Iron-57 Mossbauer Spectroscopic and X-Ray Diffraction Studies on the Mixed-valence State of Binuclear Ferrocene Derivatives with Long Alkyl Substituents†

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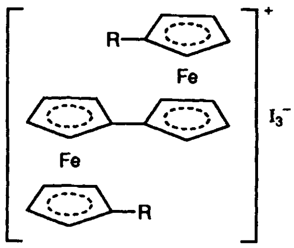
The mixed-valence states of biferrocene derivatives with long alkyl substituents, which have a layered structure, have been investigated by means of ^{57}Fe Mössbauer spectroscopy and X-ray powder diffraction. An interesting even–odd character in the number of carbon atoms of the alkyl chain is found in the relationship between the crystal structure and the mixed-valence state. The mixed-valence states of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide change in accordance with a transformation of the crystal structure in the solid state. An X-ray diffraction analysis for this salt obtained from dichloromethane at 0 °C showed that both the cation and the anion are situated at a centre of symmetry and the dodecyl substituent has the all-*trans* conformation. The layers are located in the *ab* plane.

Mixed valence in binuclear ferrocene derivatives has been mainly studied by means of ^{57}Fe Mossbauer spectroscopy to understand the mechanism of the electron-transfer process. The rate of electron transfer in the mixed-valence salts is strongly influenced by the environment about the monocation.[1,2] It is important for both fundamentals and applications to study systematically the packing effect. Our strategy for systematic design is to use derivatives with a series of long alkyl chains. We first studied 1′,1‴-bis(tetradecyl)[3] -bis(hexadecyl)[4] and -bis(dioctadecyl)[4] derivatives because it was expected that they would have a similar layered structure. From ^{57}Fe Mossbauer spectra and X-ray powder diffraction patterns, a remarkable dependence of the mixed-valence states on the crystal form was observed for 1′,1‴-bis(tetradecyl)- and -bis(hexadecyl)-1,1″-biferrocenium triiodides having a layered structure. One crystal form with a longer interlayer distance obtained from hexane showed a temperature-independent trapped-valence state, while the other with a shorter interlayer distance obtained from dichloromethane showed a 'fusion type' valence detrapping with increasing temperature. In the temperature-independent trapped-valence state two quadrupole-split doublets ascribed to ferrocene-like bivalent(Fe^{II}) and ferrocenium-like tervalent irons(Fe^{III}) were observed over all temperatures. In the 'fusion type' valence detrapping two quadrupole-split doublets observed at low temperatures approached each other with increasing temperature to converge into one doublet without significant line broadening in ^{57}Fe Mössbauer spectra.

In the present study the mixed-valance states of triiodide salts of biferrocene derivatives with a series of long alkyl chains are reported in connection with the crystal structure. An interesting even–odd character in the number of carbon atoms of the alkyl chain is found in the relationship between the interlayer distance and the mixed-valence state. The mixed-valence state of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide changes with transformation of the interlayer distances in the solid state. A single-crystal X-ray structural analysis is also reported for this compound crystallized from dichloromethane at 0 °C.

Experimental

The 1′,1‴-dialkyl-1,1″-biferrocenes were synthesized according to a method reported for the corresponding bis(tetradecyl),[3] bis(hexadecyl),[4] and bis(octadecyl)[4] compounds. They were isolated by column chromatography on alumina and purified by recrystallization from dichloromethane–hexane. For the process of acylation, tridecanoyl, pentadecanoyl, and nonadecanoyl chlorides were synthesized by reaction of the corresponding acid with thionyl chloride in the presence of pyridine, while commercial dodecanoyl chloride and heptadecanoyl chloride were used. 1′,1‴-Bis(dodecyl)-1,1″-biferrocene: m.p. = 65.0–66.5 °C; ^{1}H NMR (CDCl$_3$) δ 0.87, 1.24, 2.07, 3.81, 3.84, 4.09 and 4.22. 1′,1‴-Bis(tridecyl)-1,1″-biferrocene: m.p. = 73.5–74.5 °C; ^{1}H NMR (CDCl$_3$) δ 0.87, 1.25, 2.08, 3.83, 3.86, 4.11 and 4.23. 1′,1‴-Bis(pentadecyl)-1,1″-biferrocene: m.p. = 75.5–76.5 °C; ^{1}H NMR (CDCl$_3$) δ 0.88, 1.26, 2.09, 3.84, 3.88 4.12 and 4.25. 1′,1‴-Bis(heptadecyl)-1,1″-biferrocene: m.p. = 79.5–80.5 °C; ^{1}H NMR (CDCl$_3$) δ 0.88, 1.26, 2.11, 3.89, 3.89, 4.15 and 4.27. 1′,1‴-Bis(nonadecyl)-1,1″-biferrocene: m.p. = 83.0–84.0 °C; ^{1}H NMR (CDCl$_3$) δ 0.88, 1.26, 2.15, 3.93, 3.93, 4.19 and 4.32. It was found that cyclopentadienyl protons and methylene protons which are closest to the ring show low-field shifts, with increasing number of carbon atoms in the alkyl chain. Also the melting point rises with increasing number of carbon atoms in the alkyl chain.



R = (CH$_2$)$_n$Me n = 11,12,14,16 or 18

The ^{57}Fe Mössbauer spectra at room temperature for all the binuclear ferrocene derivatives with long alkyl substituents showed only one doublet ascribed to a ferrocene-like bivalent

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

state. There was no significant difference in the Mössbauer parameters [isomer shift (δ) = 0.44–0.46 mm s^{-1} and quadrupole splitting (ΔE_q) = 2.32–2.33 mm s^{-1}] for the present samples at room temperature. The Mössbauer parameters are summarized in Table 1.

The triiodide salts 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‴-bis(dodecyl)-1,1″-biferrocenium triiodide (from hexane): C, 48.55; H, 6.05 (from dichloromethane): C, 49.15; H, 6.15. Calc. for $C_{44}H_{66}Fe_2I_3$: C, 48.55; H, 6.05. Found for 1′,1‴-bis(tridecyl)-1,1″-biferrocenium triiodide (from hexane): C, 49.70; H, 6.45 (from dichloromethane): C, 49.90; H, 6.45. Calc. for $C_{46}H_{70}Fe_2I_3$: C, 49.50; H, 6.25. Found for 1′,1‴-bis(pentadecyl)-1,1″-biferrocenium triiodide (from hexane): C, 51.30; H, 6.75 (from dichloromethane): C, 50.90; H, 6.85. Calc. for $C_{50}H_{78}Fe_2I_3$: C, 51.20; H, 6.65. Found for 1′,1‴-bis(heptadecyl)-1,1″-biferrocenium triiodide (from hexane): C, 52.75; H, 7.05 (from dichloromethane): C, 53.05; H, 7.05. Calc. for $C_{54}H_{86}Fe_2I_3$: C, 52.80; H, 7.00. Found for 1′,1‴-bis(nonadecyl)-1,1″-biferrocenium triiodide (from hexane): C, 53.35; H, 7.25 (from dichloromethane): C, 53.15; H, 7.35. Calc. for $C_{58}H_{94}Fe_2I_3$: C, 54.20; H, 7.30%].

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

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

Three-dimensional room-temperature X-ray data for the single crystal of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide obtained from dichloromethane at 0 °C were collected in the range $2\theta < 55°$ on a Mac Science MXC3 four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Lattice parameters were determined by least-squares fitting of 27 reflections having $31 < 2\theta < 35°$. Data were collected with the ω-scan mode. All data were corrected for absorption.[5] With 4257 reflections of intensity greater than 3σ, the structure was solved by a direct method using the program MONTE CARLO-MULTAN.[6] Refinement on F was carried out by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. 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 final residuals were $R = 0.046$ and $R' = 0.045$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 ^{57}Fe Mössbauer parameters at 298 K for biferrocene derivatives with long alkyl substituents

Substituent	δ*/mm s^{-1}	ΔE_q/mm s^{-1}
Dodecyl	0.44	2.32
Tridecyl	0.45	2.32
Pentadecyl	0.46	2.33
Heptadecyl	0.45	2.33
Nonadecyl	0.45	2.33

* Isomer-shift data are reported with respect to iron foil.

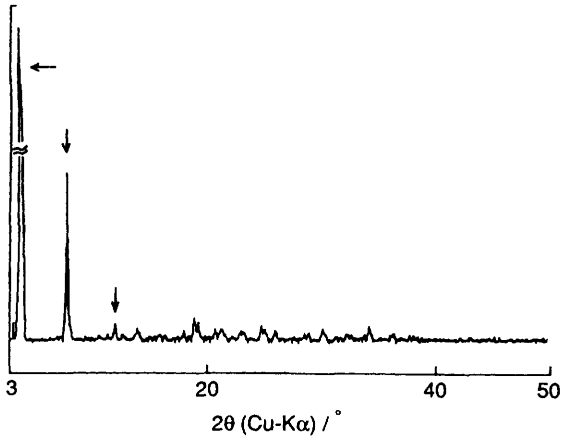

Fig. 1 X-Ray powder diffraction pattern of 1′,1‴-bis(nonadecyl)-1,1″-biferrocenium triiodide recrystallized from dichloromethane

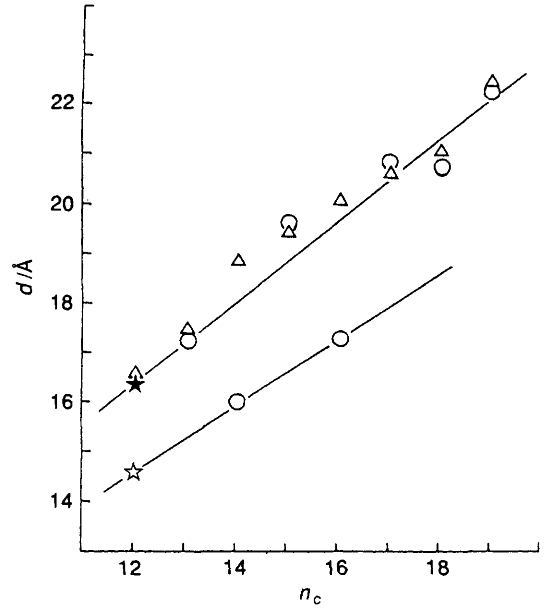

Fig. 2 Interlayer distances as a function of the number of carbon atoms (n_c) in the alkyl chain: Δ, samples from hexane; ○, samples from dichloromethane. The temperatures of crystallization are room temperature except for 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide (n_c = 12) from dichloromethane (★, 30 °C; ☆, 0 °C). Both phases transform into each other in the solid state

Results and Discussion

Correlation between Mixed-valence States and Crystal Structures of Biferrocene Derivatives with Long Alkyl Chains.— A typical X-ray powder diffraction pattern of 1′,1‴-bis(nonadecyl)-1,1″-biferrocenium triiodide is shown in Fig. 1. The most remarkable feature is that the arrowed reflections appear with an equal interval in the small-angle region, indicating a layered structure. The interlayer distance can be estimated to be 22.5 Å by assuming the first, second and third peaks to be the reflections from the (001), (002) and (003) planes, respectively. All X-ray powder diffraction patterns in the present study were similar. The interlayer distances are summarized in Fig. 2 as a function of the number of carbon atoms (n_c) in the alkyl chain. It can be seen that both samples from hexane and dichloromethane solutions show the same interlayer distances in 1′,1‴-bis(tridecyl), -bis(pentadecyl), -bis(heptadecyl), -bis(octadecyl) and -bis(nonadecyl) derivatives, while a shortening of the interlayer distance upon recrystallization from dichloromethane solution is observed in the triiodide salts of 1′,1‴-bis(dodecyl)-(16.4 to 14.6), -bis(tetradecyl)-(18.8 to 16.0) and -bis(hexadecyl)-1,1″-biferrocene (20.2 to 17.2 Å). 1′,1‴-

Bis(dodecyl)-1,1″-biferrocenium triiodide recrystallized from acetonitrile showed the shortest interlayer distance. This distance tends to increase almost linearly with increasing number of carbon atoms, which also confirms that all samples have a layered structure. It is interesting that there exist only two series (longer and shorter interlayer series) and that crystals with an intermediate distance are not obtained.

The derivatives with odd numbers of carbons tend to have structures with longer interlayer distances, while the derivatives with even numbers tend to have both types of interlayer distances, except for 1′,1‴-bis(octadecyl)-1,1″-biferrocenium triiodide. No crystal with the shorter interlayer distance could be obtained for the latter despite repeated recrystallizations from dichloromethane. It is thought that this is due to the alkyl substituent being too long.

Table 2 ^{57}Fe Mössbauer parameters for 1′,1‴-disubstituted biferrocenium triiodides with long alkyl substituents

Substituent	Solvent	T/K	δ*/mm s^{-1}	ΔE_q/mm s^{-1}
Dodecyl	Hexane	298	0.44	1.89
			0.45	0.53
		203	0.49	1.96
			0.47	0.61
		80	0.53	1.98
			0.53	0.54
	CH_2Cl_2 at 0 °C	313	0.46	1.82
			0.39	0.62
		298	0.44	1.17
		228	0.47	1.39
			0.47	0.96
		203	0.50	1.48
			0.50	0.92
		178	0.49	1.54
			0.49	0.83
		153	0.49	1.54
			0.49	0.83
		80	0.53	1.91
			0.54	0.58
Tridecyl	Hexane	298	0.45	1.89
			0.45	0.52
		203	0.46	1.94
			0.44	0.52
		80	0.54	1.98
			0.53	0.53
	CH_2Cl_2	298	0.45	1.90
			0.45	0.50
		203	0.47	1.94
			0.49	0.56
		80	0.54	1.97
			0.54	0.56
Pentadecyl	Hexane	200	0.50	1.92
			0.48	0.55
		80	0.53	1.97
			0.54	0.55
	CH_2Cl_2	200	0.49	1.93
			0.49	0.54
		80	0.54	1.98
			0.54	0.53
Heptadecyl	Hexane	200	0.46	1.93
			0.43	0.53
		80	0.50	1.98
			0.50	0.56
	CH_2Cl_2	200	0.46	1.95
			0.46	0.57
		80	0.51	1.97
			0.50	0.55
Nonadecyl	Hexane	200	0.48	1.91
			0.48	0.61
		80	0.52	1.94
			0.53	0.57
	CH_2Cl_2	200	0.49	1.92
			0.51	0.62
		80	0.52	1.95
			0.53	0.56

* Isomer-shift data are reported with respect to iron foil.

The ^{57}Fe Mössbauer spectra of 1′,1‴-bis(nonadecyl)-1,1″-biferrocenium triiodide with the longer interlayer distance are shown in Fig. 3. The spectrum was not observed at room temperature because of the decreased recoil-free fraction. Mossbauer parameters for all triiodide salts are summarized in Table 2. All samples with alkyl chains longer than $n_c > 13$ did not show spectra at room temperature. The spectra at 80 and 200 K in Fig. 3 consist of an inner and an outer doublet, with a nearly 1 : 1 ratio in area corresponding to Fe^{III} and Fe^{II}. It can easily be seen that this is a case of temperature-independent trapped valence. All the present samples with the longer interlayer distance showed this state. On the other hand, 1′,1‴-bis(dodecyl), -bis(tetradecyl)[3] and -bis(hexadecyl)-1,1″-biferrocenium[4] triiodide with the shorter interlayer distance exhibited a typical fusion-type valence detrapping, where two quadrupole-split doublets observed at low temperatures approach each other at increasing temperature, giving only one doublet ascribed to a valence state averaged over the bi-and ter-valent iron atoms without significant line broadening in the detrapping process. The intensity of the resonant absorption was stronger for the salts with the shorter interlayer distance than for those with the longer interlayer distance. The intensity of the resonant absorption associated with the Debye temperature depends on the crystal packing. It is suggested from these results that the mixed-valence states depend strongly on the crystal structure of the salts and the density of the crystal. The combined results of the Mossbauer and X-ray diffraction patterns indicate that valence detrapping of the triiodide salts of long-alkyl-chain disubstituted biferrocenes having a layered structure is observed at the shorter interlayer distances.

Coupling of the Change of Mixed-valence State and the Phase Transition of 1′,1‴-*Bis*(*dodecyl*)-1,1″-*biferrocenium Triiodide*.—X-Ray powder diffraction patterns of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide are shown in Fig. 4. The salt obtained from hexane has the longer interlayer distance (d = 16.4 Å) as mentioned above. The interlayer distance of the salt depends on the recrystallization temperature from the dichloromethane solution. The salt obtained at 0 °C has the

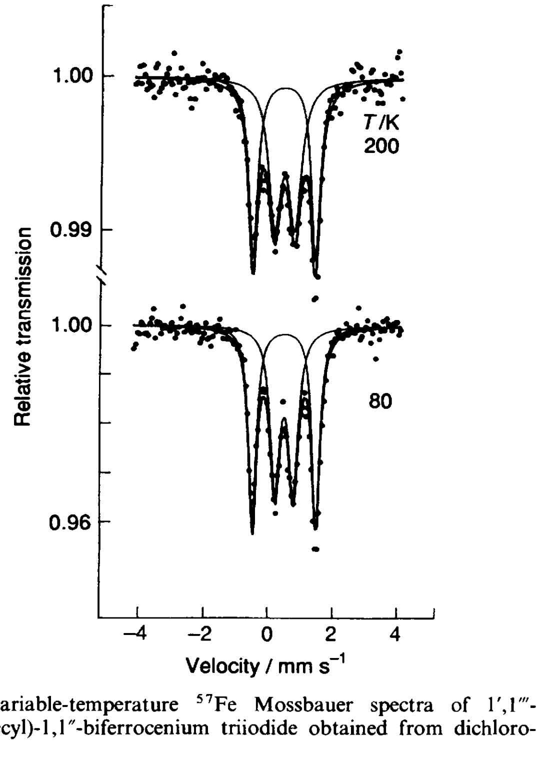

Fig. 3 Variable-temperature ^{57}Fe Mossbauer spectra of 1′,1‴-bis(nonadecyl)-1,1″-biferrocenium triiodide obtained from dichloromethane

shorter interlayer distance (d = 14.6 Å), while that obtained at 30 °C from the same solution has the longer interlayer distance. The two phases coexist in the salt obtained at 20 °C and an intermediate phase is not found. The ^{57}Fe Mossbauer spectra for the crystals with the longer interlayer distance are shown in Fig. 5, where two sets of quadrupole doublets ascribed to Fe^{II} and Fe^{III} are observed as is expected for the salts with longer interlayer distances. There is no significant temperature dependence of the mixed-valence state. Fig. 6 shows ^{57}Fe Mössbauer spectra for the crystals having the shorter interlayer distance.

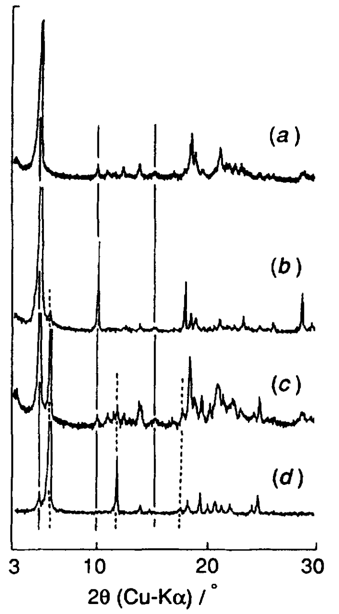

Fig. 4 X-Ray powder diffraction patterns at room temperature of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide obtained from (*a*) hexane at room temperature, (*b*) dichloromethane at 30, (*c*) at 20, and (*d*) at 0 °C

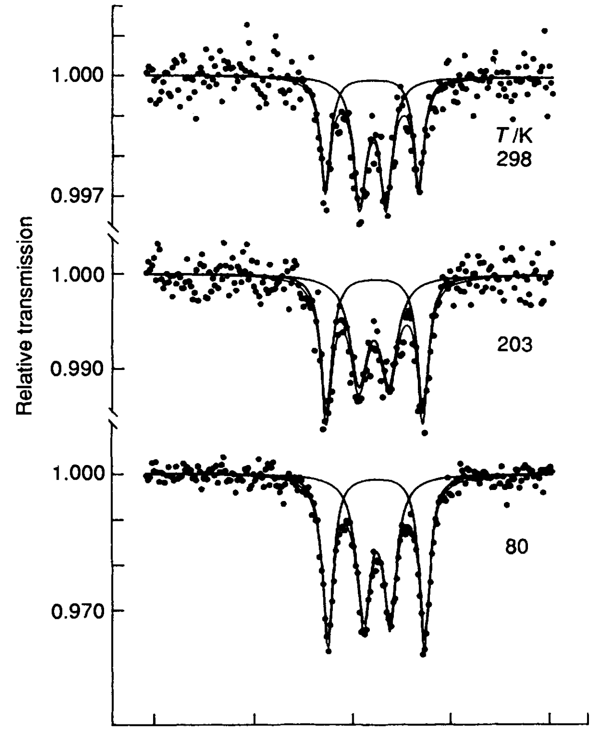

Fig. 5 Variable-temperature ^{57}Fe Mössbauer spectra of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide with the longer interlayer distance

'Fusion type' valence detrapping of the mixed-valence state is observed as is expected for the salts with shorter interlayer distances. The detrapping temperature is ≈230 K. The detrapping temperature of 1′,1‴-bis(tetradecyl)- and -bis(hexadecyl)-1,1″-biferrocenium triiodide with shorter interlayer distances are ≈205[3] and ≈220 K,[4] respectively. The detrapping temperatures for the salts with long alkyl chains are lower than those for the triiodide salts of biferrocenes with short alkyl substituents such as ethyl,[7,8] propyl[7] and butyl.[9,10] The ^{57}Fe Mossbauer spectra of the crystals obtained from dichloromethane at 20 °C consist of the superposition of those at the same temperature in Figs. 5 and 6 in accordance with the X-ray powder diffraction patterns.

The crystal structures of the salts depend strongly on the recrystallization temperature from dichloromethane solution. It is thought that the crystal structure is controlled by the recrystallization rate rather than the nature of the solvent such as its polarity. Recrystallization of the same salt from acetonitrile gave a shorter interlayer distance. The crystal structures with longer and shorter interlayer distances may be not so different to each other. In this situation it is expected that the two phases transform into each other even in the solid state. The salt with the shorter interlayer distance was heated to 30, 40 and 50 °C in turn every 20 min and then cooled to 0 °C for 1 d. All X-ray powder diffractions measured at room temperature are shown in Fig. 7. The salt with the shorter interlayer distance changes to one with the longer interlayer distance upon annealing at high temperatures. The crystals almost return to the former form in the solid state upon standing at 0 °C for 1 d. The ^{57}Fe Mössbauer spectrum at 40 °C

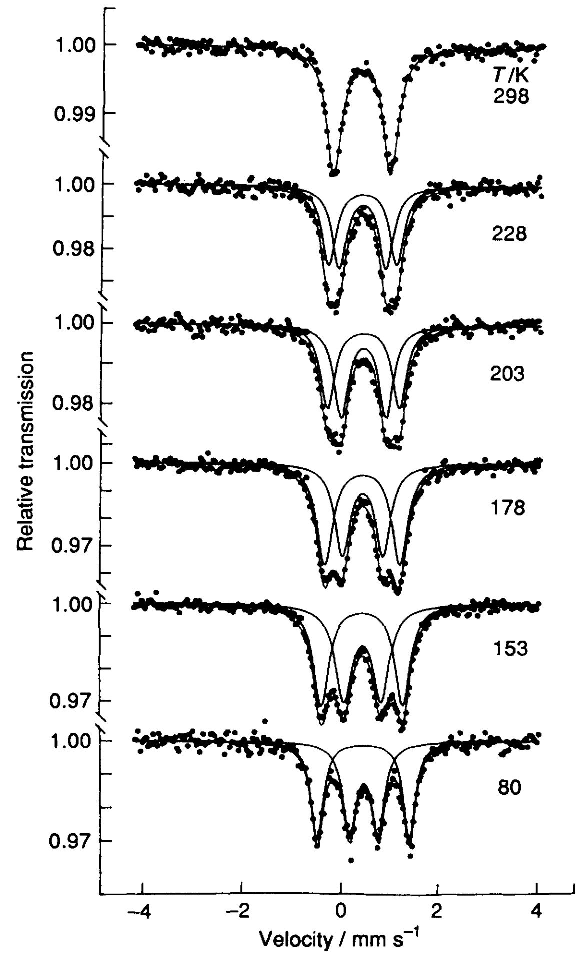

Fig. 6 Variable-temperature ^{57}Fe Mossbauer spectra of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide with the shorter interlayer distance

of the salt, which shows the averaged-valence state at room temperature, obviously indicates two sets of quadrupole doublets in spite of the poor statistics (Fig. 8). This phenomenon is in accord with the X-ray diffraction patterns. At this temperature the absorption intensities are extremely weak because of the low Debye temperature of the salt. The intensity ratio of Fe^{II} to Fe^{III} deviates considerably from 1 : 1. The difference in the intensity ratio is attributable to the slight difference in the Debye temperatures of the two iron sites. If the Fe^{III} is closer to the triiodide anion than is the Fe^{II}, the intensity of Fe^{III} will be stronger. In this situation, the environment of the monocation is asymmetric, therefore the mixed-valence state becomes valence-trapped. This is the first example of valence trapping with increasing temperature. It is thought that the phase transition between the salts with longer and shorter interlayer distances is coupled with the first ordered phase transition, while the valence detrapping is coupled with the second ordered phase transition.[11]

Crystallographic data for 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide obtained from dichloromethane at 0 °C are shown in Table 3. The positional parameters and selected bond distances and interbond angles are given in Tables 4 and 5, respectively. The crystal structure with atom labelling is shown in Fig. 9 and a stereoview of the crystal with shorter interlayer

Table 3 Crystal data for 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide having the shorter interlayer distance

Formula	$C_{44}H_{66}Fe_2I_3$
M	1087.40
T/K	296 ± 1
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.766(2)
b/Å	9.624(3)
c/Å	15.478(4)
α/°	72.62(2)
β/°	77.41(2)
γ/°	65.79(2)
U/Å^3	1129.8(6)
Z	1
D_c/g cm^{-3}	1.60
Crystal size/mm	1.00 × 0.30 × 0.20
F(000)	541
μ(Mo-Kα)/cm^{-1}	25.47
$[(\sin\theta/\lambda)_{max}]$/Å^{-1}	0.650
Total reflections measured	5690
Unique reflections	5179
Reflections used $[F_o > 3\sigma(F_o)]$	4257
R_{int}	0.01
No. of variables	328
Final residual electron density/e Å^{-3}	1.65, −1.53
S	3.35
R	0.046
R′	0.045

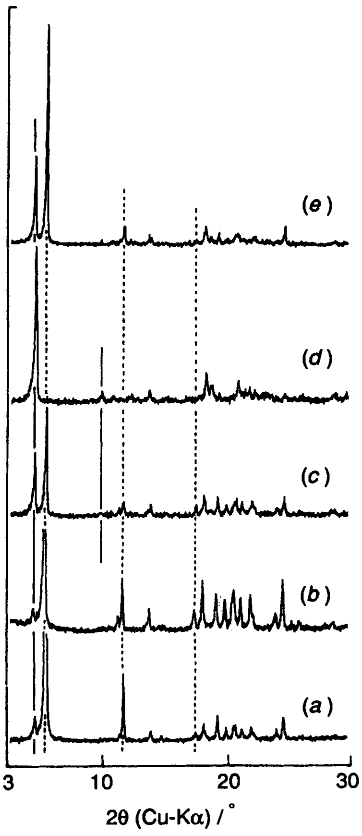

Fig. 7 X-Ray powder diffraction patterns of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide measured at room temperature: (*a*) fresh sample obtained from dichloromethane at 0 °C; (*b*) sample of (*a*) annealed at 30 °C for 20 min; (*c*) sample of (*b*) annealed at 40 °C for 20 min; (*d*) sample of (*c*) annealed at 50 °C for 20 min; (*e*) sample of (*d*) annealed at 0 °C for 1 d

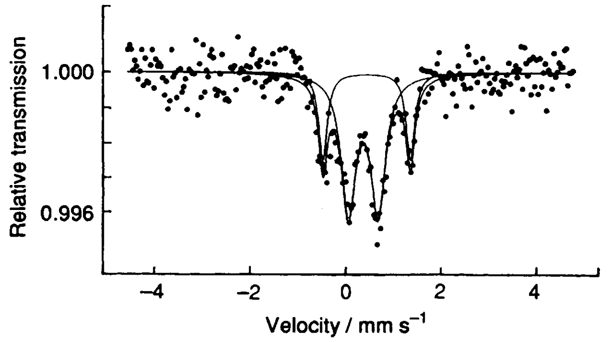

Fig. 8 ^{57}Fe Mössbauer spectrum at 313 K for crystals of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide recrystallized from dichloromethane at 0 °C

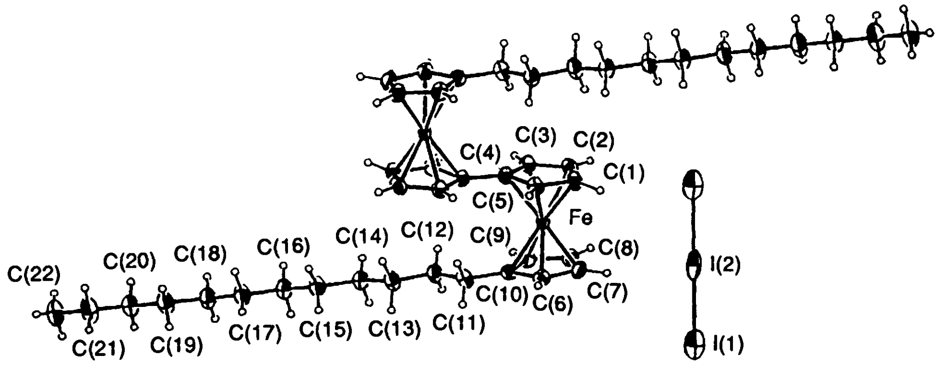

Fig. 9 Crystal structure with atom labelling of 1′, 1‴-bis(dodecyl)-1,1″-biferrocenium triiodide with the shorter interlayer distance

Table 4 Positional parameters for 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide having the shorter interlayer distance, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I(1)	0.045 21(4)	0.221 28(5)	−0.170 54(3)	H(6)	0.878(6)	0.626(6)	0.814(3)
I(2)	0	0	0	H(7)	0.924(6)	0.789(5)	0.904(3)
Fe	0.650 92(6)	0.693 16(6)	0.958 92(3)	H(8)	0.632(6)	0.991(6)	0.944(3)
C(1)	0.761 3(5)	0.546 0(4)	1.073 0(3)	H(9)	0.427(6)	0.956(6)	0.866(3)
C(2)	0.610 5(5)	0.663 1(5)	1.097 7(3)	H(11A)	0.585(6)	0.593(6)	0.791(3)
C(3)	0.476 0(5)	0.652 7(4)	1.066 2(3)	H(11B)	0.627(6)	0.704(6)	0.707(3)
C(4)	0.545 1(4)	0.523 6(4)	1.022 9(2)	H(12A)	0.316(6)	0.790(6)	0.805(4)
C(5)	0.723 3(5)	0.460 4(4)	1.026 0(3)	H(12B)	0.346(6)	0.910(6)	0.721(3)
C(6)	0.796 3(5)	0.709 2(5)	0.834 2(3)	H(13A)	0.324(7)	0.611(6)	0.727(4)
C(7)	0.817 5(5)	0.798 0(5)	0.886 1(3)	H(13B)	0.407(6)	0.714(6)	0.630(4)
C(8)	0.658 4(5)	0.912 8(5)	0.904 5(3)	H(14A)	0.149(7)	0.912(6)	0.626(4)
C(9)	0.539 7(5)	0.895 6(4)	0.863 3(3)	H(14B)	0.066(7)	0.832(7)	0.716(4)
C(10)	0.624 2(5)	0.770 4(4)	0.818 6(2)	H(15A)	0.195(7)	0.693(6)	0.564(4)
C(11)	0.555 1(6)	0.709 0(6)	0.764 8(3)	H(15B)	0.116(7)	0.608(6)	0.646(4)
C(12)	0.374 9(6)	0.791 8(6)	0.749 9(3)	H(16A)	−0.163(7)	0.835(7)	0.630(4)
C(13)	0.321 1(6)	0.718 7(6)	0.694 0(4)	H(16B)	−0.067(7)	0.915(7)	0.532(4)
C(14)	0.145 8(6)	0.806 4(7)	0.666 7(4)	H(17A)	−0.022(7)	0.668(7)	0.492(4)
C(15)	0.097 4(6)	0.721 6(7)	0.614 9(4)	H(17B)	−0.118(7)	0.618(7)	0.573(4)
C(16)	−0.072 3(7)	0.809 3(7)	0.579 5(4)	H(18A)	−0.291(8)	0.911(7)	0.454(4)
C(17)	−0.115 5(7)	0.720 8(7)	0.529 4(4)	H(18B)	−0.382(8)	0.846(7)	0.537(4)
C(18)	−0.283 1(8)	0.804 3(8)	0.491 2(4)	H(19A)	−0.224(8)	0.688(7)	0.395(4)
C(19)	−0.326 7(8)	0.713 8(7)	0.444 0(5)	H(19B)	−0.301(9)	0.622(8)	0.471(5)
C(20)	−0.492 5(7)	0.791 4(8)	0.406 1(4)	H(20A)	−0.596(7)	0.834(6)	0.459(4)
C(21)	−0.535 2(9)	0.700 7(9)	0.360 1(5)	H(20B)	−0.500(8)	0.889(7)	0.364(4)
C(22)	−0.699(1)	0.776(1)	0.322 9(6)	H(21A)	−0.434(8)	0.646(8)	0.316(4)
H(1)	0.883(6)	0.529(5)	1.076(3)	H(21B)	−0.533(9)	0.604(8)	0.404(4)
H(2)	0.598(6)	0.732(6)	1.130(3)	H(22A)	−0.798(9)	0.820(9)	0.364(5)
H(3)	0.358(6)	0.716(5)	1.073(3)	H(22B)	−0.710(9)	0.894(9)	0.279(5)
H(5)	0.795(6)	0.382(6)	1.000(3)	H(22C)	−0.72(1)	0.73(1)	0.303(5)

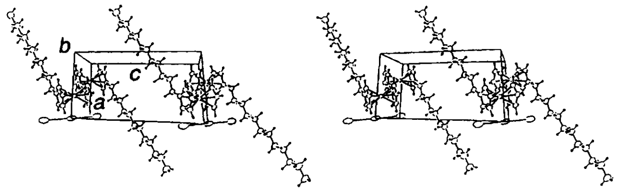

Fig. 10 Stereoview for the crystal of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide with the shorter interlayer distance

distance is illustrated in Fig. 10. The mean C–C distances (1.42 Å) and C–C–C angles (107.8°) in the ring are typical of ferrocene derivatives, the mean C–C distances (1.51 Å) and C–C–C angles (115.3°) in the alkyl chain are typical of alkyl substituents and the I–I distance 2.9221 Å is typical of the symmetric triiodide anion. The mean Fe–C (ring) distance is found to be 2.067 Å, intermediate between the values of 2.045 Å for ferrocene[12] and 2.075 Å for the ferrocenium cation,[13] indicating that the valence state is intermediate between Fe^{II} and Fe^{III}. Both the cation and anion are located at the centre of symmetry. The results are in accord with the salt exhibiting the averaged-valence state at room temperature. The dodecyl substituent has an all-*trans* conformation, which is the most thermodynamically stable. The results combined with those of the X-ray powder diffraction patterns suggest that the interlayer direction is [001]. As is discussed above this salt is very interesting because the phases with longer and shorter interlayer distances transform into each other in the solid state and the change in the mixed-valence state is coupled with the phase transition. In the case of the structure with the longer interlayer distance the crystal packing becomes worse and the interaction between the cation and anion becomes asymmetric, therefore the energy of either Fe_A^{II}–Fe_B^{III} or Fe_A^{III}–Fe_B^{II} would be low in comparison to that of the other, and the mixed-valence state becomes valence trapped. On the other hand, in the case of the structure with the shorter interlayer distance the interaction between the cation and anion is symmetric and the averaged-valence state is observed at room temperature.

Table 5 Selected bond distances (Å) and angles (°) for 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide with e.s.d.s in parentheses

I(1)–I(2)	2.9221(4)	C(7)–C(8)	1.413(5)
Fe–C(1)	2.046(4)	C(8)–C(9)	1.418(8)
Fe–C(2)	2.050(4)	C(9)–C(10)	1.422(6)
Fe–C(3)	2.063(4)	C(10)–C(6)	1.424(6)
Fe–C(4)	2.093(4)	C(10)–C(11)	1.488(8)
Fe–C(5)	2.057(4)	C(11)–C(12)	1.484(6)
Fe–C(6)	2.070(4)	C(12)–C(13)	1.51(1)
Fe–C(7)	2.058(5)	C(13)–C(14)	1.503(7)
Fe–C(8)	2.052(4)	C(14)–C(15)	1.52(1)
Fe–C(9)	2.070(3)	C(15)–C(16)	1.509(7)
Fe–C(10)	2.107(4)	C(16)–C(17)	1.50(1)
C(1)–C(2)	1.406(5)	C(17)–C(18)	1.510(8)
C(2)–C(3)	1.420(7)	C(18)–C(19)	1.49(1)
C(3)–C(4)	1.437(6)	C(19)–C(20)	1.494(9)
C(4)–C(5)	1.431(5)	C(20)–C(21)	1.47(1)
C(5)–C(1)	1.417(7)	C(21)–C(22)	1.48(1)
C(6)–C(7)	1.420(8)	C(4)–C(4′)	1.44(1)
C(1)–Fe–C(7)	105.4(2)	C(6)–C(10)–C(11)	124.1(4)
C(2)–Fe–C(8)	107.0(2)	C(9)–C(10)–C(11)	129.2(4)
C(3)–Fe–C(9)	110.7(1)	C(10)–C(11)–C(12)	117.6(4)
C(4)–Fe–C(10)	111.3(2)	C(11)–C(12)–C(13)	112.3(4)
C(5)–Fe–C(6)	108.0(2)	C(12)–C(13)–C(14)	115.6(5)
C(5)–C(1)–C(2)	108.4(4)	C(13)–C(14)–C(15)	112.6(5)
C(1)–C(2)–C(3)	108.6(4)	C(14)–C(15)–C(16)	115.2(5)
C(2)–C(3)–C(4)	107.7(3)	C(15)–C(16)–C(17)	113.4(5)
C(3)–C(4)–C(5)	107.1(4)	C(16)–C(17)–C(18)	115.6(5)
C(4)–C(5)–C(1)	108.1(3)	C(17)–C(18)–C(19)	115.1(5)
C(10)–C(6)–C(7)	108.7(4)	C(18)–C(19)–C(20)	116.9(5)
C(6)–C(7)–C(8)	107.9(4)	C(19)–C(20)–C(21)	116.5(6)
C(7)–C(8)–C(9)	107.8(4)	C(20)–C(21)–C(22)	117.2(7)
C(8)–C(9)–C(10)	108.9(3)	C(3)–C(4)–C(4′)	126.4(4)
C(9)–C(10)–C(6)	106.7(4)	C(5)–C(4)–C(4′)	126.2(4)

C(4′) is related to C(4) by the centre of symmetry.

The present study shows that the salts with the shorter interlayer distance have both the monocation and the triiodide anion at the centre of symmetry and show valence detrapping with increasing temperatures.

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