$(O_2,OH))Co(trien)]^{3+}$, 36431-46-6; $[Co(tep)(\mu\text{-}O_2)Co(tep)]^{4+}$, 36883-61-1; $[Co(en)_2(\mu\text{-}O_2)Co(en)_2]^{5+}$, 60325-91-9; $[Co(trien)(\mu\text{-}O_2)Co(trien)]^{5+}$, 60325-90-8; $[Co(tep)(\mu\text{-}O_2)Co(tep)]^{5+}$, 59200-72-5; Fe^{2+}, 15438-31-0.

References and Notes

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(2) This research was supported by a research grant, No. A-259, from the Robert A. Welch Foundation.
(3) Texas A&M University Health Fellow.
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Theoretical Study of the Electromagnetic Properties of Bis(fulvalene)diiron in Its Three Oxidation States

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An iterative extended Hückel molecular orbital calculation is used to obtain wave functions for the ground state of biferrocenylene [bis(fulvalene)diiron] and several low-lying states of the mono- and dioxidized cations. The molecular orbitals are compared to those calculated for biferrocene and to those obtained from a previous study of ferrocene and the ferrocenium ion. The calculated electron distributions are used to determine the electric field gradient at each iron nucleus for bis(fulvalene)diiron and biferrocene. A large quadrupole splitting, comparable to that calculated for ferrocene, is obtained for both compounds in agreement with experiment. The ground state of monooxidized bis(fulvalene)diiron is obtained by removal of an electron from an e_{2g} type orbital delocalized over the two ferrocene moieties due to d-orbital relaxation effects similar to those observed for the ferrocenium ion. For the monovalent cation, the electric field gradient at the iron nuclei and g values are calculated. The values are in agreement with experiment. A possible assignment of the electronic spectral transitions unique to the mixed-valence state is made. Such d-orbital relaxation effects are not observed for the dioxidized species. The ground state of the divalent cation is obtained by removal of two electrons from the highest occupied molecular orbital of the neutral species, a delocalized carbon π orbital with substantial metal–metal antibonding character. The calculated diamagnetic ground state is the basis for a consistent explanation of the unexpectedly large quadrupole splitting and other observed spectroscopic properties. Removal of electrons from a_{1g} or degenerate e_{2g} type d orbitals yields excited configurations which do not account for the observed behavior of dioxidized bis(fulvalene)diiron.

Introduction

Organometallic mixed-valence compounds form systems in which two or more atoms of the same metal exist in different formal oxidation states within one molecule. Recently there has been a growing interest in such compounds because, in contrast to the polymeric inorganic mixed-valence systems, they offer the possibility of studying on an intramolecular basis the unusual phenomena associated with the coexistence of differing valence sites in a given system. Inorganic and organometallic systems alike show a large variation in the degree of interaction between the differing sites. The range spans from firmly trapped valences, in which the properties of the compound are merely those of the component parts with little or no interaction, to complete delocalization and nonintegral valences.[1] For these latter compounds, the magnetic and spectroscopic properties do not resemble those of the constituent parts of the molecule.[2] Various theories have been advanced in an attempt to explain the observed behavior of these compounds.[1,3]

The two structurally related systems, biferrocenylene [bis(fulvalene)diiron, BFD] (Ia) and biferrocene (IIa), appear to be at opposite ends of the scale. The properties of the mixed-valence compound biferrocene(2,3) picrate (IIb) can be attributed to the constituent ferrocene and ferrocenium moieties[4-8] and those of the fully oxidized biferrocene(3,3) salt (IIc) to two ferrocenium units.[4] Although the structure of neutral BFD was determined several years ago,[9] only recently a new and more efficient synthesis[10] allowed preparation of the mono- (Ib) and dioxidized (Ic) salts and thus made possible an experimental investigation of the properties of this compound in all of its oxidation states.[10] BFD(2,3) and BFD(3,3) were found to exhibit properties distinctly different from those of ferrocene or the ferrocenium ion.[4,10]

The Mössbauer spectrum of unoxidized BFD(2,2) resembles that of ferrocene and biferrocene(2,2).[10] The spectrum of biferrocene(2,3) salts is a composite of separate ferrocene and ferrocenium transitions[11] with some recent evidence[4] for an additional low-energy equivalent iron atom component as well. On the other hand, Mössbauer results for the BFD monovalent cations indicate totally equivalent iron atoms with a spectrum resembling that of neither ferrocene nor the ferrocenium ion.[10] Mössbauer studies alone cannot determine if the apparent equivalence is due to rapid oscillation of a "trapped" valence electron between inequivalent iron(II) and iron(III) sites which exchange at a rate greater than 10^8 s^{-1} (the reciprocal of the lifetime of the Mössbauer excited state) or actual delocalization of the odd electron over two iron sites made equivalent by either a metal–metal or a metal–ligand–metal interaction, resulting in a fractional valence state. The equivalence of the iron atoms in BFD(2,3) is confirmed however by x-ray photoelectron spectroscopy (ESCA).[10]

Both the Mössbauer and ESCA studies on BFD(2,3) refute prior speculation that the compound exhibited trapped valency. This suggestion was supported by an initial electronic spectroscopy study where an absorption in the near-infrared

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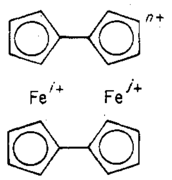
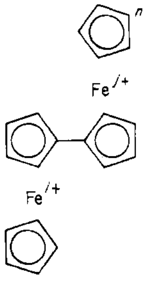


Ia, $n = 0, i = j = 2$, BFD(2,2)
b, $n = 1, i = 2, j = 3$, BFD(2,3)
c, $n = 2, i = j = 3$, BFD(3,3)



IIa, $n = 0, i = j = 2$, biferrocene(2,2)
b, $n = 1, i = 2, j = 3$, biferrocene(2,3)
c, $n = 2, i = j = 3$, biferrocene(3,3)

region, centered at 1550 nm (0.80 eV) with a shoulder at 1140 nm (1.09 eV), was assigned[12] to the intervalence transfer Fe(II)–Fe(III) → Fe(III)–Fe(II) similar to the band with a maximum at 1800–1900 nm observed for the biferrocene monovalent cation.[13] This absorption is absent from the spectra of both BFD(2,2) and BFD(3,3).[10] Another band in the visible region at 600 nm (2.07 eV), found only in the spectra of the salts of the ferrocenium ion[14] and the biferrocene mono- and divalent cations,[15] was attributed to a trapped-valence iron(III) site. Since the iron atoms of BFD(2,3) are now believed to be equivalent, the assignment of these bands is in doubt.

The ground-state configuration of BFD(2,3) has not been established. For the ferrocenium ion, electron spin resonance (ESR)[16] and magnetic susceptibility studies[17] provided the basis for a consistent assignment of an orbitally degenerate $^2E_{2g}$ $[(a_{1g})^2(e_{2g})^3]$ ground state. However, for BFD(2,3) no one configuration seems to obviously explain both the magnetic moment and the electron spin resonance behaviors. The observed temperature-independent, spin-only value of the magnetic moment[18] seems best accounted for by removal of an electron from an a_{1g} type orbital while the anisotropic g values (2.27, 2.00, 1.87)[10] can best be accounted for by removal of an electron from an orbitally degenerate e_{2g} type orbital.

The Mössbauer spectra of both the ferrocenium ion and biferrocene(3,3) salts give very small or unresolved quadrupole splittings while those of BFD(3,3) salts show an unexpectedly large splitting (3.0 mm/s).[10] Magnetic susceptibility measurements show that the BFD(3,3) salt is diamagnetic.[10] In its electronic spectra, an absorption at 600 nm typical of many ferrocenium systems is surprisingly absent.[10] To date, explanations of the observed behavior of the salts of the divalent cation have been based on the assumption that each unit of BFD(3,3) retains its formal ferrocenium features, i.e., a $[(a_{1g})^2(e_{2g})^3]$ low-spin ferric configuration. The large field gradient has then been attributed[19] to increased delocalization of the e_{2g} orbitals in BFD(3,3) and the diamagnetism to an iron–iron bonding interaction formed by direct iron orbital overlap[4] or a superexchange (antiferromagnetic) phenomenon[10] involving the π system of the fulvalene ligands. However, these assumptions have not as yet been further verified.

Thus there are many physical properties of bis(fulvalene)diiron and the salts of its mono- and divalent cations that are not completely understood from what is now known of the electronic structure of these compounds. Our recent molecular orbital calculations of the electronic structure and properties of ferrocene and the ferrocenium ion,[20] together with similar calculations for each oxidation state of BFD reported here, have allowed us to investigate the nature of the interactions of the two units upon formation of the binuclear compound and to explain the observed properties of BFD in each oxidation state. The result is a description of each state which appears to account for its observable properties in a consistent way and which contradicts existing descriptions in several important ways.

Method and Procedure

IEHT (iterative extended Hückel theory), a semiempirical all-valence electron molecular orbital method previously parameterized for iron-containing compounds,[21,22] was used in all of the calculations reported here. For BFD(2,2), a single electron configuration with pairwise occupancy of energy-ordered molecular orbitals was considered. For BFD(2,3) and BFD(3,3), several electron configurations formed by removal of a single electron or pair of electrons, respectively, from each of the highest energy filled d orbitals of a given symmetry of the neutral compound were considered. For comparison with BFD, the ground-state wave function of biferrocene(2,2) was also calculated. A more detailed study of the biferrocene system in various oxidation states is warranted. The results for the unoxidized compound are included here only to emphasize differences with BFD.

The resulting atomic orbital coefficients for each iron atom were used to calculate the electric field gradient at the iron nucleus by a procedure used previously for iron-containing complexes and explained in detail elsewhere.[23] Additionally, g values were calculated for the ground-state configuration of BFD(2,3) by the same procedure as used for the ferrocenium ion.[20] The formulation is taken from a procedure explained in detail for high-spin iron(III) ions[24] but modified to treat systems with one unpaired electron. Spin–orbit coupling between ground and specified excited states was calculated from molecular orbitals and excitation energies. By use of the spin-mixed functions obtained from the spin–orbit coupling, the Zeeman energy and principal components of the g values were calculated.

Geometry was obtained from an x-ray diffraction study of bis(fulvalene)diiron.[9] The carbon rings were assumed to be parallel regular pentagons with interatomic distances Fe–C = 2.056 Å, C–C = 1.427 Å, and C–H = 1.080 Å. The inter-ring C–C bond length was 1.476 Å. The iron atoms were separated by 3.984 Å. Consistent with previous data on iron group metallocenes,[25] no structural changes were assumed upon oxidation. An x-ray diffraction study of biferrocene[26] indicated that the two ferrocene moieties are in a trans conformation. A calculation was also performed for a perpendicular conformation with a dihedral angle of 90° between the two ferrocene axes. An undistorted cis configuration was found to be sterically impossible.

Results

The total ground-state configuration in the D_{2h} point group of BFD(2,2) has recently been calculated[27] by a contracted Gaussian basis set ab initio calculation to be $(a_g)^{18}(b_{1g})^{10}(b_{2g})^{12}(b_{3g})^7(a_u)^7(b_{1u})^{13}(b_{2u})^{10}(b_{3u})^{17}$. Both the ab initio calculation and IEHT give a valence-electron contribution of $(a_g)^{10}(b_{1g})^6(b_{2g})^7(b_{3g})^5(a_u)^5(b_{1u})^8(b_{2u})^6(b_{3u})^9$. Since the core electron contribution is neglected by IEHT, the energy ordering of the orbitals in the D_{2h} group is labeled with respect to only the valence-electron configuration. The energy and symmetry of the highest filled and lowest empty molecular orbitals together with the predominant atomic orbital contributions to these orbitals as calculated by IEHT are given

Table I. Eigenvalues and Eigenvectors Calculated for BFD(2,2)[a]

Symmetry	Energy	Occ	Atomic orbital coefficients[b]
$8b_{2g}$	−8.21	0	$0.49(d_{xz} + d'_{xz})^c$
$6a_u$	−8.68	0	$0.54(d_{yz} - d'_{yz})$
$6b_{3g}$	−8.82	0	$0.54(d_{yz} + d'_{yz})$
$9b_{1u}$	−9.32	0	$0.57(d_{xz} - d'_{xz})$
$9b_{3u}{}^e$	−11.25	2	$0.26C_1(p_z - p'_z)^d$ $+ 0.20C_3(p_z - p'_z)^d$ $+ 0.21(d_{x^2-y^2} - d'_{x^2-y^2})$
$10a_g$	−11.55	2	$0.70(d_{z^2} + d'_{z^2})$
$8b_{3u}$	−11.57	2	$0.69(d_{z^2} - d'_{z^2})$
$6b_{1g}$	−11.78	2	$0.61(d_{xy} + d'_{xy})$
$9a_g$	−11.87	2	$0.64(d_{x^2-y^2} + d'_{x^2-y^2})$
$7b_{3u}$	−11.88	2	$0.64(d_{x^2-y^2} - d'_{x^2-y^2})$
$6b_{2u}$	−11.97	2	$0.66(d_{xy} - d'_{xy})$
$5b_{1g}$	−12.04	2	$0.25C_2(p_z - p'_z)^d$
$5b_{2u}$	−12.16	2	$0.25C_2(p_z + p'_z)^d$

[a] For comparison with ferrocene, see ref 20. [b] Coordinate axes defined with the Fe–Fe vector along the *x* axis and the *z* axis perpendicular to fulvalene planes. [c] d orbitals used only for iron. Primed orbital indicates second iron center. [d] C_1 is one of four equivalent carbon atoms which bind the cyclopentadienyl rings; C_2 or C_3 is one of eight equivalent carbon atoms once or twice removed from C_1, respectively. [e] The highest occupied molecular orbital is predominantly ligand based.

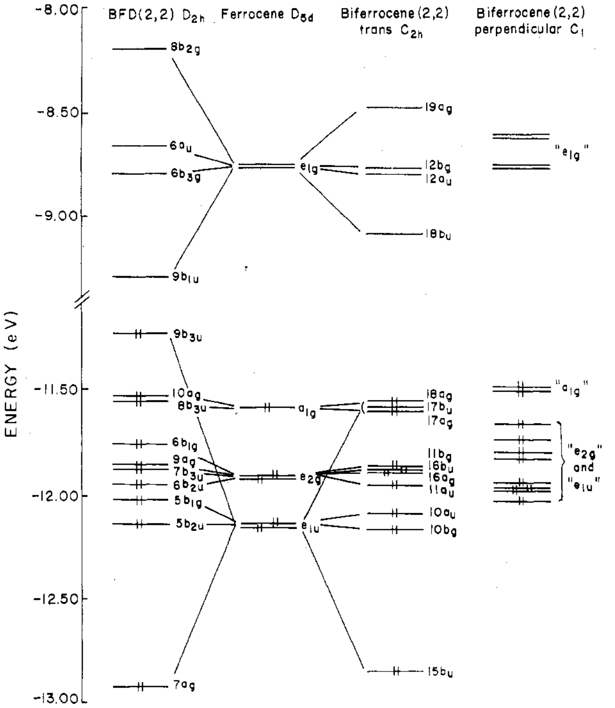


Figure 1. Energy levels calculated for ferrocene, BFD(2,2), and biferrocene(2,2).

in Table I. Figure 1 shows the orbital energy levels compared to those previously calculated for ferrocene. Orbitals with d-electron character (e_{2g}, a_{1g}, or e_{1g} symmetry) in ferrocene combine to form a set of five molecular orbitals ($d_i + d'_i$) with g and another five ($d_i - d'_i$) with u character in BFD. The degeneracy of the e^*_{1g} (d_{xz}, d_{yz}) unfilled orbitals and e_{2g} ($d_{x^2-y^2}$, d_{xy}) antibonding orbitals in ferrocene is lifted in the eight corresponding orbitals of BFD. On the other hand, the $10a_g$ and $8b_{3u}$ orbitals of BFD remain nearly degenerate and very little perturbed in energy from the a_{1g} (d_{z^2}) orbital of ferrocene. Each of these predominantly d molecular orbitals is delocalized over two equivalent iron atoms and the net charge and the total electron density in each d orbital, as indicated in Table II, are nearly identical for the ferrocene and the two equivalent BFD(2,2) iron atoms.

From Figure 1, it is evident that the major perturbation in the molecular orbitals of BFD(2,2) as compared to those of two separated ferrocene molecules is manifested in the behavior of the e_{1u} (carbon π) orbitals. These pure ligand π orbitals in ferrocene mix with appropriate symmetry combinations of d orbitals on the two iron centers upon formation of the binuclear compound. The degeneracy of these orbitals in ferrocene is split by 1.68 eV in BFD(2,2) such that the antibonding partner ($9b_{3u}$) becomes the highest occupied orbital (HOMO). This orbital has some iron–iron σ-antibonding character while the lowest energy partner ($7a_g$) has similar bonding character. The two less perturbed e_{1u} type orbitals have small amounts of iron–iron π-antibonding ($5b_{1g}$) and π-bonding ($5b_{2u}$) character. However, the main perturbation of the e_{1u} type orbitals seems to be due to direct covalent bond formation between the cyclopentadienyl rings. The highest and lowest e_{1u} type ligand orbitals have significant inter-ring (C_1–C_1') π^*-antibonding and π-bonding character, respectively, while the two relatively unperturbed orbitals do not involve the carbon atoms which form inter-ring bonds. Ab initio results[27] confirm the nature of the highest occupied orbital.

The predominant atomic orbital contributions to the molecular orbitals calculated for biferrocene(2,2) in the trans (C_{2h}) conformation are given in Table III. Again, the net charge on the iron atom and total electron density in each d orbital are similar to those found for ferrocene and BFD(2,2) as indicated in Table II. However, as shown in Figure 1, the splitting of the orbitals in biferrocene is less pronounced than that found for BFD(2,2). This splitting is reduced even more in the perpendicular conformation as the π character in the inter-ring bond is disrupted. The orbitals of a given symmetry type remain relatively close in energy and substantial mixing occurs among them. In neither conformation are the e_{1u} (carbon π) orbitals split to such a degree that a nondegenerate e_{1u} type orbital becomes HOMO. Rather, the highest energy partner of the original e_{1u} multiplets has an energy comparable to those of the a_{1g} (d_{z^2}) orbitals in the trans conformation and to those of the e_{2g} ($d_{x^2-y^2}$, d_{xy}) orbitals in the perpendicular conformation. Extensive mixing of the highest energy e_{1u}

Table II. Net Charge on Iron and Total Electron Density in Each d Orbital for the Ground-State Configurations of Ferrocene, Biferrocene, and BFD

	Electron density[a]					Net charge,[b]
	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	q_{Fe}
Ferrocene	1.98	1.91	1.91	1.08	1.08	0.28
Biferrocene(2,2) trans	1.98	1.91	1.90	1.10	1.09	0.28
Biferrocene(2,2) perpendicular	1.98	1.92	1.90	1.11	1.09	0.27
BFD(2,2)	1.98	1.92	1.90	1.09	1.09	0.28
BFD(2,3)[c]	1.98	1.56	1.91	1.17	1.17	0.34
BFD(3,3)	1.95	1.84	1.91	1.08	1.12	0.35

[a] The calculated atomic orbital occupation differs from the formal iron(II) configuration $(d_{z^2})^2(d_{x^2-y^2})^2(d_{xy})^2(d_{xz})^0(d_{yz})^0$ due to a small degree of back-donation (Fe → ligands) in the higher energy iron-based molecular orbitals and a larger degree of forward donation (ligands → Fe) in the lower energy ligand-based molecular orbitals. [b] Calculated from a Mulliken population analysis. [c] An iron(III) configuration.

Table III. Eigenvalues and Eigenvectors Calculated for Biferrocene(2,2)[a]

Symmetry[b]	Energy	Occ	Atomic orbital coefficients[c]
$19a_g$	−8.42	0	$0.51(d_{xz} + d'_{xz})$[d]
$12b_g$	−8.72	0	$0.54(d_{yz} + d'_{yz})$
$12a_u$	−8.74	0	$0.54(d_{yz} - d'_{yz})$
$18b_u$	−9.03	0	$0.55(d_{xz} - d'_{xz})$
$18a_g$[f]	−11.50	2	$0.52(d_{z^2} + d'_{z^2})$ $+ 0.19C_1(p_z - p'_z)$[e]
$17b_u$	−11.53	2	$0.70(d_{z^2} - d'_{z^2})$
$17a_g$	−11.54	2	$0.47(d_{z^2} + d'_{z^2})$ $+ 0.22C_1(p_z - p'_z)$[e]
$11b_g$	−11.81	2	$0.63(d_{xy} + d'_{xy})$
$16b_u$	−11.84	2	$0.66(d_{x^2-y^2} - d'_{x^2-y^2})$
$11a_g$	−11.84	2	$0.63(d_{x^2-y^2} + d'_{x^2-y^2})$
$11a_u$	−11.90	2	$0.66(d_{xy} - d'_{xy})$
$10a_u$	−12.04	2	$0.26C_2(p_z - p'_z)$[e]
$10b_g$	−12.10	2	$0.26C_2(p_z + p'_z)$[e]

[a] Biferrocene(2,2) in trans conformation, C_{2h} symmetry. [b] Symmetry axis defined as the rotation axis. [c] Coordinate axes defined with Fe in the *xz* plane and the *z* axis perpendicular to the fulvalene plane. [d] d orbitals used only for iron. Primed orbital indicates second iron center. [e] C_1 is one of two equivalent carbon atoms which bind the cyclopentadienyl rings; C_2 is one of four equivalent carbon atoms once removed from C_1. [f] The highest occupied molecular orbital is predominantly iron based.

orbital with the respective d orbitals of similar energy in each conformation indicates a type of metal–ligand π interaction not found in BFD. On the other hand, the ring–ring and metal–metal interactions found in the perturbed e_{1u} type orbitals of BFD are a manifestation of stronger coupling between the two ferrocene moieties in BFD than in biferrocene.

The electric field gradients at the iron nucleus were calculated for ferrocene, BFD(2,2), and biferrocene(2,2). The resulting quadrupole splittings are given in Table IVtogether with the experimental values. Similar results for each compound are expected since the differences in electron density in each orbital at each iron center are small. Although the calculated values are consistently higher than observed (no correction for the Sternheimer shielding factor has been included), large ΔE_Q values for all of these formally low-spin iron(II) systems are reproduced.

Calculations were performed for various configurations of the monocation BFD(2,3) corresponding to ionization of a single electron from one of several top-lying orbitals of BFD(2,2): the $9b_{3u}$ orbital (HOMO), the nearly degenerate $10a_g$ and $8b_{3u}$ orbitals (d_{z^2}), or different combinations of the $6b_{1g}$, $9a_g$, $7b_{3u}$, and $6b_{2u}$ orbitals ($d_{x^2-y^2}$, d_{xy}). The calculated relative stability of each configuration, as determined by the total energy differences, is given in Table IV.

As for the ferrocenium ion,[20] d-orbital relaxation effects are important in the determination of the ground state of the molecule. The calculated configuration energies for BFD(2,3) are much different from those obtained from a frozen-orbital approximation, that is, from the energy ordering of orbitals in BFD(2,2). Removal of an electron from lower energy orbitals of BFD(2,2) yields a more stable configuration than ionization from the highest occupied molecular orbital since charge relaxes back into the iron orbitals from the ligands. From the calculated energies, it appears that the ground state of BFD(2,3) is obtained upon ionization from either an a_{1g} (d_{z^2}) or an e_{2g} ($d_{x^2-y^2}$, d_{xy}) type orbital. The energy difference (0.2 eV) between the two states is too small to be conclusive. Therefore, an examination of the electromagnetic properties calculated for each of the likely ground states is necessary to distinguish the two.

The electric field gradients were calculated for each of the configurations considered and the resulting quadrupole splittings are included in Table IV. Excellent agreement with experiment is achieved for all of the configurations resulting from ionization from an e_{2g} type orbital. By contrast, the configurations resulting from ionization from an a_{1g} or an e_{1u} type orbital each yield a calculated value for the quadrupole splitting several times larger than that experimentally observed. Moreover, each e_{2g} type orbital from which the single electron may be removed is delocalized over two iron centers. Thus, the iron atoms remain equivalent upon formation of the monovalent cation. It is possible therefore to explain the experimentally observed equivalence of the iron atoms and to theoretically reproduce the lowering of ΔE_Q in BFD(2,3) with a ground-state configuration formed by ionization from an e_{2g} type orbital of either $6b_{1g}$, $9a_g$, $7b_{3u}$, or $6b_{2u}$ symmetry.

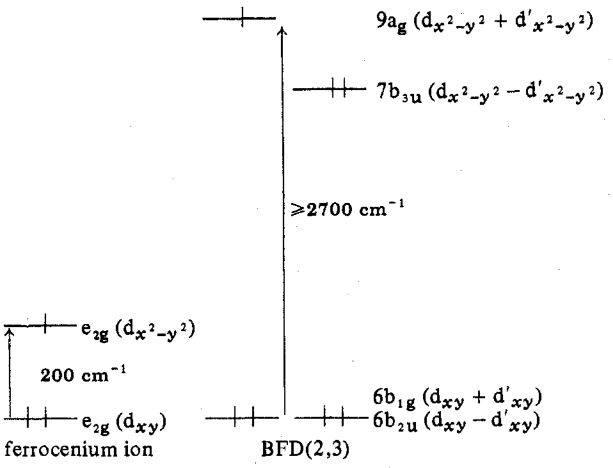
A ground state with an unpaired e_{2g} type orbital is also compatible with the observed[10] ESR spectra of BFD(2,3) ($g_{xx} = 1.87$, $g_{yy} = 2.00$, $g_{zz} = 2.27$) whereas a ground state resulting from ionization from an a_{1g} type orbital cannot account for the observed rhombicity in *g* values. An unpaired electron in a d_{z^2} orbital interacts through spin–orbit coupling only with electrons in d_{xz} and d_{yz} orbitals, which are empty, and not with electrons in the filled $d_{x^2-y^2}$ and d_{xy} orbitals. Isotropic *g* values of 2.00 were calculated for a ground state resulting from

Table IV. Calculated Quadrupole Splittings and Relative Energies for Different Configurations and Oxidation States of Ferrocene, Biferrocene, and BFD

	Orbital occ upon oxidn	Rel energy, eV	ΔE_Q(calcd),[a] mm/s	η[a]	ΔE_Q(exptl), mm/s
Ferrocene			3.30	0.0	2.40[b]
Ferrocenium	$(e_{2g})^1$		−0.21	0.0	0 (<0.01)[b]
Biferrocene(2,2)					
Trans			3.17	0.03	2.36[c]
Perpendicular		9.0	3.16	0.05	
BFD(2,2)			3.23	0.01	2.44[d]
BFD(2,3) [e_{1u} type]	$(9b_{3u})^1$	1.2	3.10	0.15	
[a_{1g} type]	$(10a_g)^{1.5}(8b_{3u})^{1.5}$		4.95	0.02	
↑	$(9a_g)^1$	0.3	1.51	0.41	
	$(9a_g)^{1.5}(7b_{3u})^{1.5}$	0.2	1.40	0.04	1.76[d]
[e_{2g} type]	$(6b_{1g})^1$	1.2	1.83	0.02	
	$(6b_{1g})^{1.5}(6b_{2u})^{1.5}$	1.2	1.75	0.03	
↓	$(9a_g)^{1.25}(7b_{3u})^{1.25}(6b_{1g})^{1.25}(6b_{2u})^{1.25}$	0.7	1.55	0.04	
BFD(3,3) [e_{1u} type]	$(9b_{3u})^0$		3.09	0.36	
[a_{1g} type]	$(10a_g)^1(8b_{3u})^1$	3.0	6.22	0.04	2.945[d]
[e_{2g} type]	$(6b_{1g})^0$	2.3	1.07	0.09	

[a] ΔE_Q calculated from $\Delta E_Q = 8Qq[(1 + \eta^2)/3]^{1/2}$ where $Q = 0.187$ b, $\langle r^{-3}\rangle_{3d} = 5.00$ au, $\langle r^{-3}\rangle_{4p} = 2.04$ au, and the principal-axis values of the field gradient are ordered $|V_{ii}| > |V_{jj}| > |V_{kk}|$ such that $q \equiv$ largest magnitude V_{ii} and $\eta \equiv (V_{kk} - V_{jj})/V_{ii}$ $(0 \leqslant \eta \leqslant 1)$. The sign of ΔE_Q is the sign of largest magnitude V_{ii}. [b] Reference 28. [c] Reference 6. [d] Reference 10.

Scheme I



ionization from an a_{1g} type orbital. Thus, such a ground state is incompatible with the behavior observed in both Mössbauer and electron spin resonances.

The rhombicity observed in the g values requires a ground state with an unpaired e_{2g} type orbital. Although there are four such nondegenerate orbitals—$6b_{1g}$, $9a_g$, $7b_{3u}$, and $6b_{3u}$–the relaxed energies of the four possible configurations as determined by the IEHT results (Table IV) correspond to two pairs of doubly degenerate states. The degenerate ground-state configurations $(6b_{2u})^2(6b_{1g})^2(7b_{3u})^2(9a_g)^1$ and $(6b_{2u})^2(6b_{1g})^2(7b_{3u})^1(9a_g)^2$ are found to be around 1.0 eV lower in energy than the degenerate excited-state configurations $(6b_{2u})^2(6b_{1g})^1(7b_{3u})^2(9a_g)^2$ and $(6b_{2u})^1(6b_{1g})^2$-$(7b_{3u})^2(9a_g)^2$. While the qualitative configuration energy orderings obtained from IEHT have proven resonable for ferrocene, the actual values of state energy differences are not reliable and therefore were varied in the calculation of the g values.

Observed g values could be accounted for with a nearly unique value of λ/Δ, the ratio of the spin–orbit coupling constant to the excitation energy between the two pairs of states. An energy difference of 0.34 eV for $\lambda = 200\ cm^{-1}$, or similarly 0.68 eV for $\lambda = 400\ cm^{-1}$, gave the values $g_{xx} = 1.85$, $g_{yy} = 1.89$, and $g_{zz} = 2.27$ in good agreement with experiment. If a small energy splitting was allowed between the $6b_{1g}$ and $6b_{2u}$ orbitals, thus lifting the degeneracy of the excited state doublet, axially symmetric g values were obtained. An energy splitting of 0.2 eV between the two higher energy orbitals $9a_g$ and $7b_{3u}$, thus lifting the degeneracy of the ground-state doublet, led to three g values $g_{xx} = 1.86$, $g_{yy} = 1.93$, and $g_{zz} = 2.39$ also in agreement with experiment. Therefore both the relaxed-energy and g-value calculations indicate a 9^2A_g, 7^2B_{3u} ground state separated by 0.34–1.0 eV from a degenerate 6^2B_{1g}, 6^2B_{2u} excited state. The ground-state doublet could possibly be split by some 0.2 eV.

Such a pattern of e_{2g} type orbital energy splittings is also compatible with the observed[13] temperature-independent spin-only value for the magnetic moment of BFD(2,3). An explanation for the difference in behavior from that observed for the ferrocenium ion is illustrated by Scheme I. In the ferrocenium ion, g values could be explained[20] if the d_{xy} and $d_{x^2-y^2}$ orbitals were separated by 200 cm^{-1}. These two states strongly interact through spin–orbit coupling and are energetically close enough to be populated by thermal excitation. Hence values of magnetic moments greater than spin-only values, a temperature dependence of the magnetic moment, and highly anisotropic g values would be expected. In BFD(2,3), these two types of orbitals are separated by at least 2700 cm^{-1}, 10 times the separation in the ferrocenium ion, and therefore would interact much less. This large splitting is due to the difference in relaxation effects on the two types of orbitals in the BFD system. Moreover, the degenerate or near-degenerate pairs have no significant spin–orbit coupling between them. These two features together account for the spin-only value and temperature independence of the magnetic moment as well as smaller anisotropy in g values observed for BFD(2,3) in contrast to the observed behavior of the ferrocenium ion in spite of the qualitatively similar ground-state configurations. Thus it is not necessary to invoke a ground state for BFD(2,3) with a hole in an a_{1g} type orbital to account for the different behavior observed for the ferrocenium ion and BFD(2,3).

The calculated description of the four energy levels allows the possible assignment of the additional peaks of the electronic spectra of BFD(2,3) not found in either BFD(2,2) or BFD(3,3). The partially resolved pair of absorptions at 1550 nm (0.80 eV) and 1140 nm (1.09 eV), previously assigned to intervalence transfer, can be assigned to the new d–d transitions corresponding to electron excitations from the orbitals $6b_{1g} \rightarrow 7b_{3u}$ and $6b_{2u} \rightarrow 9a_g$. These are symmetry-allowed transitions ($g \leftrightarrow u$) in the two centered binuclear complexes. The energy of the two transitions is calculated from IEHT at 1.0 eV and from the g value results at 0.34–0.68 eV. A splitting of 0.2 eV compatible with the calculated g values could account for the observed shoulder. The peak at 600 nm (2.07 eV), attributed to an ${}^2E_{1u} \leftarrow {}^2E_{2g}$ hole transition in the ferrocenium ion[14] and the mono- and divalent cations of biferrocene can also be assigned to the same type of transition in BFD(2,3), i.e., from several filled e_{1u} type orbitals to a hole in the e_{2g} type orbitals. The fact that BFD(2,3) is a completely delocalized system on two iron centers does not preclude such a charge-transfer transition.

The characteristics of the molecular orbitals of BFD(2,2) given in Table I do not change appreciably upon further oxidation to the divalent cation BFD(3,3). The highest occupied molecular orbitals become the near-degenerate $10a_g$, $8b_{3u}$ ($d_{z^2} \pm d_{z^2}$) orbitals when two electrons are removed from the delocalized $9b_{3u}$ (carbon π) orbital. In marked contrast to the case of BFD(2,3), removal of two electrons from the lower lying a_{1g} ($10a_g$, $8b_{3u}$) and e_{2g} ($6b_{1g}$, $9a_g$, $7b_{3u}$, $6b_{2u}$) type orbitals yields configurations with higher energy as shown in Table IV. Thus, there is less of a relaxation effect in BFD(3,3) than in BFD(2,3). The former can be described by the frozen-orbital ionization approximation while the latter cannot. The result is that BFD(3,3) has an ${}^1A_g$ ground state which differs from that of BFD(2,2) only in the depopulation of the high-lying ligand π orbital. The observed quadrupole splitting at the iron nucleus would not be expected to vanish and a straightforward calculation of ΔE_Q for the ground-state configuration of BFD(3,3) gives a magnitude in excellent agreement with experiment, as shown in Table IV.

Thus the origin of the large field gradient at the iron nucleus in BFD(3,3) and the similarity of BFD(3,3) to BFD(2,2) can be explained by a ground-state configuration for the divalent cation in which two electrons are removed from a ligand orbital with little iron character. This result is in contradiction to the hypothesis that the ground state of BFD(3,3) corresponds to removal of an electron from each of two e_{2g} type orbitals delocalized on the ferrocene moieties. From Table IV, such a configuration is 2.3 eV higher in energy than the ground state. Moreover, as indicated, such a configuration still leads to a small field gradient for BFD(3,3) despite total delocalization of the e_{2g} orbitals on both iron centers. A configuration obtained by ionization from the a_{1g} ($10a_g$, $8b_{3u}$) type orbitals is greater yet in energy and yields a value for the quadrupole splitting larger than that observed experimentally.

Although the calculated ground-state configuration can account for the magnitude of the field gradient at the iron nucleus, it does not agree with a recent determination[19] that the sign of the low-temperature value of the observed quadrupole splitting is negative. The major component of the field gradient is calculated to be positive and to be in the z direction, i.e., perpendicular to the cyclopentadienyl rings, while the two remaining principal-axis values V_{yy} and V_{xx} are negative with the order $|V_{zz}| > |V_{yy}| > |V_{xx}|$. The calculation at one iron center though does not explicitly include any lattice contributions from the adjacent ferrocenium ion moiety. Also, the conformational effects resulting from counterions in the polycrystalline sample or from cooling to liquid helium temperatures are neglected. Such environmental effects might change the direction of the major component of the field gradient and therefore also reverse the sign of the quadrupole splitting from that calculated for the dication with a geometry taken from an x-ray structure determination of the unoxidized species.

The ground state for BFD(3,3) does account for the absence of the $E_{1u} \leftarrow E_{2g}$ hole charge-transfer transition traditionally observed in ferrocenium type systems. The absence of this transition in BFD(3,3) proved difficult to explain on the basis of the current assumption of a $^2E_{2g}$ type ground state for each ferrocenium moiety. With the ground state obtained from IEHT, there is no hole in the e_{2g} manifold of states and no such absorption would be expected. Finally, the diamagnetism of the BFD(3,3) salts is also explained in a straightforward manner since the ground state is obtained upon removal of two electrons from a nondegenerate orbital. In order to arrive at such a state with the postulated $(e_{2g})^3$ configuration at each iron site, either superexchange or direct exchange interaction between the two centers had to be invoked. This added effect is no longer necessary.

Conclusion

The observed properties of bis(fulvalene)diiron and its mono- and divalent cations can be accounted for by understanding the differences between the binuclear complexes and the individual ferrocene or ferrocenium ion moieties. Biferrocene compounds have been shown experimentally to exhibit trapped valences and retain the properties of the individual units. Bis(fulvalene)diiron compounds do not.

Due to the large perturbation of the ligand π orbitals upon covalent bond formation between the cyclopentadienyl rings, a delocalized π orbital appears as the highest occupied molecular orbital in neutral bis(fulvalene)diiron. Upon oxidation to form the monovalent cation, however, it is energetically more favorable to remove a single electron from lower lying d orbitals than from the highest occupied molecular orbital due to d-electron relaxation effects similar to those found for ferrocene. The calculated ^2A_g ground state with a hole in the $(d_{x^2-y^2} + d'_{x^2-y^2})$ orbital allows a coherent explanation of the observed properties of the monooxidized species. With such a ground state and similar low-lying excited states, the electric field gradient and g values have been calculated in agreement with experiment, the observed behavior of the magnetic moment has been rationalized, and the unique ir peak and ferrocenium type electronic transitions have been assigned in the framework of a totally delocalized system.

Relaxation effects are not observed in the formation of the divalent cation as both electrons are more favorably removed from the nondegenerate ligand π orbital. BFD(3,3) is shown to be diamagnetic and to have a d-electron distribution similar to that of BFD(2,2) and therefore a large value for the electric field gradient. The absence of the hole transition $E_{1u} \leftarrow E_{2g}$ in BFD(3,3), initially a source of puzzlement, now becomes reasonable since in the calculated ground-state configuration all of the e_{2g} type orbitals are filled.

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