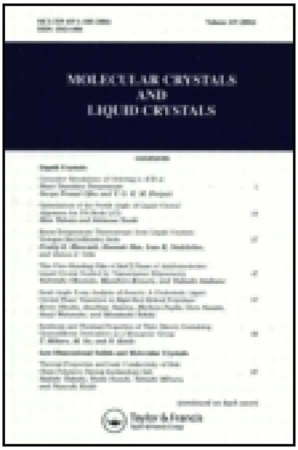

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Valence-delocalization in F_4TCNQ Salts of Biferrocenes

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Variable-temperature Mössbauer spectra were measured for biferrocenium$^+$ $F_4TCNQ^{\cdot-}$ (**2**) and 1',1'''-diethylbiferrocenium$^+$$F_4TCNQ^{\cdot-}$ (**3**) in order to elucidate their mixed-valence states, where F_4TCNQ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane. A valence-delocalization between Fe(II) and Fe(III) sites on elevating the temperature was observed for **2**; The Mössbauer spectra of **2** below 298 K consisted of two quadrupole doubets corresponding to the Fe(II) and Fe(III) atoms in **2**, and the spectrum at 320 K consisted of only one quadrupole doublet showing a single valence state of iron averaged over Fe(II) and Fe(III). On the other hand, compound **3** showed trapped-valence type spectra in the whole temperature range of 4.2 – 320 K.

Keywords: Mixed-valence compounds; Valence-delocalization

INTRODUCTION

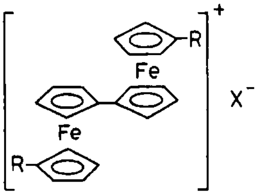
Mixed-valency is known to frequently play important roles in electro- and photochemical reactions of polynuclear metal complexes, biological electron transfer processes, and semi- and superconductors, etc[1]. A number of monocation salts of binuclear ferrocenes having formally two kinds of iron atoms, Fe(II) and Fe(III), have been studied in this research field, because of the wide variety of derivatives and their suitability for ^{57}Fe Mössbauer spectroscopy[1]. The most remarkable feature of the mixed-valence state of this system is the valence-delocalization phenomenon with the elevation of temperature[1,2]. For example, the I_3^- salt of unsubstituted biferrocene, biferrocenium$^+I_3^-$ (**1**) gives Mössbauer spectra consisting of two quadrupole doublets below ~350 K, and those consisting of single quadrupole doublet above this temperature[3], which indicates a transition from a trapped- or localized-valence state of iron atoms (Fe(II) and Fe(III)) to a state of iron averaged over Fe(II) and Fe(III) (averaged- or delocalized-valence state). The critical temperature of the transition (T_c) is known to be affected by the kind of the counter anion as well as the kind of the substituents at the cyclopentadienyl rings. However, most of the counter anions so far employed are simple inorganic anions. From the interest in the combination of binuclear-ferrocene monocations and the anion radicals of planar π-electron acceptors, we have prepared biferrocenium$^+F_4TCNQ^{\dot{-}}$ (**2**) and 1',1'''-diethylbiferrocenium$^+$ $F_4TCNQ^{\dot{-}}$ (**3**), and have investigated their mixed-valence states, where F_4TCNQ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane. The chemical structures of the compounds mentioned in this paper, including compounds **2** and **3**, are shown in Table 1 along with the T_c data.

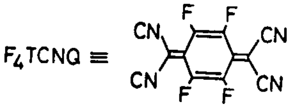
EXPERIMENTAL

Compounds **2** was prepared by the reaction of biferrocene with an equivalent amount of F_4TCNQ in a dichloromethane/acetonitrile mixture. Anal. Found: C, 59.07; H, 2.89; N, 8.54 %. Calcd for $C_{32}H_{18}N_4F_4Fe_2$: C, 59.48; H, 2.81; N, 8.67 %. Compound **3** was prepared similarly by using 1',1'''-diethylbiferrocene in place of biferrocene. Found: C,60.99; H, 3.90; N, 8.05 %. Calcd for $C_{36}H_{26}N_4F_4Fe_2$: C, 61.57; H, 3.73; N, 7.98 %. Mössbauer spectra were measured with an instrument described previously[7]. The isomer shifts are reported relative to metallic iron foil.

TABLE 1 Compounds and the critical temperatures of valence-delocalization (T_c).

Compd	R	X^-	T_c / K	Ref.
1	H	I_3^-	~350	3
2	H	$F_4TCNQ^{\dot{-}}$	~300	This work
3	C_2H_5	$F_4TCNQ^{\dot{-}}$	>320	This work
4	C_2H_5	$(TCNQ)_6^{\dot{-}}$	< 78	5
5	C_3H_7	$(TCNQ)_2^{\dot{-}}$	< 4.2	2
6	C_5H_{11}	$(TCNQ)_3^{\dot{-}}$	~90	6
7	C_2H_5	I_3^-	~270	2





RESULTS AND DISCUSSION

The Mössbauer measurements of **2** were carried out at seven different temperatures between 10 and 320 K. As can be seen in Figures 1 and 2, the Mössbauer spectral shape of **2** greatly depended upon the temperature of the measurement. The spectrum at 10 K consisted of inner and outer doublets in a nearly 1:1 ratio (Figure 1); these doublets are ascribed to the ferrocenium-like tervalent iron and ferrocene-like bivalent iron[1,2] in **2** respectively. This spectrum is of typical trapped-valence type. With the increase of temperature, however, the quadrupole splitting (ΔE_Q) of the inner doublet increased, and that of outer doublet decreased gradually. Eventually, at 320 K, compound **2** showed a typical averaged-valence spectrum which consisted of a single quadrupole doublet (Figure 2). The above spectral behavior evidenced that a valence-delocalization between the Fe(II) and Fe(III) sites occurred in **2** on the elevation of temperature.

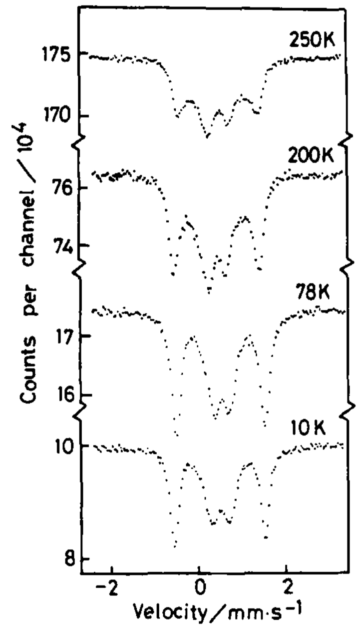


FIGURE 1 Mössbauer spectra of **2** between 10 and 250 K.

As for **3**, Mössbauer spectra were measured at 4.2, 78, 200, 298 and 320 K. Selected spectra of **3** are shown in Figure 3. The spectrum at each temperature consisted of two quadrupole doublets corresponding to ferrocenium-like and ferrocene-like iron atoms, while small changes of ΔE_Q with temperature were observed for the two kinds of iron atoms. That is, compound **3** exhibited trapped-valence type spectra in the whole temperature range. The temperature-dependences of the ΔE_Q values of **2** and **3** are shown in Figure 4, which clearly indicates the effect of the ring substitution on the T_c value of the biferrocenium-monocation/$\text{F}_4\text{TCNQ}^{\dot{-}}$ system (the T_c of **3**>320 K).

While the Fe(III)/Fe(II) area intensity ratio in the Mössbauer spectrum of **2** was estimated to be almost 1.0 for **2** at each temperature below T_c, the intensity ratio for **3** was found to change appreciably from 1.0 on elevating the temperature (1.8 at 320 K). This means that the Fe(II) and Fe(III) atoms in **3**, compared with the case of **2**, have fairly different lattice-dynamical environments in the crystal lattice[8]; such non-equivalent environments of Fe(II) and Fe(III) atoms would be unfavorable for producing the valence-delocalized state[9].

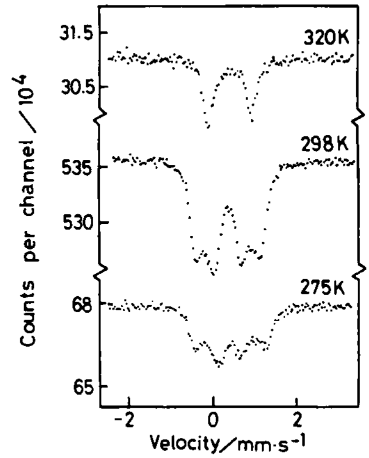


FIGURE 2 Mössbauer spectra of **2** between 275 and 320 K.

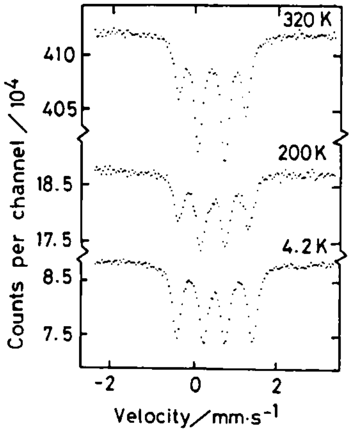


FIGURE 3 Selected Mössbauer spectra of **3**.

Variable-temperature Mössbauer spectra are reported for several TCNQ^- salts of dialkyl-biferocenium monocations [2,4-6]. As shown in Table 1 for the cases of R = C_2H_5 (**4**), C_3H_5 (**5**) and C_5H_7 (**6**), the T_c values of these TCNQ^- salts are generally fairly low; the highest value has been reported for **6** to be ~90 K[7]. The large difference in the valence-localization/delocalization behavior between **3** (T_c > 320 K) and **4** (T_c < 78 K) seems striking from the view point of the similarity of chemical structure between $\mathrm{F_4TCNQ}^{\dot{-}}$ and $\mathrm{TCNQ}^{\dot{-}}$. On the other hand, it should be noted that compound **3** is a "simple salt" and the dialkylbiferrocene-monocation/$\mathrm{TCNQ}^{\dot{-}}$ salts like compounds **4-6** are "complex salts" having a $(\mathrm{TCNQ})_n^{\dot{-}}$ anion unit (n = 2~6). It is well known that the "simple salts" of TCNQ (or a member of TCNQ family) favor an alternate stack of the cation and TCNQ molecules and the "complex salts" favor separate (segregated) cation and TCNQ stacks[10]. There is the possibility that the crystal structure of **3** is essentially different from that of **4**. In comparison with the corresponding I_3^- salt (**1**), compound **2** exhibited about 50 K lower

T_c. On the other hand, the T_c of **3** was at least 50 K higher than that of the I_3^- salt of 1',1'''-diethylbiferrocenium monocation (**7**)[2].

The above Mössbauer spectroscopic results demonstrate that the T_c of the valence-localization/delocalization transition in biferrocene-derivative monocation salts is quite sensitive to subtle variations of the chemical structure of the counter anion as well as the monocation part, while X-ray analysis data will be necessary for discussing the different T_c values in further detail. The relationship between electronic conductivity and the mixed-valence state[4] is currently under investigation for **2** and **3**.

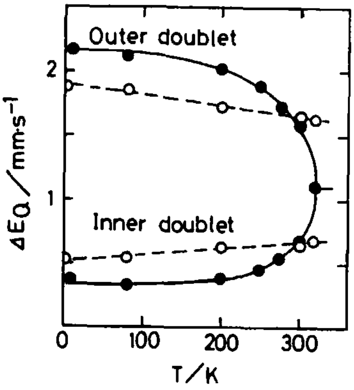


FIGURE 4 Temperature-dependences of quadrupole splittings of **2** (●) and **3** (○).

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