

Preliminary communication

Micromodulation of electron-transfer rates in mixed-valence 1',1'''-dibenzylbiferrocenium cations

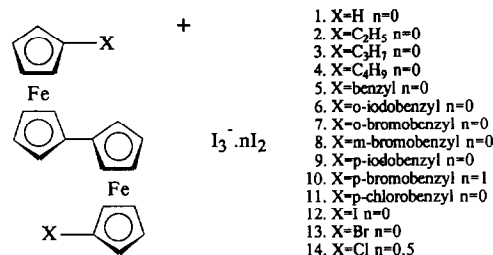
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(Received December 7th, 1990)

Abstract

X-Ray structures of 1',1'''-disubstituted biferrocenium triiodide salts have been studied and the dramatic effects of substituents on the intramolecular electron-transfer rates are described.

There has been considerable progress over the last few years [1–12] in the area of binuclear mixed-valence biferrocenium salts, examples of which are compounds 1–5. These mixed-valence compounds give insight into the factors which control electron transfer [1–5]. At temperatures below 200 K each shows two doublets in Mössbauer spectra, one representing the Fe^{II} site and the other the Fe^{III} site. Increase of temperature in each case causes the two doublets to move together with no discernible line broadening, eventually to become a single “average-valence” doublet at temperatures of 365, 275, 245, 275, and 260 K for 1–5, respectively. Furthermore, the importance of the counterion in controlling the rate of intramolecular electron transfer has been reported for 1 [8], 5 [13,14], 12 [9,15], 13 [9,15], and 14 [9]. In spite of considerable work in this area, there are still some questions that remain unanswered.



In Hendrickson's theoretical model [14], the factors of potential importance in controlling the rate of intramolecular electron transfer in the mixed-valence biferrocenium cation include (1) the extent of resistance to electron transfer in the cation, (2) the extent of resistance to charge oscillation in the anion, and (3) intermolecular cation–cation and cation–anion interactions. It has been suggested that in general

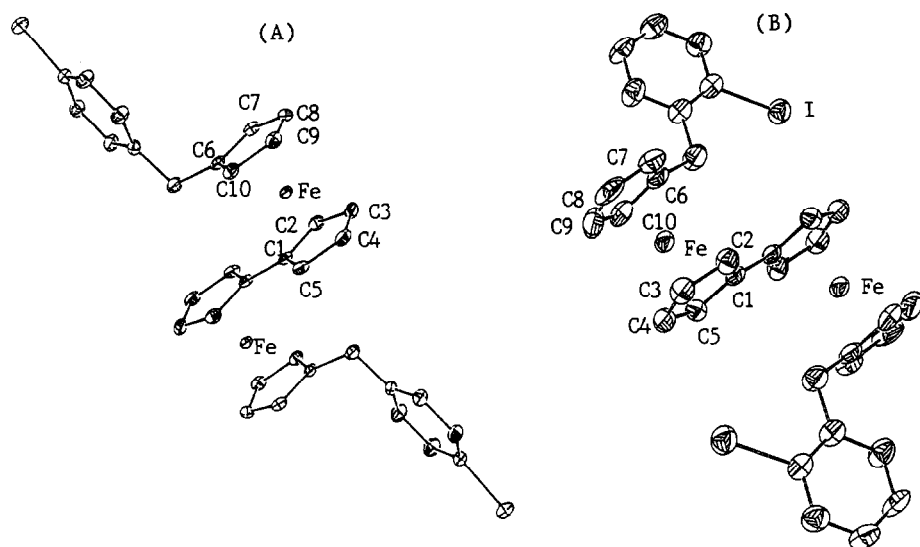


Fig. 1. ORTEP drawings of the neutral 1',1'''-di(*p*-bromobenzyl)biferrocene (**15**) (A) and cation of **6** (B).

the greater the resistance to charge oscillation in the cation or anion, the lower the electron transfer rate. Furthermore, the electron transfer rate will be decreased as the cation–anion interaction intensifies. If this suggestion is correct, then relatively minor perturbations of cation–anion interactions would have pronounced effects on the electronic structure and thus on the rate of intramolecular electron transfer. Binuclear mixed-valence compounds, such as **6**–**11**, are of use in understanding how a nearby triiodide can influence rate of electron transfer. The mixed-valence cation in each of these compounds serves as a very sensitive probe of the microscopic structure of the solid state. It is of interest to see whether the halide substituent on the benzyl unit, and therefore its intermolecular van der Waals interactions with neighbouring triiodide, affects the rate of the electron transfer in the mixed-valence cation.

Single crystal X-ray structures have been determined for **6**, **10** [16], and neutral 1',1'''-di(*p*-bromobenzyl)biferrocene (**15**)*. ORTEP drawings of the neutral compound **15** and **6** are given in Fig. 1. The packing arrangements for **6** and **10** are shown in Fig. 2. The cations in all of the above compounds have a *trans* conformation in the solid state. The fulvalenide ligand is planar in each cation and the iron

* Crystal data for **6**: $C_{34}H_{28}Fe_2I_5$, $M = 1182.81$, triclinic, space group $P\bar{1}$, $a = 8.149(4)$, $b = 9.567(3)$, $c = 12.491(4)$ Å, $\alpha = 111.78(3)$, $\beta = 85.97(4)$, $\gamma = 108.39(3)^\circ$, $V = 856.9(6)$ Å³, $Z = 1$, $\mu = 5.33$ mm⁻¹, $\lambda(\text{Mo-K}\alpha) = 0.70930$ Å, $D_c = 2.292$ g cm⁻³, 3014 unique reflections were measured to $2\theta_{\text{max}} 49.8^\circ$, 2139 reflections with $F^2 > 2.5\sigma(F^2)$ were used in the refinement, $R_f = 0.033$, and $R_w = 0.037$. Crystal data for **15**: $C_{34}H_{28}Br_2Fe_2$, $M = 708.1$, triclinic, space group $P\bar{1}$, $a = 5.853(4)$, $b = 8.380(3)$, $c = 14.2295(18)$ Å, $\alpha = 74.622(15)$, $\beta = 83.940(23)$, $\gamma = 86.69(4)^\circ$, $V = 668.8(5)$ Å³, $Z = 1$, $\mu = 4.07$ mm⁻¹, $\lambda(\text{Mo-K}\alpha) = 0.70930$ Å, $D_c = 1.758$ g cm⁻³, 2331 unique reflections were measured to $2\theta_{\text{max}} 49.8^\circ$, 2000 reflections with $F^2 > 2.5\sigma(F^2)$ were used in the refinement, $R_f = 0.029$, and $R_w = 0.037$. All crystallographic measurements were made on an Enraf–Nonius CAD4 diffractometer. The data sets were corrected for absorption. The structures were solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

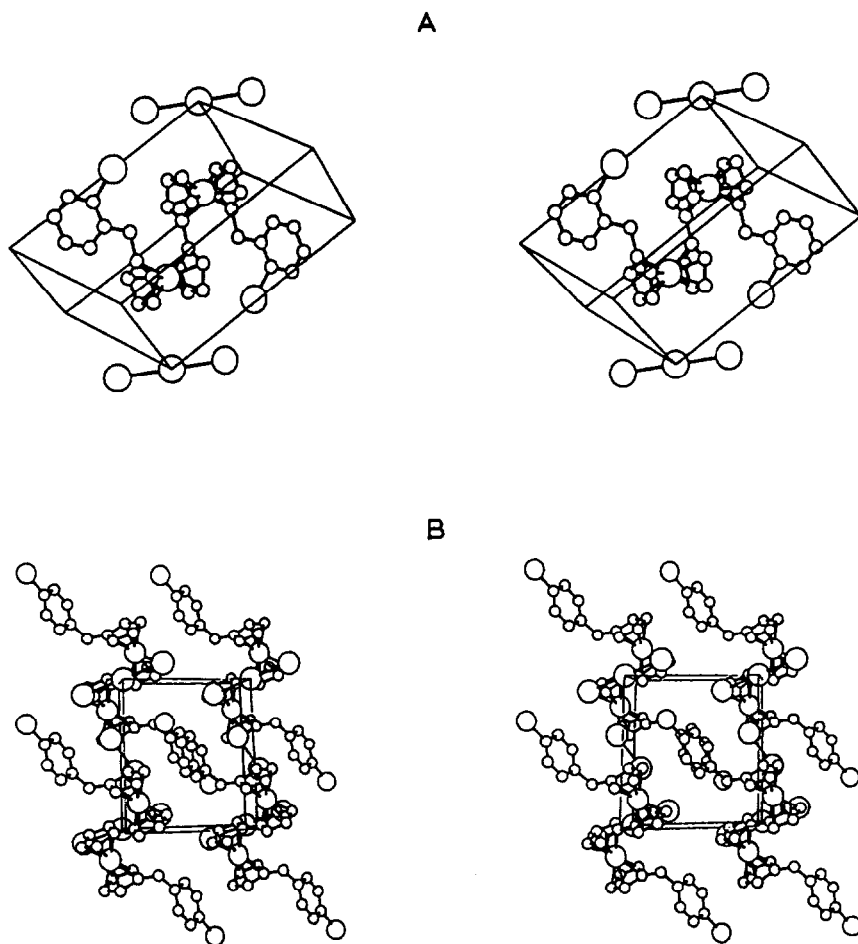


Fig. 2. Packing arrangements for **6** (A) and **10** (B) as viewed along the *c* axis.

ions are on the opposite sides of the fulvalenide ligand. There is very little change in the Fe–Fe distances for **6**, **10**, and **15**, 5.082, 5.058, and 5.119 Å, respectively. The dihedral angles between the two five-member rings of each ferrocene moiety in **6**, **10**, and **15** are 4.7, 3.3, and 0.48°, respectively. Furthermore, the average staggering angles for **6**, **10**, and **15** are 2.32, 1.2, and 1.5°, respectively. The site symmetry imposed on **6** and **10** requires that the iron centres in each cation are in equivalent positions, and this is consistent with our Mössbauer studies. We believe that the interactions between cations and anions could be changed by replacing the substituents on benzyl units. Therefore, our discussion will centre on the interactions between cations and anions. As expected, the triiodide anions in **6** are located differently, perpendicular to the fulvalenide ligand, rather than parallel to the fulvalenide ligand as in **10** (see Fig. 2). It is this dissimilarity which is probably responsible for the difference of rates of electron transfer between **6** and **10**. The most significant contact (3.87 Å) between cation and anion in **6** is the benzyl halide atom and the terminal iodine atom of the I_3^- anion. In the case of **10**, the most

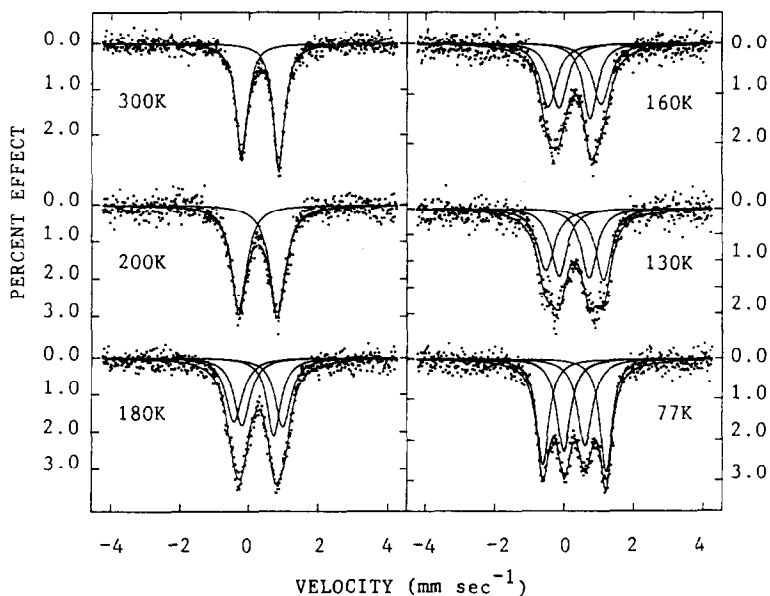


Fig. 3. Variable-temperature ^{57}Fe Mössbauer spectra for **10**.

significant contact (3.87 Å) is between the benzyl halide atom and middle iodine atom of the I_3^- anion.

There is a dramatic change in electron-transfer rate as the halide substituent on benzyl unit is moved from the *para* position to the *ortho* position. In compound **10**, at temperatures below 150 K two doublets are seen in the ^{57}Fe Mössbauer spectra. It indicates that compound **10** is valence trapped on the Mössbauer time scale (electron transfer rate is less than $\sim 10^7 \text{ s}^{-1}$) below 150 K. As shown in Fig. 3, increasing the temperature of a sample of **10** causes the two doublets to become a single "average-valence" doublet at a temperature of ~ 200 K. Furthermore, compounds **9** and **11** even show two doublets in their Mössbauer spectra at 300 K. Surprisingly, a single "average-valence" doublet ($\Delta E_{\text{O}} \approx 1.1 \text{ mm/sec}$) is seen at 77 K for **6** and **7**. The Mössbauer data clearly indicate that the intramolecular electron-transfer rates in **6** and **7** are greater than $\sim 10^7 \text{ s}^{-1}$ even at 77 K. To our belief, compounds **6** and **7** have the lowest valence-detraped transition temperature known among the dialkyl analogues. Very recent, Hendrickson found [14] that 1',1'''-dibenzylbiferrocenium PF_6 is converted from valence-trapped to valence-detraped at 170 K. Thus, in changing from the *para*-substitution to *ortho*-substitution for the 1',1'''-dibenzylbiferrocenium cation there is a change from 300 K to below 77 K for the valence-detraped transition temperature. This difference does not originate in a difference in electronic or vibronic coupling in the cations. Evidence in support of the above statement can be gleaned from the electrochemical data for the six neutral biferrocenes. Each shows two one-electron oxidation waves, and the separation (0.32 V) between the two one-electron oxidation waves is the same. The difference of electron transfer rates can be explained by the difference of packing arrangements for triiodide anions. Theoretical calculations of the effect of cation-anion interaction on the charge oscillation in the cation are in progress.

X-Band EPR spectra were run at 77 K for samples of **6–11**. An axial-type spectrum was observed for **6, 7, 9, 10, and 11**. In the case of **8**, rhombic signals are seen. The Δg values ($\Delta g = g_{\parallel} - g_{\perp}$) for **6–11** are 1.02, 1.17, 1.59, 1.29, 1.23, and 1.49, respectively. The influence of substituents on the EPR signals has been studied for a number of ferrocenium complexes [17]. In the case of binuclear mixed-valence biferrocenium ions, a reduction of Δg was seen [18]. It has been suggested that the Δg can be used to determine whether the rate of electron transfer is greater than the EPR timescale or not. If $\Delta g \leq 0.8$, then the rate of electron transfer is greater than the EPR timescale. The Δg values for **6–11** suggest that the cations in these compounds are localized on the EPR timescale at 77 K.

Supplementary material available

Tables of atomic coordinates (Table s1, 1 page), anisotropic thermal parameters (Table s2, 1 page), bond distances and angles (Table s3, 2 pages), and a listing of structure factors (Table s4, 20 pages) of **6** and tables of atomic coordinates (Table s5, 1 page), bond distances and angles (Table s6, 2 pages), thermal parameters (Table s7, 1 page), and a listing of structure factors (Table s8, 16 pages) of **15** are available from the authors.

Acknowledgement. We are grateful for support from the National Science Council.

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