure 3). If this is true, one would expect the  $\text{Fc}(e_{1u}) \rightarrow \text{Fc}^+(e_{2g})$  transition to be blue shifted in relation to the known  $\text{Fc}^+(e_{1u}) \rightarrow \text{Fc}^+(e_{2g})$  transition. Attempts to resolve this 600-nm band by spectroscopic measurements at low temperatures have only been partially successful to date.

All mixed-valence class II and III compounds prepared and studied thus far are characterized by a

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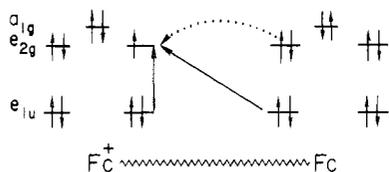
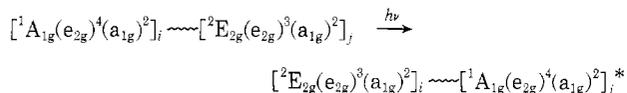


Figure 3. Possible mixed valence (electron transfer) transition in biferrocene [Fe(II)Fe(III)] picrate.

new electronic transition in the visible to near-infrared region of the spectrum. The intensity of this new transition, which is seen in the absorption spectrum of the mixed-valence species but not in the spectra of any of the equal valence precursor compounds, is an extremely sensitive gauge of the extent of interaction, even when  $\alpha$  is very small.<sup>2</sup> As such, the appearance of this new absorption band is a simple and useful diagnostic tool to identify the presence of a compound which is mixed valent in character. Mixed-valence electronic transition data for a number of new compounds are given in Table I.<sup>3,6,20-23</sup> Recently mixed-valence transitions have also been observed for mixed oxidation state ferrocene compounds prepared from terferrocene, quaterferrocene, sexiferrocene, and polyferrocene.<sup>24</sup>

For biferrocene [Fe(II)Fe(III)] picrate this transition corresponds to the intramolecular electron transfer shown in Figure 3 (-----→)



where \* indicates a vibrationally excited ground state. As such, the transition involves an electron transfer between two metallike orbitals ( $e_{2g}$ ) that interact only weakly with the  $\pi$  conjugated system of the molecule. From the following discussion it will be seen that the energy ( $\lambda$ ) of the mixed-valence transition is dependent upon differences in geometry and bond lengths in the donor and acceptor portions of the molecule but is *not* very dependent upon the extent of delocalization in the ground state ( $\alpha$ ) or upon the distance separating the donor and acceptor moieties. However, the intensity of the allowed transition is proportional to the square of the probability of finding the electron on the acceptor portion in the ground state and upon the square of the distance between the two moieties. A simple model (Figure 4) first proposed by Hush<sup>2b,c</sup> provides qualitative insight into how the various molecular parameters alter the mixed-valence transition. If we have a mixed-valence compound where the mixed-valent moieties have oxidation states  $i$  and  $j$ , respectively, then the ground-state electron distribution is  $[i,j]$ . The new absorption band is assigned to the  $[i,j] + h\nu$

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(24) (a) Unpublished observations of M. Rausch, F. Kaufman, J. Park, and D. O. Cowan. (b) Aharoni and Litt (S. M. Aharoni and M. H. Litt, *J. Organometal. Chem.*, **22**, 171, 179 (1970)) have prepared a ferrocene-ferrocenium mixed crystal; no new near-ir band was reported.

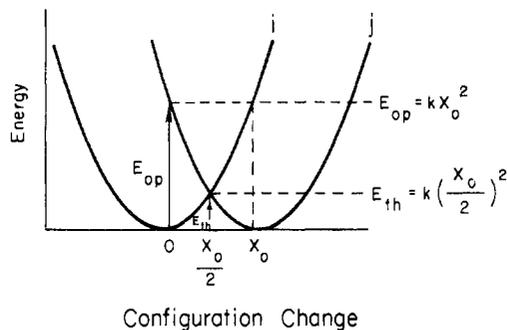
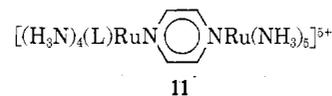


Figure 4. Potential energy-configuration diagram for a symmetrical one-electron transfer. The curves represent two weakly interacting states  $i$  and  $j$ , with different equilibrium configurations ( $0, X_0$ ). If these states are represented as harmonic oscillators [ $E(X) = k\Delta X^2$ ], then the maximum for the optical transition is equal to  $kX_0^2$  and the maximum for the thermal transition (at  $X_0/2$ ) is equal to  $k(X_0/2)^2$ ; or the thermal activation energy is one-quarter of the optical transition energy ( $E_{th} = E_{op}/4$ ) (redrawn from ref 9).

→  $[j,i]^*$  transition in which the optical excitation results in intermolecular or intramolecular electron transfer. In the limit of  $X_0 = 0$  in Figure 4, the equilibrium (configuration) normal coordinates of the  $i$  and  $j$  states would be equivalent and there would be no Franck-Condon barrier to optical electron transfer. This means that, as the electron-transfer transition in a series of mixed-valence compounds (Table I) tends toward higher energy, the atoms which are in different oxidation states find themselves in increasingly different ligand environments. This explains why the electron-transfer transition in biferrocene [Fe(II)Fe(III)] has such a low energy compared with other members of Table I. While the X-ray data<sup>8a,25</sup> are not as detailed as one would desire, we know that ferrocenium ion is structurally very similar to ferrocene. There is a very small difference in the cyclopentadienyl-iron-cyclopentadienyl distances between the two, and a small distortion from the  $D_5$  symmetry of ferrocene has been noted for the ferrocenium ion.<sup>11,12</sup> The energy of the optical transition is dependent on the difference in configuration at the two sites because structural and/or electronic reorganization is required to accommodate the intramolecular electron transfer.

If the mixed-valence compound is unsymmetrical, *i.e.*, the structure of the two moieties is different, the interpretation of the electron-transfer bands is complicated by the fact that the zero point energy levels for the initial and final states may be vertically displaced relative to each other. A case in point is provided by the mixed-valence ruthenium complexes 11 (Table I) where substitution of pyrazine (11b) for



NH<sub>3</sub> (11a) results in an electron-transfer band which is shifted to higher energy<sup>6</sup> (410-nm shift). In these complexes both configurational and energy differences between the  $[i,j]$  and the  $[j,i]$  states lead to the observed shift in wavelength maximum of the mixed-valence transition.

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Table I  
Spectral Data for Mixed Valence Compounds

Compd	Formula	$\lambda_{\max}$ , nm	$\epsilon$	Ref
1	(In text)	1900	550	3
11a	L = NH <sub>3</sub>	1570	7 × 10 <sup>8</sup>	6
11b	L = pyrazine	1160		6
12	[(NC) <sub>4</sub> Fe(CN) <sub>2</sub> Fe(CN) <sub>4</sub> ] <sup>6-</sup>	1280	5.5 × 10 <sup>8</sup>	20
13	[(R <sub>4</sub> C <sub>4</sub> S <sub>4</sub> ) <sub>2</sub> Co(DPPE)Co(R <sub>4</sub> S <sub>4</sub> C <sub>4</sub> ) <sub>2</sub> ] <sup>- a</sup>	1360		21
14	[(X) <sub>2</sub> Cu(OAc) <sub>2</sub> Cu(X) <sub>2</sub> ] <sup>- a</sup>	900		22
15	[(H <sub>3</sub> N) <sub>2</sub> Cu(Br) <sub>2</sub> Cu(Br) <sub>2</sub> Cu(NH <sub>3</sub> ) <sub>2</sub> ]	625	160	23

<sup>a</sup> DPPE = *trans*-1,2-bis(diphenylphosphino)ethylene; X = CH<sub>3</sub>OH.

The intensity of the electronic transition depends upon the magnitude of the transition dipole moment ( $M_{12}$ ) (eq 2) between the ground (1) and excited

$$M_{12} = \langle 1 | \sum_i e_i X_i | 2 \rangle \quad (2)$$

state (2); see Figure 4. Since 1 and 2 are composed of mixed donor ( $\Phi_i$ ) and acceptor ( $\Phi_j$ ) wave functions it is possible to show<sup>2c,26</sup> *via* first order perturbation theory that for a simple isolated donor-acceptor system the magnitude of  $M_{12}$  is

$$|M_{12}| = e\alpha r \quad (3)$$

where  $r$  is the distance between the donor and acceptor, and the  $\alpha$  is approximately defined in equation 1. The intensity (oscillator strength) will then depend upon the square of both the interaction parameter ( $\alpha$ ) and the distance ( $r$ ) separating the interacting donor-acceptor moieties. Based on this type of perturbation treatment it is possible to estimate  $\alpha^2$  from spectral data using the following equation

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

In this equation, the band shape of the electron transfer transition is assumed to be Gaussian,  $\epsilon_{\max}$  is the molar absorptivity at the band maximum,  $\Delta_{1/2}$  is the band half-width in wave numbers,  $\bar{\nu}$  is the frequency in wave numbers and  $r$  is the donor-acceptor distance in Å. Using this equation,  $\alpha^2$  is calculated to be  $1.610 \times 10^{-3}$  for Prussian blue<sup>2c</sup> [KFe<sup>II</sup>-Fe<sup>III</sup>(CN)<sub>6</sub>·H<sub>2</sub>O];  $0.9\text{--}1.4 \times 10^{-2}$  for biferrrocene [Fe(II)Fe(III)] picrate (1); and  $1.7 \times 10^{-2}$  for Creutz and Taube's ruthenium complex (5). All three of these compounds meet the trapped valence requirement,  $\alpha < 0.25$ .<sup>26</sup>

### Thermally Activated Electron Transfer

In addition to the optical Franck-Condon path for electron transfer, mixed-valence compounds can also undergo a thermally activated process which leads to electron exchange when the transition-state equilibrium geometry is achieved (see Figure 4). From this model it can be seen that the activation energy for the thermal electron-transfer process is equal to or greater than one-fourth the energy of the optical

transition.<sup>2c</sup> This allows one to calculate a thermally activated unimolecular electron-transfer rate constant ( $k_{th}$ ).

$$k_{th} \approx kT/h \exp[hc\bar{\nu}/(4RT)] \quad (5)$$

For biferrrocene [Fe(II)Fe(III)] picrate the calculated rate constant is  $1.3 \times 10^{10} \text{ sec}^{-1}$ . This is comparable to the unimolecular rate constant ( $4 \times 10^9 \text{ sec}^{-1}$ ) estimated from the product of the experimental second-order rate constant for the exchange of ferrocene and ferrocenium ion and a concentration term calculated so that the average iron-iron distance would be the same as that found for compound 1.<sup>3,9</sup>

A second example which involves fewer approximations in the rate calculation is the binuclear copper complex 14 (Table I) which has a mixed-valence absorption band at 900 nm.<sup>23</sup> An esr study of this compound indicates that intramolecular exchange rate is greater than  $10^8 \text{ sec}^{-1}$ , while the value calculated from the energy of the optical electron-transfer transition is  $5 \times 10^8 \text{ sec}^{-1}$ .

It seems very probable that the relationship between electronic structure and electron-transfer rates in mixed-valence compounds will be useful in defining the important rate-determining parameters in oxidation-reduction reactions. This is especially true for bimolecular reactions which proceed through a short-lived activated complex, where the rate-determining step is electron transfer within the complex.<sup>27,28</sup> The importance of precursor complex formation has been discussed for electron-transfer reactions,<sup>27</sup> and kinetic and spectral data have been used as evidence for the occurrence of certain mixed-valent complexes in the reaction mechanism. Recently it has been suggested that mixed-valence species serve as intermediates in several interesting reactions. ESR measurements during the autocatalytic decomposition of alkylcopper(I) species<sup>29a</sup> have been interpreted in terms of complexes of the RCu<sup>I</sup>Cu<sup>0</sup> type. Optical changes during the Mn(III)-catalyzed oxidative decarboxylation of acids<sup>29b</sup> are thought to be due to the formation of Mn<sup>III</sup>(RCO<sub>2</sub>)<sub>x</sub>Mn<sup>II</sup> complexes.

There are many components of living systems which contain two or more metal atoms in close proximity.<sup>30</sup> When the metal atoms of these com-

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pounds are involved in valence changes, mixed-valence effects may be important in determining physical parameters such as oxidation-reduction potentials and rates of chemical reactions. In addition, mixed-valence intermediates are involved as redox couples in the electron-transfer chains of chloroplasts and mitochondria, where a number of metal-containing proteins shuttle electrons between oxidizing and reducing substrates. In this regard, a model system for aerobic oxidation of cytochrome *c* has been prepared in which the electrons are thought to be transferred by tunneling between Fe(II)-Fe(III) potential wells.<sup>31</sup>

One group of biological compounds that can be considered as mixed valence in character is the non-heme iron proteins.<sup>30a,32</sup> These substances, which have active sites of the type (Fe-S)<sub>*n*</sub>, where *n* = 1-8, have been examined by a variety of physical techniques which indicate that the iron atoms (*n* > 2) can be in close structural and electronic proximity.<sup>33</sup> The 2.5-Å resolution X-ray map of bacterial ferredoxin (*n* = 8) indicates that there are two clusters of tetrahedrally arranged 4Fe-4S units in the molecule.<sup>34</sup> Magnetic susceptibility and Mossbauer measurements on a number of these iron-sulfur proteins indicate that the oxidized form is diamagnetic, while the reduced form has one unpaired electron, which is delocalized over all the iron atoms in the active site.<sup>33b</sup> A model with antiferromagnetically coupled Fe(III) atoms (oxidized form) and Fe(II)-Fe(III) atoms (reduced form) has been suggested to account for these results.<sup>35</sup> Spinach ferredoxin and beef adrenodoxin, on the other hand, have Fe-S active sites which are not characterized by a high degree of metal-metal interaction. Circular dichroism and absorption spectra of these substances have transitions at about 11,000 cm<sup>-1</sup> that have been interpreted as mixed-valence bands due to weak Fe(III)-Fe(II) orbital overlap.<sup>32</sup> The weak coupling hypothesis is consistent with the low mixed-valence band intensity and the presence of the individual component transitions in the Mossbauer and electronic absorption spectra.

Many of the iron-sulfur proteins have unique physical properties, such as extremely low oxidation-reduction potentials (near the value of the H<sub>2</sub> electrode) and *g* values of less than 2 as measured by esr experiments for the reduced (mixed-valence) forms. The reasons for the extraordinary properties of individual species, or the explanation for differences in the behavior of related iron-sulfur proteins, is not immediately apparent from the structural data on the active sites. For example, ferredoxin and HiPIP have structurally similar Fe-S clusters,<sup>34</sup> yet their *E*<sub>0</sub> values differ by 0.7 V.<sup>36</sup>

It is possible that geometrical distortions from the normal geometry may be important in determining the properties of these systems.

### Structural Change

It is expected that interaction between the appropriate atoms in a mixed-valence compound [*i,j*] may manifest itself in discrete structural changes relative to the [*i,i*] or [*j,j*] parent species. These changes are expected to depend on the nature of the interaction between the HOMO levels and the structural rigidity of the molecular framework. A major distortion in structure may result in bonding changes which will be reflected in new bond lengths and bond angles that can be easily measured by X-ray crystallography. On the other hand, some subtle geometric distortions could elude X-ray detection.

Mixed-valence organometallic chalcogen complexes have been prepared and studied by X-ray crystallography in order to determine the stereochemical consequences of removing a valence electron. The tetramercapto-bridged Mo(III) dimer, [Mo(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(SCH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, and the corresponding mixed-valence cation were prepared and found to have very similar bond distances and bond angles.<sup>37</sup> These results were in strong contrast to those found for the mixed-valence iron-sulfur dimer [Fe(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)(SC-H<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>+</sup>. The latter compound has an iron-iron distance of 2.925 Å which was a decrease of 0.46 Å relative to that found for the diamagnetic neutral dimer.<sup>38</sup> The decrease in the metal-metal distance was also reflected as a large distortion (16°) of the bridging Fe-S-Fe angle (98° neutral species).

The difference in sensitivity to mixed-valence interaction upon removal of one valence electron from the Mo *vs.* Fe dimer was ascribed to the presence of angular strain in the bridging ligands of the former compound which prevented any shortening of the Mo-Mo bond upon oxidation. This interpretation is consistent with the very small bridging Mo-S-Mo angles (64°) found in the neutral dimer.

The decrease in the Fe-Fe bond length of the dimercapto mixed-valence compound was attributed to the formation of a one-electron metal-metal bond upon removal of a single electron from the completely filled  $\sigma$  antibonding orbital by oxidation of the neutral dimer.

Geometrical changes have also been detected in ferrocene dimers<sup>12</sup> upon the removal of one or more valence electrons, even though the metal orbitals involved in the valence change are only weakly coupled and nonbonding in character. Biferrocene can exist in three stable oxidation states, the diamagnetic [2,2] and the two paramagnetic states [2,3] and [3,3]. The choice of one- *vs.* two-electron oxidation depends upon the oxidizing agent used.<sup>9</sup> The paramagnetic derivatives, which contain one [2,3] and two

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**Table II**  
Electrical Conductivity at 298 K and Activation Energy ( $E_a$ )

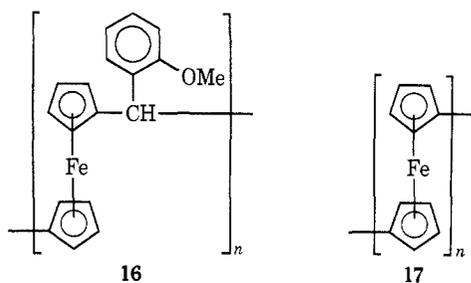
Compd	$\sigma$ , ( $\Omega$ cm) $^{-1}$	$E_a$ , eV	Ref
Ferrocene	$10^{-14}$	0.90	9
Ferricenium picrate	$10^{-13}$	...	9
1	$10^{-8}$	0.43	3
2	100	0.023 <sup>b</sup>	4b
3	250		2a
4	0.25	0.19	5
4 reduced	$10^{-12}$		5
6	0.3–120	0.085 <sup>b</sup>	7c

<sup>a</sup> Conductivity data for 4 was determined on a pellet; all other data were from single crystal measurements. <sup>b</sup> Low-temperature activation energy.

[3,3] unpaired electrons respectively, can be studied by magnetic susceptibility and electron spin resonance. The differences in observed behavior indicate that geometric distortions in these compounds can lead to changes in electronic structure.

### Electrical Conductivity

Table II gives electrical conductivity data for several mixed-valence compounds and their non-mixed-valence parents. The electrical conductivity of single crystals of the biferrocene [Fe(II)Fe(III)] picrate were found to be  $10^6$  times larger than that of ferrocene or ferrocenium picrate.<sup>3,9</sup> Measurement of the conductivity as a function of temperature indicated that compound 1 was an intrinsic semiconductor, with an activation energy for the conduction of 0.43 eV. This is in comparison to an activation energy of 0.9 eV found for ferrocene. The difference between the activation energy for electrical conduction (0.43 eV) and the thermal activation energy for intramolecular electron transfer (0.16 eV) indicates that the rate-limiting process in the conduction is electron hopping between the individual molecules in the crystal. The electrical conductivity of ferrocene polymers (16, 17) can be dramatically increased when the polymers are converted into mixed-valence poly salts.<sup>1</sup>



A simple electron-hopping model for the electrical conductivity is consistent with the observations that the conductivity is relatively insensitive to the anion structure, or to conjugation, but is very sensitive to the fraction of the ferrocene units oxidized. The higher conductivity for compounds 2, 4, and 6 which stack in one-dimensional chains is probably due to (a) stronger interaction between individual units and (b) appropriate molecular orientation within the crystal for interaction between more than two of the molecular units. However, recent experimental<sup>39</sup> and theoretical<sup>40</sup> work suggest that the probability of finding a very highly conducting one-dimensional system is quite low. This is a consequence of the fact that even small random potentials (caused, for example, by counterions) will result in the localization of an otherwise extensively delocalized system.

The organic compound with the highest known electrical conductivity combines the cation of compound 4, tetrathiafulvalenium cation (TTF<sup>+</sup>), with the tetracyano-*p*-quinodimethane anion (TCNQ<sup>-</sup>).<sup>41</sup> Single crystals of this material have a conductivity of 650  $\Omega^{-1}$  cm<sup>-1</sup> at room temperature and a value of 15,000  $\Omega^{-1}$  cm<sup>-1</sup> at 77 K.

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