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# Electron transfer in mixed-valence 1',1'''-bis(*m*-bromobenzyl)biferrocenium triiodide

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## Abstract

The solid-state physical properties of the new mixed-valence 1',1'''-bis(*m*-bromobenzyl)biferrocenium triiodide are reported. Mössbauer spectra of a microcrystalline sample indicated the presence of both delocalized and localized species. In the case of a recrystallized sample, below 200 K there are two doublets in the  $^{57}\text{Fe}$  Mössbauer spectra which, on increasing the temperature, become a single "average-valence" doublet at *ca.* 250 K. The effects of the nature of the motion of charge in counterion and cation–anion interactions on solid-state electron transfer were investigated by studying intramolecular electron transfer for a series of 1',1'''-bis(halobenzyl)biferrocenium salts in solution.

## 1. Introduction

The study of intramolecular electron transfer in mixed-valence compounds has enabled systematic and creative investigation of the factors that affect rates of electron transfer in solution redox processes, solid-state materials, and biological electron-transport chains [1–4]. The two most thoroughly studied mixed-valence complexes are ruthenium amine complexes [4] and binuclear biferrocenium salts [5]. Mixed-valence trinuclear iron acetate complexes have received attention recently [5].

In the case of the mixed-valence biferrocenium salts 1–8 (Scheme 1), considerable progress has been made in understanding which factors influence the rate of intramolecular electron transfer in the solid state [6–10]. Compounds 5–8 give unusual temperature-dependent Mössbauer spectra [7]. Furthermore, pronounced dependency of the sample history on electron-transfer rates has been noted [7] for compounds 7 and 8. X-ray structures have been reported at 298 and 110 K for 6 [9] and at 363, 298, and 150 K for 7 [7]. Very recently, we prepared a series of binuclear mixed-valence compounds 9–13 which are of use in understanding how a nearby triiodide can influence the rate of electron

transfer [11]. We found that the cation–anion van der Waals interactions between the halide substituent in the benzyl unit and the neighbouring triiodide can have a dramatic influence on the rate of electron transfer of compounds 11 and 13. Variable-temperature (77–300 K) Mössbauer spectra reveal that the cations are localized on the time-scale of the Mössbauer technique (electron-transfer rates less than *ca.*  $10^7 \text{ s}^{-1}$  at 300 K). In the case of 12, at temperatures below 150 K there are two doublets in the  $^{57}\text{Fe}$  Mössbauer spectra and increasing the temperature causes them to become a single "average-valence" doublet at a temperature of *ca.* 200 K. In comparison with 11–13, a single "average-valence" doublet is seen even at 77 K for 14 and 15. Thus, there is a dramatic change in electron-transfer rate as the position of the halide substituent in the benzyl unit is changed from *para* to *ortho*. We proposed that the dramatic difference in electron-transfer rates results from the difference of packing arrangements for triiodide anions in the solid state.

In the solid state, the rate of electron transfer for a given mixed-valence cation is influenced by various structural factors and by lattice dynamics, including the electronic and vibronic couplings between two metal ions, the nature of the counterion, and cation–anion interactions. To provide further confirmation for our explanation for the difference of electron-transfer rates in the cations of 9–13, we have investigated the elec-

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tron-transfer rates of **9–13** in solution. In this paper, we also report the physical properties of the new mixed-valence compound **14** in both solid and solution states.

## 2. Experimental section

### 2.1. General information

All manipulations involving air-sensitive materials were carried out by using standard Schlenk techniques under nitrogen. Chromatography was performed on neutral alumina oxide (activity II), eluting with hexane-CH<sub>2</sub>Cl<sub>2</sub>. Dichloromethane was dried over P<sub>2</sub>O<sub>5</sub>. The sample of biferrocene was prepared according to the literature [12].

### 2.2. 1',1'''-Bis(m-bromobenzoyl)biferrocene

This compound was prepared according to our procedure [11] for 1',1'''-bis(benzoyl)biferrocenes, using *m*-bromobenzoyl chloride/AlCl<sub>3</sub> as acylating reagent. The properties of this compound are as follows. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.88 (t, 2H), 7.63 (m, 2H), 7.60 (m, 2H), 7.23 (m, 2H), 4.64 (t, 4H), 4.38 (t, 4H), 4.26 (t, 4H), and 4.18 (t, 4H).

### 2.3. 1',1'''-Bis(m-bromobenzyl)biferrocene

The same method described for the preparation of the neutral compounds of **9–13** [11] was used to synthesize the desired compound. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.19 (m, 4H), 7.05 (t, 2H), 6.90 (d, 2H), 4.29 (t, 4H), 4.17 (t, 4H), 3.92 (t, 4H), 3.87 (t, 4H), 3.33 (s, 4H). Mass spectrum, M<sup>+</sup>/z at 706, 708, and 710 (M + 2).

### 2.4. Mixed-valence compound **14**

The sample of **14** was prepared according to the simple procedure previously reported [11] for **9–13**. A microcrystalline compound results when a solution of I<sub>2</sub> in benzene is slowly added to a solution of biferrocene in benzene. Anal. Found: C, 37.20; H, 2.54. C<sub>34</sub>H<sub>30</sub>Br<sub>2</sub>Fe<sub>2</sub>I<sub>3</sub> calc.: C, 37.51, H, 2.59%.

### 2.5. Physical methods

At the Academia Sinica, <sup>57</sup>Fe Mössbauer measurements were made on a constant-acceleration instru-

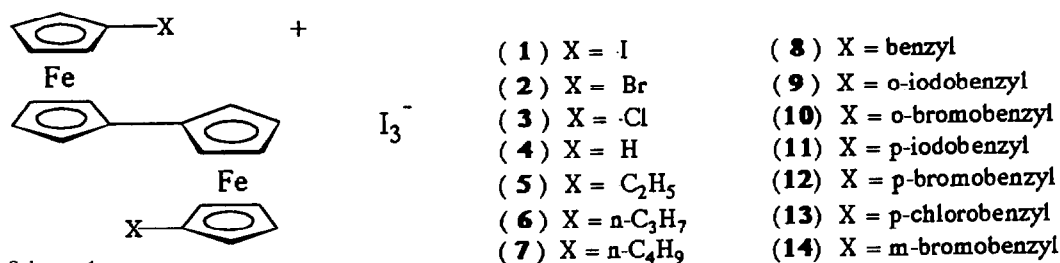
ment. The source, which originally consisted of 35 mCi of <sup>57</sup>Co diffused into a 12 μm rhodium matrix, is connected to a Ranger Scientific model VT-900 velocity transducer. An Ortec Model 5600 multichannel analyzer, scanned over 1024 channels, receives the logic pulses from the single-channel analyzer. Velocity calibrations were made using a 99.99% pure 10 μm iron foil at 300 K.

<sup>1</sup>H NMR spectra were run on a Bruker MSL 200 spectrometer. Mass spectra were obtained with a VG250-70S system. Electron paramagnetic resonance data (X-band) were collected with a Bruker ER200D-SRC spectrometer. The magnetic field was calibrated with a Bruker ER035M NMR gaussmeter. DPPH was used to gauge the microwave frequency. A direct-immersion dewar, which was inserted into the cavity, was used to obtain data at 77 K.

## 3. Results and discussion

### 3.1. Physical properties of **14** in the solid state

Pronounced dependency of sample history on the <sup>57</sup>Fe Mössbauer spectral properties of compounds **7** and **8** has been reported [11]. In the series of 1',1'''-di(substituted-benzyl)biferrocenium triiodide salts, we find that only compound **14** shows this phenomenon. A microcrystalline sample of **14** was prepared as described in the Experimental section. The variable-temperature <sup>57</sup>Fe Mössbauer spectra of this microcrystalline sample are shown in Fig. 1. The various absorption peaks in each spectrum were fitted to Lorentzian lines. Examination of the 77 K Mössbauer spectrum of this microcrystalline sample reveals that it consists of valence-trapped (Fe<sup>II</sup>, ΔE<sub>q</sub> = 2.11 mm s<sup>-1</sup>; Fe<sup>III</sup>, ΔE<sub>q</sub> = 0.461 mm s<sup>-1</sup>) and valence-detraped (Fe<sup>II/III</sup>, ΔE<sub>q</sub> = 1.231 mm s<sup>-1</sup>) signals. As the temperature of the sample is increased, the intensity of the detraped signal grows at the expense of the trapped signal. At temperatures above 230 K, the spectrum of this microcrystalline sample shows a single quadrupole-split doublet which is characteristic of valence-detraped cation in which the intramolecular electron-transfer rate exceeds ca. 10<sup>7</sup> s<sup>-1</sup>. There is a dramatic change in the



Scheme 1

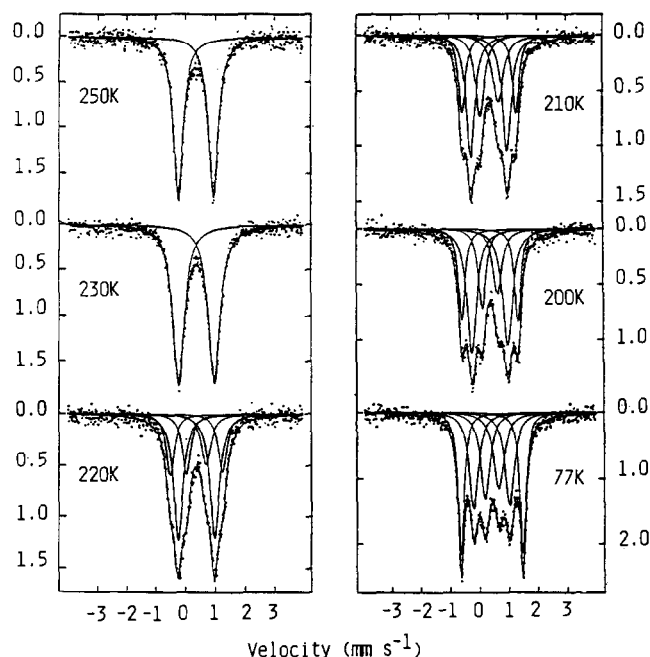


Fig. 1.  $^{57}\text{Fe}$  variable-temperature Mössbauer spectra for a microcrystalline sample of **14**.

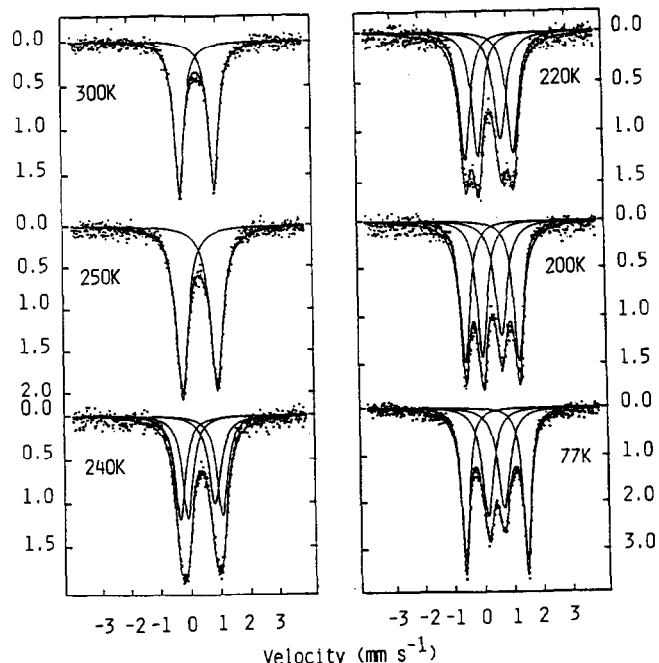


Fig. 2.  $^{57}\text{Fe}$  variable-temperature Mössbauer spectra for a recrystallized sample of **14**.

$^{57}\text{Fe}$  Mössbauer characteristics for the recrystallized sample prepared by redissolving the initial microcrystalline sample in  $\text{CH}_2\text{Cl}_2$  and then evaporating to dryness. The Mössbauer spectra of this recrystallized sample are shown in Fig. 2. At temperatures below 240 K, only two doublets are shown in the  $^{57}\text{Fe}$  Mössbauer spectra of the recrystallized sample, indicating that the cation is valence-trapped on the Mössbauer time scale (electron-transfer rate is less than *ca.*  $10^7 \text{ s}^{-1}$ ) below 240 K. As shown in Fig. 2, increasing the temperature causes two doublets to become a single “valence-de-trapped” doublet at temperature *ca.* 250 K (electron-transfer rate is greater than *ca.*  $10^7 \text{ s}^{-1}$ ). This phenomenon is similar to the spectral properties of 1',1''-dibenzylbiferrocenium triiodide (**8**) [7,13]. It has been shown that the intramolecular electron transfer in **8** is sensitive to the environmental perturbation caused by differences in crystal packing arrangements. Hendrickson proposed [13] that a 1',1''-dibenzylbiferrocenium cation situated close to a defect such as a dislocation would become trapped due to the induction of a zero-point energy difference between the two vibronic descriptions of the cation ( $\text{Fe}_a^{\text{III}}\text{Fe}_b^{\text{II}}$  and  $\text{Fe}_a^{\text{II}}\text{Fe}_b^{\text{III}}$ ).

It has been reported that the EPR technique can be used as a rough estimate of the nature of the electronic ground state for a given mixed-valence biferrocenium cation [7,13]. At low temperature, the EPR spectrum for a given ferrocenium cation consists of an axial-type ( $g_{\parallel}$  and  $g_{\perp}$ ) signal [14–16]. The  $g$ -tensor anisotropy,  $\Delta g = g_{\parallel} - g_{\perp}$ , is 3.09 for ferrocenium triiodide. In the

case of binuclear mixed-valence biferrocenium cation, a reduction of  $\Delta g$  was seen [17]. It has been suggested that  $\Delta g$  can be used to determine whether the rate of electron transfer is greater than the EPR time scale or not. If  $\Delta g < 0.8$ , then the rate of intramolecular electron transfer in biferrocenium cation is greater than the EPR time scale ( $10^9\text{--}10^{10} \text{ s}^{-1}$ ).

X-band EPR spectra were run for the microcrystalline and recrystallized samples of **14** at 77 K. The  $g$  values extracted from the spectra are collected in Table 1. The spectrum of the microcrystalline sample of **14** is clearly a superposition of two distinct signals. The feature at  $g = 3.31$  is the  $g_{\parallel}$  edge of an axial pattern where the  $g_{\perp}$  feature occurs at 1.90. The second  $g_{\parallel}$  feature occurs at  $g = 3.95$  and the  $g_{\perp}$  signal is  $g = 1.54$ . The  $g$ -tensor values of these two distinct signals are 1.41 and 2.41, respectively, and it indicates that compound **14** is localized on the EPR time scale. Further-

TABLE 1. EPR data at 77 K

Compound	$g_{\parallel}$	$g_{\perp}$	$\Delta g^a$
<b>14</b> <sup>b</sup>	3.31	1.90	1.41
	3.95	1.54	2.41
<b>14</b> <sup>c</sup>	3.06	1.94	1.12
	3.63	1.55	2.08
<b>14</b> <sup>d</sup>	3.23	1.90	1.33

<sup>a</sup>  $\Delta g = g_{\parallel} - g_{\perp}$ . <sup>b</sup> Microcrystalline sample in solid state. <sup>c</sup> Recrystallized sample in solid state. <sup>d</sup> In  $\text{CH}_2\text{Cl}_2$ /toluene.

TABLE 2. Characteristic IT bands of **9–14** in CD<sub>2</sub>Cl<sub>2</sub> solution

Compound	$\nu_{\max}^a$	$\epsilon_{\max}^b$	$\Delta\nu_{1/2}^a$	$\alpha$	$H_{ab}$	$k_{et}^c$
<b>9</b>	4651	848	3082	0.0957	445	$1.07 \times 10^{14}$
<b>10</b>	4651	952	3082	0.1014	472	$1.20 \times 10^{14}$
<b>11</b>	4651	1008	3096	0.1095	486	$1.27 \times 10^{14}$
<b>13</b>	4651	792	3082	0.0925	430	$9.96 \times 10^{13}$
<b>14</b>	4651	1016	3044	0.1041	484	$1.26 \times 10^{14}$

<sup>a</sup> In units of cm<sup>-1</sup>, <sup>b</sup> In units of cm<sup>-1</sup> M<sup>-1</sup>, <sup>c</sup> In units of s<sup>-1</sup>.

more, these two distinct signals cannot be attributed to the Mössbauer delocalized and localized species. One possible origin for these signals arises from a weak magnetic exchange interaction which develops between valence-trapped cations. The 77 K EPR spectrum of the recrystallized sample of **14** and the EPR spectrum of **14** in a CH<sub>2</sub>Cl<sub>2</sub>/toluene glass can support the above suggestion. First, the 77 K EPR spectrum of the recrystallized sample of **14** is similar to the EPR spectrum of the microcrystalline sample. At 77 K, the <sup>57</sup>Fe Mössbauer spectrum of the recrystallized sample shows only two doublets which are attributed to the valence-trapped species. Thus, the two distinct signals cannot arise from the valence-detraped and valence-trapped species. Second, the X-band EPR spectrum of **14** in a frozen CH<sub>2</sub>Cl<sub>2</sub>/toluene solution consists of a typical axial pattern ( $g_{\parallel} = 3.33$  and  $g_{\perp} = 1.90$ ) with no  $g_{\parallel} = 3.95$  and  $g_{\perp} = 1.54$  signals. Consequently, this indicates that the  $g_{\parallel} = 3.95$  and  $g_{\perp} = 1.54$  signals seen for the microcrystalline and recrystallized samples are probably the result of intermolecular interactions in a crystalline lattice.

### 3.2. Electron-transfer rates of **9–14** in solution

Electronic absorption spectroscopy, and in particular the energy and line-shape of the intervalence transition (IT) band in the near-IR region are useful for determining the photo-induced electron transfer rate of a given mixed-valence compound. Cowan *et al.* have applied the PKS model to mixed-valence ions of biferrocene and bis(fulvalene)diiron in solution [18].

In common with most other mixed-valence complexes, **9–14** have a near-IR transition at 2150 nm which is not present for the neutral or dioxidized ion. According to Hush's model [19], the bandwidth ( $\Delta\nu_{1/2}$ ) of a symmetric mixed-valence compound is given by eqn. (1), where  $E_{op}$  is the energy of the optical transition maximum. At room temperature, eqn. (1) yields eqn. (2)

$$\Delta\nu_{1/2} = [16(\ln 2)K_B T E_{op}]^{1/2} \quad (1)$$

$$\Delta\nu_{1/2} = [2310E_{op}]^{1/2} \quad (2)$$

Thus, the IT bands of **9–14** are about 6% sharper than that estimated on the basis of eqn. (2) ( $\Delta\nu_{1/2} = ca. 3080 \text{ cm}^{-1}$  compared with a calculated value of  $3278 \text{ cm}^{-1}$ ). Agreement to within about 10% for the  $\Delta\nu_{1/2}$  (calc) and the  $\Delta\nu_{1/2}$  (obs) values is usually taken as an indication that the Hush model is a satisfactory description of a mixed-valence system.

As shown in Table 2, the magnitude of the delocalization can be obtained by a calculation of the delocalization parameter  $\alpha^2$  and electronic coupling  $H_{ab}$  from eqns. (3) and (4):

$$\alpha^2 = \{4.24 \times 10^{-4} \epsilon_{\max} (\Delta\nu_{1/2})\} / \{\nu_{\max} d^2\} \quad (3)$$

$$H_{ab} = \nu_{\max} \alpha \quad (4)$$

In eqns. (3) and (4) the  $\epsilon_{\max}$  is the extinction coefficient,  $d$  is the donor-acceptor distance,  $\Delta\nu_{1/2}$  is the bandwidth at half-height, and  $\nu_{\max}$  is the frequency. The average Fe-Fe distance (5.1 Å) in **6** [9], **7** [7], **9** [11], and **12** [11] is taken as the donor-acceptor distance.

Finally, the thermal electron-transfer barrier,  $\Delta G^*$ , for compounds **9–14** can be estimated using eqn. (5). The rate constant ( $k_{et}$ ) of intramolecular electron transfer in **9–14**

$$\Delta G^* = E_{op}/4 \quad (5)$$

can be calculated from eqn. (6), where  $\nu_{et}$  is the hopping frequency. Furthermore, our system

$$k_{et} = \nu_{et} \exp(-\nu_{\max}/4K_B T) \quad (6)$$

$$\nu_{et} = (2\pi/\hbar) H_{ab}^2 (\pi/K_B T \nu_{\max})^{1/2}$$

should be considered as adiabatic [3], since

$$4.6 \times 10^{-3} H_{ab} (\nu_{\max})^{-1/2} (\text{in cm}^{-1}) > 1$$

## 4. Conclusions

Mössbauer spectra indicating the presence of both delocalized and localized species have been observed for a microcrystalline sample of **14**. In the case of a recrystallized sample of **14**, only the localized species has been observed below 240 K. Above 250 K, the delocalized species can be observed.

The energy and the line-shape of the IT band clearly indicate that the intramolecular electron-transfer rates in each of **9–14** in solution are greater than in the solid state. In solid state, we have demonstrated [11] that relatively minor perturbations caused by interactions with neighbouring cations and anions in **9–14** experiencing weak or moderate electronic coupling between two Fe centres have pronounced effects on the electronic structure and rate of intramolecular electron transfer. We suggested [11] that the position of the  $I_3^-$  anion exerts a dramatic influence on the rates of electron transfer. In solution, the manner in which the mixed-valence cation is solvated also influences the rate of intramolecular electron transfer. If ion pairing is present, the anion must move rapidly so as not to limit the rate of intramolecular electron transfer. For **9–14** in solution, we believe that the solvent molecules solvating the cation can adjust rapidly so that the electron transfer rate is not limited.

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