

⁵⁷Fe Mössbauer spectra and X-ray structural analyses of iodide salts for 1',1'''-bis(α- and β-naphthylmethyl)-1,1''-biferrocenes

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Abstract

The relation between the mixed-valence state and crystal structure of iodide salts for 1',1'''-bis(α- and β-naphthylmethyl)-1,1''-biferrocenes has been studied by means of ⁵⁷Fe Mössbauer spectroscopy and X-ray structural analysis. Time change of ⁵⁷Fe Mössbauer spectroscopy was first observed for only the α-naphthylmethyl derivative; the trapped-valence state (metastable phase) of the Fe atom in the salt gradually changes into the detrapped-valence state (stable phase) on standing at room temperature for one month. There are two independent monocations in the β-naphthylmethyl derivative. Both salts (α-naphthylmethyl derivative in stable phase and β-naphthylmethyl derivative) gave the detrapped-valence state of ⁵⁷Fe Mössbauer spectra, implying the equivalence of the oxidation state of the two Fe atoms. X-ray diffraction studies of both salts support the above results, i.e. both monocations sit on the center of symmetry and the Fe–C(Cp) distances (2.064(2) Å for the α-naphthylmethyl derivative and 2.061(9) and 2.056(7) Å for the β-naphthylmethyl derivative) are close to the mean values of ferrocene and ferrocenium ion. © 1997 Elsevier Science S.A.

Keywords: Mixed-valence state; Binuclear ferrocene derivatives; ⁵⁷Fe Mössbauer spectroscopy; X-ray structural analysis

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]. Especially, a number of ⁵⁷Fe Mössbauer spectroscopic and other studies on mixed-valence binuclear ferrocene derivatives have provided us with important information on electron-transfer processes, i.e. the rate of electron transfer in the mixed-valence salts is strongly concerned with the packing of the cations and anions [2–11]. In addition, systematic change of the alkyl group showed an interesting even–odd character in the number of carbon atoms of the substituent in the relationship between the crystal structure and the mixed-valence state [6–11]. In the second stage our strategy is the use of the derivative attached to a planar substituent. In the present study, the relation between

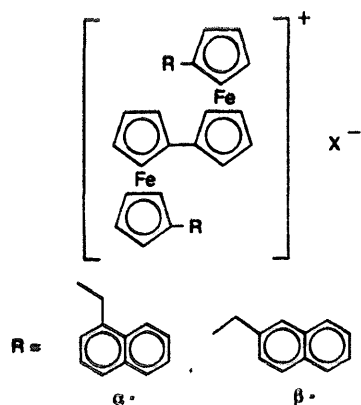
the mixed-valence state and the crystal structure of iodide salts for 1',1'''-bis(α- and β-naphthylmethyl)-1,1''-biferrocenes is investigated by means of ⁵⁷Fe Mössbauer spectroscopy and X-ray structural analysis.

2. Experimental

2.1. Syntheses

1',1'''-Bis(α- and β-naphthylmethyl)-1,1''-biferrocenes were synthesized according to a method reported for a series of biferrocenes disubstituted with alkyl substituents [4–11]. The products were isolated by column chromatography on alumina and purified by recrystallization from dichloromethane–hexane. 1',1'''-Bis(α-naphthylmethyl)-1,1''-biferrocene: m.p. 221–223 °C. ¹H NMR (δ/ppm, CDCl₃): 7.94 (2H), 7.82 (2H), 7.65 (2H), 7.48 (4H), 7.31 (2H), 7.10 (2H) (naphthyl); 4.42 (4H), 4.29 (4H), 4.01 (8H) (Fc); 3.78 (4H) (–CH₂–).

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Scheme 1. 1',1''-Bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide and 1',1''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaoidide ($X = I_3$ or I_5).

1',1''-Bis(β -naphthylmethyl)-1,1''-biferrocene: m.p. 172–174°C. ^1H NMR (δ /ppm, CDCl_3): 7.71 (6H), 7.48 (2H), 7.39 (6H) (naphthyl); 4.34 (4H), 4.20 (4H), 3.95 (8H) (Fc); 3.58 (4H) ($-\text{CH}_2-$). The ^{57}Fe Mössbauer spectra for 1',1''-bis(α - and β -naphthylmethyl)-1,1''-biferrocenes at room temperature show only one doublet ascribed to ferrocene-like Fe^{II} . There are no significant differences in the Mössbauer parameters between the α - and β -naphthylmethyl derivatives. Both showed the same isomer shift value, $\delta = 0.44 \text{ mm s}^{-1}$ and quadrupole splitting value, $\Delta E_q = 2.29 \text{ mm s}^{-1}$.

1',1''-Bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide (Scheme 1) was prepared by adding a stoichiometric amount of I_2 dissolved in chloroform to a chloroform solution of 1',1''-bis(α -naphthylmethyl)-1,1''-biferrocene. The sample was recrystallized from dichloromethane. Anal. Found for 1',1''-bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide: C, 48.87; H, 3.34. $\text{C}_{42}\text{H}_{34}\text{Fe}_2\text{I}_3$ Calc.: C, 48.92; H, 3.32%. 1',1''-Bis(β -naphthylmethyl)-1,1''-biferrocenium pentaoidide (Scheme 1) was obtained, although 3/2 times the amount of I_2 was added to 1',1''-bis(β -naphthylmethyl)-1,1''-biferrocene in chloroform. Anal. Found for 1',1''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaoidide: C, 39.70; H, 2.83. $\text{C}_{42}\text{H}_{34}\text{Fe}_2\text{I}_5$ Calc.: C, 38.50; H, 2.41%.

2.2. ^{57}Fe Mössbauer spectroscopic measurements

A $^{57}\text{Co}(\text{Rh})$ source moving in a constant-acceleration mode was used for ^{57}Fe Mössbauer spectroscopic measurements. Variable-temperature Mössbauer spectra were obtained by using 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 $\text{Cu K}\alpha$ radiation (Rigaku) at room temperature.

Three-dimensional room temperature X-ray data for the single crystal of 1',1''-bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide were collected in the range $2\theta < 55^\circ$ on a Mac Science MX3 four-circle diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). 1',1''-Bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide ($\text{C}_{42}\text{H}_{34}\text{Fe}_2\text{I}_3$) crystallized in the triclinic space group $P\bar{1}$, with $a = 9.820(5) \text{ \AA}$, $b = 10.439(7) \text{ \AA}$, $c = 10.650(6) \text{ \AA}$, $\alpha = 62.81(4)^\circ$, $\beta = 86.12(5)^\circ$, $\gamma = 69.71(4)^\circ$, $V = 905.4(9) \text{ \AA}^3$, and $Z = 1$. All data were corrected for absorption [12]. The initial structure was solved by a direct method using the program MONTE CARLO-MULTAN [13]. Refinement of F was carried out by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares method. All hydrogen atoms could be found on a Fourier-difference map; these coordinates were included in the refinement with isotropic thermal parameters. All the computations were carried out on a Titan-750 computer. The refinement based on 3217 observed reflections ($I > 3.0\sigma(I)$) converged to an R (R') factor of 5.4% (4.6%).

1',1''-Bis(β -naphthylmethyl)-1,1''-biferrocenium pentaoidide ($\text{C}_{42}\text{H}_{34}\text{Fe}_2\text{I}_5$) crystallized in the triclinic space group $P\bar{1}$, with $a = 11.263(2) \text{ \AA}$, $b = 18.272(4) \text{ \AA}$, $c = 10.813(3) \text{ \AA}$, $\alpha = 99.43(2)^\circ$, $\beta = 104.15(2)^\circ$, $\gamma = 74.86(1)^\circ$, $V = 2071.1(8) \text{ \AA}^3$, and $Z = 2$. The X-ray data were collected at a temperature of $23 \pm 1^\circ\text{C}$ using the ω - 2θ scan technique to a maximum 2θ value of 50° on a Rigaku AFC6A four-circle diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation. The data were corrected for Lorentz and polarization effects. Lattice parameters were determined by least-squares fitting of 25 reflections having $22.11^\circ < 2\theta < 24.76^\circ$. 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 3167 observed reflections ($I > 2.00\sigma(I)$) converged to an R (R') factor of 7.0% (9.5%).

3. Results and discussion

3.1. 1',1''-Bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide

1',1''-Bis(α -naphthylmethyl)-1,1''-biferrocene was oxidized by using a stoichiometric amount of I_2 in chloro-

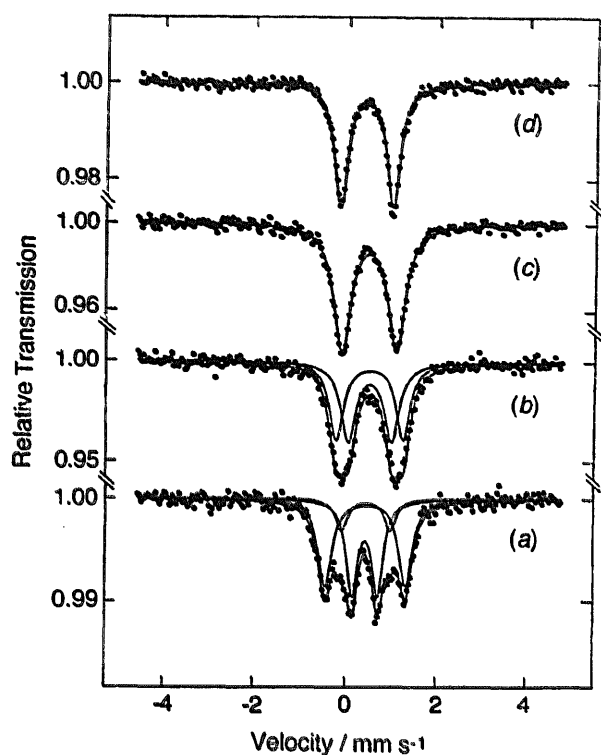


Fig. 1. Variable-temperature ^{57}Fe Mössbauer spectra of 1',1'''-bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide: (a) fresh sample at 298 K; (b) sample at 4.2 K of (a) allowed to stand at room temperature for one month; (c) sample at 80 K of (b); (d) sample at 298 K of (b).

form to give the triiodide salt. The most striking feature of the salt is found in the time change of ^{57}Fe Mössbauer spectra, i.e. the fresh salt gives two kinds of Fe states (Fe^{II} and Fe^{III}), although the spectra are not reasonable in spite of several days measurements because the oxidation state of the Fe atoms in the cation is not fixed during the measurements. About 7 days later a relatively reasonable ^{57}Fe Mössbauer spectrum was observed at room temperature (as shown in Fig. 1; the Mössbauer parameters are summarized in Table 1) which contains the trapped-valence state (in which the Fe^{II} and Fe^{III} are observed independently) and a small amount of the detrapped-valence state (where Fe^{II} and Fe^{III} are not distinguished). These results suggest that the fresh salt crystallized first is in metastable phase with trapped-valence Fe state and this phase gradually changes into the stable one with detrapped-valence Fe state on standing at room temperature. To verify the speculation, the same ^{57}Fe Mössbauer spectroscopy using the same salt and allowed to stand at room temperature for one month was carried out. Strikingly, only one doublet (detrapped-valence state) was observed at room temperature, as shown in Fig. 1(d). The slight difference of the Mössbauer parameters (especially the quadrupole splitting value) found in Fig. 1(d) and the detrapped one in Fig. 1(a) is due to the difficulty in the analysis of the spectrum for Fig. 1(a). Although no significant spectral

Table 1

^{57}Fe Mössbauer parameters for 1',1'''-bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide and 1',1'''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide

Substituent	T (K)	δ^a (mms^{-1})	ΔE_q (mms^{-1})
α -Naphthylmethyl	298 ^b	0.45	1.77
		0.44	0.56
	298 ^c	0.46	1.07
		0.43	1.15
		0.46	1.16
		0.48	1.17
		0.50	1.18
		0.50	1.19
β -Naphthylmethyl	298	0.53	1.47
		0.54	0.95
	204	0.43	1.14
		0.46	1.35
		0.46	0.94
		0.50	1.42
		0.51	0.92
		0.51	1.43
80	0.49	0.90	
	0.51	1.52	
		0.52	0.87

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

^b Fresh sample.

^c Sample allowed to stand at room temperature for one month.

change was observed by cooling the sample to 80 K, a broader spectrum was observed at 4.2 K, which can be correctly analysed by using two doublets ascribed to $\text{Fe}^{\text{II}+\delta}$ and $\text{Fe}^{\text{III}-\delta}$. The facts provide us with the information that the oxidation states of the two Fe atoms are equivalent to each other in 1',1'''-bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide in the stable phase above

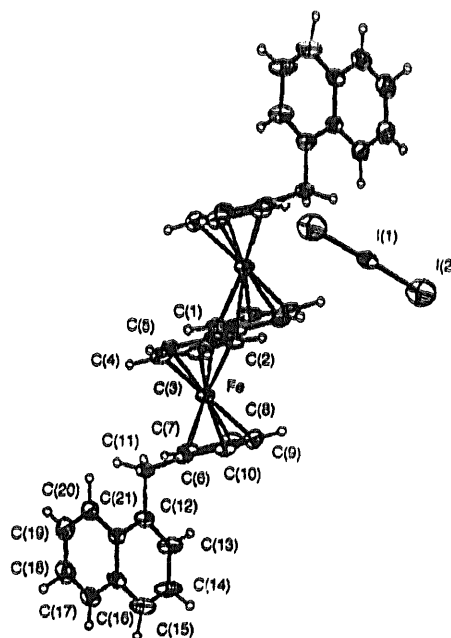


Fig. 2. Molecular structure of 1',1'''-bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide recrystallized from dichloromethane.

80 K, although they are somewhat different from each other at 4.2 K.

The results of X-ray powder diffraction patterns are concerned with the above results, i.e. the change of powder pattern is observed from the fresh sample by standing it at room temperature for one month. Thus, it can be concluded that the metastable phase with trapped-valence state of Fe is crystallized at first by the oxidation in chloroform and the phase gradually changes into the stable one which contains detrapped-valence state.

The results of X-ray diffraction of the sample prepared by the slow recrystallization from dichloromethane confirmed the above conclusion (the X-ray powder diffraction patterns of the sample correspond to those of the stable sample). An ORTEP drawing of the salt is shown in Fig. 2 and the crystal data, positional parameters and selected bond distances and angles are shown in Tables 2–4 respectively. X-ray structural analysis shows that both the cation and the anion are located at the center of symmetry. Two metallocene halves have a *trans* conformation, which is found in most ferrocene derivatives and their salts. The I–I distance (2.8943(7) Å) is typical of the symmetric triiodide anion, but is slightly shorter than that (2.9221(4) Å) of

Table 2

Crystal data for 1',1'''-bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide (stable phase) and 1',1'''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaliodide

Formula	α -Fe ₂ C ₄₂ H ₃₄ I ₃	β -Fe ₂ C ₄₂ H ₃₄ I ₅
<i>M</i>	1031.10	1284.95
<i>T</i> (K)	296	296
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	9.820(5)	11.263(2)
<i>b</i> (Å)	10.439(7)	18.272(4)
<i>c</i> (Å)	10.650(6)	10.813(3)
α (°)	62.81(4)	99.43(2)
β (°)	86.12(5)	104.15(2)
γ (°)	69.71(4)	74.86(1)
<i>V</i> (Å ³)	905.4(9)	2071.1(8)
<i>Z</i>	1	2
<i>D_c</i> (g cm ⁻³)	1.89	2.064
Crystal size (mm ³)	0.65 × 0.32 × 0.12	0.10 × 0.20 × 0.20
<i>F</i> (000)	497	1210
μ (Mo K α) (cm ⁻¹)	31.77	44.56
$[\sin \theta / \lambda]_{\max}$ (Å ⁻¹)	0.650	0.595
Total reflections measured	4458	6280
Unique reflections	4169	5873
Reflections used	3217 [$F_o > 3\sigma(F_o)$]	3167 [$F_o > 2\sigma(F_o)$]
<i>R_{int}</i>	0.02	0.048
No. of variables	271	442
Final residual electron density (e Å ⁻³)	2.33, -1.76	5.56, -0.78
<i>S</i>	3.64	2.62
<i>R</i>	0.054	0.070
<i>R'</i>	0.046	0.095

Table 3

Positional parameters for 1',1'''-bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide with estimated standard deviations (e.s.d.s) in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
I(1)	0.0	-0.5	0.0
I(2)	-0.25480(7)	-0.44302(8)	0.14764(7)
Fe	0.19120(8)	-0.24477(9)	0.18482(7)
C(1)	0.0769(6)	-0.0444(6)	0.0027(5)
C(2)	0.1320(8)	-0.1722(6)	-0.0258(5)
C(3)	0.2879(8)	-0.2314(9)	0.0042(6)
C(4)	0.3250(8)	-0.1420(9)	0.0536(7)
C(5)	0.1970(7)	-0.0289(6)	0.0554(6)
C(6)	0.2813(6)	-0.4709(6)	0.3425(5)
C(7)	0.3010(6)	-0.3667(7)	0.3839(5)
C(8)	0.1633(6)	-0.2621(8)	0.3848(6)
C(9)	0.0579(7)	-0.3056(8)	0.3449(6)
C(10)	0.1290(6)	-0.4300(7)	0.3175(6)
C(11)	0.4014(7)	-0.6035(6)	0.3367(6)
C(12)	0.4493(6)	-0.7454(6)	0.4822(5)
C(13)	0.3644(7)	-0.7582(7)	0.5909(6)
C(14)	0.4063(8)	-0.8896(8)	0.7240(7)
C(15)	0.5350(8)	-1.0061(8)	0.7499(7)
C(16)	0.6275(6)	-0.9986(6)	0.6426(6)
C(17)	0.7644(8)	-1.1166(7)	0.6671(7)
C(18)	0.8548(9)	-1.1093(8)	0.5657(8)
C(19)	0.8126(8)	-0.9812(8)	0.4297(8)
C(20)	0.6815(7)	-0.8634(7)	0.3995(7)
C(21)	0.5843(6)	-0.8675(6)	0.5054(5)
H(2)	0.069(8)	-0.213(8)	-0.056(7)
H(3)	0.348(8)	-0.332(9)	-0.010(8)
H(4)	0.414(9)	-0.148(8)	0.085(7)
H(5)	0.180(8)	0.046(8)	0.087(7)
H(7)	0.386(8)	-0.364(8)	0.403(6)
H(8)	0.128(8)	-0.178(8)	0.398(7)
H(9)	-0.024(8)	-0.257(9)	0.351(7)
H(10)	0.089(7)	-0.486(8)	0.289(6)
H(11A)	0.498(7)	-0.588(7)	0.313(6)
H(11B)	0.369(7)	-0.638(7)	0.267(6)
H(13)	0.270(8)	-0.670(8)	0.573(7)
H(14)	0.337(8)	-0.882(8)	0.798(8)
H(15)	0.570(8)	-1.108(8)	0.835(7)
H(17)	0.794(8)	-1.203(8)	0.752(8)
H(18)	0.926(9)	-1.210(9)	0.590(8)
H(19)	0.882(9)	-0.980(9)	0.361(8)
H(20)	0.646(8)	-0.772(8)	0.302(7)

1',1'''-bis(dodecyl)-1,1''-biferrocenium triiodide [9]. The mean Fe–C (cyclopentadienyl (Cp) ring) distance is found to be 2.064(2) Å, intermediate between the values of 2.033 Å for ferrocene [14] and 2.075(3) Å for ferrocenium cation [15], indicating that the valence state is intermediate between Fe^{II} and Fe^{III}. This is in accord with the result that the stable phase of the salt shows the detrapped-valence state at room temperature. In almost all the disubstituted derivatives the substituent sits on the opposite half of binuclear ferrocene. In the present salt the two α -naphthyl substituents point in unusual directions away from the cation, which is similar to the case of [1',1'''-dibenzyl-1,1''-biferrocenium] [SbF₆] [16]. The packing arrangement is also similar to that of

Table 4
Selected bond distances (Å) and angles (°) for 1',1'''-bis(α -naphthylmethyl)-1,1''-biferrocenium triiodide with e.s.d.s in parentheses

I(1)–I(2)	2.8943(7)
Fe–C(1)	2.087(4)
Fe–C(2)	2.064(6)
Fe–C(3)	2.054(7)
Fe–C(4)	2.046(8)
Fe–C(5)	2.054(6)
Fe–C(6)	2.075(4)
Fe–C(7)	2.042(5)
Fe–C(8)	2.061(7)
Fe–C(9)	2.076(6)
Fe–C(10)	2.077(7)
C(1)–C(2)	1.42(1)
C(2)–C(3)	1.43(1)
C(3)–C(4)	1.41(1)
C(4)–C(5)	1.400(9)
C(5)–C(1)	1.43(1)
C(6)–C(7)	1.42(1)
C(7)–C(8)	1.416(8)
C(8)–C(9)	1.42(1)
C(9)–C(10)	1.40(1)
C(10)–C(6)	1.414(8)
C(6)–C(11)	1.498(8)
C(11)–C(12)	1.527(6)
C(12)–C(13)	1.364(8)
C(13)–C(14)	1.404(7)
C(14)–C(15)	1.352(9)
C(15)–C(16)	1.401(9)
C(16)–C(17)	1.414(8)
C(16)–C(21)	1.429(6)
C(17)–C(18)	1.34(1)
C(18)–C(19)	1.409(9)
C(19)–C(20)	1.367(9)
C(20)–C(21)	1.422(9)
C(21)–C(12)	1.424(7)
C(1)–C(1')	1.46(1)
C(1)–Fe–C(9)	112.2(2)
C(2)–Fe–C(10)	111.0(3)
C(3)–Fe–C(6)	107.5(2)
C(4)–Fe–C(7)	106.0(3)
C(5)–Fe–C(8)	107.0(3)
C(2)–C(1)–C(5)	108.2(5)
C(1)–C(2)–C(3)	107.2(7)
C(4)–C(3)–C(2)	107.7(7)
C(5)–C(4)–C(3)	109.0(7)
C(4)–C(5)–C(1)	107.8(7)
C(10)–C(6)–C(7)	106.6(5)
C(8)–C(7)–C(6)	109.7(6)
C(7)–C(8)–C(9)	105.7(7)
C(10)–C(9)–C(8)	109.5(6)
C(9)–C(10)–C(6)	108.4(7)
C(10)–C(6)–C(11)	128.0(7)
C(7)–C(6)–C(11)	125.3(6)
C(6)–C(11)–C(12)	112.1(5)
C(13)–C(12)–C(21)	119.0(4)
C(13)–C(12)–C(11)	121.1(4)
C(21)–C(12)–C(11)	119.9(5)
C(12)–C(13)–C(14)	121.4(5)
C(15)–C(14)–C(13)	120.8(6)
C(14)–C(15)–C(16)	120.2(5)
C(15)–C(16)–C(17)	121.6(5)
C(15)–C(16)–C(21)	119.6(5)
C(17)–C(16)–C(21)	118.8(6)

Table 4 (continued)

C(18)–C(17)–C(16)	122.1(5)
C(17)–C(18)–C(19)	119.5(6)
C(20)–C(19)–C(18)	121.1(7)
C(19)–C(20)–C(21)	120.5(5)
C(20)–C(21)–C(12)	123.1(4)
C(20)–C(21)–C(16)	117.9(5)
C(12)–C(21)–C(16)	118.9(5)
C(2)–C(1)–C(1')	126.4(8)
C(5)–C(1)–C(1')	125.0(8)

C(1') is related to C(1) by the center of symmetry.

[1',1'''-dibenzyl-1,1''-biferrocenium] [SbP₆], i.e. it consists of stacks of relatively large mixed-valence cations, with the I₃⁻ anions sandwiched between the stacks of cations.

3.2. 1',1'''-Bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide

1',1'''-Bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide was obtained by adding I₂ dissolved in chloroform to a chloroform solution of 1',1'''-bis(β -naphthylmethyl)-1,1''-biferrocene, although the ratio of I₂ to 1',1'''-bis(β -naphthylmethyl)-1,1''-biferrocene was 3/2. The composition was confirmed by elemental analysis and X-ray structural analysis.

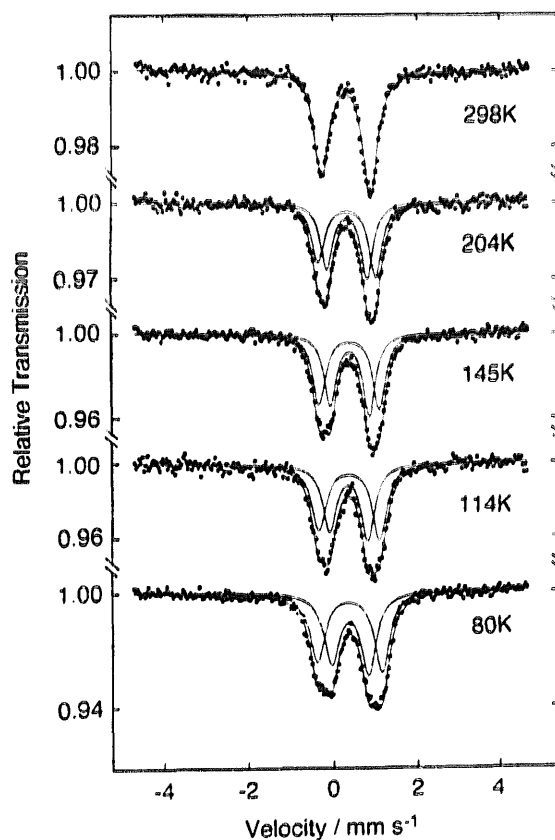


Fig. 3. Variable-temperature ⁵⁷Fe Mössbauer spectra of 1',1'''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide.

Table 5

Positional parameters for 1',1''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide with e.s.d.s in parentheses

Atom	x	y	z
K(1)	0.5648(2)	0.1588(1)	0.9201(2)
K(2)	0.7293(2)	0.2306(1)	0.8568(2)
K(3)	0.9123(2)	0.3128(1)	0.7851(2)
K(4)	1.1407(2)	0.1809(1)	0.8853(2)
K(5)	1.3315(2)	0.0597(2)	0.9830(2)
Fe(1)	0.7620(3)	0.0449(2)	0.4683(4)
Fe(2)	0.2972(3)	0.4670(2)	0.8688(3)
C(1)	0.722(2)	-0.053(2)	0.516(3)
C(2)	0.655(3)	-0.035(2)	0.391(3)
C(3)	0.577(2)	0.041(2)	0.399(3)
C(4)	0.596(3)	0.069(2)	0.531(3)
C(5)	0.686(3)	0.012(2)	0.602(3)
C(6)	0.952(2)	0.035(1)	0.477(3)
C(7)	0.881(3)	0.041(2)	0.349(3)
C(8)	0.794(3)	0.111(2)	0.356(3)
C(9)	0.804(3)	0.147(2)	0.483(4)
C(10)	0.903(3)	0.099(2)	0.560(3)
C(11)	0.808(2)	-0.129(1)	0.549(3)
C(12)	0.727(2)	-0.183(1)	0.545(3)
C(13)	0.690(3)	-0.195(1)	0.646(3)
C(14)	0.608(2)	-0.239(1)	0.638(3)
C(15)	0.556(3)	-0.248(2)	0.740(3)
C(16)	0.469(3)	-0.292(2)	0.720(4)
C(17)	0.430(3)	-0.330(2)	0.597(5)
C(18)	0.473(3)	-0.323(2)	0.504(4)
C(19)	0.559(2)	-0.276(1)	0.518(3)
C(20)	0.602(3)	-0.267(2)	0.411(3)
C(21)	0.682(3)	-0.223(2)	0.424(3)
C(22)	0.233(2)	0.440(2)	1.017(3)
C(23)	0.134(2)	0.490(1)	0.944(2)
C(24)	0.116(2)	0.458(1)	0.819(2)
C(25)	0.197(2)	0.386(1)	0.808(2)
C(26)	0.269(2)	0.373(1)	0.928(3)
C(27)	0.462(2)	0.506(2)	0.935(2)
C(28)	0.358(2)	0.564(1)	0.893(3)
C(29)	0.308(2)	0.545(2)	0.763(3)
C(30)	0.379(2)	0.472(1)	0.720(2)
C(31)	0.477(3)	0.445(2)	0.829(2)
C(32)	0.281(2)	0.451(1)	1.159(2)
C(33)	0.204(2)	0.422(1)	1.236(2)
C(34)	0.134(2)	0.372(1)	1.185(2)
C(35)	0.064(2)	0.347(1)	1.254(2)
C(36)	-0.007(3)	0.294(1)	1.202(2)
C(37)	-0.072(3)	0.271(1)	1.273(3)
C(38)	-0.065(3)	0.301(2)	1.403(3)
C(39)	0.001(3)	0.352(2)	1.457(2)
C(40)	0.068(2)	0.378(1)	1.381(2)
C(41)	0.141(2)	0.431(2)	1.437(2)
C(42)	0.208(2)	0.454(2)	1.363(3)
H(2)	0.6626	-0.0704	0.3119
H(3)	0.5177	0.0681	0.3278
H(4)	0.5543	0.1181	0.5673
H(5)	0.7175	0.0145	0.6973
H(7)	0.8915	0.0058	0.2724
H(8)	0.7318	0.1330	0.2822
H(9)	0.7548	0.1972	0.5071
H(10)	0.9312	0.1110	0.6472
H(11a)	0.8630	-0.1239	0.6337
H(11b)	0.8643	-0.1490	0.4898
H(13)	0.7219	-0.1689	0.7311
H(15)	0.5829	-0.2217	0.8291

Table 5 (continued)

Atom	x	y	z
H(16)	0.4306	-0.2952	0.7946
H(17)	0.3790	-0.3655	0.5922
H(18)	0.4429	-0.3485	0.4167
H(20)	0.5737	-0.2935	0.3271
H(21)	0.7141	-0.2177	0.3497
H(23)	0.0902	0.5402	0.9757
H(24)	0.0542	0.4811	0.7463
H(25)	0.2033	0.3498	0.7298
H(26)	0.3359	0.3271	0.9503
H(28)	0.3272	0.6112	0.9424
H(29)	0.2379	0.5771	0.7070
H(30)	0.3648	0.4453	0.6343
H(31)	0.5392	0.3970	0.8293
H(32a)	0.3681	0.4255	1.1816
H(32b)	0.2754	0.5050	1.1845
H(34)	0.1282	0.3525	1.0950
H(36)	-0.0131	0.2742	1.1134
H(37)	-0.1230	0.2332	1.2383
H(38)	-0.1066	0.2806	1.4561
H(39)	0.0030	0.3732	1.5471
H(41)	0.1435	0.4528	1.5271
H(42)	0.2540	0.4940	1.4001

Temperature-dependent ^{57}Fe Mössbauer spectra of 1',1''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide are shown in Fig. 3. The Mössbauer parameters are summarized in Table 1. The structural relaxation was not observed in the β -naphthylmethyl derivative, which is the most important difference from the α -naphthylmethyl derivative in the Mössbauer spectra. The spectrum at room temperature shows only one doublet averaged over Fe^{II} and Fe^{III} . 1',1''-Bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide shows the 'fusion type' valence detrapping as is shown in the α -naphthylmethyl derivative in the stable phase. The detrapping temperature is higher than that of the α -naphthylmethyl derivative. The quadrupole splitting values of the β -naphthylmethyl derivative are very close to each other even at 80 K. This shows the insufficient valence trapping with decreasing temperature. The temperature region for the detrapping process is wider than those of 1',1''-dialkyl-1,1''-biferrocenium triiodides [3,4,17].

Slow recrystallization from dichloromethane gave good single crystals suitable for X-ray crystal structural analysis. The crystal data are shown in Table 2. The positional parameters and selected bond distances and angles are shown in Tables 5 and 6 respectively. There are two independent monocations (Cation 1 and Cation 2) sitting on the center of symmetry. Metallocene halves in Cation 1 and Cation 2 have a *trans* conformation. The conformation of naphthylmethyl substituent is shown in Fig. 4, which shows the difference between Cation 1 and Cation 2. The conformation in Cation 1 is rotated about 90° to the conformation in Cation 2. Its counter anion is pentaiodide in general position. The

Table 6

Selected bond distances (Å) and angles (°) for 1',1''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide with e.s.d.s in parentheses

I(1)–I(2)	2.793(3)
I(2)–I(3)	3.143(3)
I(3)–I(4)	3.139(3)
I(4)–I(5)	2.795(3)
Fe(1)–C(1)	2.12(3)
Fe(1)–C(2)	2.08(3)
Fe(1)–C(3)	2.05(3)
Fe(1)–C(4)	2.07(3)
Fe(1)–C(5)	2.09(3)
Fe(1)–C(6)	2.08(2)
Fe(1)–C(7)	2.05(3)
Fe(1)–C(8)	2.00(3)
Fe(1)–C(9)	2.02(3)
Fe(1)–C(10)	2.05(3)
C(1)–C(2)	1.41(4)
C(2)–C(3)	1.44(4)
C(3)–C(4)	1.42(4)
C(4)–C(5)	1.43(4)
C(5)–C(1)	1.42(4)
C(6)–C(6')	1.52(6)
C(6)–C(7)	1.42(4)
C(7)–C(8)	1.39(4)
C(8)–C(9)	1.42(5)
C(9)–C(10)	1.41(4)
C(10)–C(6)	1.42(4)
C(1)–C(11)	1.51(4)
C(11)–C(12)	1.50(3)
C(12)–C(13)	1.32(3)
C(13)–C(14)	1.36(4)
C(14)–C(15)	1.42(4)
C(14)–C(19)	1.41(4)
C(15)–C(16)	1.38(5)
C(16)–C(17)	1.42(5)
C(17)–C(18)	1.25(5)
C(18)–C(19)	1.42(4)
C(19)–C(20)	1.40(4)
C(20)–C(21)	1.33(4)
C(21)–C(12)	1.44(4)
Fe(2)–C(22)	2.09(2)
Fe(2)–C(23)	2.10(2)
Fe(2)–C(24)	2.03(2)
Fe(2)–C(25)	2.03(2)
Fe(2)–C(26)	2.05(2)
Fe(2)–C(27)	2.08(2)
Fe(2)–C(28)	2.01(2)
Fe(2)–C(29)	2.01(3)
Fe(2)–C(30)	2.06(2)
Fe(2)–C(31)	2.10(3)
C(22)–C(23)	1.41(3)
C(23)–C(24)	1.37(3)
C(24)–C(25)	1.40(3)
C(25)–C(26)	1.37(3)
C(26)–C(22)	1.46(3)
C(27)–C(27')	1.48(5)
C(27)–C(28)	1.39(3)
C(28)–C(29)	1.40(4)
C(29)–C(30)	1.44(4)
C(30)–C(31)	1.46(4)
C(31)–C(27)	1.47(3)
C(22)–C(32)	1.50(3)
C(32)–C(33)	1.57(3)
C(33)–C(34)	1.32(3)

Table 6 (continued)

C(34)–C(35)	1.41(3)
C(35)–C(36)	1.38(3)
C(35)–C(40)	1.40(3)
C(36)–C(37)	1.36(3)
C(37)–C(38)	1.41(4)
C(38)–C(39)	1.33(4)
C(39)–C(40)	1.45(3)
C(40)–C(41)	1.40(4)
C(41)–C(42)	1.40(3)
C(42)–C(33)	1.40(4)
I(1)–I(2)–I(3)	179.4(1)
I(2)–I(3)–I(4)	89.56(8)
I(3)–I(4)–I(5)	175.6(1)
C(1)–Fe(1)–C(6)	113(1)
C(2)–Fe(1)–C(7)	108(1)
C(3)–Fe(1)–C(8)	104(1)
C(4)–Fe(1)–C(9)	104(1)
C(5)–Fe(1)–C(10)	110(1)
C(2)–C(1)–C(5)	107(2)
C(1)–C(2)–C(3)	109(2)
C(2)–C(3)–C(4)	106(2)
C(3)–C(4)–C(5)	108(2)
C(4)–C(5)–C(1)	108(2)
C(6')–C(6)–C(7)	125(3)
C(6')–C(6)–C(10)	123(3)
C(7)–C(6)–C(10)	110(2)
C(6)–C(7)–C(8)	104(2)
C(7)–C(8)–C(9)	111(2)
C(8)–C(9)–C(10)	106(2)
C(9)–C(10)–C(6)	107(2)
C(2)–C(1)–C(11)	125(2)
C(5)–C(1)–C(11)	127(2)
C(1)–C(11)–C(12)	107(2)
C(11)–C(12)–C(13)	124(2)
C(11)–C(12)–C(21)	118(2)
C(13)–C(12)–C(21)	117(2)
C(12)–C(13)–C(14)	123(2)
C(13)–C(14)–C(15)	125(2)
C(13)–C(14)–C(19)	119(2)
C(15)–C(14)–C(19)	114(2)
C(14)–C(15)–C(16)	120(3)
C(15)–C(16)–C(17)	120(3)
C(16)–C(17)–C(18)	120(3)
C(17)–C(18)–C(19)	121(3)
C(14)–C(19)–C(18)	122(2)
C(14)–C(19)–C(20)	118(2)
C(18)–C(19)–C(20)	119(2)
C(19)–C(20)–C(21)	119(2)
C(12)–C(21)–C(20)	121(2)
C(22)–Fe(2)–C(27)	112.7(9)
C(23)–Fe(2)–C(28)	108.2(10)
C(24)–Fe(2)–C(29)	105(1)
C(25)–Fe(2)–C(30)	106.5(10)
C(26)–Fe(2)–C(31)	110(1)
C(23)–C(22)–C(26)	106(2)
C(22)–C(23)–C(24)	107(2)
C(23)–C(24)–C(25)	110(2)
C(24)–C(25)–C(26)	107(2)
C(25)–C(26)–C(22)	108(2)
C(27')–C(27)–C(28)	130(2)
C(27')–C(27)–C(31)	119(3)
C(28)–C(27)–C(31)	109(2)
C(27)–C(28)–C(29)	108(2)
C(28)–C(29)–C(30)	109(2)

Table 6 (continued)

C(29)–C(30)–C(31)	107(2)
C(30)–C(31)–C(27)	105(2)
C(23)–C(22)–C(32)	125(2)
C(26)–C(22)–C(32)	127(2)
C(22)–C(32)–C(33)	112(1)
C(32)–C(33)–C(34)	123(2)
C(32)–C(33)–C(42)	116(2)
C(34)–C(33)–C(42)	120(2)
C(33)–C(34)–C(35)	123(2)
C(34)–C(35)–C(36)	123(2)
C(34)–C(35)–C(40)	116(2)
C(36)–C(35)–C(40)	119(2)
C(35)–C(36)–C(37)	121(2)
C(36)–C(37)–C(38)	119(2)
C(37)–C(38)–C(39)	121(2)
C(38)–C(39)–C(40)	118(2)
C(35)–C(40)–C(39)	119(2)
C(35)–C(40)–C(41)	120(2)
C(39)–C(40)–C(41)	120(2)
C(40)–C(41)–C(42)	119(2)
C(33)–C(42)–C(41)	119(2)

C(6') and C(27') are related to C(6) and C(27) respectively by the center of symmetry.

pentaiodide has a V shape. The I–I distances are 2.793(3) Å, 3.143(3) Å, 3.139(3) Å, 2.795(3) Å, and $\angle I(2)–I(3)–I(4) = 89.56(8)^\circ$, showing symmetric planar V-shaped ions consisting of an I^- ion very weakly bonded to two polarized I_2 molecules, as is shown in Fig. 5. In $N(CH_3)_4I_5$ there are V-shaped I_5^- ions and the I–I distances are 2.81 Å, 3.17 Å, 3.17 Å, 2.81 Å and the angle corresponding to $\angle I(2)–I(3)–I(4)$ in the present study is 95° [18]. The structure of the present pentaiodide is similar to that of $N(CH_3)_4I_5$. The mean

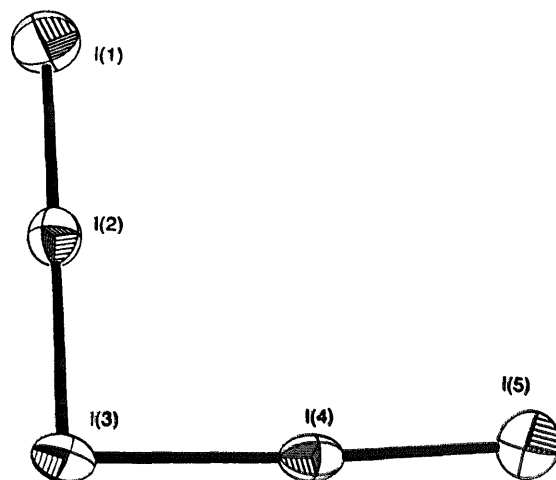


Fig. 5. Structure of pentaiodide of 1,1''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide.

Fe–C(Cp ring) distance is found to be 2.061(9) Å in Cation 1 and 2.056(7) Å in Cation 2, intermediate between the values of 2.033 Å for ferrocene [14] and 2.075(3) Å for the ferrocenium cation [15]. This is in accord with the result that the salt shows the detrapped-valence state at room temperature. The iron atoms do not sit on the center between the Cp ring and fluvalene. The iron atoms are somewhat closer to the fluvalene than to the Cp ring (Fe(1)–Cp 1.69(2) Å, Fe(1)–fluvalene 1.65(2) Å, Fe(2)–Cp 1.68(2) Å, and Fe(2)–fluvalene 1.65(2) Å). The two independent cations might reflect the slight broadness of the Mössbauer spectra. The substituents sit on the opposite half of binuclear ferrocene, which is different from the case of α -naphthylmethyl derivative.

The projection of the unit cell to the ab plane is shown in Fig. 6. The columns of Cation 1 and Cation 2 can be seen respectively. The projection to the bc plane is shown in Fig. 7. It can be seen that the naphthylmethyl substituent in Cation 1 is close to the naphthylmethyl substituent in Cation 2. The distance between C(13) in Cation 1 and C(35) in Cation 2 is 3.47(3) Å, which is close to twice the value (3.40 Å) of the van der Waals radius of carbon, which suggests that Cation 1 interacts weakly with Cation 2 through π – π interaction between the naphthylmethyl substituents. The difference in the conformation of the naphthylmethyl substituents affects the interaction between Cation 1 and Cation 2. In this structure, the change of the valence state from the trapped to the detrapped-valence state can be transferred to other cations. The packing of the β -naphthylmethyl derivative gives a hint for the structural relaxation in the α -naphthylmethyl derivative. One possibility is the change of the conformation of the naphthylmethyl substituent.

Dong et al. showed that the deviations of the Cp rings from the parallel position correlate with the va-

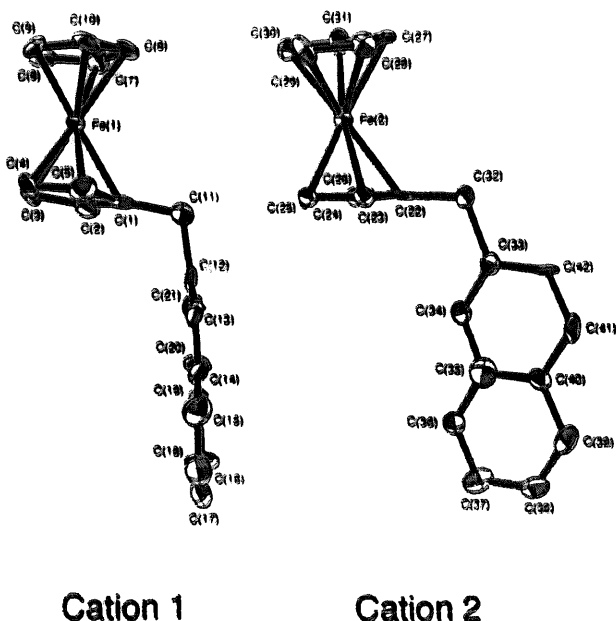


Fig. 4. Conformation of substituent for Cations 1 and 2 in 1,1''-bis(β -naphthylmethyl)-1,1''-biferrocenium pentaiodide. The counterparts by the center of symmetry are omitted.

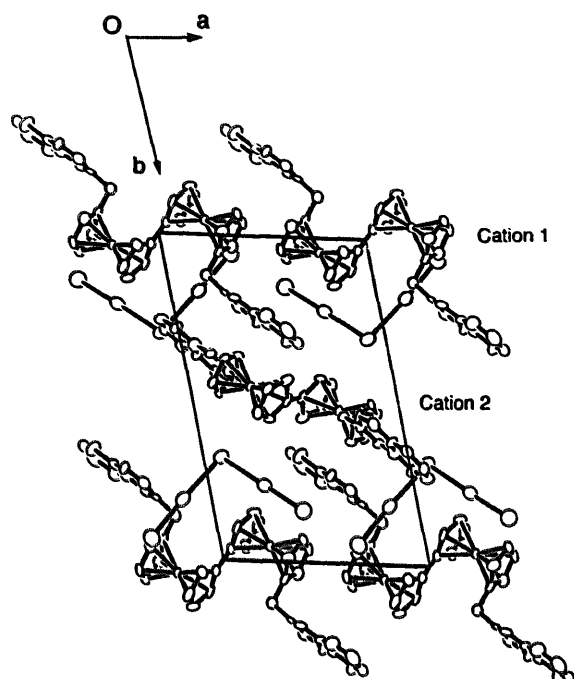


Fig. 6. Projection of the unit cell of 1',1'''-bis(β -naphthylmethyl)-1,1'''-biferrocenium pentafluoroborate to the ab plane.

lence detrapping temperature in mixed-valence polyalkyl-substituted biferrocenium cations [19]. The deviations of the Cp rings from the parallel position are 7.89° for Cation 1 and 5.99° for Cation 2 in 1',1'''-bis(β -naphthylmethyl)-1,1'''-biferrocenium pentafluoroborate. According to Dong et al., these angles correspond to the ~ 200 K valence detrapping temperature, which is very roughly in agreement with the present result. On the other hand, the deviation is 2.89° in 1',1'''-bis(α -naph-

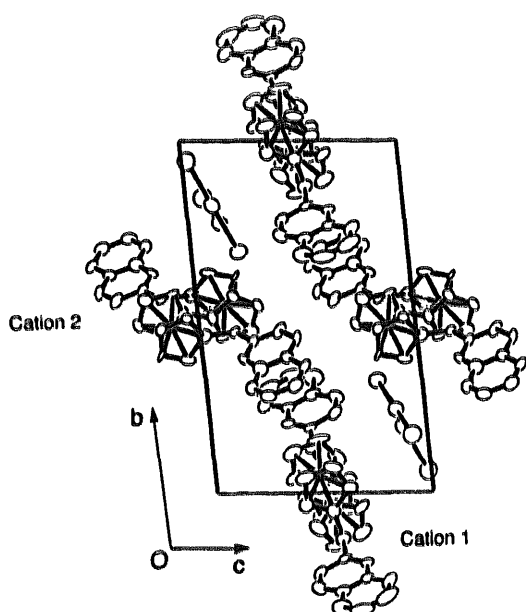


Fig. 7. Projection of the unit cell of 1',1'''-bis(β -naphthylmethyl)-1,1'''-biferrocenium pentafluoroborate to the bc plane.

thylmethyl)-1,1'''-biferrocenium triiodide. The present result shows that the detrapping temperature is near 4.2 K, while the detrapping temperature is expected to be near room temperature according to the correlation between the deviation of the Cp rings from the parallel position and the detrapping temperature. The discrepancy from the correlation indicates the important role of the intermolecular interaction in the mixed-valence state.

The mixed-valence state of 1',1'''-dibenzyl-1,1'''-biferrocenium triiodide is reported [20,21]. The needle crystals of the benzyl derivative showed a wide temperature range of detrapped-valence state, and even at 25 K showed the component of the detrapped-valence state. In the present study, 1',1'''-bis(α - and β -naphthylmethyl)-1,1'''-biferrocenium salts show that the environments around Fe^{II} and Fe^{III} are relatively similar even at low temperatures. The wide temperature range of the detrapped-valence state in the benzyl and naphthyl derivatives might reflect the π - π interaction. It might be interesting that the tetracyanoquinodimethane (TCNQ) salts of 1',1'''-dialkyl-1,1'''-biferrocenes which have a π -system in the anion show a wide temperature range of detrapped-valence state [22].

Acknowledgements

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