Mixed-Valence States of 1′,1‴-Bis(2-phenylbutyl)-1,1″-biferrocenium(1+) Triiodides: Effects of the Cation Symmetry and Counter Anion on the Electron-Transfer Rate

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The effects of cation symmetry and packing on the mixed-valence state of binuclear ferrocene derivatives are discussed by using chiral isomers and the racemic modification of 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium(1+) triiodide. Although the three chiral isomers showed trapped-valence states at 78 K, only the (*R*,*S*) isomer showed a perfect detrapped-valence state at room temperature in the three isomers. The racemic modification consisted of the (*R*,*R*) and the (*S*,*S*) isomers showed a perfect detrapped-valence state at room temperature. This shows that the packing effect overcomes the effect of cation asymmetry. The electron-transfer rate for each pentaiodide salt was faster than that of the corresponding triiodide salt. A comparison between the (*S*,*S*) triiodide and the (*S*,*S*) pentaiodide salts reveals an important packing effect. The polymeric pentaiodide skeleton forced the (*S*,*S*) cation to have pseudo-inversion center.

The nature of electron transfer between well-separated metal sites in mixed-valence compounds has been discussed in connection with studies of superconductive materials and biological systems.[1,2] ^{57}Fe Mössbauer spectroscopy and X-ray structural analysis had a great role on understanding the mixed-valence state of dinuclear and trinuclear iron complexes.[2–4] The study of mixed-valence state has expanded, especially by using mono-oxidized (mixed-valence) binuclear ferrocene derivatives, since binuclear ferrocenes have an advantage of ease for molecular design. Many studies have been made on the two determination factors of the mixed-valence state. One is a cation symmetry effect,[5] and the other is a packing effect.[6]

We revealed the relation between the effects of cation symmetry and packing by using optically active 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium(1+) pentaiodides.[7] Namely, the (*R*,*S*) isomer having an inversion center showed a perfect detrapped-valence state even at 78 K, while the (*R*,*R*) and the (*S*,*S*) isomers having no inversion center showed a trapped-valence state even at room temperature. The two doublets observed by ^{57}Fe Mössbauer spectra were very close to each other, which could be understood based on the symmetry of circumstances around the cation. In this situation, two questions arise: 1. Why does not the 2-fold axis contribute to valence detrapping? 2. Why are the two doublets so close? Concerning question 2, two speculations arise: (A) The (*R*,*R*) and the (*S*,*S*) cations are distorted from structure having a 2-fold axis due to centrosymmetric circumstances. (B) The centrosymmetric circumstances force the asymmetric (*R*,*R*) and (*S*,*S*) cations to a more symmetric structure. The former effect (A) decelerates the electron-transfer rate, while the latter effect (B) accelerates it. In order to answer the above two questions, and to know which is more effective between (A) and (B), a study of the corresponding triiodide salts will be essential.

In the present study, the mixed-valence states of 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium(1+) triiodides were investigated. We discuss the relation between the structure and the mixed-valence state from the same viewpoint in the corresponding pentaiodide salt. Moreover, the differences between 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium(1+) triiodides and their pentaiodides are discussed, and an anion structural effect on the mixed-valence state is also discussed.

Experimental

Preparations. 1′,1‴-Bis(2-phenylbutyl)-1,1″-biferrocenium(1+) triiodides were prepared by the following method. Each neutral derivative, 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocene, was prepared by the reported method.[7] Each isomer of 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocene was mono-oxidized by adding a stoichiometric amount (3/2 times) of I_2 to an acetone solution of the neutral derivative. The triiodide salts were recrystallized from an acetone solution under a hexane atmosphere at 0 °C. Black plate-shape crystals were obtained. Found for 1′,1‴-bis((*R*)-2-phenylbutyl)-1,1″-biferrocenium(1+) triiodide: C, 45.60; H, 3.91%. Found for 1′,1‴-bis((*S*)-2-phenylbutyl)-1,1″-biferrocenium(1+) triiodide: C, 46.19; H, 4.64%. Found for 1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocenim(1+) triiodide: C, 44.16; H, 4.14%. Calcd for $C_{40}H_{42}Fe_2I_3$: C, 47.33; H, 4.17%.

The racemic modification was prepared by using equimolar 1′,1‴-bis((*R*)-2-phenylbutyl)-1,1″-biferrocene and 1′,1‴-bis((*S*)-2-phenylbutyl)-1,1″-biferrocene in a one-electron oxidation process. The methods for oxidation and recrystallization were the same as in the case of other 1′,1‴-bis(2-phenylbutyl)-1,1″-bi-

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ferroceneium(1+) triiodides. Found for the racemic modification: C, 45.48; H, 3.94%. Calcd for $C_{40}H_{42}Fe_2I_3$: C, 47.33; H, 4.17%.

^{57}Fe Mössbauer Spectroscopic Measurements. A ^{57}Co(Rh) source moving in a constant-acceleration mode was used for ^{57}Fe Mössbauer spectroscopic measurements. ^{57}Fe Mössbauer spectra at 78 K and room temperature were obtained by using a Wissel spectrometer. The measurement condition, such as the distance from a source to the detector, was different between 78 K and room temperature. The ^{57}Fe Mössbauer parameters were obtained by a least-squares fitting to Lorentzian peaks. The isomer shift values are referred to metallic iron.

X-ray Crystal Structural Analyses. Single crystals for the X-ray crystallography of 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium(1+) triiodides were obtained by the following method. Each salt was dissolved in acetone, and was then put in a hexane atmosphere at 0 °C. After several days, single crystals for an X-ray structural analysis were obtained as black plate-shape crystals. The single crystal was selected so that the longest side was less than 0.5 mm. All measurements were made on Mac Science DIP 2030 imaging plate area detector using graphite-monochromated Mo-Kα radiation. The cell parameters and intensities for the reflection were estimated by a program package of MacDENZO.[8] The crystal structure of 1′,1‴-bis((*S*)-2-phenylbutyl)-1,1″-biferrocenium(1+) triiodide was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. All calculations were performed with the CrystalStructure crystallographic software packages of Rigaku and Molecular Structure Corporation.[9,10] Table 1 summarizes the crystallographic data and experimental details. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 215490.

Table 1. Details of Crystal Structure Determinations for 1′,1‴-Bis(2-phenylbutyl)-1,1″-biferrocenium(1+) Triiodides

	The (*S*,*S*) isomer	The racemic modification
Formula	$C_{40}H_{42}Fe_2I_3$	$C_{40}H_{42}Fe_2I_3$
Formula weight	1015.18	1015.18
Crystal appearance	Black plate	Black plate
Crystal size/mm	0.25 × 0.15 × 0.10	0.34 × 0.23 × 0.03
Crystal system	Monoclinic system	Monoclinic system
Space group	$P2_1$	—a)
T/K	293	293
a/Å	11.8380(3)	11.8330(4)
b/Å	10.9790(4)	10.9790(4)
c/Å	15.8610(5)	15.9140(6)
β/degree	109.246(2)	108.452(1)
V/Å^3	1946.23(10)	1961.2(1)
Z	2	2
ρ_{calcd}/g cm^{-3}	1.732	1.719
Number of reflections	4736	4880
Observed reflections[b]	3996	4227
R[c]	0.075	—a)
R_w[d]	0.069	—a)

a) Molecular structure was not obtained. b) $I > 3.00\sigma(I)$. c) $R = \Sigma||F_O| - |F_C||/\Sigma|F_O|$. d) $R_w = (\Sigma w(|F_O| - |F_C|)^2/\Sigma w|F_O|^2)^{1/2}$.

Powder X-ray Diffraction Patterns. Powder X-ray diffraction patterns were measured by using graphite-monochromated Cu-Kα radiation (RIGAKU) at room temperature.

Results and Discussion

It was very hard to obtain stoichiometric compounds of 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium(1+) triiodides. By using hexane as an oxidizing solvent, the triiodide salts were not obtained, although a stoichiometric amount (3/2 times) of I_2 was added.[11] When triiodide salt prepared in an acetone solution was recrystallized in a dichloromethane solution, the composition of the crystal was close to that of the pentaiodide salt. Even though it was recrystallized in a more polar solvent, it was hard to prepare a perfect triiodide salt. This means that 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium(1+) polyiodide prefers the pentaiodide form to the triiodide form. However, this is a very rare case that polyiodide salts of 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenes have both forms of triiodide and pentaiodide salts. Therefore, it becomes possible to discuss a subtle effect of the counteranion.

1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocenim(1+), 1′,1‴-bis((*R*)-2-phenylbutyl)-1,1″-biferrocenium(1+), and 1′,1‴-bis((*S*)-2-phenylbutyl)-1,1″-biferrocenim(1+) triiodides are abbreviated to the (*R*,*S*), (*R*,*R*), and (*S*,*S*) triiodide salts, respectively. The racemic modification is abbreviated to the racemic triiodide salt. 'The pentaiodide salt' denotes 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium(1+) pentaiodide in the present paper.

^{57}Fe Mössbauer Spectroscopy. Figure 1 shows the ^{57}Fe Mössbauer spectra of the (*R*,*S*) triiodide salt, and their Mössbauer parameters are listed in Table 2. The mixed-valence state is trapped at 78 K, although two valence states are slightly closer to each other than those in a typical trapped-valence state.[12] The mixed-valence state at room temperature is perfectly

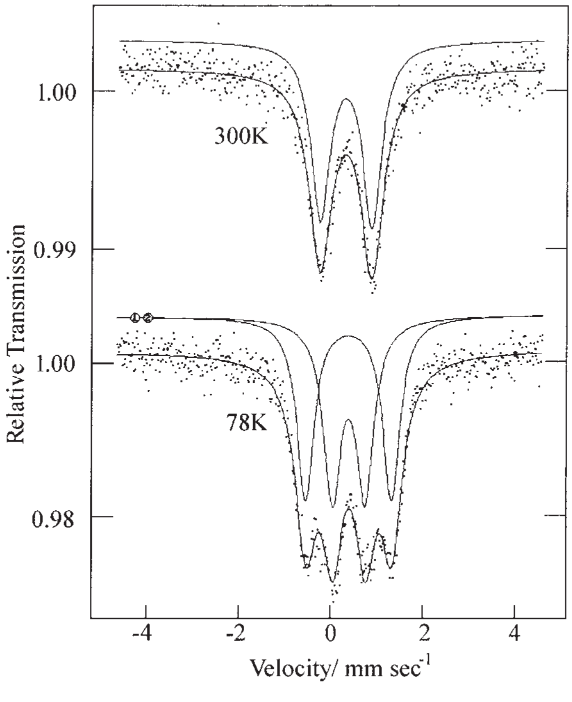

Fig. 1. ^{57}Fe Mössbauer spectra of the (*R*,*S*) triiodide salt.

Table 2. Mössbauer Parameters of $1',1'''$-Bis(2-phenylbutyl)-$1,1''$-biferrocenium(1+) Triiodides

T/K	*I.S.*[a] /mm sec^{-1}	*Q.S.* /mm sec^{-1}	Γ /mm sec^{-1}
		The (*R*,*S*) isomer	
300	0.45	1.13	0.50
78	0.52	1.87	0.46
	0.52	0.71	0.45
		The (*R*,*R*) isomer	
300	0.45	1.49	0.25
	0.45	0.83	0.25
78	0.50	1.68	0.25
	0.50	0.70	0.25
		The (*S*,*S*) isomer	
300	0.44	1.53	0.23
	0.45	0.82	0.21
78	0.53	1.92	0.24
	0.54	0.61	0.24
		The racemic modification	
300	0.45	1.11	0.47
78	0.52	1.92	0.24
	0.54	1.24	0.57
	0.54	0.65	0.24

a) Isomer shift data are reported with respect to iron foil.

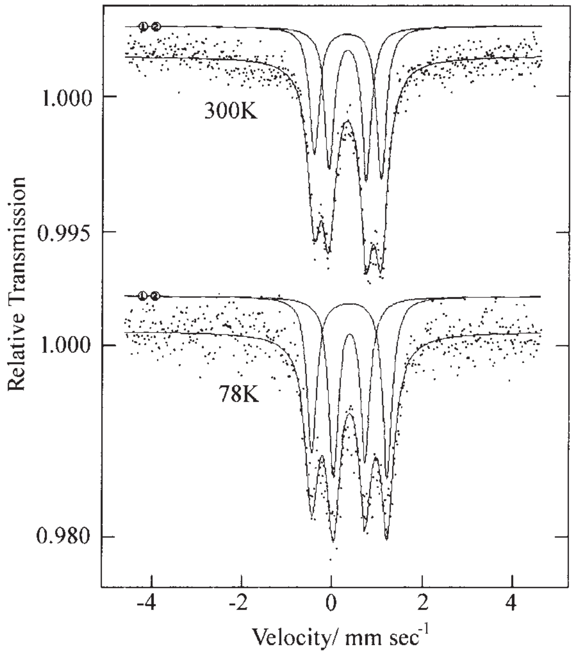

Fig. 2. ^{57}Fe Mössbauer spectra of the (*R*,*R*) triiodide salt.

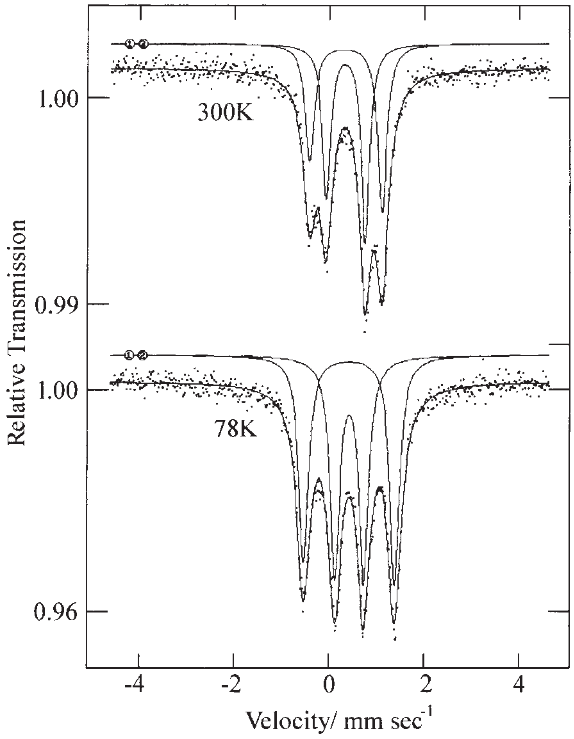

Fig. 3. ^{57}Fe Mössbauer spectra of the (*S*,*S*) triiodide salt.

detrapped. Figures 2 and 3 show the ^{57}Fe Mössbauer spectra of the (*R*,*R*) and the (*S*,*S*) triiodide salts, respectively, and their Mössbauer parameters are listed in Table 2. Their mixed-valence states have a similar trend, i.e., both salts show almost perfect trapped-valence states at 78 K and closer trapped-valence states at room temperature. Three isomers show a similar mixed-valence state at 78 K, but a cation symmetry effect comes into play at room temperature. The results demonstrate the importance of a cation symmetry effect on the mixed-valence state, i.e., the (*R*,*S*) cation is possible to have an inversion center, but the (*R*,*R*) and the (*S*,*S*) cations are intrinsically impossible.

Table 3 summarizes the information of the mixed-valence state for $1',1'''$-bis(2-phenylbutyl)-$1,1''$-biferrocenium(1+) pentaiodides and triiodides. The triiodide salt has a larger difference (Δ*Q.S.*) in the quadrupole splitting values between the ferrocene-like and the ferrocenium-like valence doublets than the corresponding pentaiodide salt[7] in each isomer. In particular, the (*R*,*S*) isomers at 78 K show a large contrast between them. These results indicate that the pentaiodide salt has a faster electron-transfer rate than the corresponding triiodide salt in $1',1'''$-bis(2-phenylbutyl)-$1,1''$-biferrocenium(1+) salt.

The (*R*,*R*) and the (*S*,*S*) triiodide salts show a slight difference in the valence state, i.e., the (*R*,*R*) triiodide salt shows a closer trapped-valence state. This reflects the difference in composition; that is, the (*R*,*R*) triiodide salt includes a more pentaiodide salt-like composition than the (*S*,*S*) triiodide salt, judging from an elemental analysis.

The adiabatic potential-energy surface of the cation is characterized by two minima.[13] The two vibronic states are described as $[\mathrm{Fe_A}^{\mathrm{II}}\mathrm{Fe_B}^{\mathrm{III}}]$ and $[\mathrm{Fe_A}^{\mathrm{III}}\mathrm{Fe_B}^{\mathrm{II}}]$. When intramolecular electron transfer occurs, the molecular structure is inevitably distorted from its original form. This distortion is established by the aid of the antisymmetric breathing vibrational mode. Although the (*R*,*R*) and the (*S*,*S*) cations have a possibility to have a 2-fold axis, the present result shows that the (*R*,*R*) and the (*S*,*S*) cations never show a detrapped-valence state. This is perhaps due to the fact that the distortion is established by the aid of an antisymmetric breathing vibrational mode under symmetric circumstances. If the distortion is established by the aid of the antisymmetric breathing vibrational mode under 2-fold circumstances, the (*R*,*R*) and the (*S*,*S*) cations would show a de-

Table 3. Comparison of Mixed-Valence State between 1′,1‴-Bis(2-phenylbutyl)-1,1″-biferrocenium(1+) Pentaiodides[7] and the Corresponding Triiodides

		Mixed-valence state		$\Delta Q.S.$ (mm sec^{-1})	
		300 K	78 K	300 K	78 K
The (*R*,*S*) isomer	Pentaiodide	Detrapped	Detrapped	—	—
	Triiodide	Detrapped	Trapped	—	1.16
The (*R*,*R*) isomer	Pentaiodide	Trapped	Trapped	0.42	0.73
	Triiodide	Trapped	Trapped	0.66	0.98
The (*S*,*S*) isomer	Pentaiodide	Trapped	Trapped	0.43	0.61
	Triiodide	Trapped	Trapped	0.71	1.31

trapped-valence state. Mixed-valence trinuclear iron carboxylate complexes, [Fe$^{III}_2$Fe^{II}O(O$_2$CR)$_6$L$_3$]S, are also a suitable system for studying the mixed-valence properties of discrete molecules in a solid. It is known that the mixed-valence state is dependent on whether Fe$_3$O complexes have a 3-fold axis or not.[4]

Figure 4 shows the ^{57}Fe Mössbauer spectra of the racemic triiodide salt. The racemic triiodide salt shows a perfect detrapped-valence state at room temperature as well as the racemic pentaiodide salt.[7] However, it is hard to estimate the best-fitting lines for the spectrum at 78 K by two doublets, and it is necessary to add a third doublet as a detrapped-valence state. There are two ideas concerning assignment of the third doublet. One idea is that the racemic triiodide salt has a coexistence-type temperature-dependence, in which the trapped-valence and detrapped-valence states coexist and the area ratio changes with the temperature. The other idea is that the third doublet is divided into two closer doublets as given in the racemic pentaiodide salt because the elemental analysis suggests a slight coexistence of the pentaiodide salt.

1′,1‴-Bis(2-phenylbutyl)-1,1″-biferrocenium(1+) triiodides have the same trend among (*R*,*S*), (*R*,*R*), (*S*,*S*), and racemic samples with their pentaiodide salts in the mixed-valence states. However, the trend to show the detrapped-valence state is not so apparent in the triiodide salts.

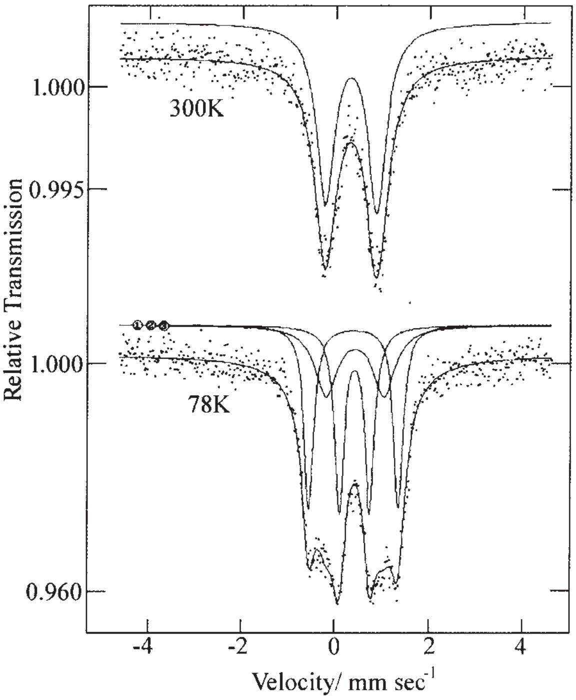

Fig. 4. ^{57}Fe Mössbauer spectra of the racemic triiodide salt.

X-ray Crystallography. An ORTEP drawing of the (*S*,*S*) triiodide salt at 293 K is shown in Fig. 5. Crystallographic data for the (*S*,*S*) triiodide salt are listed in Table 1, and selected bond distances and angles are given in Table 4. The space group for the (*S*,*S*) triiodide salt is $P2_1$, indicating that the (*S*,*S*) cation has no inversion center and the analysis is consistent with the result of an ^{57}Fe Mössbauer measurement. The average distance between iron and carbon atoms in Cp rings (Fe–C(Cp)$_{\text{average}}$) reflects the valence state, i.e., ferrocene has a smaller value (2.045 Å)[14] and ferrocenium cation has a larger one (2.075 Å).[15] The Fe–C(Cp)$_{\text{average}}$ distances in the (*S*,*S*) triiodide salt are 2.077(4) Å for Fe(1) and 2.061(4) Å for Fe(2), indicating that Fe(1) is trivalent and Fe(2) is divalent.

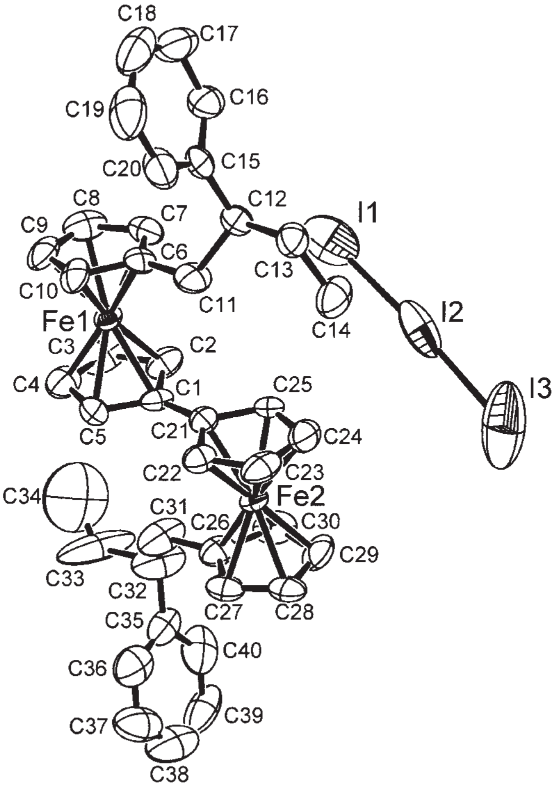

Fig. 5. ORTEP drawing of the (*S*,*S*) triiodide salt with 50% probability drawing ellipsoids.

Table 4. Selected Bond Lengths (Å) and Angles (degree) for 1′,1‴-Bis((*S*)-2-phenylbutyl)-1,1″-biferrocenium(1+) Triiodide

	Bond lengths		
I(1)–I(2)	2.917(3)	I(2)–I(3)	2.902(4)
Fe(1)–C(1)	2.104(11)	Fe(1)–C(2)	2.079(13)
Fe(1)–C(3)	2.036(12)	Fe(1)–C(4)	2.034(15)
Fe(1)–C(5)	2.073(14)	Fe(1)–C(6)	2.129(11)
Fe(1)–C(7)	2.091(13)	Fe(1)–C(8)	2.089(14)
Fe(1)–C(9)	2.070(13)	Fe(1)–C(10)	2.094(12)
Fe(2)–C(21)	2.073(11)	Fe(2)–C(22)	2.026(13)
Fe(2)–C(23)	2.052(13)	Fe(2)–C(24)	2.075(15)
Fe(2)–C(25)	2.050(11)	Fe(2)–C(26)	2.097(14)
Fe(2)–C(27)	2.055(13)	Fe(2)–C(28)	2.055(13)
Fe(2)–C(29)	2.071(14)	Fe(2)–C(30)	2.052(13)
	Bond angle		
I(1)–I(2)–I(3)	175.57(8)		

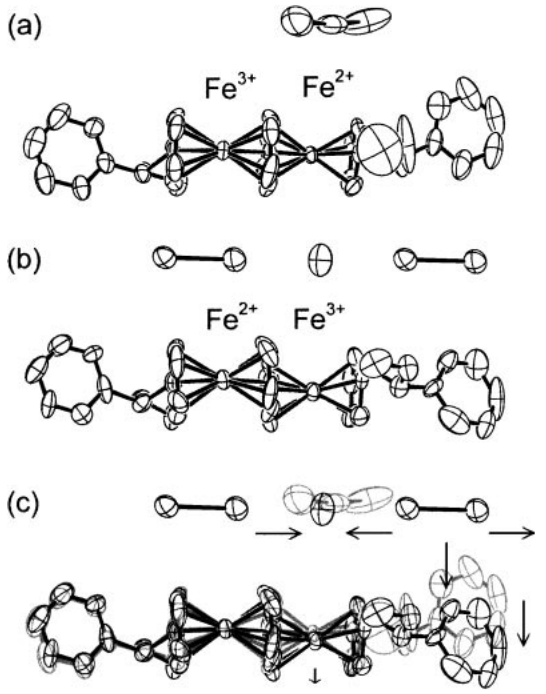

Fig. 6. Comparison of the (*S*,*S*) cation structures between (a) triiodide and (b) pentaiodide salts. The overwriting is shown in (c).

The tilt angles between the Cp rings are 4.44° and 3.19° in each ferrocene unit containing Fe(1) and Fe(2), respectively. It is reported that a mixed-valence biferrocene derivative having a larger tilt angle has stronger interaction between two irons and shows a detrapped-valence state at lower temperatures.[16] The tilt angles in the (*S*,*S*) triiodide salt are smaller than those in the corresponding (*S*,*S*) pentaiodide salt.[7] The relationship between the tilt angle and the electron-transfer rate is applicable in the present case, although they are trapped-valence states.

The triiodide anion in the (*S*,*S*) triiodide salt has a slight vending unsymmetrical structure: I(1)–I(2) = 2.917(3) Å, I(2)–I(3) = 2.902(4) Å and I(1)–I(2)–I(3) = 175.57(8)°. The result suggests that I(1) has a slightly larger charge than I(3). The difference of two I–I distances is smaller than that in the triiodide anion unit in the corresponding pentaiodide salt. Although we expect that (*S*,*S*) triiodide salt shows a smaller Δ*Q.S.* in this situation, the result is opposite. This is explained later using Fig. 6. Comparing the distance between an iron and its nearest iodine atom, Fe(1)–I(1) is 5.385 Å and Fe(2)–I(3) is 5.564 Å, suggesting that Fe(1) is trivalent and Fe(2) is divalent. This finding is consistent with the result of the Fe–$\mathrm{C(Cp)}_{\mathrm{average}}$ distances. Each Fe–I distance in the (*S*,*S*) triiodide salt is longer than that in the (*S*,*S*) pentaiodide salt in spite of a reduction of the unit-cell parameters.

The lattice parameters for the racemic triiodide salt estimated from an X-ray crystal analysis, are a monoclinic system: $a = 11.8330(4)$ Å, $b = 10.9790(4)$ Å, $c = 15.9140(6)$ Å, and $\beta = 108.452(1)°$, as listed in Table 1. The *c*-axis is extended and the β-angle is reduced compared with those of the (*S*,*S*) triiodide salt. This indicates that the (*R*,*R*) and the (*S*,*S*) cations coexist in a crystal of the racemic triiodide salt. However, a reasonable molecular structure was not obtained. At the present stage, we comment that the triiodide anion is unsymmetrical, and that the distance between the most negative iodine and an iron atom is farther than that between another terminal iodine and an iron atom, as well as the pentaiodide salt.[7]

We will discuss the difference between the (*S*,*S*) pentaiodide and triiodide salts. Figure 6 shows ORTEP drawings of the (*S*,*S*) triiodide and pentaiodide salts, which are shown from the same direction. The phenyl rings in the (*S*,*S*) pentaiodide salt are located on the *anti*-position each other. This structure means that the (*S*,*S*) cation has a pseudo-inversion center. We comment here that it is possible to analyze the (*S*,*S*) pentaiodide by using space group $P2_1/n$, although we analyzed it by using space group $P2_1$ to give the best result. On the other hand, the phenyl rings are located on the *syn*-position in the (*S*,*S*) triiodide salt and the cation loses a pseudo-inversion center. Figure 6(c) shows the static effects of an ‘extra’ iodine molecule by arrows. A significant movement of the right phenyl ring and a slight movement of the left phenyl ring are found in Fig. 6(c). The iodine molecule unit in the pentaiodide anion chain barges between two triiodide anion units, and shifts the position of triiodide anion unit to a more parallel position against the fulvalene plane. The iodine molecule unit also moves the phenyl ring to have a pseudo-inversion center in the cation. The environments around two ferrocene moieties result in forming to be more equivalent to each other in the pentaiodide salt, and therefore the (*S*,*S*) pentaiodide salt shows a smaller Δ*Q.S.*, i.e., the exchange rate is faster. It is interesting that the valence state of each iron atom changes between the pentaiodide and the triiodide salts. This is related to the relative shift of the triiodide anion unit to the ferrocene moiety.

Figure 7 shows the powder X-ray diffraction patterns of the (*R*,*S*), (*R*,*R*), (*S*,*S*), and racemic triiodide salts. The crystallinity of the present triiodide salts was worse compared with that of the corresponding pentaiodide salts. Nevertheless, it can be seen that all diffraction patterns show no remarkable difference. This suggests that each triiodide salt has the same crystal structure basically. The (*R*,*S*), (*R*,*R*), (*S*,*S*), and racemic pentaiodide salts also showed similar crystal structures, although a slight difference, such as the space group of $P2_1$ or

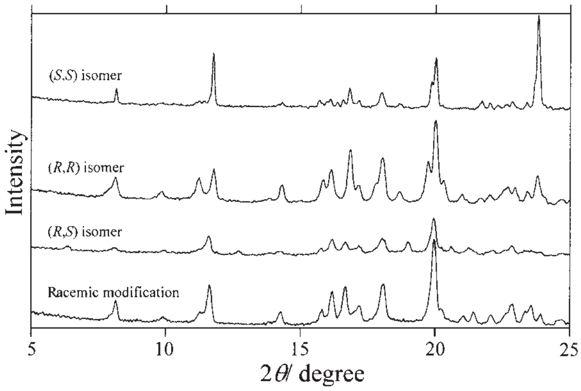

Fig. 7. Powder X-ray diffraction patterns for the (*R*,*S*), (*R*,*R*), (*S*,*S*) triiodide salts and the racemic modification at room temperature.

$P2_1/n$, was observed.[7] Therefore, the change in the packing effect and the environment around the cation from pentaiodide to triiodide salts should affect the mixed-valence state, even in the (*R*,*S*) cation. Actually, the valence state of the (*R*,*S*) triiodide salt is trapped at 78 K, in contrast to the detrapped-valence state of the (*R*,*S*) pentaiodide salt at 78 K.

Conclusion

The importance of the cation symmetry effect was identified in 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium(1+) triiodides. Namely, only the (*R*,*S*) isomer shows a perfect detrapped-valence state at room temperature in three isomers. The racemic modification, which consists of the (*R*,*R*) and the (*S*,*S*) isomers, showed a detrapped-valence state at room temperature. This reveals that the cation asymmetry effect was overcome by the packing effect. The difference in mixed-valence states between the (*S*,*S*) triiodide and pentaiodide salts could also be understood by a packing effect. The phenyl ring was forced to move to have a pseudo-inversion center in the cation by changing from triiodide to pentaiodide salts. These findings demonstrated that the centrosymmetric circumstances around the cation in the pentaiodide salts imposed the asymmetric (*R*,*R*) and (*S*,*S*) cations to change to a more symmetric structure.

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