Even−Odd Character and Dynamic Electronic State in the Binuclear Ferrocene Derivatives with Long Alkyl Substituents

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X-ray powder diffraction patterns revealed that 1′,1‴-diheptyl- and 1′,1‴-dioctyl-1,1″-biferrocenium triiodides obtained from hexane and from dichloromethane have a layered structure with longer interlayer distances. 1′,1‴-Diheptyl-1,1″-biferrocenium triiodide falls under the category reported before, while 1′,1‴-dioctyl-1,1″-biferrocenium triiodide becomes exception; it shows a valence detrapping with increasing temperature despite the longer interlayer series. The difference in the crystal structure between longer and shorter interlayer distance series was reflected in the difference of the space group. 1′,1‴-Diheptyl-1,1″-biferrocenium triiodide ($C_{34}H_{46}Fe_2I_3$) crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 27.209(10)$ Å, $b = 9.6480(6)$ Å, $c = 14.042(10)$ Å, $\beta = 98.572(4)°$, and $Z = 4$, while 1′,1‴-dioctyl-1,1″-biferrocenium triiodide ($C_{36}H_{50}Fe_2I_3$) crystallizes in the monoclinic space group $P2_1/c$ with $a = 20.758(6)$ Å, $b = 9.80(1)$ Å, $c = 37.88(2)$ Å, $\beta = 90.44(3)°$, and $Z = 8$. Both salts in the present study have a space group of $P2_1/c$, which is different from the shorter interlayer series; 1′,1‴-dihexyl- and 1′,1‴-didodecyl-1,1″-biferrocenium triiodides have a space group of $P\bar{1}$. The difference in the structure between the 1′,1‴-diheptyl derivative and the 1′,1‴-dioctyl derivative is also discussed. There is a difference in the symmetry of the monocation between the two salts, while both show the unsymmetrical triiodide anion. The difference between them makes the difference of the cation−cation interaction. The structure of the cations agrees with the result of ^{57}Fe Mössbauer spectroscopy. The cation−cation interaction in the stacking is observed in 1′,1‴-dioctyl derivative, while such interaction is disturbed by the adjacent stacking in 1′,1‴-diheptyl derivative.

1. Introduction

The nature of electron transfer between well-separated metal sites has been discussed in connection with studies of superconductive materials and biological systems.[1,2] D. O. Cowan and F. Kaufman provided us with mixed-valence states of binuclear ferrocenes.[3] Recently, M. Watanabe et al. found an interesting mixed-valence state in binuclear ruthenocenes.[4] The mixed-valence binuclear ferrocene derivatives are recognized as a good model compound in studying the intramolecular electron-transfer process because of the ease of synthetic design and of various selectivities for counteranions. Recent progress of understanding of the mixed-valence state for binuclear ferrocene derivatives is due to the discovery of a temperature-dependent mixed-valence state in 1′,1‴-diethyl-1,1″-biferrocenium triiodide, in which two quadrupole-split doublets observed at low temperatures converge into one doublet and no significant broadening of the half-width in ^{57}Fe Mössbauer spectra is observed in the detrapping process.[5] Hendrickson's and Sano's groups suggested the important role of environment in the mixed-valence state.[2,6,7]

For a long time, the present authors have studied the mixed-valence state of binuclear ferrocene derivatives, especially by means of ^{57}Fe Mössbauer spectroscopy and X-ray structural analyses, in order to clarify the important role of environment in the mixed-valence state.[8−11] Recently, our attention has been concentrated on the triiodide salts of binuclear ferrocenes with long alkyl substituents, exhibiting layered structures. Those structures are divided into two groups: one has longer interlayer distances and the other has shorter interlayer distances. Systematic change of the alkyl group showed an interesting even−odd character in the relationship between the interlayer distance and the number of carbon atoms of the substituent.[12−17] That is, the salts with odd-numbered carbons in the alkyl substituent

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only indicate the longer interlayer distances. On the other hand, the salts with even-numbered carbons can indicate two interlayer distances (shorter or longer) by the conditions of preparation. Both salts give quite different ^{57}Fe Mössbauer spectra; i.e., the longer interlayer distance salts give a temperature-independent trapped-valence state, while the shorter interlayer distance salts give the "fusion-type" valence detrapping like the case of 1′,1‴-diethyl-1,1″-biferrocenium triiodide.

The present authors have already reported the X-ray structural analyses for the derivatives with even-numbered carbons in the alkyl group ($n = 6$, 12).[15,17] To advance the chemistry of the mixed-valence state, it is important to investigate the crystal structure for the triiodide salts with odd-numbered carbons in the substituent. The aim of the present study is to investigate the ^{57}Fe Mössbauer spectra and the crystal structure of 1′,1‴-diheptyl- and 1′,1‴-dioctyl-1,1″-biferrocenium triiodides in connection with those of previous analogues. The difference between the longer and shorter interlayer series is discussed. The difference of the carbon number in the alkyl substituents affecting the mixed-valence state in the longer interlayer distance series is also discussed.

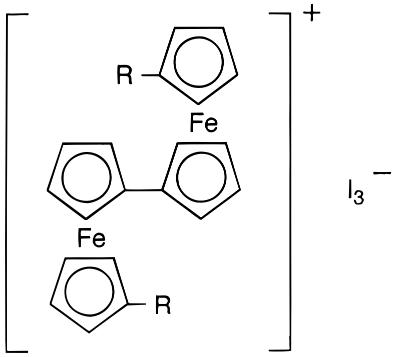
2. Experimental Section

2.1. Syntheses. 1′,1‴-Diheptyl- and 1′,1‴-dioctyl-1,1″-biferrocenes (Chart 1) were synthesized according to a method reported for a series of biferrocenes disubstituted with alkyl substituents.[8−17] The products were isolated by column chromatography on alumina and purified by recrystallization from dichloromethane−hexane.

1′,1‴-Diheptyl-1,1″-biferrocene. ^{1}H NMR (δ/ ppm, $CDCl_3$): 4.24 (4H), 4.11 (4H), 3.87 (4H), 3.83 (4H) (Fc); 2.09 (4H), 1.22 (20H), 0.87 (6H) (heptyl). Found for 1′,1‴-diheptyl-1,1″-biferrocene: C, 72.44; H, 8.31. Calcd for $C_{34}H_{46}Fe_2$: C, 72.10; H, 8.19.

1′,1‴-Dioctyl-1,1″-biferrocene. ^{1}H NMR($CDCl_3$): 4.24 (4H), 4.11 (4H), 3.87 (4H), 3.83 (4H) (Fc); 2.09 (4H), 1.24 (24H), 0.88 (6H) (octyl). Found for 1′,1‴-dioctyl-1,1″-biferrocene: C, 72.80; H, 8.55. Calcd for $C_{36}H_{50}Fe_2$: C, 72.73; H, 8.48. The ^{57}Fe Mössbauer spectra for 1′,1‴-diheptyl- and 1′,1‴-dioctyl-1,1″-biferrocenes at room temperature showed only one doublet ascribed to ferrocene-like Fe^{II}. The Mössbauer parameters are summarized in Table 1. There was no significant difference in the Mössbauer parameters between the 1′,1‴-diheptyl and 1′,1‴-dioctyl derivatives.

Chart 1. 1′,1‴-Diheptyl-1,1″-biferrocenium Triiodide ($R = C_7H_{15}$) and 1′,1‴-Dioctyl-1,1″-biferrocenium Triiodide ($R = C_8H_{17}$)



1′,1‴-Diheptyl- and 1′,1‴-dioctyl-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‴-dialkyl-1,1″-biferrocenes. About one-half of the sample prepared in the above manner was recrystallized from a dichloromethane solution. Found for 1′,1‴-diheptyl-1,1″-biferrocenium triiodide: (from hexane) C, 43.19; H, 4.66; (from dichloromethane) C, 44.34; H, 5.01. Calcd for $C_{34}H_{46}Fe_2I_3$: C, 43.14; H, 4.90. Found for 1′,1‴-dioctyl-1,1″-biferrocenium triiodide: (from hexane) C, 44.25; H, 4.81; (from dichloromethane) C, 44.35; H, 5.12. Calcd for $C_{36}H_{50}Fe_2I_3$: C, 44.34; H, 5.17.

2.2. ^{57}Fe Mössbauer Spectroscopic Measurements. A ^{57}Co(Rh) source moving in constant-acceleration mode was used for ^{57}Fe Mössbauer spectroscopic measurements. Variable-temperature ^{57}Fe Mössbauer spectra were obtained with a Toyo Research spectrometer and a continuous-flow cryostat. 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 X-ray powder diffraction patterns were measured by using graphite-monochromated Cu Kα radiation (Rigaku) at room temperature.

Single crystals for X-ray crystallography of 1′,1‴-diheptyl- and 1′,1‴-dioctyl-1,1″-biferrocenium triiodide were obtained by the following method. The corresponding 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.

1′,1‴-Diheptyl-1,1″-biferrocenium triiodide ($C_{34}H_{46}Fe_2I_3$) crystallized in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 27.209(10)$ Å, $b = 9.6480(6)$ Å, $c = 14.042(10)$ Å, $\beta = 98.572(4)°$, $V = 3645(4)$ Å^3, and $Z = 4$. The X-ray data were collected at 23 ± 1 °C using the ω scan technique to a maximum 2θ value of 63.1° on a Mac Science DIP3000 diffractometer equipped with a graphite monochromator. Oscillation and nonscreen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo Kα radiation ($\lambda = 0.710\,73$ Å), and the data reduction was made by the Mac DENZO program system. Lattice parameters were determined by least-squares fitting of 25 reflections having $22.11 < 2\theta < 24.76°$. 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. All hydrogen atoms were fixed at the calculated positions; these coordinates were included in the refinement with isotropic thermal parameters. The refinement based on 3013 observed reflections ($F_o > 2.50\sigma(F_o)$) converged to the $R(R_w)$ factor of 7.0% (8.5%).

1′,1‴-Dioctyl-1,1″-biferrocenium triiodide ($C_{36}H_{50}Fe_2I_3$) crystallized in the monoclinic space group $P2_1/c$, with $a = 20.758(6)$ Å, $b = 9.80(1)$ Å, $c = 37.88(2)$ Å, $\beta = 90.44(3)°$, $V = 7708(9)$ Å^3, and $Z = 8$. The X-ray data were collected at 23 ± 1 °C using the $\omega{-}2\theta$ scan technique to a maximum 2θ value of 52° on a Rigaku AFC6A four-circle diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. Lattice parameters were determined by least-squares fitting of 25 reflections having $22.23 < 2\theta < 24.96°$. The initial structure was solved by a direct method and expanded using Fourier techniques. All non-

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Table 1. ^{57}Fe Mössbauer Parameters for 1′,1‴-Diheptyl- and 1′,1‴-Dioctyl-1,1″-biferrocene and Their Triiodide Salts

T/K	δ^a/mm s^{-1}	ΔE_q/mm s^{-1}	Γ/mm s^{-1}	relative area/%
		1′,1‴-Diheptyl-1,1″-biferrocene		
298	0.45	2.32	0.24	100
		1′,1‴-Dioctyl-1,1″-biferrocene		
298	0.44	2.34	0.27	100
		1′,1‴-Diheptyl-1,1″-biferrocenium Triiodide from Hexane		
298	0.45	1.81	0.30	54.8
	0.44	0.59	0.31	45.2
203	0.49	1.92	0.36	53.7
	0.49	0.57	0.41	46.3
80	0.52	1.97	0.36	50.4
	0.53	0.57	0.40	49.6
		1′,1‴-Diheptyl-1,1″-biferrocenium Triiodide from Dichloromethane		
268	0.46	1.87	0.26	45.8
	0.46	0.59	0.31	54.2
203	0.49	1.91	0.29	47.8
	0.48	0.58	0.34	52.2
80	0.53	1.96	0.35	49.4
	0.53	0.56	0.38	50.6
		1′,1‴-Dioctyl-1,1″-biferrocenium Triiodide from Hexane		
298	0.42	1.09	0.27	100
258	0.44	1.17	0.41	100
243	0.46	1.18	0.40	100
233	0.46	1.37	0.32	50.3
	0.47	1.01	0.31	49.7
223	0.48	1.39	0.30	47.4
	0.46	0.95	0.34	52.6
213	0.48	1.65	0.35	51.1
	0.48	0.75	0.37	48.9
203	0.50	1.72	0.34	52.4
	0.51	0.70	0.35	47.6
173	0.49	1.76	0.28	50.5
	0.49	0.67	0.33	49.5
97	0.52	1.89	0.42	48.6
	0.53	0.60	0.50	51.4
80	0.53	1.89	0.31	50.9
	0.53	0.57	0.32	49.1
		1′,1‴-Dioctyl-1,1″-biferrocenium Triiodide from Dichloromethane		
268	0.45	1.18	0.29	100
223	0.47	1.18	0.36	100
203	0.48	1.40	0.38	55.4
	0.49	0.96	0.36	44.6
193	0.48	1.56	0.32	50.2
	0.49	0.85	0.35	49.8
183	0.49	1.63	0.32	51.6
	0.49	0.79	0.34	48.4
173	0.49	1.65	0.30	49.9
	0.49	0.77	0.34	50.1
93	0.51	1.84	0.32	51.1
	0.51	0.66	0.34	48.9
80	0.52	1.86	0.30	50.4
	0.53	0.63	0.32	49.6

[a] Isomer-shift data are reported with respect to iron foil.

hydrogen atoms were refined anisotropically by the full-matrix least-squares method. All hydrogen atoms were fixed at the calculated positions; these coordinates were included in the refinement with isotropic thermal parameters. The refinement based on 4098 observed reflections ($F_o > 2.00\sigma(F_o)$) converged to the R (R_w) factor of 5.5% (6.6%).

3. Results

3.1. 1′,1‴-Diheptyl-1,1″-biferrocenium Triiodide. As is mentioned in the Introduction, the structures for the triiodide salts of binuclear ferrocenes with long alkyl substituents are divided into two groups, i.e., one is a longer interlayer distance group and the other is a shorter one. The X-ray powder diffraction pattern showed that the interlayer distances of 1′,1‴-diheptyl-1,1″-biferrocenium triiodides from hexane and dichloromethane are 13.5 and 13.8 Å, respectively, which belong to the longer interlayer series on the basis of results of our previous studies.[12−17] The results come under the category reported before; i.e., the triiodide salts with odd-numbered carbons in the alkyl chain have a longer interlayer distance. The variable-temperature ^{57}Fe Mössbauer spectra of the triiodide salt from dichloromethane are shown in Figure 1. The Mössbauer parameters for both salts from hexane and dichloromethane are summarized in Table 1. The spectra consist of an inner and an outer doublet, with a nearly 1:1 ratio in area corresponding to Fe^{III} and Fe^{II} and this salt is the typical temperature-independent trapped-valence type, as is expected for the triiodide salts with odd-numbered carbon atoms in the alkyl substituent. Figure 1 shows a dramatic departure from the symmetric doublets. It is known that the unsymmetrical doublet is due to a preferred orientation and/or an anisotropy of lattice vibration (Gol'danskii−Karyagin effect).[18] The degree of departure from the symmetric doublet does not show the temperature dependence. The scanning electron microscope (SEM) picture of 1′,1‴-diheptyl-

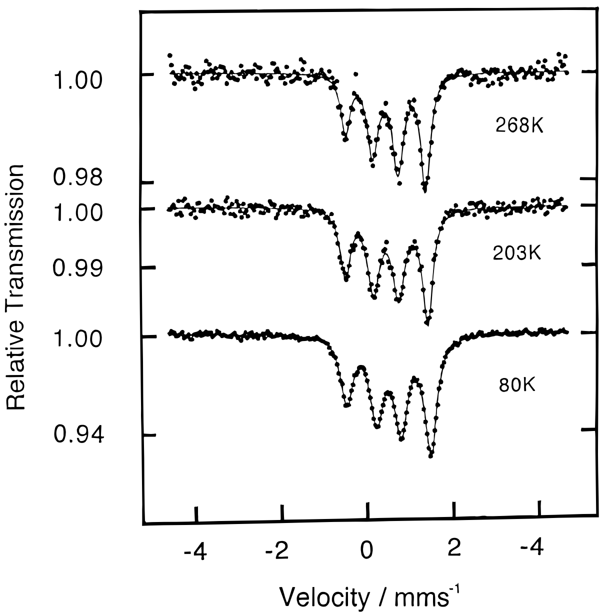

Figure 1. Variable-temperature ^{57}Fe Mössbauer spectra of 1′,1‴-diheptyl-1,1″-biferrocenium triiodide from dichloromethane.

Table 2. Crystallographic Data for 1′,1‴-Diheptyl-1,1″-biferrocenium Triiodide and 1′,1‴-Dioctyl-1,1″-biferrocenium Triiodide

empirical formula	$Fe_2C_{34}H_{46}I_3$	$Fe_2C_{36}H_{50}I_3$
fw	947.14	975.20
T/K	296	296
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a/Å	27.209(10)	20.758(6)
b/Å	9.6480(6)	9.80(1)
c/Å	14.042(10)	37.88(2)
β/deg	98.572(4)	90.44(3)
V/Å^3	3645(4)	7708(9)
Z	4	8
D_c/g cm^{-3}	1.726	1.680
μ(Mo Kα)/cm^{-1}	33.57	31.77
radiation/Å	Mo Kα, 0.710 73	Mo Kα, 0.710 73
R^a	0.070 ($F_o > 2.5\sigma(F_o)$)	0.055($F_o > 2.0\sigma(F_o)$)
$R_w{}^b$	0.085	0.066

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

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1′,1‴-Diheptyl-1,1″-biferrocenium Triiodide with Esd's in Parentheses

I(1)−I(2)	2.945(2)	Fe(2)−C(14)	2.07(2)	C(8)−C(9)	1.39(2)	C(1)−C(21)	1.52(3)
I(2)−I(3)	2.859(3)	Fe(2)−C(15)	2.04(1)	C(9)−C(10)	1.43(2)	C(21)−C(22)	1.33(4)
Fe(1)−C(1)	2.13(2)	Fe(2)−C(16)	2.06(2)	C(10)−C(6)	1.44(2)	C(22)−C(23)	1.66(5)
Fe(1)−C(2)	2.09(2)	Fe(2)−C(17)	2.04(2)	C(6)−C(11)	1.43(1)	C(23)−C(24)	1.66(4)
Fe(1)−C(3)	2.06(2)	Fe(2)−C(18)	2.08(1)	C(11)−C(12)	1.41(2)	C(24)−C(25)	1.50(4)
Fe(1)−C(4)	2.07(2)	Fe(2)−C(19)	2.04(1)	C(12)−C(13)	1.41(2)	C(25)−C(26)	1.27(5)
Fe(1)−C(5)	2.08(2)	Fe(2)−C(20)	2.09(2)	C(13)−C(14)	1.39(2)	C(26)−C(27)	1.41(4)
Fe(1)−C(6)	2.14(1)	C(1)−C(2)	1.50(2)	C(14)−C(15)	1.45(2)	C(16)−C(28)	1.52(2)
Fe(1)−C(7)	2.10(1)	C(2)−C(3)	1.44(2)	C(15)−C(11)	1.46(2)	C(28)−C(29)	1.50(2)
Fe(1)−C(8)	2.08(1)	C(3)−C(4)	1.33(2)	C(16)−C(17)	1.42(2)	C(29)−C(30)	1.53(2)
Fe(1)−C(9)	2.01(2)	C(4)−C(5)	1.41(2)	C(17)−C(18)	1.38(2)	C(30)−C(31)	1.39(2)
Fe(1)−C(10)	2.06(1)	C(5)−C(1)	1.39(3)	C(18)−C(19)	1.36(2)	C(31)−C(32)	1.55(3)
Fe(2)−C(11)	2.07(1)	C(6)−C(7)	1.47(2)	C(19)−C(20)	1.48(2)	C(32)−C(33)	1.43(4)
Fe(2)−C(12)	2.05(1)	C(7)−C(8)	1.41(2)	C(20)−C(16)	1.38(2)	C(33)−C(34)	1.61(3)
Fe(2)−C(13)	2.01(1)						

I(2)−I(1)−I(3)	179.15(5)	C(6)−C(7)−C(8)	108(1)	C(19)−C(20)−C(16)	101(1)
C(1)−Fe(1)−C(6)	110.8(6)	C(7)−C(8)−C(9)	107(1)	C(2)−C(1)−C(21)	122(2)
C(2)−Fe(1)−C(7)	108.6(6)	C(8)−C(9)−C(10)	111(1)	C(5)−C(1)−C(21)	130(2)
C(3)−Fe(1)−C(8)	107.7(6)	C(9)−C(10)−C(6)	106(1)	C(1)−C(21)−C(22)	113(2)
C(4)−Fe(1)−C(9)	109.5(6)	C(7)−C(6)−C(11)	126(1)	C(21)−C(22)−C(23)	110(3)
C(5)−Fe(1)−C(10)	108.9(6)	C(10)−C(6)−C(11)	126(1)	C(22)−C(23)−C(24)	121(3)
C(11)−Fe(2)−C(16)	111.4(5)	C(6)−C(11)−C(12)	127(1)	C(23)−C(24)−C(25)	119(3)
C(12)−Fe(2)−C(17)	109.5(6)	C(6)−C(11)−C(15)	125(1)	C(24)−C(25)−C(26)	120(4)
C(13)−Fe(2)−C(18)	105.7(6)	C(15)−C(11)−C(12)	107(1)	C(25)−C(26)−C(27)	127(4)
C(14)−Fe(2)−C(19)	108.4(6)	C(11)−C(12)−C(13)	108(1)	C(17)−C(16)−C(28)	123(1)
C(15)−Fe(2)−C(20)	108.2(6)	C(12)−C(13)−C(14)	110(1)	C(20)−C(16)−C(28)	125(1)
C(5)−C(1)−C(2)	106(1)	C(13)−C(14)−C(15)	107(1)	C(16)−C(28)−C(29)	117(1)
C(1)−C(2)−C(3)	104(1)	C(14)−C(15)−C(11)	106(1)	C(28)−C(29)−C(30)	113(1)
C(2)−C(3)−C(4)	109(1)	C(20)−C(16)−C(17)	110(1)	C(29)−C(30)−C(31)	115(1)
C(3)−C(4)−C(5)	111(1)	C(16)−C(17)−C(18)	109(1)	C(30)−C(31)−C(32)	110(1)
C(4)−C(5)−C(1)	108(1)	C(17)−C(18)−C(19)	105(1)	C(31)−C(32)−C(33)	111(2)
C(10)−C(6)−C(7)	106.4(10)	C(18)−C(19)−C(20)	113(1)	C(32)−C(33)−C(34)	111(3)

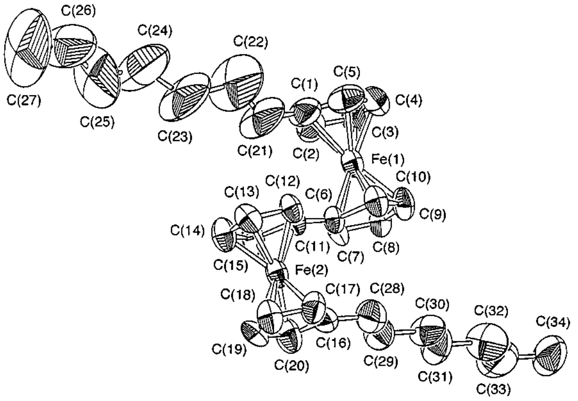

Figure 2. Structure of the cation with atom labeling of 1′,1‴-diheptyl-1,1″-biferrocenium triiodide from dichloromethane. The thermal ellipsoids are drawn at the 50% probability level.

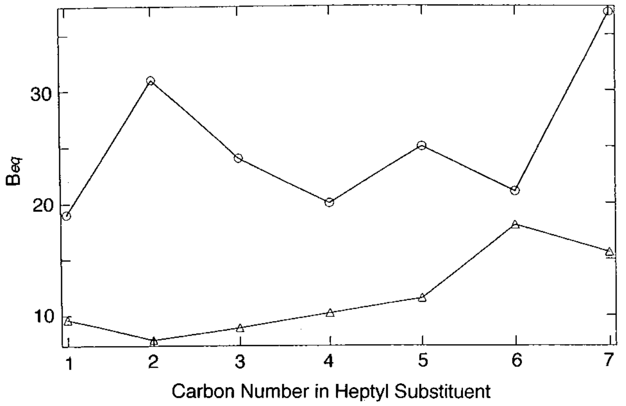

Figure 3. Thermal parameters of carbon atoms in heptyl substituents of 1′,1‴-diheptyl-1,1″-biferrocenium triiodide from dichloromethane.

1,1″-biferrocenium triiodide from dichloromethane showed a cleavage plane.[19] It is assumed that the unsymmetrical doublets are due to this texture. The salt prepared from hexane also showed the similar ^{57}Fe Mössbauer spectra with the salt from dichloromethane, and both salts revealed the typical feature of the longer interlayer distance series.

Crystallographic data for 1′,1‴-diheptyl-1,1″-biferrocenium triiodide are shown in Table 2. The selected bond distances and angles are given in Table 3. This is the first example of the X-ray crystal analysis with odd-numbered carbons in the alkyl chain except for 1′,1‴-dipropyl-1,1″-biferrocenium triiodide[20] (short alkyl chain). The space group is found to be $P2_1/c$. 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,[21] and the value for ferrocenium cation is 2.075 Å.[22] The Cp−Cp distance also becomes a diagnosis for the valence state; i.e., the value for ferrocene is 3.32 Å,[23] and the value for ferrocenium cation is 3.40 Å.[22] The mean Fe−C(ring) distances for the present cation were different (2.082 and 2.055 Å) and the Cp−Cp distance is also different (3.39 and 3.33 Å), indicating that the valence state is a trapped-valence state at room temperature, which is in accordance with the results of ^{57}Fe Mössbauer spectra constituted from two kinds of the quadrupole doublets.

The structure of the cation with atom labeling is shown in Figure 2. It can be seen that the two substituents are not

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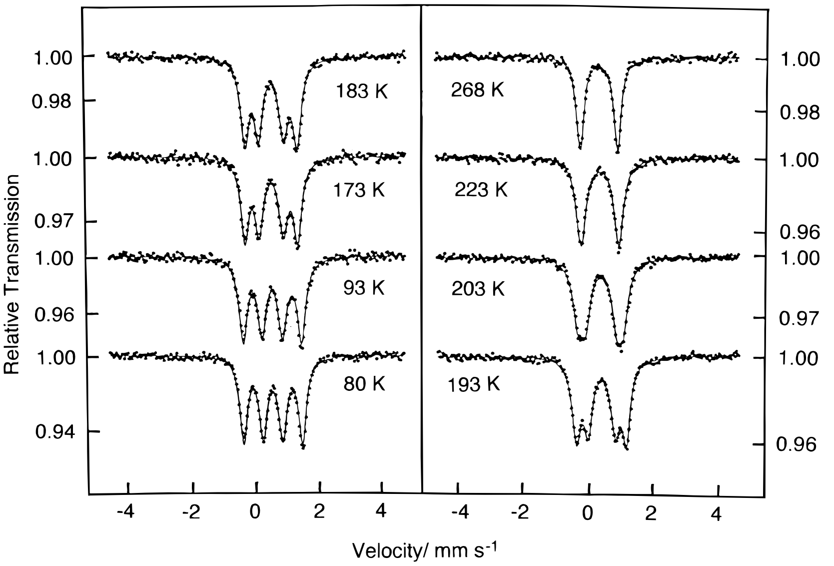

Figure 4. Variable-temperature ^{57}Fe Mössbauer spectra of 1′,1‴-dioctyl-1,1″-biferrocenium triiodide from dichloromethane.

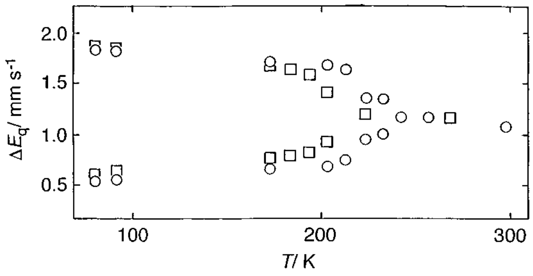

Figure 5. Temperature dependence of the quadrupole splitting values (ΔE_q) of 1′,1‴-dioctyl-1,1″-biferrocenium triiodide. (○) Hexane results; (□) dichloromethane results.

symmetric. One of them orients parallel to the Cp ring, while the other orients perpendicular to the Cp ring. Thermal parameters of carbon atoms in heptyl substituents are summarized in Figure 3. The thermal parameters for the carbons in the perpendicular alkyl chain are larger than those in the parallel one.

The I−I distances of the counteranion (I_3^-) are found to be 2.945 and 2.859 Å. The I−I−I angle is 179.17°. The result shows a linear unsymmetrical triiodide anion. The unsymmetrical triiodide anion has a good correlation with unsymmetrical monocation. ^{129}I Mössbauer spectrum of 1′,1‴-diundecyl-1,1″-biferrocenium triiodide with odd numbered carbons in the alkyl chain is reported.[16] This salt also shows a linear unsymmetrical triiodide anion.

The packing of 1′,1‴-diheptyl-1,1″-biferrocenium triiodide combined with those of the X-ray powder diffraction patterns suggests that the interlayer direction is [200]. This reflects the result that the crystal has a cleavage plane.

3.2. 1′,1‴-Dioctyl-1,1″-biferrocenium Triiodide. The X-ray powder diffraction pattern showed that the interlayer distances of 1′,1‴-dioctyl-1,1″-biferrocenium triiodides from hexane and dichloromethane are the same 13.8 Å, which belong to the longer interlayer series. 1′,1‴-Dioctyl-1,1″-biferrocenium triiodide becomes the exception to the reported result that the salt with even-numbered carbons in the alkyl chain obtained from dichloromethane can have a shorter interlayer distance. The variable-temperature ^{57}Fe Mössbauer spectra of 1′,1‴-dioctyl-1,1″-biferrocenium triiodide from dichloromethane are shown in Figure 4. The Mössbauer parameters for both salts from hexane and dichloromethane are summarized in Table 1. Typical fusion-type valence detrapping is observed, where two sets of quadrupole doublets ascribed to Fe^{II} and Fe^{III} are observed at lower temperatures and the two doublets approach each other with increasing temperature to converge into one doublet without significant line broadening. The results obtained from hexane also showed a similar temperature dependence. The temperature dependence of the quadrupole splitting values (ΔE_q) is compared in Figure 5. It can be seen that the detrapping temperature of the salt from dichloromethane is somewhat lower than that of the same salt from hexane. This might reflect the difference in the number of defect in the lattice, which supports the cooperativity of the fusion-type valence detrapping. This becomes the exception to the reported result that the salts with longer interlayer distances show the temperature-independent trapped-valence state, thus it is important to investigate the structure of the salt by means of X-ray diffraction.

Crystallographic data for 1′,1‴-dioctyl-1,1″-biferrocenium triiodide are shown in Table 2. The selected bond distances and angles are given in Table 4. The space group for the salt is found to be $P2_1/c$. The interesting thing is that the present salts (heptyl and octyl derivatives) with longer interlayer distances have a space group of $P2_1/c$, while the salts (hexyl[15] and dodecyl[17] derivatives) with shorter interlayer distances have a space group of $P\bar{1}$. Two independent pairs of cations (Cations A and B) and anions (Anions A and B) exist. The structures of the cations with atom labeling are shown in Figure 6. The mean Fe−C(ring) distances for the two independent cations were 2.062 and 2.062 Å in Cation A and 2.051 and 2.050 Å in Cation B, between the values of 2.045 Å[21] for ferrocene and of 2.075 Å[22] for ferrocenium cation, indicating that the valence states for both salts are between Fe^{II} and Fe^{III}. The result is in accordance with the result of ^{57}Fe Mössbauer spectra constituted from one kind of the quadrupole doublet.

The alkyl substituents are not in an all-trans conformation, which might lead to close packing. The difference of the crystal packing between 1′,1‴-diheptyl- and 1′,1‴-dioctyl-1,1″-biferrocenium triiodide will be discussed later.

Thermal parameters of carbon atoms in octyl substituents are summarized in Figure 7. In the octyl substituent the thermal parameters increase at the outer carbons. The two substituents in the same cation have a relatively similar value, which is different from the result of the heptyl derivative. It might be said that the large difference of the thermal parameters between the alkyl substituents in the heptyl derivative causes the valence

Table 4. Selected Bond Distances (Å) and Angles (deg) for 1′,1‴-Dioctyl-1,1″-biferrocenium Triiodide with Esd's in Parentheses

I(1)−I(2)	2.860(2)	C(1)−C(2)	1.41(2)	C(23)−C(24)	1.28(3)	Fe(4)−C(48)	2.04(1)	C(50)−C(51)	1.39(2)
I(2)−I(3)	2.920(2)	C(2)−C(3)	1.33(2)	C(24)−C(25)	1.44(3)	Fe(4)−C(49)	2.02(1)	C(51)−C(47)	1.47(2)
I(4)−I(5)	2.869(2)	C(3)−C(4)	1.41(3)	C(25)−C(26)	1.23(3)	Fe(4)−C(50)	2.02(1)	C(52)−C(53)	1.40(3)
I(5)−I(6)	2.924(2)	C(4)−C(5)	1.38(2)	C(26)−C(27)	1.40(3)	Fe(4)−C(51)	2.02(1)	C(53)−C(54)	1.42(2)
Fe(1)−C(1)	2.10(2)	C(5)−C(1)	1.44(3)	C(27)−C(28)	1.22(4)	Fe(4)−C(52)	2.07(2)	C(54)−C(55)	1.39(3)
Fe(1)−C(2)	2.05(2)	C(6)−C(7)	1.45(2)	C(16)−C(29)	1.61(2)	Fe(4)−C(53)	2.07(2)	C(55)−C(56)	1.38(3)
Fe(1)−C(3)	2.03(2)	C(7)−C(8)	1.43(2)	C(29)−C(30)	1.27(4)	Fe(4)−C(54)	2.07(2)	C(56)−C(52)	1.42(3)
Fe(1)−C(4)	2.05(2)	C(8)−C(9)	1.41(2)	C(30)−C(31)	1.62(3)	Fe(4)−C(55)	2.01(2)	C(37)−C(57)	1.48(3)
Fe(1)−C(5)	2.01(2)	C(9)−C(10)	1.39(2)	C(31)−C(32)	1.25(4)	Fe(4)−C(56)	2.07(2)	C(57)−C(58)	1.15(4)
Fe(1)−C(6)	2.09(1)	C(10)−C(6)	1.42(2)	C(32)−C(33)	1.75(3)	C(37)−C(38)	1.43(3)	C(58)−C(59)	1.65(4)
Fe(1)−C(7)	2.07(1)	C(6)−C(11)	1.49(2)	C(33)−C(34)	1.11(5)	C(38)−C(39)	1.40(2)	C(59)−C(60)	1.16(4)
Fe(1)−C(8)	2.09(1)	C(11)−C(12)	1.40(2)	C(34)−C(35)	1.94(5)	C(39)−C(40)	1.42(2)	C(60)−C(61)	1.64(5)
Fe(1)−C(9)	2.07(1)	C(12)−C(13)	1.38(2)	C(35)−C(36)	0.90(5)	C(40)−C(41)	1.36(2)	C(61)−C(62)	0.96(6)
Fe(1)−C(10)	2.06(1)	C(13)−C(14)	1.39(2)	Fe(3)−C(37)	2.11(2)	C(41)−C(37)	1.42(3)	C(62)−C(63)	1.50(4)
Fe(2)−C(11)	2.07(1)	C(14)−C(15)	1.39(2)	Fe(3)−C(38)	2.04(2)	C(42)−C(43)	1.44(2)	C(63)−C(64)	0.82(4)
Fe(2)−C(12)	2.03(1)	C(15)−C(11)	1.41(2)	Fe(3)−C(39)	2.04(2)	C(43)−C(44)	1.42(2)	C(52)−C(65)	1.45(3)
Fe(2)−C(13)	2.06(1)	C(16)−C(17)	1.41(2)	Fe(3)−C(40)	2.02(2)	C(44)−C(45)	1.41(2)	C(65)−C(66)	1.27(3)
Fe(2)−C(14)	2.05(1)	C(17)−C(18)	1.41(2)	Fe(3)−C(41)	2.04(2)	C(45)−C(46)	1.40(2)	C(66)−C(67)	1.52(3)
Fe(2)−C(15)	2.02(1)	C(18)−C(19)	1.41(2)	Fe(3)−C(42)	2.07(1)	C(46)−C(42)	1.43(2)	C(67)−C(68)	1.10(3)
Fe(2)−C(16)	2.09(1)	C(19)−C(20)	1.41(2)	Fe(3)−C(43)	2.06(1)	C(42)−C(47)	1.40(2)	C(68)−C(69)	1.56(3)
Fe(2)−C(17)	2.09(2)	C(20)−C(16)	1.37(2)	Fe(3)−C(44)	2.02(1)	C(47)−C(48)	1.44(2)	C(69)−C(70)	1.02(3)
Fe(2)−C(18)	2.04(2)	C(1)−C(21)	1.52(2)	Fe(3)−C(45)	2.04(2)	C(48)−C(49)	1.41(2)	C(70)−C(71)	1.51(3)
Fe(2)−C(19)	2.07(1)	C(21)−C(22)	1.42(3)	Fe(3)−C(46)	2.08(2)	C(49)−C(50)	1.38(2)	C(71)−C(72)	1.02(4)
Fe(2)−C(20)	2.10(2)	C(22)−C(23)	1.51(3)	Fe(4)−C(47)	2.11(1)				

I(1)−I(2)−I(3)	179.02(6)	C(2)−C(1)−C(21)	129(2)	C(43)−C(44)−C(45)	109(1)
I(4)−I(5)−I(6)	178.25(5)	C(5)−C(1)−C(21)	129(2)	C(44)−C(45)−C(46)	108(1)
C(1)−Fe(1)−C(6)	110.1(6)	C(1)−C(21)−C(22)	116(2)	C(45)−C(46)−C(42)	109(1)
C(2)−Fe(1)−C(7)	110.1(6)	C(21)−C(22)−C(23)	115(2)	C(43)−C(42)−C(47)	125(1)
C(3)−Fe(1)−C(8)	108.5(6)	C(22)−C(23)−C(24)	127(2)	C(46)−C(42)−C(47)	127(1)
C(4)−Fe(1)−C(9)	106.9(6)	C(23)−C(24)−C(25)	131(2)	C(42)−C(47)−C(48)	128(1)
C(5)−Fe(1)−C(10)	110.9(7)	C(24)−C(25)−C(26)	128(2)	C(42)−C(47)−C(51)	127(1)
C(11)−Fe(2)−C(16)	114.6(5)	C(25)−C(26)−C(27)	121(2)	C(51)−C(47)−C(48)	104(1)
C(12)−Fe(2)−C(17)	108.4(6)	C(26)−C(27)−C(28)	121(3)	C(47)−C(48)−C(49)	110(1)
C(13)−Fe(2)−C(18)	107.1(6)	C(17)−C(16)−C(29)	130(2)	C(48)−C(49)−C(50)	107(1)
C(14)−Fe(2)−C(19)	107.0(6)	C(20)−C(16)−C(29)	119(2)	C(49)−C(50)−C(51)	111(1)
C(15)−Fe(2)−C(20)	110.7(6)	C(16)−C(29)−C(30)	110(2)	C(50)−C(51)−C(47)	108(1)
C(5)−C(1)−C(2)	102(1)	C(29)−C(30)−C(31)	107(2)	C(56)−C(52)−C(53)	105(1)
C(1)−C(2)−C(3)	111(2)	C(30)−C(31)−C(32)	118(3)	C(52)−C(53)−C(54)	111(2)
C(2)−C(3)−C(4)	112(1)	C(31)−C(32)−C(33)	116(3)	C(53)−C(54)−C(55)	105(1)
C(3)−C(4)−C(5)	103(2)	C(32)−C(33)−C(34)	98(3)	C(54)−C(55)−C(56)	109(2)
C(4)−C(5)−C(1)	113(2)	C(33)−C(34)−C(35)	91(4)	C(55)−C(56)−C(52)	110(2)
C(10)−C(6)−C(7)	106(1)	C(34)−C(35)−C(36)	100(4)	C(38)−C(37)−C(57)	129(2)
C(6)−C(7)−C(8)	108(1)	C(37)−Fe(3)−C(42)	109.6(6)	C(41)−C(37)−C(57)	126(2)
C(7)−C(8)−C(9)	107(1)	C(38)−Fe(3)−C(43)	110.0(7)	C(37)−C(57)−C(58)	125(3)
C(8)−C(9)−C(10)	109(1)	C(39)−Fe(3)−C(44)	106.8(6)	C(57)−C(58)−C(59)	112(3)
C(9)−C(10)−C(6)	110(1)	C(40)−Fe(3)−C(45)	106.6(7)	C(58)−C(59)−C(60)	102(3)
C(7)−C(6)−C(11)	127(1)	C(41)−Fe(3)−C(46)	107.7(6)	C(59)−C(60)−C(61)	129(3)
C(10)−C(6)−C(11)	127(1)	C(47)−Fe(4)−C(52)	109.7(6)	C(60)−C(61)−C(62)	133(5)
C(6)−C(11)−C(12)	126(1)	C(48)−Fe(4)−C(53)	110.4(6)	C(61)−C(62)−C(63)	139(5)
C(6)−C(11)−C(15)	124(1)	C(49)−Fe(4)−C(54)	106.2(6)	C(62)−C(63)−C(64)	170(6)
C(15)−C(11)−C(12)	109(1)	C(50)−Fe(4)−C(55)	107.3(6)	C(53)−C(52)−C(65)	125(2)
C(11)−C(12)−C(13)	107(1)	C(51)−Fe(4)−C(56)	109.9(7)	C(56)−C(52)−C(65)	131(2)
C(12)−C(13)−C(14)	108(1)	C(41)−C(37)−C(38)	105(2)	C(52)−C(65)−C(66)	128(3)
C(13)−C(14)−C(15)	109(1)	C(37)−C(38)−C(39)	110(2)	C(65)−C(66)−C(67)	135(2)
C(14)−C(15)−C(11)	106(1)	C(38)−C(39)−C(40)	105(1)	C(66)−C(67)−C(68)	134(3)
C(20)−C(16)−C(17)	111(1)	C(39)−C(40)−C(41)	111(2)	C(67)−C(68)−C(69)	127(3)
C(16)−C(17)−C(18)	104(1)	C(40)−C(41)−C(37)	109(2)	C(68)−C(69)−C(70)	124(3)
C(17)−C(18)−C(19)	111(1)	C(46)−C(42)−C(43)	107(1)	C(69)−C(70)−C(71)	134(3)
C(18)−C(19)−C(20)	105(1)	C(42)−C(43)−C(44)	107(1)	C(70)−C(71)−C(72)	129(3)
C(19)−C(20)−C(16)	109(1)				

trapping because of the unsymmetrical environment, while the relatively similar values in the octyl derivative cause the valence detrapping because of the relatively symmetric environment.

The I−I distances of two independent counteranions are 2.920 and 2.860 Å for Anion A and 2.924 and 2.869 Å for Anion B. The I−I−I angles are 179.02° for Anion A and 178.25° for Anion B. Both anions show a linear unsymmetrical triiodide anion. The interesting thing is that the salt shows the detrapped-valence state despite the unsymmetrical triiodide anion, which is different from the result of the heptyl derivative. In the present salt, the mixed-valence state was not related to the symmetry of the counteranion. There is another example for the inconsistency between the symmetry of cation and anion. Biferrocenium triiodide shows a trapped-valence state from low temperature to room temperature despite the symmetric triiodide.[24]

The packing of 1′,1‴-dioctyl-1,1″-biferrocenium triiodide combined with those of the X-ray powder diffraction patterns suggests that the interlayer distance direction is [102].

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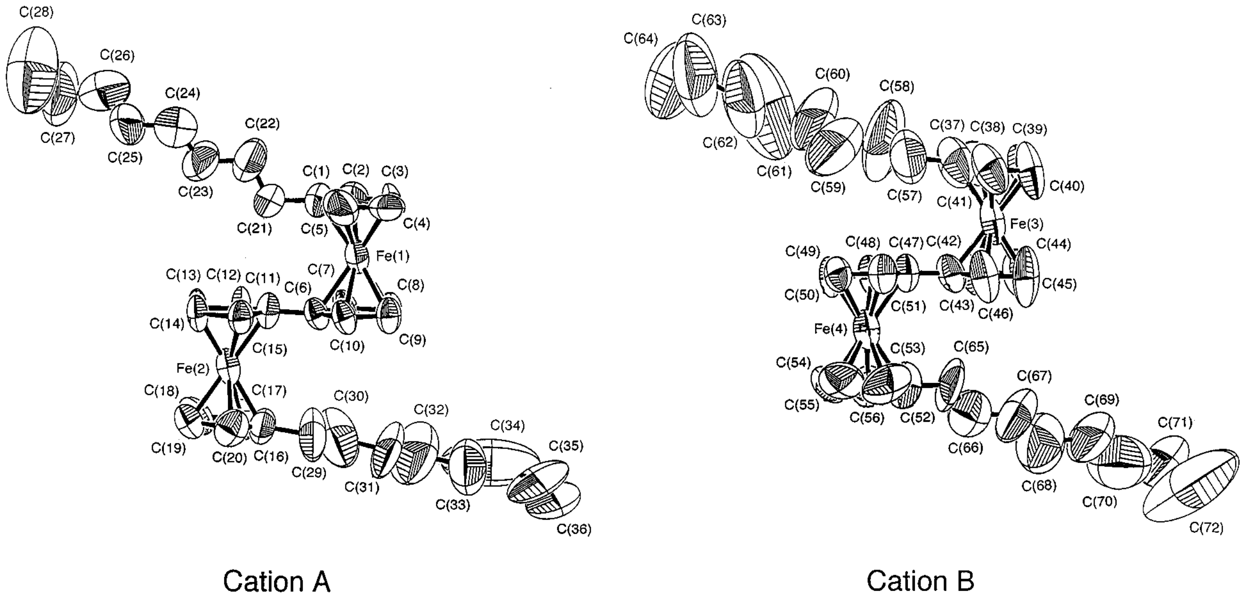

Cation A

Cation B

Figure 6. Structure of the cations (Cation A and B) with atom labeling of 1′,1‴-dioctyl-1,1″-biferrocenium triiodide from dichloromethane. The thermal ellipsoids are drawn at the 50% probability level.

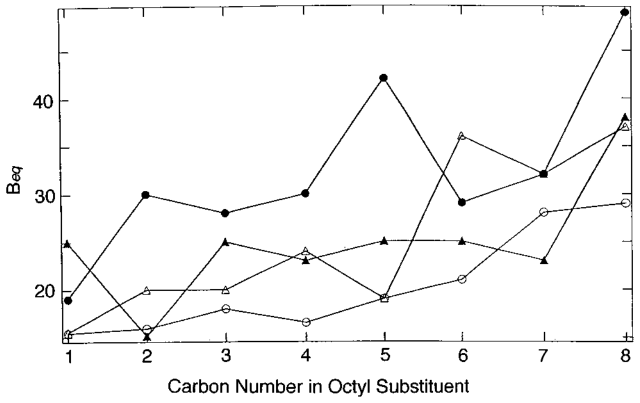

Figure 7. Thermal parameters of carbon atoms in octyl substituents of 1′,1‴-dioctyl-1,1″-biferrocenium triiodide from dichloromethane. (○, △) Cation A results; (●, ▲) Cation B results.

Table 5. Tilt Angles between Least-Squares-Fitted Cp Rings

compound	tilt angle/deg
1′,1‴-diheptyl-1,1″-biferrocenium triiodide	4.17, 2.97
1′,1‴-dioctyl-1,1″-biferrocenium triiodide	
Cation A	2.43, 4.67
Cation B	4.06, 4.23

4. Discussion

Dong et al. showed that the deviations of the Cp rings from the parallel position correlate with the valence-detrapping temperature in mixed-valence polyalkyl-substituted biferrocenium cations.[25] The deviations of the Cp rings from the parallel position in the present salts are summarized in Table 5. The values are similar between the two salts, while the two salts show the absolutely different mixed-valence state. This emphasizes the important role of the intermolecular interaction in the mixed-valence state.

One may ask what is the difference between 1′,1‴-diheptyl- and 1′,1‴-dioctyl-1,1″-biferrocenium triiodide because 1′,1‴-diheptyl-1,1″-biferrocenium triiodide shows the temperature-independent trapped-valence state and 1′,1‴-dioctyl-1,1″-biferrocenium triiodide shows the valence detrapping despite both having the longer interlayer distance structure and the unsymmetrical triiodide anion. The alkyl substituents show the difference in the two heptyl substituents. As was shown in the Results, one of them orients parallel to the Cp ring, while the other orients perpendicular to the Cp ring. On the other hand, the octyl substituents are relatively symmetric. Such a difference of the substituents is already reported in 1′,1‴-dibutyl-1,1″-biferrocenium triiodide. The salt has a polymorphism. One is needlelike crystals, and the other is platelike crystals. The former has unsymmetrical substituents and shows the temperature-independent trapped-valence state, while the latter has relatively symmetric substituents and shows the valence detrapping.[9,10] The relation between the symmetry of the substituents and the mixed-valence state in the present study is similar to the relation observed in the two polymorphisms in 1′,1‴-dibutyl-1,1″-biferrocenium triiodide.

To understand why 1′,1‴-diheptyl- and 1′,1‴-dioctyl-1,1″-biferrocenium triiodides show the difference in the temperature dependence of the mixed-valence state, we have to consider the difference in the cation−cation interaction between them, because both triiodide anions are unsymmetrical. The packings are shown in Figures 8 and 9, respectively, to show the difference between them easily. It can be seen that the packing arrangement in the octyl derivative continues in one direction in the column, while the arrangement in heptyl derivative does not continue in one direction in the column. The perpendicular heptyl substituent interacts with the perpendicular heptyl substituent in the adjacent stacking, although the parallel heptyl substituent interacts with the parallel substituent in the same column. Thus the present result may suggest the important role of the cation−cation interaction in the column. It may be concluded that the difference of the carbon number in the alkyl substituents in the longer interlayer series affects the intermolecular cation−cation interaction in the column. It may be considered that the interaction between cation and cation exceeds the interaction between cation and anion in the octyl derivative, while the cation−cation interaction cannot exceed the cation−anion interaction in the heptyl derivative because of the disturbance from the adjacent column.

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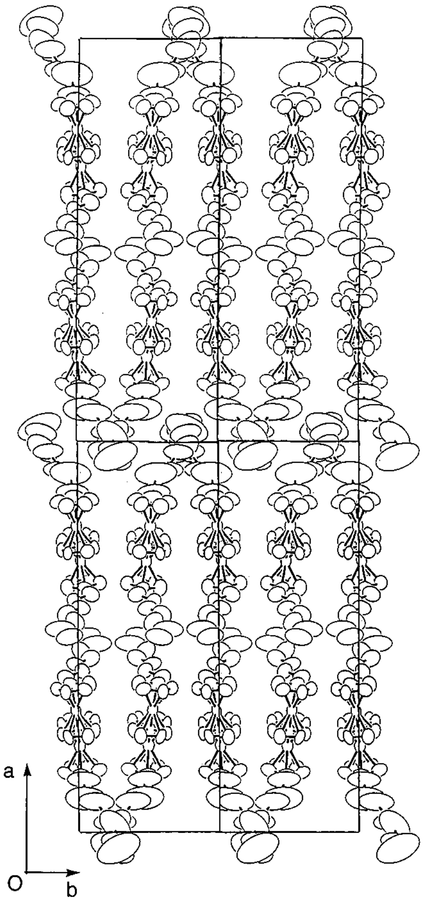

Figure 8. Projection of 1′,1‴-diheptyl-1,1″-biferrocenium triiodide to the *ab* plane.

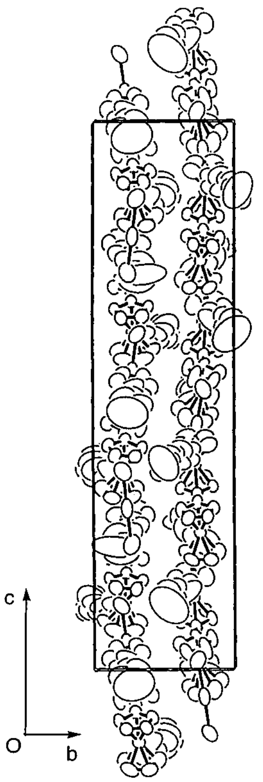

Figure 9. Projection of 1′,1‴-dioctyl-1,1″-biferrocenium triiodide to the *bc* plane.

Here we discuss the relation among the mixed-valence state, the symmetry of cation and anion, and crystal packing. To this aim we recall the relation between the crystal structure and the mixed-valence state of 1,1″-biferrocenium triiodide and 1′,1‴-diethyl-1,1″-biferrocenium triiodide.[11] The temperature dependence of the mixed-valence state of 1′,1‴-diethyl-1,1″-biferrocenium triiodide is coupled with a change in the symmetry of the triiodide anion.[11] On the other hand, 1,1″-biferrocenium triiodide shows the valence detrapping at higher temperatures than room temperature, although the symmetry of the triiodide anion remains symmetric at all temperatures.[24] One of several possible explanations was that the structural difference between 1,1″-biferrocenium triiodide and 1′,1‴-diethyl-1,1″-biferrocenium triiodide, and thus the difference in crystal packing might be responsible for the way of valence-detrapping. In the 1,1″-biferrocenium triiodide crystal, the monocations and triiodide anions are stacked in independent columns.[7,26] There exists Cp−Cp overlap between cations in a steplike stack of cations. On the other hand, in 1′,1‴-diethyl-1,1″-biferrocenium triiodide crystal, each monocation is surrounded by triiodide anions and vice versa.[27] In this case $\pi-\pi$ or $\mathrm{CH}-\pi$ interactions between cations would not be expected. Therefore the difference between 1,1″-biferrocenium triiodide and 1′,1‴-diethyl-1,1″-biferrocenium triiodide was that the cations in the former can interact directly while the cations in the latter need to interact through the triiodide anions. Such consideration allowed us to suggest that the temperature dependence of the mixed-valence state is independent of the counteranion in 1,1″-biferrocenium triiodide, while it depends on the symmetry change of the counteranion in 1′,1‴-diethyl-1,1″-biferrocenium triiodide. In the present study cations both in 1′,1‴-dioctyl- and 1′,1‴-diheptyl-1,1″-biferrocenium triiodides are stacked in the columns as the case of 1,1″-biferrocenium triiodide. In this case, cations have a possibility to interact in the cation stacking. The cations of 1′,1‴-dioctyl-1,1″-biferrocenium triiodide can interact with each other, which shows valence detrapping, while the cations of 1′,1‴-diheptyl-1,1″-biferrocenium triiodide cannot interact in the cation column because of the disturbance from the adjacent column, which does not show valence detrapping. The importance of the cation−cation interaction is also indicated in 1′,1‴-bis(β-naphthylmethyl)-1,1″-biferrocenium pentaiodide.[28] There remains, however, as question why there is a difference in the symmetry of the triiodide anion between 1,1″-biferrocenium triiodide and 1′,1‴-dioctyl-1,1″-biferrocenium triiodide despite both showing valence detrapping.

Supporting Information Available: Tables listing detailed crystallographic data, positional parameters, and least-squares planes (10 pages). Ordering information is given on any current masthead page.

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