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Mixed-Valence State of Optically Active 1′,1‴-Bis(2-phenylbutyl)-1,1″-biferrocenium Pentaiodide: Effects of Cation Symmetry and Intermolecular Interaction on Trapped-/Detrapped-Valence States

Takashi Oda,[†] Satoru Nakashima,*,[‡] and Tsutomu Okuda*,[†]

Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama,
Higashi-Hiroshima 739-8526, Japan, and Natural Science Center for Basic Research and
Development (N-BARD), Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526, Japan

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The effects of cation symmetry and packing on the mixed-valence state of binuclear ferrocene derivatives are discussed separately by using chiral isomers and racemic modification of 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium pentaiodide. The pentaiodide anion has a polymeric structure and is composed of triiodide anion and iodine molecule units. The (*R*,*S*) isomer having an inversion center shows a detrapped-valence state even at 78 K. On the other hand, the (*R*,*R*) and the (*S*,*S*) isomers having no inversion center show a trapped-valence state at room temperature. The racemic modification, however, consisting of the (*R*,*R*) and the (*S*,*S*) isomers shows a perfect detrapped-valence state at room temperature. This finding shows that the packing effect overcomes the effect of cation asymmetry.

Introduction

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] The study of the mixed-valence state has been expanded especially by using monooxidized (mixed-valence) binuclear ferrocene derivatives, since binuclear ferrocenes have an advantage of the ease of molecular design.[3] This progress in the last two decades is due to the discovery of a temperature-dependent mixed-valence state in 1′,1‴-diethyl-1,1″-biferrocenium triiodide.[4] The investigations for many mixed-valence biferrocenium derivatives revealed that the important factors to control the mixed-valence states are cation symmetry and packing effect.[2,5−9] Study on the mixed-valence state of binuclear ferrocene derivatives is still expanding.[10,11] Nevertheless, it is difficult to decide which of the two is the more important factor concerning the mixed-valence state. The effect of cation asymmetry has already been discussed by many researchers.[12] To compare the degree of the two effects, we started studying

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* To whom correspondence should be addressed. E-mail: snaka@hiroshima-u.ac.jp (S.N.)

[†] Department of Chemistry, Hiroshima University

[‡] N-BARD, Hiroshima University.

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the mixed-valence state of binuclear ferrocenes having chiral substituents.[13−15] Because the (*R*,*S*) isomer has an inversion center in itself but the (*R*,*R*) and the (*S*,*S*) isomers cannot intrinsically, the racemic modification which consists of the (*R*,*R*) and the (*S*,*S*) isomers has a possibility of throwing light upon the packing effect.

Previously we have reported interesting mixed-valence states in 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenium salts.[14,15] This (*R*,*S*) sample showed a perfect detrapped-valence state at room temperature, while the (*R*,*R*) and the (*S*,*S*) samples never showed the perfect detrapped-valence state. These results were explained by cation symmetry effect; i.e., the former has an inversion center, but the latter never has it intrinsically. The problem was, however, that these samples were neither perfect triiodide salts nor pentaiodide ones but intermediate forms between them. We could not obtain the pure triiodide and pentaiodide salts from hexane solution by adding 3/2 and 5/2 times the molarity of I_2 to neutral binuclear ferrocenes, respectively.

In this study, we isolated the pentaiodide salts for (*R*,*R*), (*S*,*S*), and (*R*,*S*) isomers and the racemic modification of 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocene. We have discussed the cation symmetry and packing effect on the mixed-valence state independently by using ^{57}Fe Mössbauer spectroscopy and an X-ray crystal structural analysis. We have revealed an important factor of cation symmetry on the mixed-valence state and also an interesting packing effect overcoming the cation asymmetry.

Experimental Section

Syntheses. 1′,1‴-Bis((*R*)-2-phenylbutyl)-1,1″-biferrocene and 1′,1‴-bis((*S*)-2-phenylbutyl)-1,1″-biferrocene were synthesized according to the method reported for a series of ferrocene derivatives with alkyl substituents.[16] (*S*)-(+)- and (*R*)-(−)-2-phenylbutyryl chlorides were used in the acylation for the (*R*,*R*) and the (*S*,*S*) compounds, respectively. The products were isolated by column chromatography on alumina. Anal. Found for 1′,1‴-bis((*R*)-2-phenylbutyl)-1,1″-biferrocene: C, 75.59; H, 6.68. Calcd for $C_{40}H_{42}Fe_2$: C, 75.72; H, 6.67. ^{1}H NMR (*δ*/ppm, $CDCl_3$): 7.22 (4H), 7.13 (2H), 7.00 (4H) (phenyl ring); 4.18 (4H), 4.06 (4H), 3.81 (4H), 3.75 (4H) (Cp ring); 3.55 (2H) (on chiral carbon), 2.39 (4H) ($\mathrm{CpC}H_2-$); 1.52 (4H) ($-CH_2\mathrm{CH}_3$); 0.67 (6H) ($-\mathrm{CH}_2CH_3$). Anal. Found for 1′,1‴-bis((*S*)-2-phenylbutyl)-1,1″-biferrocene: C, 75.42; H, 6.10. Calcd for $C_{40}H_{42}Fe_2$: C, 75.72; H, 6.67. ^{1}H NMR (*δ*/ppm, $CDCl_3$): 7.22 (4H), 7.13 (2H), 6.99 (4H) (phenyl ring); 4.17 (4H), 4.06 (4H), 3.81 (4H), 3.74 (4H) (Cp ring); 3.54 (2H) (on chiral carbon), 2.38 (4H) ($\mathrm{CpC}H_2-$); 1.49 (4H) ($-CH_2\mathrm{CH}_3$); 0.66 (6H) ($-\mathrm{CH}_2CH_3$).

1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocene was synthesized by using the equimolar mixture of 1′-(*R*)-2-phenylbutyl-1-bromoferrocene and 1′-((*R*)-2-phenylbutyl)-1-bromoferrocene in the Ullman coupling reaction.[17] After extraction with dichloromethane, the mixture was isolated by column chromatography on alumina. The first and second bands were ((*R*)-2-phenylbutyl)ferrocene and 1′,1‴-bis((*R*)-2-phenylbutyl)-1,1″-biferrocene eluted with hexane, respectively. The third band was ((*R*)-2-phenylbutyryl)ferrocene eluted with hexane/benzene mixed solution (7:3). The forth band was 1′-((*R*)-2-phenylbutyl)-1‴-((*R*)-2-phenylbutyryl)-1,1″-biferrocene eluted with benzene. The fifth band was 1′,1‴-bis((*R*)-2-phenylbutyryl)-1,1″-biferrocene eluted with dichloromethane. Then, 1′-((*R*)-2-phenylbutyl)-1‴-((*R*)-2-phenylbutyryl)-1,1″-biferrocene was reduced by $LiAlH_4$ with $AlCl_3$. Anal. Found for 1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocene: C, 75.34; H, 5.75. Calcd for $C_{40}H_{42}Fe_2$: C, 75.72; H, 6.67. ^{1}H NMR (*δ*/ppm, $CDCl_3$): 7.21 (4H), 7.13 (2H), 6.99 (4H) (phenyl ring); 4.16 (4H), 4.06 (4H), 3.81 (4H), 3.74 (4H) (Cp ring); 3.55 (2H) (on chiral carbon), 2.41 (4H) ($\mathrm{CpC}H_2-$); 1.50 (4H) ($-CH_2\mathrm{CH}_3$); 0.67 (6H) ($-\mathrm{CH}_2CH_3$).

These 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenes were oxidized by adding stoichiometric amount (5/2 times) of I_2 dissolved in dichloromethane to dichloromethane solution of the neutral complexes. The pentaiodide salts were recrystallized from dichloromethane solution under hexane atmosphere at 0 °C. Then, black column-shape crystals were obtained. Anal. Found for 1′,1‴-bis((*R*)-2-phenylbutyl)-1,1″-biferrocenium pentaiodide: C, 38.12; H, 2.82. Found for 1′,1‴-bis((*S*)-2-phenylbutyl)-1,1″-biferrocenim pentaiodide: C, 38.54; H, 2.91. Found for 1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocenim pentaiodide: C, 38.66; H, 2.84. Calcd for $C_{40}H_{42}Fe_2I_5$: C, 37.86; H, 3.34.

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 the one-electron oxidation process. The methods for oxidation and recrystallization were the same as the case of other 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocene. Anal. Found for the racemic modification: C, 38.44; H, 2.74. Calcd for $C_{40}H_{42}Fe_2I_5$: C, 37.86; H, 3.34.

^{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 Toyo-Research spectrometer. The ^{57}Fe Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shift values are referred to metallic iron.

X-ray Crystal Structural Analyses. Single crystals for X-ray crystallography of 1′,1‴-bis(2-phenybutyl)-1,1″-biferrocenium pentaiodides were obtained by the following method. Each salt was dissolved in dichloromethane, and then it was put in the hexane atmosphere at 0 °C. After several days single crystals for X-ray structural analysis were obtained as black column-shape crystals. They were cut 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 program package of MacDENZO.[18] The crystal structures were 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

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Table 1. Crystallographic Data for 1′,1‴-Bis(2-phenylbutyl)-1,1″-biferrocenium Pentaiodides

	(*R*,*S*) isomer	(*R*,*R*) isomer	(*S*,*S*) isomer	racemic modification
formula	$C_{40}H_{42}Fe_2I_5$	$C_{40}H_{42}Fe_2I_5$	$C_{40}H_{42}Fe_2I_5$	$C_{40}H_{42}Fe_2I_5$
fw	1268.99	1268.99	1268.99	1268.99
T/°C	20	20	20	20
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$	$P2_1$	$P2_1$
a/Å	12.0410(2)	12.0130(2)	12.0140(2)	12.0390(6)
b/Å	10.9440(3)	10.9310(2)	10.9170(2)	10.9330(6)
c/Å	16.7840(4)	16.8790(4)	16.8900(5)	16.8560(10)
β/deg	110.8190(10)	110.4860(10)	110.5250(10)	110.378(2)
V/Å^3	2067.33(8)	2076.28(7)	2074.61(7)	2079.8(2)
Z	2	2	2	2
ρ_{calcd}/g cm^{-3}	2.038	2.030	2.031	2.026
μ(Mo Kα)/mm^{-1}	44.62	44.43	44.47	44.36
R^a	0.070	0.054	0.067	0.079
$R_w{}^b$	0.088	0.065	0.071	0.086

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

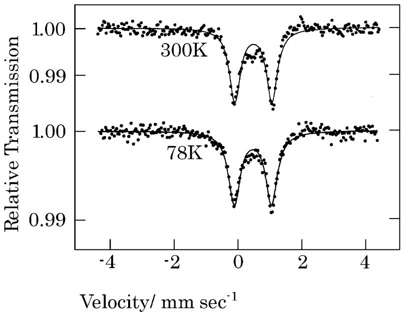

Figure 1. Variable-temperature ^{57}Fe Mössbauer spectra of the (*R*,*S*) pentaiodide salt.

Table 2. Mössbauer Parameters of 1′,1‴-Bis(2-phenylbutyl)-1,1″-biferrocenium Pentaiodides

T/K	IS^a/mm s^{-1}	QS/mm s^{-1}	area ratio/%
	(*R*,*S*) Isomer		
300	0.44	1.16	100
78	0.49	1.16	100
	(*R*,*R*) Isomer		
300	0.48	1.41	44.9
	0.49	0.99	55.1
78	0.54	1.62	43.5
	0.55	0.89	56.5
	(*S*,*S*) Isomer		
300	0.42	1.38	50.0
	0.44	0.95	50.0
78	0.50	1.49	55.1
	0.51	0.88	44.9
	Racemic Modification		
300	0.45	1.19	100
78	0.56	0.95	53.0
	0.55	1.53	47.0

^{a} Isomer shift data are reported with respect to iron foil.

packages of Rigaku and Molecular Structure Corp.[19,20] Table 1 summarizes crystallographic data and experimental details.

As the analysis of the racemic modification is difficult, the structure was analyzed by using $P2_1$ to compare with other pentaiodide salts.

Results and Discussion

It was not easy to obtain a stoichiometric mixed-valence compound of 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenes. By using hexane as oxidizing solvent the triiodide salts were not obtained, although a stoichiometric amount (3/2 times) of I_2 was added. Moreover, by adding 5/2 times amount of I_2, the perfect pentaiodide salt was never obtained.[14,15] In this study we succeeded in obtaining the pentaiodide salts by using dichloromethane as oxidizing solvent. This will be seen in the X-ray structural analysis later. Nevertheless, it was not easy to obtain perfect elementary analysis results.

1′-((*R*)-2-Phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocenium Pentaiodide. 1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocenium pentaiodide is abbreviated as the (*R*,*S*) pentaiodide salt.

Figure 1 shows the ^{57}Fe Mössbauer spectra of the (*R*,*S*) pentaiodide salt at 78 and 300 K, and their Mössbauer parameters are listed in Table 2. Only one doublet is detected in ^{57}Fe Mössbauer spectra at each temperature. The quadrupole splitting (QS) value is 1.16 mm s^{-1} at both temperatures and intermediate between typical ferrocene and typical ferrocenium doublets. The value is similar to that of other detrapped-valence samples,[7] indicating that the valence state is detrapped even at 78 K.

The ORTEP drawing of the (*R*,*S*) pentaiodide salt at 293 K is shown in Figure 2. Crystallographic data for the (*R*,*S*) pentaiodide salt are listed in Table 1, and selected bond distances and angles are given in Table 3. The space group for the (*R*,*S*) pentaiodide salt is $P2_1/n$ (No. 14), indicating that the cation has inversion center and two ferrocene units are identical. This finding is consistent with the result of perfect detrapped-valence state in ^{57}Fe Mössbauer spectrum. One is the *R*-substituent and the other is the *S*-substituent, suggesting that their configurations are maintained in the crystal. By paying attention to the structure of ferrocene unit, we find the tilt angle between the Cp (cyclopentadienyl) ring and fulvalene is 6.00° and the average distance of iron to carbon atom in the Cp rings is 2.061(2) Å, which is intermediate between 2.045 Å for ferrocene[21] and 2.075 Å for ferrocenium cation.[22]

The structure of the pentaiodide anion in a mixed-valence binuclear ferrocenium derivative has been reported as

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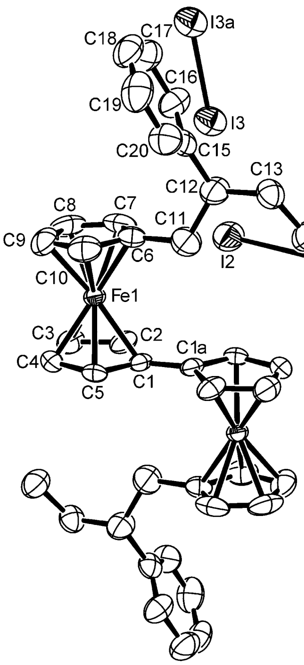

Figure 2. ORTEP drawing for the (*R*,*S*) pentaiodide salt at 293 K. The thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for the (*R*,*S*) Pentaiodide Salt

Bond Lengths			
I(1)−I(2)	2.8910(10)	I(2)−I(3)	3.3340(10)
I(3)−I(3a)	2.7680(10)	Fe(1)−C(1)	2.111(6)
Fe(1)−C(2)	2.069(7)	Fe(1)−C(3)	2.041(8)
Fe(1)−C(4)	2.052(7)	Fe(1)−C(5)	2.048(6)
Fe(1)−C(6)	2.092(7)	Fe(1)−C(7)	2.042(7)
Fe(1)−C(8)	2.038(7)	Fe(1)−C(9)	2.045(8)
Fe(1)−C(10)	2.072(8)	C(1)−C(1a)	1.421(13)
C(1)−C(2)	1.428(10)	C(1)−C(5)	1.439(10)
C(2)−C(3)	1.415(11)	C(3)−C(4)	1.431(13)
C(4)−C(5)	1.396(10)	C(6)−C(7)	1.384(13)
C(6)−C(10)	1.392(12)	C(7)−C(8)	1.381(13)
C(8)−C(9)	1.37(1)	C(9)−C(10)	1.411(13)
Bond Angles			
I(2)−I(1)−I(2a)	180	I(1)−I(2)−I(3)	101.30(2)
I(2)−I(3)−I(3a)	177.86(4)		

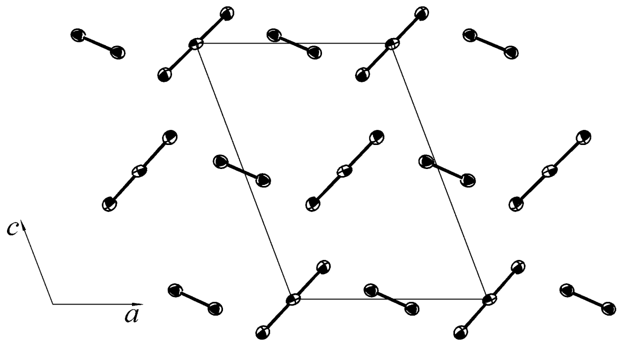

Figure 3. Polymeric anion structure of zigzag chain projected to the *ac* plane in the (*R*,*S*) pentaiodide salt.

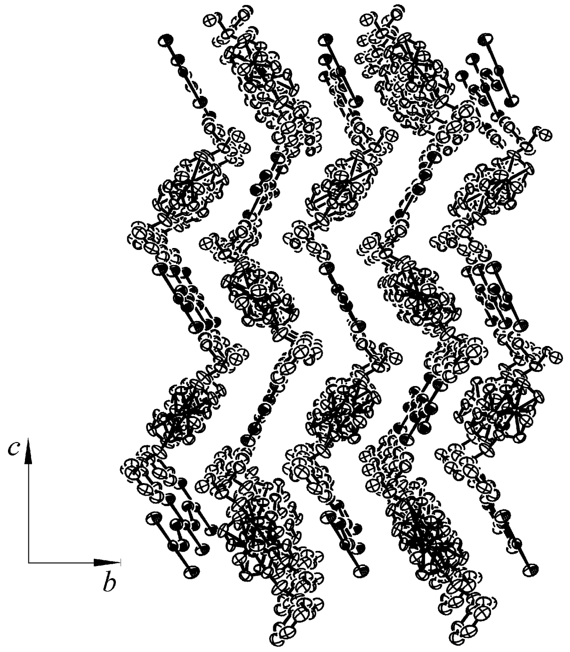

Figure 4. Packing view projected to the *bc* plane in the (*R*,*S*) pentaiodide salt.

polymeric zigzag[10b,23] or an isolated V-shaped symmetric structure.[24] The anion structure in the present derivatives is considered to be the former, which is composed of triiodide anion and iodine molecule units. The polymeric anion of the zigzag chain lies along the *a*-axis as illustrated in Figure 3. The triiodide anion unit was analyzed to be linear and symmetric, and the I(1)−I(2) bond length is 2.8910(10) Å. The symmetric triiodide anion was found in the most detrapped-valence binuclear ferrocenium derivatives.[25] The triiodide units are linked by the iodine molecule unit. The bridging I(2)−I(3) distance is 3.3340(10) Å, and the I(1)−I(2)-I(3) angle is 101.30(2)°. The bond distance is obviously shorter than the sum of the van der Waals radii for iodine atoms. The I−I distance in this iodine molecule unit is 2.7680(10) Å, which is longer than that of usual iodine molecule (2.68 Å).[26] The bond distances are in the range of other polyiodide anions[27] and similar to the reported polymeric pentaiodide anions in the mixed-valence binuclear ferrocenium derivatives.[10b,23]

The packing view of the (*R*,*S*) pentaiodide salt projected to the *bc* plane is shown in Figure 4. The cation and anion chain columns are packed alternately. In the cation column the Cp rings are not overlapped between neighboring cations but stacked stepwise. The cation columns are divided by the anion chain column. The Cp ring and phenyl ring in the next column are close, and the C−H bond in the Cp ring is directed to the center of C−C bond in the phenyl ring. This makes us expect the existence of a CH−π interaction. The distance, however, is about 3.8 Å and near the sum of the

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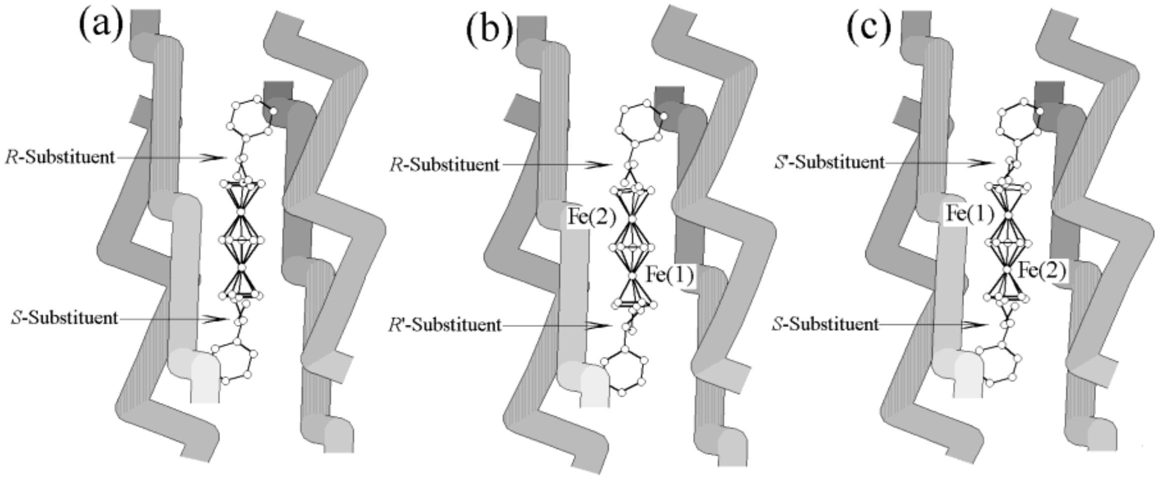

Figure 5. Illustrated drawing for the cation and its surrounding anion chains: (a) the (*R*,*S*) cation; (b) the (*R*,*R*) cation; (c) the (*S*,*S*) cation.

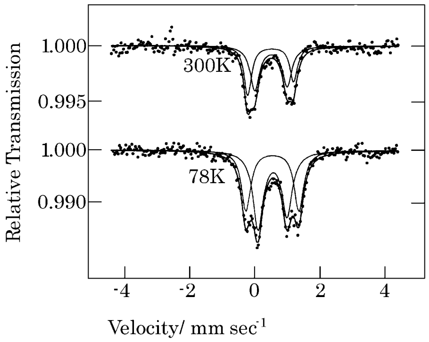

Figure 6. Variable-temperature ^{57}Fe Mössbauer spectra of the (*R*,*R*) pentaiodide salt.

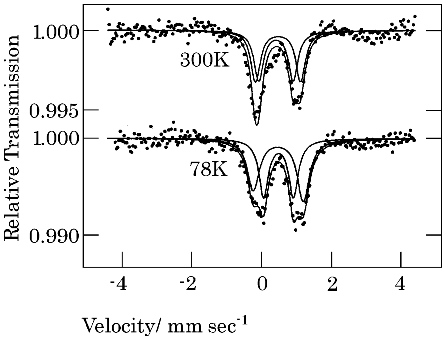

Figure 7. Variable-temperature ^{57}Fe Mössbauer spectra of the (*S*,*S*) pentaiodide salt.

van der Waals radii. Therefore, the interaction between cations is considered to be not very strong.

The packing view of the (*R*,*S*) cation and its surrounding anion chains (illustrated by gray columns) is shown in Figure 5a. It looks like that anion chains enclose the cation. Especially, the phenyl rings in substituents are surrounded by anion chains. The shortest distance between a carbon atom in the phenyl ring and the iodine atom is about 4.1 Å. The distance is close to the sum of the van der Waals radii in C(H)−I. That is, interactions between cation−cation and cation−anion columns are on the order of a “van der Waals interaction”. Although the interaction is not so strong, it can be thought that a rigid polymeric anion structure controls the cation structure.

1′,1‴-Bis((*R*)-2-phenylbutyl)-1,1″-biferrocenium Pentaiodide and 1′,1‴-Bis((*S*)-2-phenylbutyl)-1,1″-biferrocenium Pentaiodide. 1′,1‴-Bis((*R*)-2-phenylbutyl)-1,1″-biferrocenium pentaiodide and 1′,1‴-bis((*S*)-2-phenylbutyl)-1,1″-biferrocenium pentaiodide are abbreviated as the (*R*,*R*) and the (*S*,*S*) pentaiodide salts, respectively.

Figures 6 and 7 show the ^{57}Fe Mössbauer spectra of the (*R*,*R*) and the (*S*,*S*) pentaiodide salts, respectively, and their Mössbauer parameters are listed in Table 2. The shapes of the spectra of the (*R*,*R*) and the (*S*,*S*) pentaiodide salts are very similar to each other, because it is well-known that there is no difference in properties between enantiomers without polarization. Two doublets are observed at 78 K. The outer doublet is assigned to a ferrocene-like valence state (Fe^{2+}), and the inner doublet is assigned to a ferrocenium-like valence state (Fe^{3+}). The two QS values (1.62 and 0.89 mm s^{-1} for the (*R*,*R*) isomer and 1.49 and 0.88 mm s^{-1} for the (*S*,*S*) isomer) approach from the typical ferrocene-like and ferrocenium-like doublets. The QS values reflect the circumstances around the cation.[28] It is judged that the circumstances around the cation are relatively symmetric, which will be discussed later. The two valence states are approaching each other with increasing temperature. But they never fuse into one doublet even at room temperature; i.e., a very close trapped-valence state is observed.

We have already reported the mixed-valence state of the nonstoichiometric polyiodide salt composed of triiodide and pentaiodide.[15] The (*R*,*S*) isomer shows the coexistent type valence detrapping, and the (*R*,*R*) and the (*S*,*S*) isomers are of the trapped-valence type. By comparison of these results and the present results, it is noted that the temperature dependence of valence state is affected by the coexistence of triiodide and pentaiodide in the (*R*,*S*) isomer, while the coexistence does not significantly affect the mixed-valence state in the (*R*,*R*) and the (*S*,*S*) isomers.

The ORTEP drawing of the (*R*,*R*) pentaiodide salt at 293 K is shown in Figure 8. Crystallographic data for the (*R*,*R*) pentaiodide salt are listed in Table 1, and selected bond distances and angles are given in Table 4. The space group

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(28) Nakashima, S.; Nishimori, A.; Masuda, Y.; Sano, H.; Sorai, M. *J. Phys. Chem. Solids* **1991**, *52*, 1169.

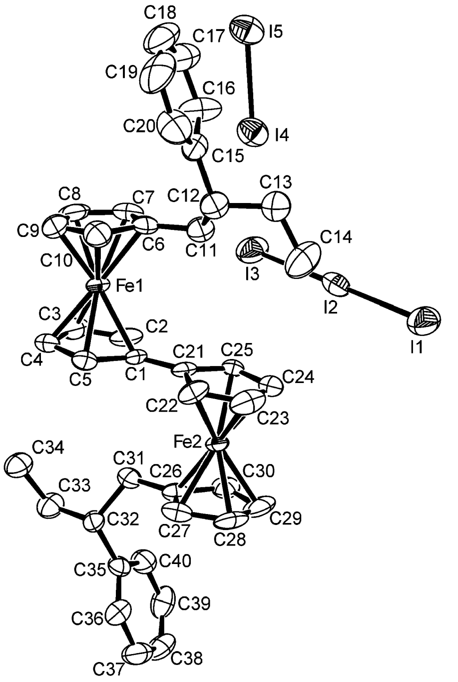

Figure 8. ORTEP drawing for the (*R*,*R*) pentaiodide salt at 293 K. The thermal ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for the (*R*,*R*) Pentaiodide Salt

	Bond Lengths		
I(1)−I(2)	2.8680(10)	I(1)−I(5)	3.4050(10)
I(2)−I(3)	2.9160(10)	I(3)−I(4)	3.3000(10)
I(4)−I(5)	2.7660(10)	Fe(1)−C(1)	2.115(8)
Fe(1)−C(2)	2.061(11)	Fe(1)−C(3)	2.056(13)
Fe(1)−C(4)	2.048(12)	Fe(1)−C(5)	2.061(10)
Fe(1)−C(6)	2.135(11)	Fe(1)−C(7)	2.121(11)
Fe(1)−C(8)	2.054(10)	Fe(1)−C(9)	2.014(11)
Fe(1)−C(10)	2.058(12)	Fe(2)−C(21)	2.101(8)
Fe(2)−C(22)	2.056(10)	Fe(2)−C(23)	2.031(11)
Fe(2)−C(24)	2.060(12)	Fe(2)−C(25)	2.061(9)
Fe(2)−C(26)	2.084(11)	Fe(2)−C(27)	2.037(11)
Fe(2)−C(28)	2.042(9)	Fe(2)−C(29)	2.067(11)
Fe(2)−C(30)	2.055(11)	C(1)−C(2)	1.41(2)
C(1)−C(5)	1.48(2)	C(1)−C(21)	1.423(11)
C(2)−C(3)	1.41(2)	C(3)−C(4)	1.44(2)
C(4)−C(5)	1.45(2)	C(6)−C(7)	1.42(2)
C(6)−C(10)	1.46(2)	C(7)−C(8)	1.41(2)
C(8)−C(9)	1.40(2)	C(9)−C(10)	1.39(2)
C(21)−C(22)	1.44(2)	C(21)−C(25)	1.42(2)
C(22)−C(23)	1.38(2)	C(23)−C(24)	1.39(2)
C(24)−C(25)	1.38(2)	C(26)−C(27)	1.40(2)
C(26)−C(30)	1.40(2)	C(27)−C(28)	1.44(2)
C(28)−C(29)	1.35(2)	C(29)−C(30)	1.44(2)
	Bond Angles		
I(1)−I(2)−I(3)	179.79(5)	I(1)−I(5)−I(4)	178.57(5)
I(2)−I(1)−I(5)	102.99(4)	I(2)−I(3)−I(4)	98.47(4)
I(3)−I(4)−I(5)	176.16(4)		

for the (*R*,*R*) pentaiodide salt is $P2_1$ (No. 4), indicating that the cation loses the inversion center and the two ferrocene units are unequal. The tilt angles between Cp rings are 7.21 and 6.05°, and the average distances of Fe(1) and Fe(2) to a carbon atom in the Cp rings are 2.071(3) and 2.059(3) Å, respectively. The average Fe−C(Cp)$_{av}$ distance is considered to become a diagnostic for the valence state of the ferrocene; i.e., the distance is 2.045 Å for ferrocene[20] and 2.075 Å for the ferrocenium cation.[21] It can be judged that Fe(1) is trivalent and Fe(2) is bivalent. The slight difference in the environment around two iron atoms is in accordance with the result of ^{57}Fe Mössbauer spectrum constituted from close two doublets. Therefore, very close trapped-valence states are explained by a small difference in the average distance of iron to a carbon atom in the Cp rings. Both of the 2-phenylbutyl substituents are of the *R*-configuration (hydrogen atoms on chiral carbons are located in front of the paper in Figure 8) and keep their chirality in the crystal.

The counteranion is composed of triiodide anion and iodine molecule units as is the case of the (*R*,*S*) pentaiodide salt. It is known that the trapped-valence biferrocenium cation is accompanied by an asymmetric anion.[13] In the present case, the triiodide anion unit in the (*R*,*R*) pentaiodide salt is asymmetric: I(1)−I(2) = 2.8680(10) Å, I(2)−I(3) = 2.9160(10) Å, and I(1)−I(2)−I(3) = 179.79(5)°. The iodine molecule unit is not also placed in the center between two triiodide units. It approaches the most negatively charged iodine atom (I(3)) in the triiodide anion unit; i.e., I(3)−I(4) = 3.3000(10) and I(1)−I(5) = 3.4050(10) Å. In a comparison of the distance of each iron atom to the nearest iodine atom, the distance of Fe(1)−I(3) is closer than that of Fe(2)−I(1). This finding indicates that Fe(1) is trivalent. This assignment is consistent with the judgment concerning the distance between the iron atom and C(Cp)$_{av}$.

Figure 5b shows the packing illustrations of a cation in the anion chains for the (*R*,*R*) pentaiodide salt. It can be seen that the anion chains create a centrosymmetric space in the (*R*,*S*) pentaiodide salt that should pack the cation. The centrosymmetric space is maintained in the crystal of the (*R*,*R*) pentaiodide salt in the same way as that of the (*R*,*S*) pentaiodide salt except for very small differences. As the interspace constructed by anion chains has a centrosymmetric structure, the (*R*,*S*) cation having an inversion center can be packed without troubles, maintaining the symmetric structure. On the other hand, the (*R*,*R*) cation does not have a centrosymmetric structure intrinsically. Although one ferrocene unit having an *R*-substituent is packed in the same way as that in the (*R*,*S*) cation, the other moiety is required to jam into the space which should be packed by the ferrocene unit having an *S*-substituent in the (*R*,*S*) cation (shown as *R*′-substituent in Figure 5b). It is thought that the tilt angles between Cp rings bear testimony to this phenomenon. That is, one tilt angle is the same as that in the (*R*,*S*) cation and the other is larger. The Fe−C(Cp)$_{av}$ distance in the unit having the larger tilt angle is larger than the other, showing that the iron atom is the ferrocenium type. As the structures of two ferrocene units differ from each other, the valence state becomes trapped as a result.

The ORTEP drawing of the (*S*,*S*) pentaiodide salt at 293 K is shown in Figure 9. Crystallographic data for the (*S*,*S*) pentaiodide salt are listed in Table 1, and selected bond distances and angles are given in Table 5. The cation and anion structures are similar to those in the (*R*,*R*) pentaiodide salts. All substituents have an *S*-configuration (hydrogen atoms on chiral carbons are located in front of the paper in Figure 9). The (*S*,*S*) and the (*R*,*R*) cations are related via enantiomorphism. The (*S*,*S*) cation also has two different ferrocene units. One tilt angle between Cp rings is large

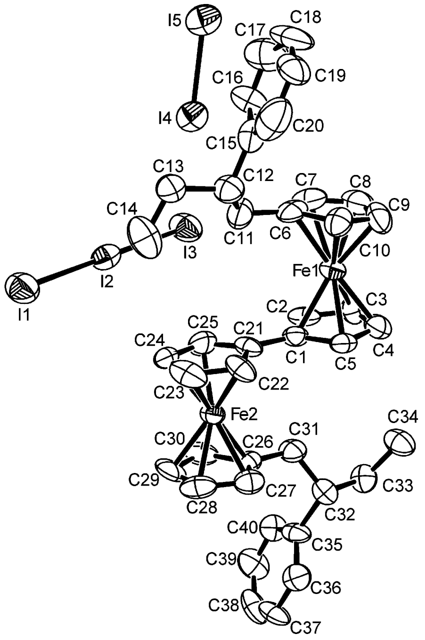

Figure 9. ORTEP drawing for the (*S*,*S*) pentaiodide salt at 293 K. The thermal ellipsoids are drawn at the 50% probability level.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for the (*S*,*S*) Pentaiodide Salt

Bond Lengths			
I(1)−I(2)	2.869(2)	I(1)−I(5)	3.405(2)
I(2)−I(3)	2.920(2)	I(3)−I(4)	3.305(2)
I(4)−I(5)	2.764(2)	Fe(1)−C(1)	2.10(2)
Fe(1)−C(2)	2.02(2)	Fe(1)−C(3)	2.04(2)
Fe(1)−C(4)	2.05(2)	Fe(1)−C(5)	2.10(2)
Fe(1)−C(6)	2.13(2)	Fe(1)−C(7)	2.09(2)
Fe(1)−C(8)	2.04(2)	Fe(1)−C(9)	2.03(2)
Fe(1)−C(10)	2.06(2)	Fe(2)−C(21)	2.08(2)
Fe(2)−C(22)	2.05(2)	Fe(2)−C(23)	2.03(2)
Fe(2)−C(24)	2.02(2)	Fe(2)−C(25)	2.00(2)
Fe(2)−C(26)	2.09(2)	Fe(2)−C(27)	2.10(2)
Fe(2)−C(28)	2.06(2)	Fe(2)−C(29)	2.03(2)
Fe(2)−C(30)	2.05(2)	C(1)−C(2)	1.41(3)
C(1)−C(5)	1.45(2)	C(1)−C(21)	1.44(2)
C(2)−C(3)	1.40(3)	C(3)−C(4)	1.42(3)
C(4)−C(5)	1.42(3)	C(6)−C(7)	1.44(3)
C(6)−C(10)	1.47(3)	C(7)−C(8)	1.34(3)
C(8)−C(9)	1.43(4)	C(9)−C(10)	1.39(3)
C(21)−C(22)	1.44(3)	C(21)−C(25)	1.37(3)
C(22)−C(23)	1.41(3)	C(23)−C(24)	1.41(4)
C(24)−C(25)	1.37(3)	C(26)−C(27)	1.43(2)
C(26)−C(30)	1.43(3)	C(27)−C(28)	1.44(3)
C(28)−C(29)	1.39(4)	C(29)−C(30)	1.40(3)
Bond Angles			
I(1)−I(2)−I(3)	179.68(10)	I(1)−I(5)−I(4)	178.66(7)
I(2)−I(1)−I(5)	102.88(7)	I(2)−I(3)−I(4)	98.42(6)
I(3)−I(4)−I(5)	176.21(6)		

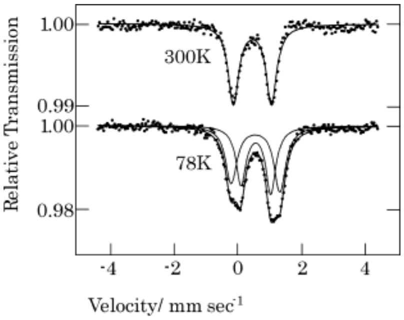

Figure 10. Variable-temperature ^{57}Fe Mössbauer spectra of the racemic pentaiodide salt.

(8.46°), and this ferrocene unit has a ferrocenium-type valence state as in the (*R*,*R*) pentaiodide salt from the viewpoint of the Fe−C(Cp)$_{av}$ distance. Figure 5c shows the packing illustration of a cation in the anion chains for the (*S*,*S*) pentaiodide salt. All illustrations in Figure 5 are seen from the same direction. In comparison of the (*S*,*S*) cation with the (*R*,*S*) cation, one ferrocene unit having an *S*-substituent is packed in the same way as that in the (*R*,*S*) cation, and the other moiety is required to jam into the space which should be packed by the ferrocene unit having the *R*-substituent in the (*R*,*S*) cation (shown as an *S*′-substituent in Figure 5c). In the illustrations of the (*R*,*R*) and the (*S*,*S*) cations, the trivalent Fe(1) exists on the opposite site of each other and has a distorted substituent. Therefore, the one part of ferrocene is distorted by the counteranions and consequently adopts the ferrocenium-type valence state in this series. Thus, the (*R*,*R*) and the (*S*,*S*) cations become valence-trapped.

The crystal data in Table 1 indicate that the volume of the (*R*,*S*) pentaiodide salt is smaller than those of the (*R*,*R*) and the (*S*,*S*) pentaiodide salts. This is due to the difference of the lattice parameters, mainly the *c*-axis. In comparison of the anion structures among the isomers, the I−I bond distance in the triiodide anion unit in the (*R*,*S*) pentaiodide salt is similar to the average distance between the I(1)−I(2) and I(2)−I(3) bond distances in other isomers. But the distance between triiodide anion and iodine molecule units in the (*R*,*S*) pentaiodide salt is shorter than the average distance between I(3)−I(4) and I(1)−I(5) bond distances in other isomers. This might reflect the good fit of the cation in the centrosymmetric space in the (*R*,*S*) pentaiodide salt as is discussed above, and the structures of the anion chains in the (*R*,*R*) and the (*S*,*S*) pentaiodide salts are distorted by cations.

Racemic Modification (Mixture of 1′,1‴-Bis((*R*)-2-phenylbutyl)-1,1″-biferrocenium Pentaiodide and 1′,1‴-Bis((*S*)-2-phenylbutyl)-1,1″-biferrocenium Pentaiodide). The racemic pentaiodide salt has equimolar amounts of the (*R*,*R*) and the (*S*,*S*) cations.

^{57}Fe Mössbauer spectra of the racemic pentaiodide salt are shown in Figure 10, and their Mössbauer parameters are listed in Table 2. The trapped-valence state at 78 K is the same as those in the (*R*,*R*) and the (*S*,*S*) pentaiodide salts. However, a perfect detrapped-valence state is observed at 300 K. This is a bizarre and interesting result because the racemic pentaiodide salt shows a temperature dependence different from those of the component (*R*,*R*) and (*S*,*S*) pentaiodide salts. The racemic pentaiodide salt adopts a perfect detrapped-valence state despite the lack of inversion center at room temperature, indicating that the packing effect overcomes the effect of cation asymmetry. This finding cannot be suitably explained by the cation symmetry effect, and it is necessary to take into account the results of the crystal structural analysis.

The crystal structure was analyzed by using space group $P2_1$ to compare with other pentaiodide salts. This cation

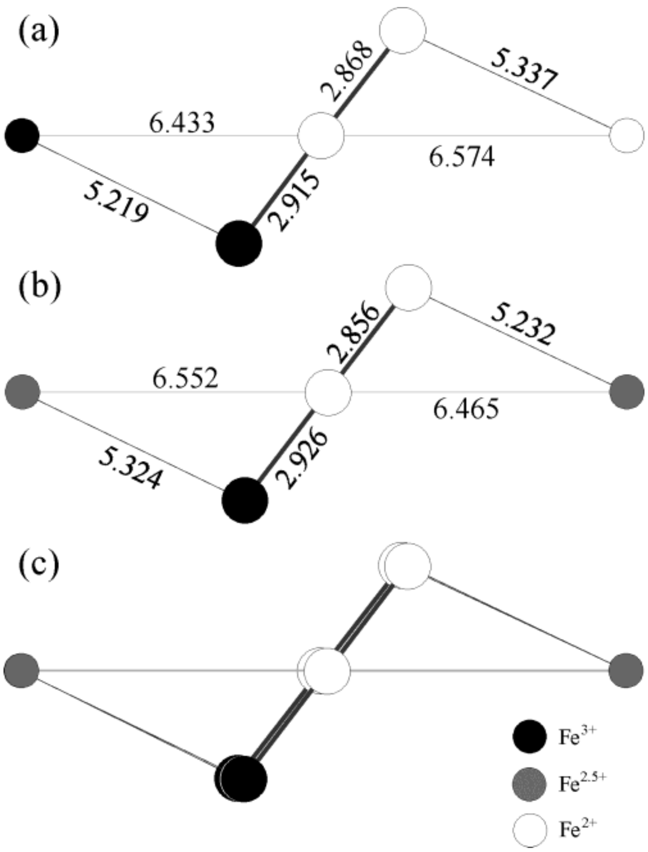

Figure 11. Geometry between the triiodide anion unit and the each nearest iron atom and selected bond distances (Å) in (a) the (*R*,*R*) pentaiodide salt and (b) the racemic pentaiodide salt. (c) Overwriting of (a) and (b).

Table 6. Bond Lengths (Å) and Angles (deg) for the Pentaiodide Anion in the Racemic Pentaiodide Salt

	Bond Lengths		
I(1)−I(2)	2.926(4)	I(1)−I(5)	3.355(3)
I(2)−I(3)	2.855(4)	I(3)−I(4)	3.328(3)
I(4)−I(5)	2.767(2)		
	Bond Angles		
I(1)−I(2)−I(3)	179.28(18)	I(1)−I(5)−I(4)	178.23(9)
I(2)−I(1)−I(5)	101.3(1)	I(2)−I(3)−I(4)	101.2(1)
I(3)−I(4)−I(5)	178.04(9)		

structure is similar to those of the other pentaiodide salts, and its substituents present a mean structure between the (*R*,*R*) and the (*S*,*S*) cations. Meanwhile, the pentaiodide anion is not a mean structure between them in the (*R*,*R*) and the (*S*,*S*) pentaiodide salts. The I−I distances in the triiodide anion unit are 2.926(4) and 2.855(4) Å; the triiodide anion unit is asymmetric as well as the (*R*,*R*) and the (*S*,*S*) pentaiodide salts despite valence-derapping in the racemic pentaiodide salt as listed in Table 6.

Figure 11 shows the geometry between the triiodide anion unit and each of the nearest iron atoms. In the distances between an iron and the nearest iodine atoms, the most negatively charged iodine atom (larger black circle) is farther than another terminal iodine atom from each of the nearest iron atoms as shown in Figure 11b. The selected five atoms are approximately in a plane, and the distances between the selected iron atoms are almost equal in each pentaiodide salt. The triiodide anion unit shifts in parallel by 0.1 Å from the (*R*,*R*) pentaiodide salt to the racemic pentaiodide salt, which balances out the electrostatic interaction without delocalization on the anion as in the case of biferrocenium bromodiiodide.[7a,29]

Table 7. Summary of the Mixed-Valence States and Cation Symmetry for 1′,1‴-Bis(2-phenylbutyl)-1,1″- biferrocenium Pentaiodides

		(*R*,*S*) isomer	(*R*,*R*) isomer	(*S*,*S*) isomer	racemic modification
valence state	300 K	detrapped	trapped	trapped	detrapped
	78 K	detrapped	trapped	trapped	trapped
cation symmetry		symmetric	asymmetric	asymmetric	

It is hard to decide whether the anion arrangement dominates the detrapped-valence state in the racemic pentaiodide salt or a detrapped-valence state displaces the triiodide anion unit to a position achieving an electrostatic balance. It is very important, however, that the coexistence of the (*R*,*R*) and the (*S*,*S*) cations in the crystal makes the valence detrapped, clearly showing that the packing effect overcomes the effect of cation asymmetry.

Conclusion

In this study, we synthesized pure pentaiodide salts of the (*R*,*S*), the (*R*,*R*), the (*S*,*S*), and the racemic modification for 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocene. The results from ^{57}Fe Mössbauer spectra and X-ray structural analyses are summarized in Table 7. The (*R*,*S*) isomer has an inversion center in itself and showed the detrapped-valence state. On the other hand, the (*R*,*R*) and the (*S*,*S*) isomers cannot have an inversion center intrinsically and showed the trapped-valence state. This shows that the cation symmetry is an important factor in the mixed-valence state. The racemic modification which consists of the (*R*,*R*) and the (*S*,*S*) isomers showed the detrapped-valence state at room temperature. This reveals that the cation asymmetry effect was overcome by the packing effect.

Acknowledgment. We thank Mrs. Emi Ohta, Natural Science Center for Basic Research and Development, Hiroshima University, for the elemental analyses.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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