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References and Notes

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Bis(fulvalene)diiron, Its Mono- and Dications. Intramolecular Exchange Interactions in a Rigid System

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Abstract: Biferrocenylene [bis(fulvalene)diiron, BFD] was synthesized by two independent routes: an Ullman coupling of dibromoferrocene and the reaction of the fulvalene dianion with ferrous chloride. It was chemically oxidized to the mixed valence monocation and to the dication. These derivatives were characterized by optical, Mössbauer, ESR, and x-ray photoelectron spectra and magnetic susceptibility. The Mössbauer spectra of the mixed valence salts at 298 and 77 K indicate that both iron atoms are equivalent. X-Ray photoelectron spectra similarly attest to this equivalence. An asymmetry in the intensity of the Mössbauer lines is due to a Karyagin effect. The Mössbauer spectrum of the dication shows a quadrupole splitting of 3.0 mm/s which is unusually large for a ferrocenium-type derivative. The magnetic susceptibility of BFD (2,3) picrate, measured in the 2–300 K range, follows a Curie law with a room temperature moment very close to the spin-only value. The dicationic fluoroborate salt is diamagnetic. The ESR spectra of the monocationic picrate and fluoroborate salts are characterized by narrow lines and a small rhombic anisotropy. An absorption in the near-infrared centered at 1550 nm is observed in the spectra of the monocations, but not the neutral or dicationic derivatives. The assignment of this band is discussed with respect to the results of the other physical measurements.

By definition, mixed valence compounds contain two or more atoms of the same element in different formal states of oxidation.² Theory³ predicts that new (e.g., magnetic and spectroscopic) properties will arise from interactions between valence electrons in unique oxidation states. Many inorganic mixed valence systems have been found to possess properties beyond those derived by simple addition from the component parts of the molecule.⁴

The term "mixed valence" was chosen by Robin and Day^{3b} with the intent that it be all encompassing. Systems ranging from no interaction and firmly trapped valences to complete delocalization and nonintegral valences are included. The former group is termed class I; the latter is class III. An intermediate classification, class II, houses those compounds in which there is some delocalization, but the properties of the components are still discernible.

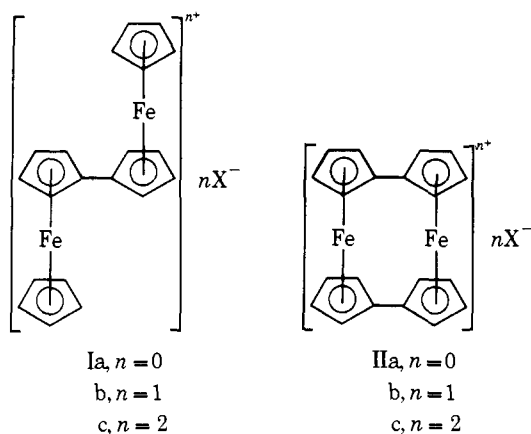
Our objective has been to investigate the variation of properties with change in structure in binuclear mixed valence metallocenes. According to the theory of Hush,^{3a} the rate of electron transfer in mixed valence systems depends on the amount of reorganizational energy necessary to make the mixed valence sites identical; i.e., if the coordination geometry

of the two sites is very different, the rate of transfer is very slow. In this regard, the iron group metallocenes are notable candidates for rapid electron transfer since crystallographic data on ferrocene⁵ and ferrocenium salts⁶ have shown that the oxidation state of iron has a small effect on interatomic distances.

The organometallic mixed valence compound biferrocene [Fe(II)Fe(III)] picrate (Ib) has been characterized as a class II species.² Its Mössbauer,⁷ ESCA,⁸ magnetic,⁹ and optical¹⁰ properties have features attributable to the constituent ferrocene and ferrocenium portions in addition to features ascribable to its mixed-valence nature. Moreover, the fully oxidized biferrocene [2Fe(III)] salt (Ic), although unstable in solution and more difficult to characterize, displays properties that are essentially the sum of two ferrocenium units.^{7,9} This is in sharp contrast to the observed behavior of the mono- (Iib) and dioxided (Iic) salts of biferrocenylene (bis(fulvalene)diiron, BFD), whose syntheses and properties are discussed herein.

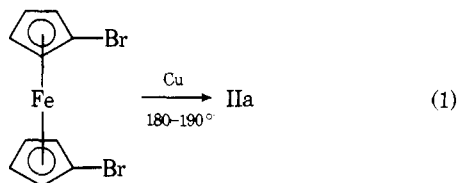
Synthesis

Bis(fulvalene)diiron (IIa) has been reported in the literature as a product of the Ullmann coupling of 1,1'-diiodoferrocene¹¹

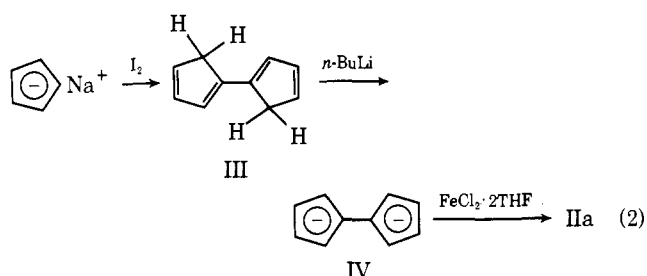


and as a by-product in the pyrolysis of polymercycloferrocenylene.¹² In the course of our studies, two other methods of preparation were developed.^{13,14}

The yield of BFD from the Ullmann coupling ranged from 2 to 30% depending on the purity of the 1,1'-diiodoferrocene.¹⁵ The major impurity in diiodoferrocene when prepared by the method of Kovar et al.¹⁶ is iodoferrocene which lowers the yield and complicates the isolation of BFD by increasing polymer formation. As diiodoferrocene is difficult to purify by conventional measures, 1,1'-dibromoferrocene was used instead. This compound is a solid and can be purified by fractional sublimation and repeated recrystallizations. The coupling of the dibromide (eq 1) requires higher temperature than that of the diiodide, and was carried out with biphenyl as solvent. Reaction for 19 h at 180–190° in the presence of activated copper gave a 20–25% yield of biferrocenylene (IIa).



The second approach, through the intermediacy of the fulvalene dianion and without the isolation of any intermediates, proved to be a most efficient route (eq 2).¹⁴



Sodium cyclopentadienide (CpNa) was converted to dihydrofulvalene (III) according to the procedure given by Doering and Matzner.¹⁷ This reaction was found to proceed with approximately 70–80% conversion (based on the ratio of the final ferrocene products). The first step of this reaction presumably involves the initial formation of 5-iodocyclopentadiene which was described as stable by Breslow.¹⁸ We considered that the inverse addition of CpNa to iodine might lead to a more complete conversion, but no major change in product distribution was achieved in this case.

Addition of *n*-butyllithium afforded the fulvalene dianion, contaminated chiefly by cyclopentadienide. Addition of the stable FeCl₂·2THF complex¹⁹ in THF produced BFD together with ferrocene and polyferrocenes. The yield of BFD was 20–40% based on starting CpNa.

Table I. Mössbauer Parameters

	<i>T</i> , K	QS, mm/s	IS, ^a mm/s
BFD	298	2.44	0.455
	77	2.46	0.535
BFD (2,3) picrate	298	1.75	0.436
	77	1.78	0.525
BFD (2,3) (TCNQ) ₂	298	1.759	0.440
	77	1.781	0.512
BFD (2,3) BF ₄	298	1.772	0.439
	77	1.803	0.516
BFD (2,3) I ₃ ^b	4.2	1.756	0.542
BFD (3,3) 2BF ₄ ^c	298	2.945	0.468
	77	3.025	0.534
Ferrocene ^d	77	2.40	0.475
Ferrocenium DDQ ^d	77	0	0.466
Biferrocene (2,3) picrate ^e			
Fe(II)	77	2.14	0.510
Fe(III)	77	0.288	0.518
Biferrocene (3,3) 2BF ₄	298	0.568	0.392
	77	0.581	0.489

^a Isomer shift relative to iron foil. ^b Reference 24. ^c Contaminated with (2,3) salt. ^d Reference 23. ^e Reference 7.

This synthetic scheme has proved to be general and was also used successfully by Davison and Smart²⁰ in the synthesis of bis(fulvalene)dnicobalt(III,III) bishexafluorophosphate, the isoelectronic cobalt analogue of BFD.

Monocationic salts of BFD were obtained by oxidation with benzoquinone in the presence of picric acid or boron trifluoride etherate to give the (2,3) picrate and fluoroborate salts, respectively. (For simplicity, the notation (2,2) is used for neutral BFD, IIa, with formal iron(II)–iron(II) oxidation states. Similarly, the notations (2,3) and (3,3) denote the monocation, IIb, and dication, IIc, respectively.) Recrystallization from chloroform, acetonitrile, or methanol gave dark green needles which decomposed without melting above 200 °C.

BFD was readily oxidized by TCNQ (TCNQ = tetracyanoquinodimethane) in methylene chloride or acetonitrile to give the 1:2 complex salt, BFD (2,3) (TCNQ)₂.

BFD was fully oxidized in acetonitrile to the (3,3) fluoroborate salt by excess benzoquinone in the presence of boron trifluoride etherate.²¹ The salt was isolated as thin leaflets by slow cooling to –30° or as microcrystalline powder by the addition of dry ether. Pure (3,3) salt appears to be stable in air at room temperature but darkens above 250 °C without melting. In the absence of an oxidizing agent, solutions of BFD (3,3) salts decompose rapidly, forming the (2,3) salt. Similar behavior was observed for biferrocene (3,3) 2BF₄.⁷

The Oxidation State of Iron in the [2,3] Salts: Trapped or Fractional Valency?

Mössbauer Spectra. It is well known that Mössbauer spectroscopy is often able to identify the oxidation states of iron in mixed valence compounds.²² The quadrupole splittings and isomer shifts are generally very different for Fe(II) and Fe(III).

For ferrocene derivatives, the quadrupole splitting parameter has been particularly useful in defining the 3d configuration of the iron atom. Ferrocene itself has a large quadrupole splitting (see Table I), while removal of an electron to form the ferrocenium ion leads to a vanishingly small quadrupole splitting.²³

Biferrocene picrate (Ib) was shown to have “trapped” valences by Mössbauer spectroscopy.^{7,24} Its four-line spectrum is a composite of ferrocene and ferrocenium transitions. The rate of electron transfer in the solid must therefore be slower

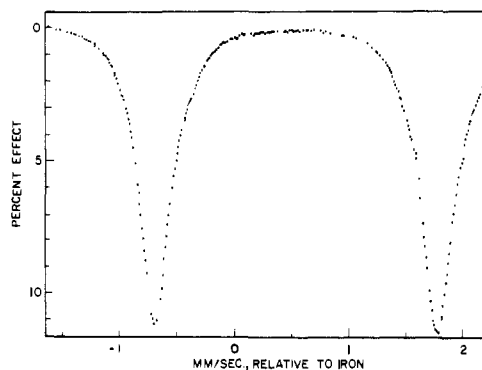


Figure 1. Mössbauer spectrum of bis(fulvalene)diiron (BFD) at 77 K.

than 10^8 s^{-1} , the reciprocal of the lifetime of the Mössbauer excited state. It should be noted, however, that in comparison to isolated ferrocene and ferrocenium systems, the QS for the ferrocene part is decreased in (2,3) by about 0.3 mm/s, while the ferrocenium half shows a QS increased by the same amount. For the (3,3) system, the QS again shows the same increase to 0.8 mm/s for the two equivalent iron sites.

Figures 1, 2, and 3 show the Mössbauer spectra of BFD and its mono- and dicationic salts at 77 K. Unoxidized BFD has Mössbauer parameters similar to those observed for ferrocene and biferrocene. In contrast to biferrocene (2,3) salts, however, BFD monocations have two-line spectra, indicating that, on the Mössbauer time scale, both iron atoms are equivalent.²⁵ Furthermore, this equivalence is not a function of temperature; spectra at 298, 77, and 4 K²⁴ all show the presence of only one type of iron.

This apparent equivalence could arise from either very rapid electron exchange or delocalization of the odd electron, resulting in fractional formal valence. The quadrupole splitting of 1.78 mm/s is intermediate between that of ferrocene and ferrocenium, which neither supports nor eliminates either of the two possibilities. For rapidly oscillating (2,3) compounds, the observed quadrupole splitting is not invariably the average of the quadrupole splittings for the (2,2) and (3,3) derivatives.²⁶

The Mössbauer lines, however, are not identical. There is an asymmetry in the intensity, the left peak being stronger for the (TCNQ)₂ and picrate salts, while the right peak is stronger for the BF₄ and triiodide²⁴ salts. Moreover, the asymmetry increases at higher temperature.

In the Mössbauer spectrum, one of the peaks arises from transitions to the $m = \pm 3/2$ states of excited ⁵⁷Fe, and the other from transitions to the $m = \pm 1/2$ states. An asymmetry in the intensity of these peaks could be caused by one of four factors: orientation of sample, magnetic relaxation, a Karyagin effect, or slightly different iron sites.²⁷

Selective orientation of the sample can effect the line intensities, as the intensity ratio is dependent on θ , the angle between the principle EFG axis and the direction of the γ ray. For powdered samples, however, random orientation is secured, and all values of θ are averaged.

A magnetic relaxation could broaden and weaken the $\pm 3/2$ transition line more than the $\pm 1/2$ transition. For this mode of relaxation, however, the peak asymmetry would be greater at lower temperature, and this is contrary to the observed behavior.

If the two iron sites are slightly different, the resultant spectrum would be the sum of two doublets. The areas would be the same and the deeper peak would have the narrower line width. Such is the case for the picrate and triiodide salts, but not for the fluoroborate and TCNQ derivatives. Since other spectroscopic properties of BFD monocations are the same

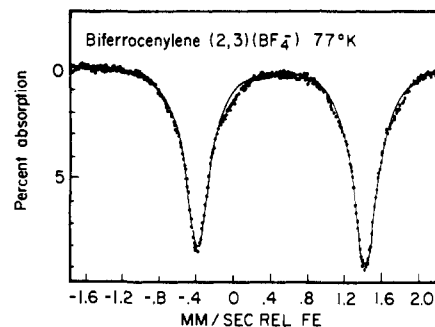


Figure 2. Mössbauer spectrum of BFD (2,3) BF₄ at 77 K.

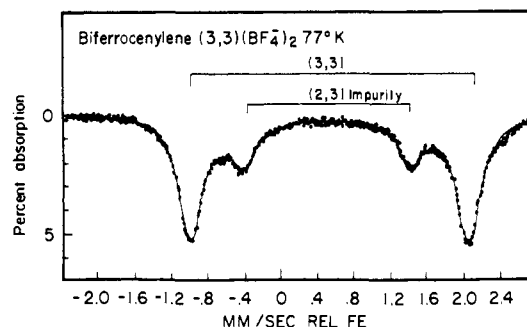


Figure 3. Mössbauer spectrum of BFD (3,3) 2BF₄ at 77 K.

regardless of the counterion, we are forced to conclude that the two iron atoms are chemically identical on a Mössbauer time scale and the asymmetry is due to a Karyagin effect.

Karyagin²⁸ shows that the recoilless fraction of Mössbauer events may be locally anisotropic. That is, a difference in the mean square amplitude of molecular vibrations of the iron nucleus may exist so that Mössbauer transitions to the $m = \pm 3/2$ and $m = \pm 1/2$ states occur with different probabilities. This vibrational anisotropy increases as the temperature increases and thus would account for the observed temperature dependence.

Class II mixed valence compounds, under the categories defined by Day,^{3b} show spectroscopic evidence for discrete oxidation states. Likewise, this criterion is imposed by Hush^{3a} for establishing a weak ground-state interaction. Class II compounds that have been studied by Mössbauer spectroscopy generally show composite spectra.^{22,29} In the case of certain class II trinuclear iron acetates,²⁶ rapid electron transfer results in a one-line spectrum at room temperature, but as the temperature is lowered the spectrum is resolved into separate quadrupole splittings. Implicit in the "class II" description is an activation energy for electron transfer; rapid electron transfer at very low temperature is incompatible with the description unless an alternative mechanism such as tunneling becomes operative.

A delocalized, or class III, description has generally been assigned to those mixed valence iron compounds which exhibit only one doublet at low temperature.^{22,30} For such compounds, isomer shifts with values intermediate between the ranges found for integral oxidation states are generally found.

For ferrocene and its derivatives, a large change in isomer shift upon oxidation is not observed; removal of an electron apparently does not change the s-electron density significantly. Similar results for cyclopentadienyl iron clusters have been interpreted to mean that electrons are being withdrawn primarily from the ligand system with negligible change in the iron electron environment.³¹ This interpretation is false in principle but correct in the final net result: ab initio calculations^{32a,32b} on ferrocene and ferrocenium ion show that upon oxidation the electron is removed from the metal and that this process is followed by considerable relaxation and redistribu-

Table II. ESCA Parameters

	E_b (eV) ^a	Line width (eV)
BFD	707.6	1.8
BFD (2,3) (TCNQ) ₂	707.9	2.2
BFD (2,3) BF ₄	707.7	2.4
BFD (3,3) 2BF ₄	708.5	2.4
Ferrocene ^b	707.6	1.7
Ferrocenium BF ₄ ^b	709.4	3.3
Biferrocene (2,3) picrate ^c		
Fe(II)	707.7	2.0
Fe(III)	711.1	4.0

^a Binding energy of Fe 2p_{3/2} relative to 285.2 eV for C-1s. ^b R. Gleiter, R. Seeger, H. Bindu, E. Fluck, and M. Cais, *Angew. Chem., Int. Ed. Engl.*, **11**, 1028 (1972) (values adjusted to 285.2 eV for C-1S). ^c Reference 8.

tion of electronic charge, so that the Fe atom in the ferrocenium ion is only slightly more positive^{32b} (1.46 vs. 1.39) than in the neutral ferrocene.

The Mössbauer spectrum of BFD (3,3) 2BF₄ shows equivalent iron sites and a surprisingly large quadrupole splitting of 3.0 mm/s. (Since all samples of (3,3) salts were contaminated with (2,3) species, the (2,3) spectrum was subtracted.) Similar results have been obtained by Morrison and Hendrickson for the corresponding DDQ salt.²⁴

In contrast, most ferrocenium ions, including biferrocene (3,3) 2BF₄ (Ic), give small or unresolved splittings. A value of 3.0 mm/s has been found for high-spin ferrous compounds,²⁷ where it is characteristic of a single uncompensated 3d electron on each iron.

ESCA Measurements. Significant information concerning the oxidation state of metal atoms in mixed valence compounds can be derived from x-ray photoelectron spectroscopy (ESCA). This technique is capable of monitoring electron density rapidly ($\sim 10^{-17}$ s) and is thus well suited to the study of charge distributions in compounds with rapidly oscillating valences.³³ For biferrocene (2,3) picrate,⁸ as well as other class II mixed valence compounds,^{34,35} the nonequivalence of the metal atoms is sometimes discernible from their x-ray photoelectron spectra.³⁶

Binding energies and line widths for the Fe 2p_{3/2} transitions of several ferrocene derivatives are listed in Table II. The relative positions of the bands refer to the C-1s lines, for which an energy of 285.2 eV has been taken.

Decomposition under the influence of x rays was observed for several of these compounds. The intensity of the peaks diminished with time, although the shapes and ESCA parameters did not change. Spectra were recorded immediately upon insertion to minimize this effect. Comparable results were obtained on three distinct spectrometers, increasing the likelihood that the results are intrinsic of the molecule and not its decomposition products.

BFD has an Fe 2p_{3/2} transition similar in shape and position to that of ferrocene and biferrocene. The spectra of its (2,3) derivatives, however, do not resemble those of biferrocene (2,3) picrate,⁸ or other substituted biferrocene cations.³⁷ No transition of shape and position similar to ferrocenium ion is observed. The Fe 2p_{3/2} transition is unsymmetrical with a shoulder at higher binding energy. The integrated area of this satellite, however, is only a small fraction of the total peak area. Several phenomena can lead to secondary structures in x-ray photoelectron spectra.³⁸

The peak position for BFD (2,3) salts is very close to that of neutral BFD, indicating a similar partial charge on iron in both species. BFD (3,3) 2BF₄ shows one transition from the Fe 2p_{3/2} level at a binding energy of 708.5 eV.

The line widths of BFD (2,3) and BFD (3,3) salts are relatively narrow as compared to other oxidized ferrocenes. Reduction in exchange splitting for paramagnetic species can be attributed to a large degree of delocalization of the valence electrons.³⁹

The combined Mössbauer and ESCA data attest to the equivalence of the iron atoms in the BFD (2,3) cation. Both techniques reveal properties of the solid salts which, more than likely, also pertain to the ions in solution. (ESR spectra of the solid monocation and of solutions are very similar.)⁴⁰ The equivalence of the metal atoms rules out "trapped" valences, but does not, in itself, prove fractional (2½, 2½) valency.⁴¹ Electronic distributions which, in effect, result in 2Fe(III) plus a delocalized ligand-based electron, or 2Fe(II) plus a delocalized ligand-based radical are also consistent with two equivalent iron atoms. These alternatives do not seem viable in view of the quadrupole splittings observed for the (2,2), (2,3), and (3,3) derivatives. In systems with extensive delocalization, the formal metal oxidation state becomes a quantity of little significance.

Magnetic Properties

The ESR and magnetic susceptibility studies of ferrocenium compounds were of great value in elucidating the ground state electronic configuration of this system. Magnetic susceptibility measurements of various substituted ferrocenium salts and carborene analogues give moments which differ significantly from the spin-only value.⁴² Furthermore, ESR spectra reveal a highly anisotropic *g* tensor.^{43,44} These studies provide the basis for the assignment of an orbitally degenerate ²E_{2g} [(a_{1g})²(e_{2g})³] ground state configuration for the d⁵ metallocenes.⁴⁵

The magnetic susceptibility was determined for BFD (2,3) picrate in the 2–300 K range.²⁵ The measured susceptibility, corrected for diamagnetism, follows a Curie law and can be expressed by $\chi = (0.372/T + 250 \times 10^{-6}) \text{ cm}^3 \text{ mol}^{-1}$. The spin-only value of the Curie constant is $\chi(T) = C = N\beta^2 g^2 S(S+1)/3k = 0.375 \text{ (cm}^3 \text{ K)/mol}$ for $S = 1/2$ and $g = 2$.

The effective magnetic moment, calculated by $\mu_{\text{eff}} = 2.828C^{1/2}$ is 1.72 μ_B for BFD (2,3) picrate, which is in close agreement with the spin-only value of 1.73 μ_B .⁴⁶ Other ferrocenium and dicarbollide complexes, including biferrocene (2,3) picrate, have room temperature moments ranging from 2.3 to 2.6 μ_B .⁴²

The ESR spectrum of solid BFD (2,3) I₃ has been reported.⁴⁰ In order to ascertain the effect, if any, of different counterions on the spectrum of the BFD ion, we recorded the spectra of the picrate and fluoroborate salts as solids and CH₂Cl₂-EtOH glasses at 77 and 160 K. The picrate and fluoroborate salts have the same *g* values in the solid and in glasses. The most precise values ($g_1 = 1.87$, $g_2 = 2.00$, $g_3 = 2.27$) were obtained from the glass spectra, which showed very narrow lines (see Figure 4). (These values differ somewhat from those reported for the triiodide.)⁴⁰ The resolution was dependent on trace amounts of oxygen, but reproducible line widths were obtained by careful degassing. We were unable to resolve any additional hyperfine structure (due to coupling with Fe⁵⁷ or ring protons) under a variety of microwave energies and modulation amplitudes. The narrow lines and small rhombic anisotropy are in marked contrast to the axial symmetry and broad lines found in ferrocenium⁴³ and ferrocenium⁹ cations. The effective magnetic moment calculated from the ESR results by $\mu = [(1/3)(g_1^2 + g_2^2 + g_3^2)S(S+1)]^{1/2} = 1.78 \mu_B$ is in agreement with the directly measured value (1.72 μ_B).

Neither of the criteria used to assign the ²E_{2g} ground state to ferrocenium pertains to the BFD (2,3) ion. Several discussions in the literature have considered the possibility of a

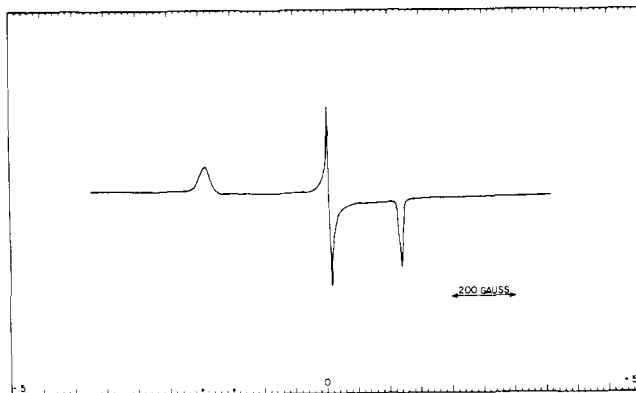


Figure 4. ESR spectrum of BFD (2,3) picrate in $\text{CH}_2\text{Cl}_2/\text{EtOH}$ at 160 K. Zero is 3210 G; microwave frequency is 9.062 GHz.

spin-only moment for the ferrocenium ion. For a ${}^2E_{2g}$ ground state experiencing a large Jahn–Teller distortion, German and Dyatkina⁴⁷ have shown that the effective magnetic moment would approach the spin-only value and would be temperature independent. Alternatively, a ${}^2A_{1g} [(a_{1g})^1(e_{2g})^4]$ ground state as found for d^5 bisarene complexes and recently suggested for dicyclopentadienylmanganese from photoelectron spectra⁴⁸ is compatible with the magnetic data. In the absence of a low-symmetry crystal field perturbation, the g value for the ${}^2A_{1g}$ configuration is expected to be very nearly isotropic and equal to 2.

If, as seems likely, the BFD (2,3) cation is a class III compound, its magnetic properties cannot be discussed in terms of theories developed for substituted ferrocenium ions. In that case, the magnetic properties are a consequence of the delocalization of the valence electrons.

The magnetic susceptibility of BFD (3,3) 2BF_4 was measured in the 2–300 K range, and was found to be small but measurable. Varying amounts of paramagnetic impurities were present in the samples measured (up to 30% by weight). These were shown to be the (2,3) species by Mössbauer spectroscopy. Subtraction of the susceptibility due to the impurity from the measured value gives a net diamagnetism. The observed diamagnetism could be explained by either a distinct iron bond formed by direct iron orbital overlap or a superexchange phenomenon involving the π -system of the fulvalene ligands.

Further evidence for the diamagnetism comes from the NMR spectrum of the dicationic salt. In spite of the instability of aqueous solutions of (3,3), the spectrum was obtained in D_2O by virtue of the fact that the (2,3) salt is essentially insoluble in water. The spectrum consists of two sharp peaks at τ 3.64 and 5.92 with a width at half height of 6 Hz and a 1:1 proton ratio. Efforts to detect the expected resolution of the two peaks into triplets were not successful. The ring protons are deshielded with respect to protons in neutral BFD (NMR in benzene- d_6 : triplets ($J = 2$ Hz) at τ 4.78 and 6.27),¹¹ but shielded with respect to the protons of bis(fulvalene)dibis(hexafluorophosphate) (NMR in CH_3CN : triplets ($J = 1$ Hz) at τ 2.52 and 4.52), the isoelectronic cobalt analogue of biferrocenylene.²⁰

Electronic Spectroscopy

The visible and near-infrared spectra of the BFD (2,3) and biferrocene (2,3) ions are shown in Figure 5. An absorption in the near-infrared, centered at 1550 nm (0.80 eV; ϵ 2100, acetonitrile) is observed in the spectra of the BFD (2,3) fluoroborate, picrate, and TCNQ salts. This absorption is absent from the spectra of both the (2,2) and (3,3) species. In this respect, it is similar to the intervalence transfer band observed at 1800–1900 nm for the biferrocene monocation.² Closer in-

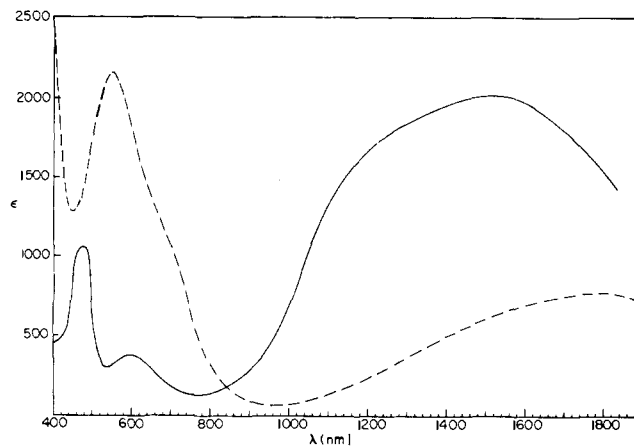


Figure 5. Visible and near-infrared spectra of BFD (2,3) BF_4 in acetonitrile (—) and biferrocene (2,3) in acetonitrile containing 0.1 M Et_4NClO_4 (---).

spection of the 1550-nm band for BFD (2,3) in the frequency linear representation reveals the presence of a second transition at 1140 nm (1.09 eV) and of lower intensity.¹⁴ This feature is not observed in the biferrocene (2,3) spectrum.

In addition, there is a band in the visible at 600 nm in the spectra of the BFD (2,3) fluoroborate and picrate salts that is not observed in neutral BFD. (This portion of the spectrum is obscured by anion absorptions in the BFD (2,3) (TCNQ)₂ salt.) Absorptions in the 600-nm region are typical of ferrocenium ions⁴⁹ and biferrocene mono- and dicationic salts.⁵⁰ The intensity of the band in BFD (2,3) (ϵ 370), however, is much lower than that observed for other biferrocene monocations. Fully oxidized BFD (3,3) does not absorb in this region. Its lowest energy transition occurs at 465 nm (ϵ 2755).

Summary

The electronic spectrum of BFD (2,3) is qualitatively similar to that of biferrocene (2,3). It is tempting, therefore, to analyze the spectral results for BFD (2,3) in terms that were used successfully for the biferrocene monocation. The observation of a 600-nm band in BFD (2,3) would seem to satisfy the “weak interaction” requirement for the Hush model.^{3a} The model is one which correlates rates of electron transfer with intervalence transfer band energies. From an analysis of the near-infrared band maxima, the model predicts a faster rate of electron exchange in the biferrocene cation than in BFD (2,3). From the intensity of the 1550-nm band, the model predicts only 3% delocalization in the ground state of the BFD (2,3) ion. Neither prediction is in accordance with the Mössbauer and ESCA results.

In light of the Mössbauer, ESCA, and magnetic results, we assign a class III description to BFD (2,3). Its electronic properties must, therefore, be interpreted differently from those of the class II biferrocene (2,3) ion. The excitation energies in class II are dependent on reorganization energy; in class III, the electronic transitions are those of the total binuclear complex. If the visible and near-ir absorptions in BFD (2,3) are due to transitions to a half-filled molecular orbital delocalized over both metal centers, then we might expect to see similar transitions, shifted somewhat in frequency, in the spectrum of BFD (3,3). The disappearance of these bands in the doubly oxidized species is puzzling.⁵¹

The small structural change in going from biferrocene to BFD has produced a radical change in the physical properties of the ions. The question remains as to whether the delocalized nature of the BFD ion results from greater direct metal–metal interaction due to the proximity of the iron atoms in the cis conformation, or from interactions through the π -system of

the fused fulvalene ligands. Several lines of evidence point to the latter.

Based on an analogy to cobalt d^7 systems, an iron-iron distance of 3.98 Å, as found in neutral BFD,⁵² seems to preclude the possibility of direct overlap of metal d orbitals. In the cobalt system, direct overlap has been invoked to account for the diamagnetism of bis(pentalene)dnicobalt where the Co-Co distance is about 2.5 Å.⁵³ The bis(*as*-indacenyl)dnicobalt compound, however, is paramagnetic, presumably because the metal-metal distance, estimated to be about 4 Å, is too large for bond formation. Unless considerable structural reorganization occurs in BFD (2,3) as compared to BFD (2,2), the possibility of a distinct metal-metal bond is remote.

Furthermore, there is evidence to show that the proximity of the metal atoms is not a necessary or sufficient condition for strong metal-metal interactions. From a model of [1.1]ferrocenophane, the iron-iron distance may be as close as 3.9 Å, but no intervalence transfer transition is observed for the monooxidized salt in the near-infrared.^{14,32} On the other hand, acetylene bridged biferrocenes, with iron-iron distances estimated to be greater than 6.5 Å, exhibit intense near-infrared bands.^{54,55} One can visualize the electron transfer process as a simultaneous Fe(II) → ligand, ligand* → Fe(III) process. This is a superexchange phenomenon analogous to transmittance of magnetic interactions between ions through intervening ligands.⁵⁶ The essential condition in class II and class III mixed valence biferrocenes appears to be intact π -bridging ligands between the metal atoms.

In their review of mixed valence chemistry,^{3b} Robin and Day remind us that an important feature of resonance among degenerate structures is that no one structure adequately describes the ground state. For example, the pentamethinium ion, $(\text{CH}_3)_2\text{N}(\text{CH}=\text{CH})_2\text{CH}=\text{N}^+(\text{CH}_3)_2$, must be described by two degenerate structures, since the nitrogens can assume two valences. This, of course, is the typical description of a delocalized organic compound. Robin and Day go on to say that, "There is ample reason to believe that exactly similar results would follow if a molecule could be synthesized in which the nitrogens were replaced by, say Fe(II) and Fe(III)." The evidence presented in this paper suggests that the BFD (2,3) cation is such a fully delocalized, resonance stabilized ion.

Experimental Section

Instrumentation and Procedures. Mössbauer spectroscopy was performed on an apparatus that has been previously described.⁵⁷ The quadrupole splitting parameter (QS) and isomer shift (IS) values in units of millimeters per second have an estimated error of not more than 0.03 mm/s.

The magnetic susceptibility of the samples was determined in the 2–298 K range by a modified Faraday method.⁵⁸ The measurements were run with the samples cooled by a heat exchange gas (He or N_2). The temperatures above 77 K were measured with a calibrated copper-constantan thermocouple. In the 2–4 K range, the temperature was determined from the vapor pressure of the liquid helium used as the coolant. Corrections were always made for the sample container and for the diamagnetism of the material. The diamagnetic corrections were obtained by direct measurement and are as shown below

Species	Diamagnetism ($\times 10^6$), cgsu
BFD	-190
Picric acid	-85
BF_4^-	-40

X-Ray photoelectron spectra were performed on a DuPont 650 electron spectrometer and a Hewlett-Packard 5950A ESCA spectrometer.

Electronic spectra were obtained on a Cary 14 recording spectrophotometer.

ESR spectra were recorded on a Varian E-12 spectrometer with 100-kHz modulation. The field was standardized by use of DPPH at two different microwave frequencies. Samples were dissolved in 1:1 (v/v) CH_2Cl_2 -EtOH, and transferred to thin-walled Pyrex tubes. The

solutions were degassed on a vacuum line by ten freeze-thaw cycles and sealed off.

The NMR spectrum of BFD (3,3) 2BF_4 was recorded with sodium 2,2-dimethyl-2-silapentanesulfonate as internal standard. D_2O containing the standard was added to a sample of the BFD (3,3) salt, the solution was filtered immediately into an NMR tube, and the spectrum was recorded within 1 min after dissolving the sample.

Melting points were taken in evacuated tubes and are uncorrected.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of $\text{FeCl}_2 \cdot 2\text{THF}$.⁵⁹ In a 1000-ml round-bottom flask with magnetic stirrer, reflux condenser, and nitrogen bubbler, 50 g of anhydrous ferrous chloride⁶⁰ was suspended in 500 ml of dry THF. The slurry was refluxed for 2 h with stirring in an atmosphere of dry nitrogen. After cooling the mixture in an ice/methanol bath, the brown THF solution was decanted and the residual slurry poured through a funnel into the paper thimble of a nitrogen flushed hot vapor extraction apparatus.⁶¹ After extraction with 500 ml of dry THF and cooling with ice/methanol, $\text{FeCl}_2 \cdot 2\text{THF}$ separated as white crystals from the light-brown solution. The product was filtered under nitrogen, washed once with cold absolute THF, then several times with dry ether, and finally with pentane, and dried in a stream of nitrogen (removal of all ethereal solvent is essential for air stability, since ether moist samples will immediately turn brown upon exposure to air). In some cases where the product was not completely white, it was extracted a second time with fresh dry THF.

BFD via Fulvalene Dianion.^{17b} A 1000-ml four-necked flask with mechanical stirrer, a reflux condenser (topped by a nitrogen bubbler), addition funnel, and a low temperature thermometer was carefully flushed with pure, dry nitrogen. A sodium cyclopentadienide solution in THF (0.2 mol, 103 ml of 1.9 M solution) was added and cooled to -70°C by an acetone/dry ice bath. To this solution 0.1 mol of iodine (25.4 g), dissolved in 150 ml of absolute THF, was slowly added during 1 h. The temperature inside the reaction flask was kept below -60°C . After the addition was complete, the reaction mixture was stirred at -60°C for 1 h after which time 0.2 mol of *n*-butyllithium in hexane (125 ml of a 1.6 M solution) was gradually added. The reaction mixture was allowed to warm to -30°C . Then 30 g (0.11 mol) of $\text{FeCl}_2 \cdot 2\text{THF}$, partially dissolved in 300 ml of THF, was added. The dark brown reaction mixture was stirred for 4 h, hydrolyzed with 10 ml of water and evaporated under reduced pressure. Benzene (1000 ml) was added to the dark brown residue and the mixture was heated to reflux for 10 min and filtered hot.⁶² The residue, which contained BFD together with oligomeric and polymeric material, was washed twice with 100 ml of warm benzene, placed in an extractor, and extracted for 2 days with refluxing benzene. BFD crystallized from the solution of this first extraction and was purified by repeating the extraction. The yield of pure bis(fulvalene)diiron was 3.7–7.4 g (20–40%): NMR (in benzene- d_6 at 60°C) τ 4.78 (t, 8 H) and 6.27 (t, 8 H); uv (CHCl_3) λ_{max} (ϵ), 315 (1820), 465 (450). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{Fe}_2$: C, 65.27; H, 4.38. Found: C, 65.21; H, 4.34.

BFD via Ullmann Coupling. 1,1'-Dibromoferrocene, prepared by the literature procedure,¹⁶ was purified by fractional sublimation at 60° (0.1 mm) and recrystallization from methanol: mp 54 – 55° (lit.¹⁶ mp 55 – 56°). A mixture of 3.7 g (0.01 mol) of 1,1'-dibromoferrocene, 12.0 g of activated⁶³ copper bronze, and 500 g of biphenyl was heated under nitrogen at 180 – 190° for 19 h. The mixture was filtered hot and diluted to a volume of 2 l. with hexane to precipitate the BFD. The dark residue was extracted well with boiling benzene and the benzene was evaporated. The red crystalline residue was recrystallized several times from benzene to produce 0.35 g (18%) of BFD: mp 340° dec (lit.^{11,12} mp $>300^\circ$ dec).

BFD (2,3) (TCNQ)₂ (Method A). A suspension of BFD (38 mg, 0.1 mmol) in 50 ml of acetonitrile was heated to reflux under nitrogen. A solution of TCNQ (48 mg, 0.2 mmol) in 25 ml of acetonitrile was added. The mixture was stirred at reflux for 6 h. Upon cooling, a dark precipitate was collected and recrystallized from acetonitrile to give 56 mg (70%) of BFD (2,3) (TCNQ)₂. Anal. Calcd for $\text{C}_{44}\text{H}_{24}\text{N}_8\text{Fe}_2$: C, 68.07; H, 3.11; N, 14.42. Found: C, 67.98; H, 3.22; N, 14.21.

BFD (2,3) (TCNQ)₂ (Method B). Bis(fulvalene)diiron (370 mg, 1 mmol) was extracted from a paper thimble by 300 ml of boiling dry methylene chloride containing 420 mg (2 mmol) of tetracyanoquinodimethane, while the entire extraction system was kept in an atmosphere of nitrogen. After 2 days the extraction was complete and the precipitate of fine felt-like clusters of needles was filtered and recrystallized from absolute acetonitrile (about 2000 ml) to yield 550

mg (71%) of fine dark green needles. Anal. Calcd for $C_{44}H_{24}N_8Fe_2$: C, 68.07; H, 3.11. Found: C, 68.34; H, 3.30. Uv (acetonitrile) λ_{max} (ϵ) 234 (21 200), 270 (12 300), 394 (88 900), 743 (16 800), 762 (14 400), 822 (22 260), 842 (32 700), 1550 (1900).

BFD (2,3) Picrate. Bis(fulvalene)diiron (300 mg, 0.8 mmol) suspended in 100 ml of dry benzene was stirred for 5 days in a nitrogen atmosphere with 0.6 g (2.00 mmol) of picric acid and 73 mg (0.675 mmol) of benzoquinone. The green slurry was filtered and recrystallized from methanol to give 300 mg (63%) of green needles which decomposed at about 230 °C. Anal. Calcd for $C_{26}H_{18}N_3O_7Fe_2$: C, 52.38; H, 3.04; N, 7.05. Found: C, 52.38; H, 3.35; N, 6.85. Uv (acetonitrile) λ_{max} (ϵ) 375 (32 510), 595 (366), 1550 (1950).

BFD (2,3) BF₄. Bis(fulvalene)diiron (740 mg, 2 mmol), benzoquinone (108 g, 1.0 mmol), and boron trifluoride etherate (3.25 g, 5 ml, 23 mmol) in 100 ml of dry acetonitrile were stirred in a nitrogen atmosphere for 10 h. After addition of 300 ml of dry ether, the dark green precipitate was filtered off and recrystallized from methanol to yield 520 mg (57%) of tetrafluoroborate as dark green needles. Anal. Calcd for $C_{20}H_{16}Fe_2BF_4$: C, 52.81; H, 3.55. Found: C, 52.72; H, 3.75. Uv (acetonitrile) λ_{max} (ϵ) 240 (16 500), 270 (11 800), 330 (5600), 468 (1100), 600 (372), 1550 (2120).

BFD (3,3) 2BF₄. A suspension of BFD (40 mg, 0.11 mmol) in 4 ml of dry acetonitrile was stirred under nitrogen in a small Schlenk tube. Boron trifluoride etherate (0.1 ml) and benzoquinone (30 mg, 0.28 mmol) were added. The solution was allowed to stir 1 h, at which time anhydrous ether was added (10 ml) to completely precipitate an orange-brown solid. The solid was filtered under nitrogen, washed with dry ether, and dried under vacuum to give 47 mg (93%) of BFD (3,3) 2BF₄. Anal. Calcd for $C_{20}H_{16}B_2F_8Fe_2$: C, 44.35; H, 2.98. Found: C, 44.32; H, 2.95.

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