Division of the Effects of Cation Symmetry and Its Packing on the Mixed-Valence State of 1′,1‴-Bis(2-methylbutyl)-1,1″-biferrocenium Triiodide Having Asymmetric Carbon in the Substituent

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The effects of the cation symmetry and packing on the mixed-valence state of binuclear ferrocene derivatives are discussed separately by paying attention on the differences between the racemic and (*S*,*S*) samples and between the salts from hexane and from dichloromethane in 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide having asymmetric carbon. An (*R*,*S*) isomer can sit on the center of symmetry, while (*S*,*S*) and (*R*,*R*) isomers cannot. Such a difference plays an important role on the mixed-valence state in the samples from dichloromethane but not in the samples from hexane. Both the racemic and (*S*,*S*) salts in the disordered state showed the same temperature-dependent mixed-valence state. The disordered state of racemic and (*S*,*S*) salts from hexane changed to the ordered state by recrystallization from dichloromethane. The ordered state for (*S*,*S*) salts showed a typical temperature-independent trapped-valence state. The packing effect in the present salts appears different from that of the derivatives with long alkyl chain. (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide ($Fe_2C_{30}H_{38}I_3$) crystallized in a triclinic system with space group *P*1 and unit cell parameters $a = 10.242(1)$ Å, $b = 13.380(2)$ Å, $c = 13.797(1)$ Å, $\alpha = 109.358(6)°$, $\beta = 93.015(6)°$, $\gamma = 113.214(4)°$, and $Z = 4$. The ordered racemic sample changed to the disordered state in the solid state at room temperature as time proceeded, while the ordered (*S*,*S*) sample changed to the disordered state by annealing at high temperature, which were followed by the change of mixed-valence state.

1. Introduction

The nature of electron transfer between well-separated metal sites in the mixed-valence binuclear ferrocene derivatives has been discussed in connection with studies of superconductive materials and biological systems.[1,2] The important role of the cation symmetry and its packing effect in the mixed-valence state has been shown.[2−4] Study on the mixed-valence state of binuclear ferrocene derivatives is still expanding.[5,6] There is a problem, however, in the understanding of the steric effect; i.e., it is difficult to separate the contribution of the symmetry of the cation from that of the packing effect in the crystal. In many cases, the symmetry of the cation depends on the crystal structure; e.g., 1′,1‴-dipropyl-1,1″-biferrocenium triiodide shows the valence detrapping with increasing temperature, which is accompanied by both the changes of crystal structure and the symmetry of cation.[7] We have studied the polymorphism and its mixed-valence state for 1′,1‴-dibutyl-1,1″-biferrocenium triiodide[4b,e] and found that the mixed-valence state is strongly affected by the crystal structure. The valence detrapping is also affected by the crystallinity.[4a] The question is, which is more adequate between the effect of the cationic symmetry and the packing effect? Is there a balance between the two contributions (the effect of the cationic symmetry and the packing effect) on the valence detrapping? Is it possible to detrap all kinds of mixed-valence binuclear ferrocene derivatives by controlling the crystal structure? Is the symmetry of mixed-valence cation still important to detrap the mixed-valence state? One of the ways to control the packing is the use of the substituent's conformation change by changing the crystallizing solvent. The important role of order−disorder transition is suggested on the valence-

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detrapping of the mixed-valence state of binuclear ferrocene derivatives.[8] We pay attention here to the ordered and disordered states of the rotational conformations of the substituent. We believe that the ordered and disordered Fe^{II}-Fe^{III} states are concerned with their rotational conformations.

In the present study, we used the binuclear ferrocene derivatives with asymmetric carbons in the substituent to consider the effect of the cationic symmetry and the packing effect separately on the mixed-valence state. The differences between the racemic and (*S*,*S*) samples and between the salts from hexane and from dichloromethane are discussed for 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide in order to reveal the effect of the cationic symmetry and the packing effect independently. We also controlled the ordered and disordered states by annealing the sample at high temperature and allowed the mixed-valence state to change in order to reveal the difference between the racemic and (*S*,*S*) salts.

2. Experimental Section

2.1. Syntheses. 1′,1‴-Bis(2-methylbutyl)-1,1″-biferrocenes were synthesized according to the method reported for a series of biferrocenes disubstituted with alkyl substituents.[6] In the acylation, DL-2-methylbutyryl chloride or (*S*)-(+)-2-methylbutyric anhydride was used. The products were isolated by column chromatography on alumina and purified by recrystallization from dichloromethane−hexane. Found for racemic 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocene: C, 70.38; H, 7.83. Mp 55.2−56.0 °C. ^{1}H NMR(δ/ppm, $CDCl_3$) 4.23 (4H), 4.10 (4H), 3.87 (4H), 3.81 (4H) (Fc), 2.02 (4H), 1.26 (4H), 1.01 (2H), 0.80 (6H), 0.73 (6H) (alkyl). Calcd for $C_{30}H_{38}Fe_2$: C, 70.65; H, 7.51. Found for (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocene: C, 70.38; H, 7.91. Mp 56.1−56.9 °C. ^{1}H NMR(δ/ppm, $CDCl_3$) 4.25 (4H), 4.12 (4H), 3.88 (4H), 3.83 (4H) (Fc), 2.03 (4H), 1.24 (4H), 1.01 (2H), 0.80 (6H), 0.72 (6H) (alkyl). Calcd for $C_{30}H_{38}Fe_2$: C, 70.65; H, 7.51. The racemic and (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodides were prepared by adding a stoichiometric amount of I_2 dissolved in hexane to a hexane solution of the corresponding 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenes. About one-half of the sample prepared in the above manner was recrystallized from a dichloromethane solution. Found for racemic 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from hexane: C, 40.57; H, 4.57; mp 114.6−115.7 °C. From dichloromethane: C, 40.43; H, 4.30; mp 113.5−115.9 °C. Calcd for $C_{30}H_{38}Fe_2I_3$: C, 40.45; H, 4.27. Found for (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from hexane: C, 40.49; H, 4.37; mp 113.8−117.2 °C. From dichloromethane: C, 40.40; H, 4.31; mp 114.6−117.8 °C. Calcd for $C_{30}H_{38}Fe_2I_3$: C, 40.45; H, 4.27.

2.2. ^{57}Fe Mössbauer Spectroscopic Measurements. A ^{57}Co(Rh) source moving in a constant-acceleration mode was used for ^{57}Fe Mössbauer spectroscopic measurements. Variable-temperature ^{57}Fe Mössbauer spectra were obtained by using a Toyo Research spectrometer and a continuous-flow cryostat or handmade high-temperature apparatus. The Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shift values are referred to metallic iron.

2.3. X-ray Crystallography. All powder X-ray diffraction patterns were measured by using graphite-monochromated Cu Kα radiation (Rigaku) at room temperature.

Single crystals for X-ray crystallography of (*S*,*S*)-bis-1′,1‴-(2-methylbutyl)-1,1″-biferrocenium triiodide were obtained by the following method. The salt was dissolved in dichloromethane solution and then it was put in the hexane atmosphere at 0 °C. After several days well-formed single crystals were obtained. (*S*,*S*)-1′,1‴-Bis(2-methylbutyl)-1,1″-biferrocenium triiodide ($Fe_2C_{30}H_{38}I_3$) crystallized in the triclinic system with space group $P1$ and unit cell parameters a = 10.242(1) Å, b = 13.380(2) Å, c = 13.797(1) Å, α = 109.358(6)°, β = 93.015(6)°, γ = 113.214(4)°, V = 3204.8(3) Å^3, and Z = 4. The X-ray data were collected at a temperature of 25 ± 1 °C using the $\theta/2\theta$ scan technique to a maximum 2θ value of 58.16° on a Mac Science MXC18 diffractometer equipped with a graphite monochromator. The initial structure was solved by a direct method and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares method. Hydrogen atoms were fixed at the calculated positions; these coordinates were included in the refinement with isotropic thermal parameters. The refinement based on 5278 observed reflections ($F_o > 2.0\sigma(F_o)$) converged to the R (R_w) factor of 7.2% (8.6%).

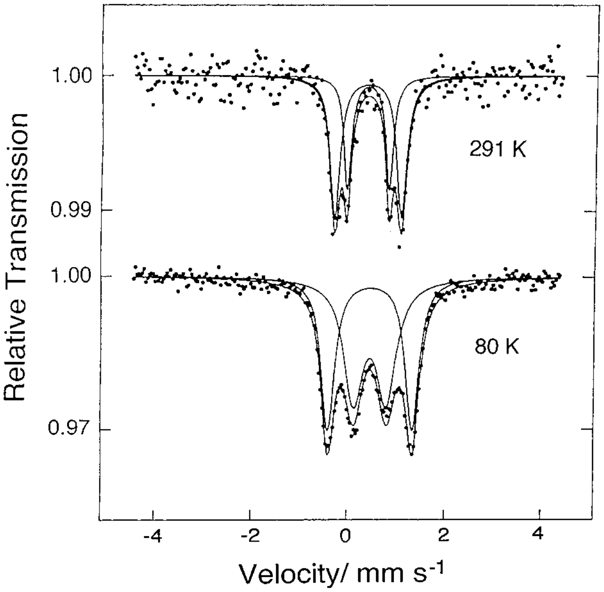

Figure 1. ^{57}Fe Mössbauer spectra of (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from hexane at room temperature and 80 K.

3. Results and Discussion

We refer to the binuclear ferrocene derivatives synthesized from DL-2-methylbutyryl chloride and (*S*)-(+)-2-methylbutyric anhydride for the acylation as racemic and (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocene, respectively.

The ^{57}Fe Mössbauer spectra of racemic and (*S*,*S*) samples for 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocene showed a typical ferrocene-like doublet. The parameters are similar to each other and to those of a series of 1′,1‴-dialkyl-1,1″-biferrocenes.[6] There is no difference among a series of neutral 1′,1‴-dialkyl-1,1″-biferrocenes, while there is a diversity of mixed-valence states in their monooxidized salts as will be shown below.

The ^{57}Fe Mössbauer spectra of (*S*,*S*) samples for 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from hexane and dichloromethane at 80 and 291 K are shown in Figures 1 and 2, respectively. Ferrocene- and ferrocenium-like doublets are observed independently at all temperatures in the samples from both hexane and dichloromethane. But it can be seen that the quadrupole splitting doublet (ΔE_q) values are different between the salts from hexane and dichloromethane. The ΔE_q values for the sample from hexane approach to each other with increasing temperature, while the values from dichloromethane do not show the significant temperature dependence. The ΔE_q values for the former are closer to each other than those for the latter even at 80 K.

This finding is interesting because the closer state in which the close two doublets observed for the sample from hexane changes to the apparently different state by recrystallizing it from dichloromethane, showing a big contrast with the derivatives having long alkyl chains in the substituent.[6d,e] The derivatives with even-numbered carbon atoms in the long alkyl chains show a change of mixed-valence state by recrystallization

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[8] Masuda, Y.; Sano, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2674.

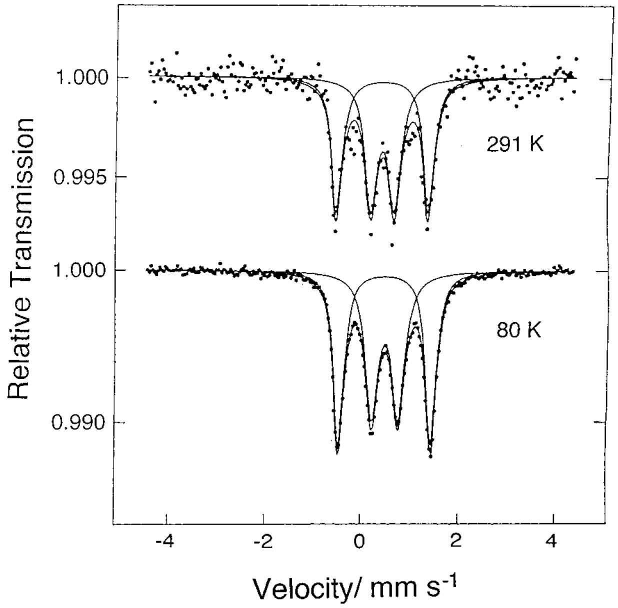

Figure 2. ^{57}Fe Mössbauer spectra of (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from dichloromethane at room temperature and 80 K.

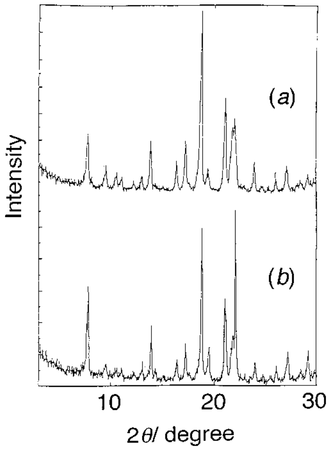

Figure 3. Powder X-ray diffraction patterns at room temperature of (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from (a) hexane and (b) dichloromethane.

from dichloromethane. The crystals from dichloromethane show the valence detrapping with increasing temperature, while the crystals from hexane show the typical temperature-independent trapped-valence state. This typical temperature-independent trapped-valence state is the same as the present salt from dichloromethane. The Fe^{II} and Fe^{III} states in the mixed-valence state become closer by recrystallization from dichloromethane for the salts with long alkyl chain. For the long alkyl derivatives the change in the valence state is followed by a big change in the powder X-ray diffraction pattern; i.e., this reveals a change of interlayer distance in the layered structure. But in the present case, there is not a significant difference in the powder X-ray diffraction pattern between the samples from hexane and dichloromethane as is shown in Figure 3. The positions of the reflections are the same to each other. The only difference is the sharpness of the reflections. The diffraction for the salt from dichloromethane is sharper than that from hexane. The difference reflects the crystallinity; i.e., the packing effect. This finding indicates that the crystallinity of the salt from dichloromethane is better than that from hexane. It is thought that the difference in the crystallinity reflects the difference in the conformation of the substituent. The sample from hexane can have a several rotational isomers in the crystal because of quick precipitation. The rotational isomers may be disordered in the crystal. But the sample from dichloromethane has the most stable isomer because of slow recrystallization. They can be ordered in the crystal. Therefore, we thought that the crystallinity of the sample from dichloromethane is better than that from hexane in the present case, while the salts with long alkyl chain show a big change of crystal structure between the salts from hexane and dichloromethane. The ΔE_q values of the mixed-valence binuclear ferrocene derivatives are easily influenced by making the mixed crystals.[4d] We believe that the fact that the salts from hexane show the approaching doublet in the present study has a close connection with mixed crystals experiment.

The stereoscopic views of the (*S*,*S*) sample recrystallized from dichloromethane in the hexane atmosphere are shown in Figure 4. The crystal data are listed in Table 1. There are two independent cations and anions in the unit cell. The mean Fe−C(cyclopentadienyl ring (Cp ring)) distance becomes a diagnosis for the valence state of the ferrocene; i.e., the value for ferrocene is 2.045 Å,[9] and the value for ferrocenium cation is 2.075 Å.[10] The mean Fe−C(Cp) distances are 2.039(4) and 2.075(4) Å in one cation and 2.035(4) and 2.053(4) Å in the other cation, showing that the two irons in each cation are different from each other. This reveals that Fe(1) and Fe(3) are divalent and Fe(2) and Fe(4) are trivalent. These results are consistent with the ^{57}Fe Mössbauer spectrum at room temperature. The I−I−I angles for anions A and B are 177.9(1)° and 178.5(5)°, respectively, showing that they are almost linear. The I−I distances are 2.927(3) and 2.850(3) Å in anion A and 2.942(12) and 2.837(16) Å in anion B. The triiodide anion is considered to consist of I_2 and I^- and, therefore, the anion is unsymmetrical. We think that the trapped-valence state of the cation is connected with the unsymmetrical anion. It was difficult to determine the proton in the two positions of the asymmetric carbons, therefore it was difficult to judge that they are the *S* isomers.

Variable-temperature ^{57}Fe Mössbauer spectra of racemic sample from hexane are shown in Figure 5. Although the temperature dependence of the mixed-valence state can be seen, ferrocene- and ferrocenium-like doublets are observed independently at all temperatures. The ΔE_q values are 1.83 and 0.66 mm s^{-1} at 80 K and 1.39 and 0.90 mm s^{-1} at 293 K. These values are similar to those for the (*S*,*S*) sample from hexane at 80 and 291 K but not to those for the (*S*,*S*) sample from dichloromethane. It is interesting because the significant difference is not observed between the racemic and (*S*,*S*) samples from hexane. This suggests the similarity in the packing state between the (*S*,*S*) and racemic samples. Both the positions and half widths in the powder X-ray diffraction patterns are very similar to each other as will be shown later in Figure 8. This similarity may be due to the disorder of the rotational conformers of the substituents. When the rotational conformers are disordered, the difference between the (*S*,*S*) and racemic samples will not be striking. The temperature dependence of ΔE_q values is shown in Figure 6. Although the quadrupole splitting values are approaching at room temperature, the two doublets never fuse into one doublet with increasing temperature. An interesting point is that the approaching occurs at lower temperatures and over 150 K the ΔE_q values are almost constant. The DTA measurement did not show the thermal anomaly in this temperature region. Another interesting point is that the two doublets have a trend to depart slightly over room temperature. One may expect that all kinds of the mixed-valence compounds show the valence detrapping at higher temperatures. But this

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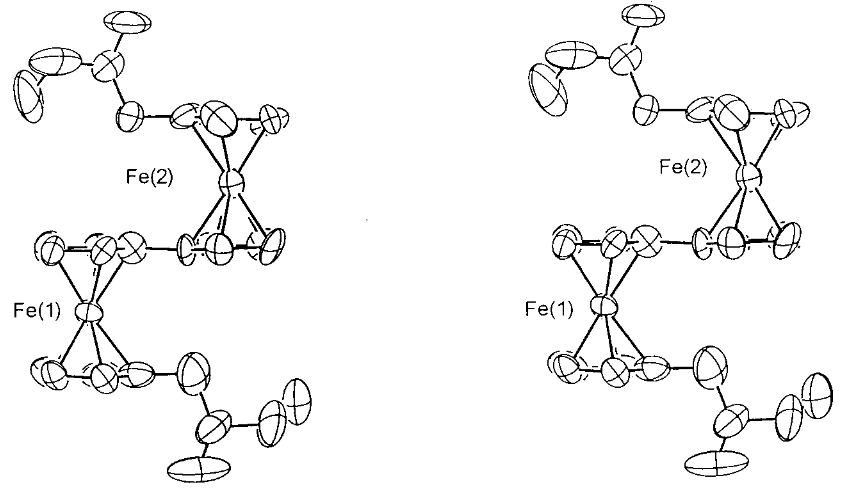
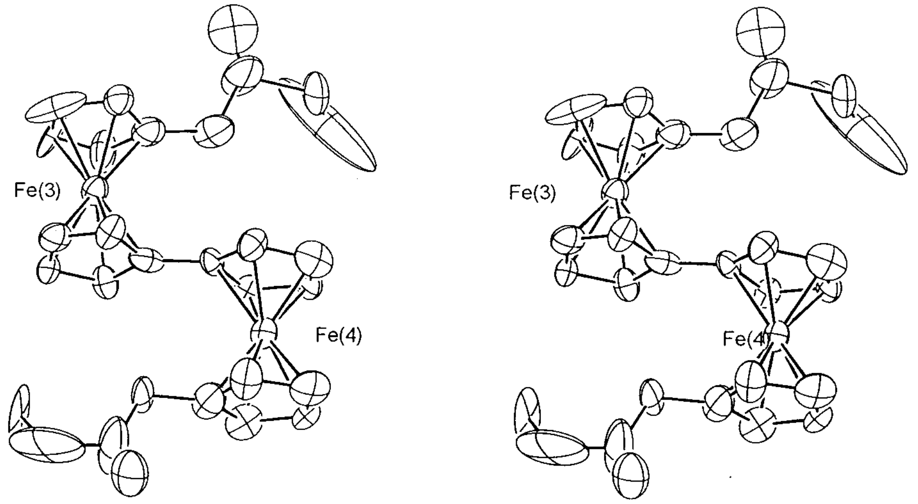
[9] Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B.* **1978**, *35*, 1068.

[10] Mammano, N. J.; Zalkin, A.; Landers, A.; Rheingold, A. L. *Inorg. Chem.* **1977**, *16*, 297.



Cation A



Cation B

Figure 4. Stereoscopic views of cation for (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from dichloromethane. There are two independent cations (cations A and B). The thermal ellipsoids are drawn at 50% probability level.

Table 1. Crystallographic Data for (*S*,*S*)-Bis(2-methylbutyl)-1,1″-biferrocenium Triiodide from Dichloromethane

empirical formula	$Fe_2I_3C_{30}H_{38}$
fw	891.04
space group	$P1$
a/Å	10.242(1)
b/Å	13.380(2)
c/Å	13.797(1)
α/deg	109.358(6)
β/deg	93.015(6)
γ/deg	113.214(4)
V/Å^3	3204.8(3)
Z	4
T/K	298
λ/Å	0.71073
ρ_{calcd}/g cm^{-3}	1.846
μ(Mo Kα)/mm^{-1}	38.34
R^a	0.072 ($F_o > 2.0\sigma(F_o)$)
$R_w{}^b$	0.086

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

trend reveals that the present salt does not show the perfect valence detrapping. This suggests the important role of the structure of cation on the mixed-valence state. This also suggests that the salts are divided into two groups: one shows valence detrapping and the other does not. It was suggested that the order−disorder transition is important to the valence detrapping of binuclear ferrocene derivatives.[8] The present results reveal that the disordered state is not the satisfactory condition for the perfect valence detrapping. In the present case, the salts are considered to be disordered from the results of powder X-ray diffraction patterns as will be shown later in Figure 8. Why does the present salt not show the perfect valence detrapping? One of the possibilities is that the (*S*,*S*) and (*R*,*R*) isomers in the salts never have a center of symmetry.

Figure 7 shows the ^{57}Fe Mössbauer spectra of the racemic samples at room temperature. The samples were recrystallized under the several conditions described in Figure 7. It can easily be seen that the spectra depend on the recrystallization condition. When the recrystallization is slow, the coexistence of the typical trapped-valence state (first and second doublet) and the detrapped-valence state (third doublet) is observed. It is difficult, however, to judge that the third doublet is due to a detrapped-valence state. Another possibility is that the third doublet might

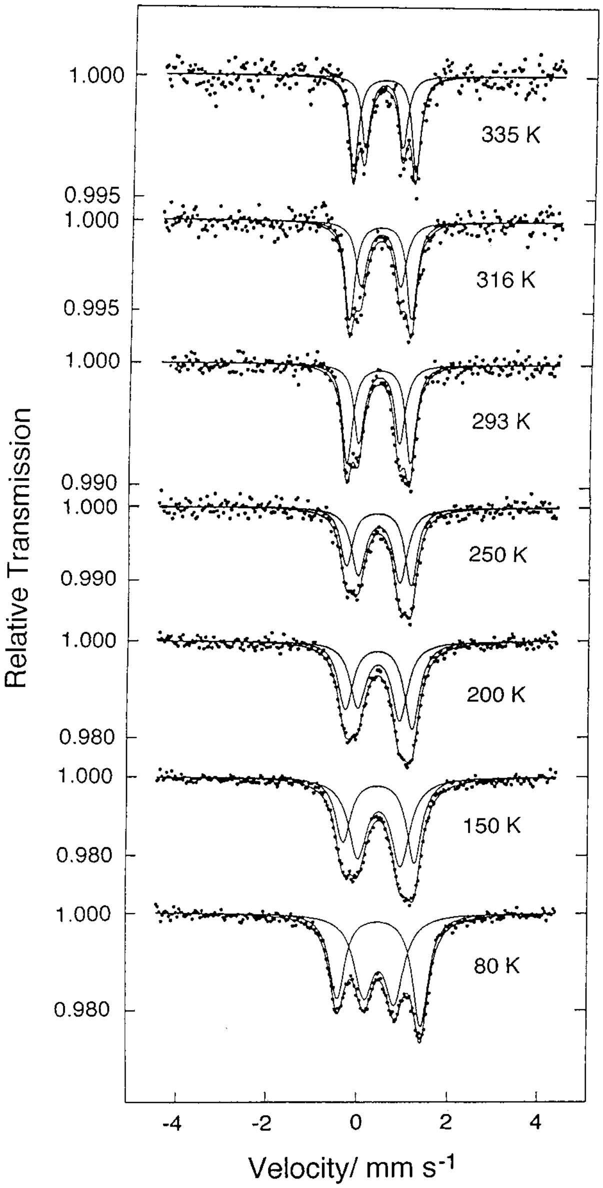


Figure 5. Variable-temperature ^{57}Fe Mössbauer spectra of racemic 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from hexane.

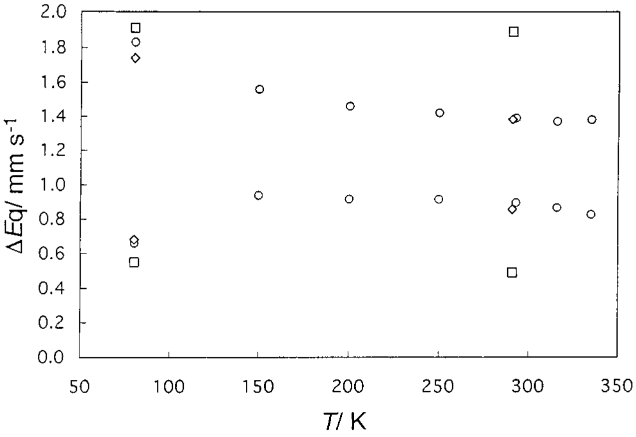


Figure 6. Temperature dependence of quadrupole splitting values (ΔE_q) for the racemic compound from hexane (○), the (*S*,*S*) compound from hexane (◇), and the (*S*,*S*) compound from dichloromethane (□) in 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide.

be divided into two closer doublets such as those in the salt from hexane shown in Figure 5. The first and second doublets

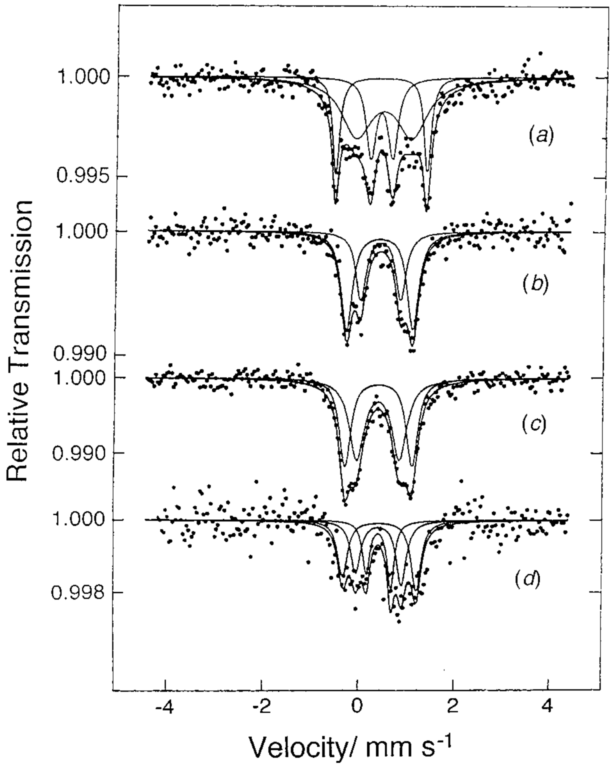


Figure 7. ^{57}Fe Mössbauer spectra of racemic 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from dichloromethane at room temperature: (a) first measurement; (b) 4 months later from (a); (c) recrystallized for a few days; (d) recrystallized for 1 week.

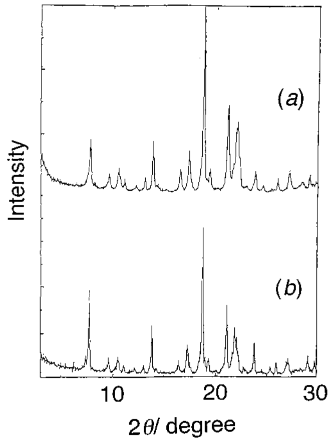


Figure 8. Powder X-ray diffraction patterns at room temperature of racemic 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from (a) hexane and (b) dichloromethane.

in this sample are similar to those of the (*S*,*S*) sample from dichloromethane shown in Figure 2. When the recrystallization is fast, the two doublets are closer and are similar to those from hexane. Such a change in the spectrum was not observed in the recrystallization of (*S*,*S*) sample.

The difference between the racemic and (*S*,*S*) samples from dichloromethane was also observed in the time dependence of the mixed-valence state. The mixed-valence state of the (*S*,*S*) sample obtained from dichloromethane was unchanged with the passage of time, but that of the racemic sample changed at room temperature. Three doublets observed in the racemic sample from dichloromethane changed during 4 months at room temperature to two closer doublets as is shown in Figure 7, whose Mössbauer parameters are equal to those of the sample from hexane. This finding shows that the state in the racemic sample obtained by slow recrystallization from dichloromethane changed to the new state similar to that from hexane. Such a change in the solid state has been observed in 1′,1‴-bis(α-naphthylmethyl)-1,1″-biferrocenium triiodide.[11] In that case the coexistence of the trapped- and detrapped-valence states changed to the presence of only the detrapped-valence state, indicating that in the α-naphthylmethyl derivative the stable state is the detrapped-valence state. However, in the present case, the stable state is a trapped-valence state. What is the difference between the two? One of factors is a center of symmetry in the salt.

Powder X-ray diffraction patterns for the racemic salts both from hexane and dichloromethane are shown in Figure 8. The powder X-ray diffraction patterns are similar to each other, and they are similar to the patterns for the (*S*,*S*) samples. The only difference between the racemic salts from hexane and dichloromethane is the sharpness of the diffractions.

The difference between the racemic and (*S*,*S*) samples from dichloromethane is observed in the effect of the symmetry of the cation. The present results can be explained by the difference in the structure of the cation. The racemic sample consists of (*R*,*R*), (*S*,*S*), and (*R*,*S*) isomers. The *S* isomer can be moved to the *R* isomer by the center of symmetry. Therefore, the (*R*,*S*) cation can sit on the center of symmetry. But the (*S*,*S*) and (*R*,*R*) cations cannot sit on the center of symmetry. In the (*S*,*S*) sample, which cannot sit on the center of symmetry, the most stable isomer crystallized from dichloromethane. In this case the unsymmetrical cation and anion order, and then the mixed-valence state is valence trapped. The ordered Fe^{II}-Fe^{III} state changes the mixed-valence state to a temperature-independent trapped state. In the disordered case from hexane, however, the environment around the cation becomes relatively similar statistically, therefore two doublets approach according to a packing effect. In the racemic sample, the (*S*,*S*), (*R*,*R*), and (*R*,*S*) isomers are ordered independently in the crystal by slow recrystallization. Only the (*R*,*S*) isomer shows valence detrapping while (*S*,*S*) and (*R*,*R*) isomers show the trapped-valence state. This explains the coexistence of the detrapped- and trapped-valence states in the racemic sample. When the third doublet observed above is divided into two doublets, the coexistence of the typical trapped-valence state and the approaching state is observed. When the racemic sample is left to stand at room temperature for several months, the isomers become disordered in the solid state and the mixed-valence state is changed. On the other hand, in the pure (*S*,*S*) sample from dichloromethane, the cation and anion are ordered and hardly become disordered at room temperature because of the more perfect crystal. But when the samples are left at high temperatures, they become disordered, as will be shown later. It is interesting that the coexistence of (*S*,*S*), (*R*,*R*), and (*R*,*S*) conformers assists the state to become disordered easily than the pure (*S*,*S*) sample.

To know whether the (*S*,*S*) sample from dichloromethane changes to the new state in the solid state or not, (*S*,*S*) sample from dichloromethane was annealed at 30, 40, 50, and 60 °C for 20 min, and then the powder X-ray diffraction patterns were measured at room temperature. The patterns are shown in Figure 9. It can be seen that these patterns were changed from that of the fresh sample. The patterns broadened slightly and are similar to those of the sample from hexane. The ^{57}Fe Mössbauer spectra at room temperature of (*S*,*S*) samples from dichloromethane are shown in Figure 10. It can be seen that the spectrum changed from a typical trapped-valence state to the closer doublets. The spectrum for the annealed sample is similar to that of the sample from hexane. This is the same change with time dependence observed at room temperature in the racemic sample. The difference between the racemic and (*S*,*S*) samples is the transition temperature, which is around room temperature for the racemic sample and higher for the (*S*,*S*) sample.

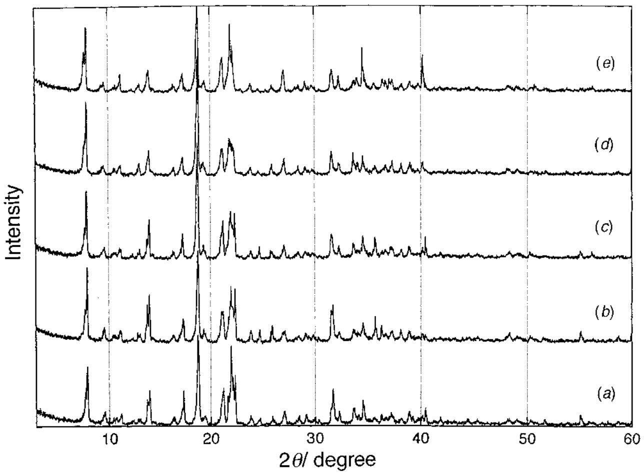


Figure 9. Powder X-ray diffraction patterns at room temperature of (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide annealed at several temperatures: (a) fresh sample obtained from dichloromethane at 0 °C; (b) sample of (a) annealed at 30 °C for 20 min; (c) sample of (b) annealed at 40 °C for 20 min; (d) sample of (c) annealed at 50 °C for 20 min; (e) sample of (d) annealed at 60 °C for 20 min.

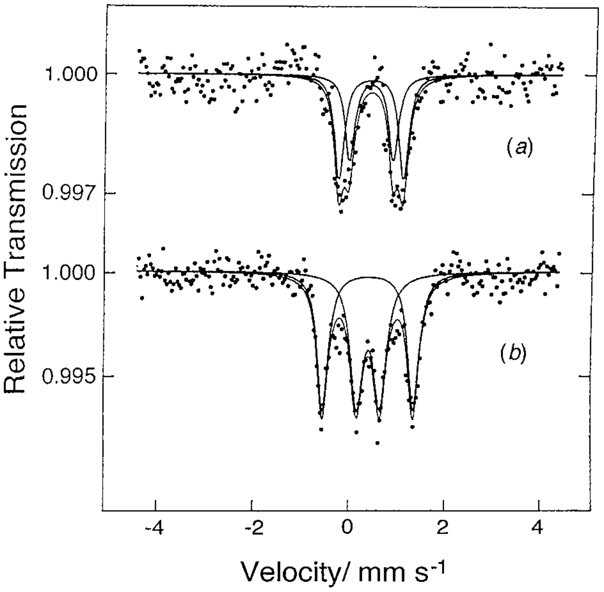


Figure 10. ^{57}Fe Mössbauer spectra at room temperature of (*S*,*S*)-1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from dichloromethane: (a) annealed sample; (b) fresh sample.

The importance of both the structure of cation and the packing effect in the mixed-valence states of binuclear ferrocene derivatives is obviously revealed in the present study independently. The packing effect supports the valence detrapping, but the perfect valence detrapping is dependent on the structure of cation.

Supporting Information Available: Tables listing ^{57}Fe Mössbauer parameters, detailed crystallographic data, positional parameters, anisotropic thermal parameters, and all intramolecular bond lengths and angles and a figure of the crystal structure showing the labeling of atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Nakashima, S.; Hori, A.; Sakai, H.; Watanabe, M.; Motoyama I. *J. Organomet. Chem.* **1997**, *542*, 271.