Phase transition in triiodide salts of binuclear ferrocene derivatives having long alkyl chains accompanied by a change in mixed-valence state

Satoru Nakashima,*[a] **Yutaka Ueki,**[b] **Hiroshi Sakai***[c] **and Yutaka Maeda**[d]

[a] *Radioisotope Center, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739, Japan*
[b] *Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739, Japan*
[c] *Department of Chemistry, Faculty of Science, Konan University, Higashi-Nada, Kobe 658, Japan*
[d] *Research Reactor Institute, Kyoto University, Kumatori, Sennan, Osaka 590-04, Japan*

The relation between the mixed-valence state and crystal structure of 1′,1‴-didecyl- and 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodide has been studied by means of ^{57}Fe Mössbauer spectroscopy and X-ray powder diffraction. The salts with even numbers of carbon atoms in the alkyl chain show a phase transition between two types of layered structures, accompanied by a change in mixed-valence state. Iodine-129 Mössbauer spectroscopy was applied to determine the electronic state of the triiodide anion in the biferrocenium salts. A change in the electronic state accompanied by a phase transition was observed in the case of the 1′,1‴-didecyl derivative.

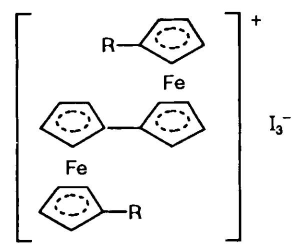
Mixed-valence binuclear ferrocene derivatives are good model compounds to study electron-transfer processes. The rate of electron transfer in the mixed-valence salts is strongly influenced by the environment about the monocation.[1,2] We have studied the mixed-valence states of binuclear ferrocene derivatives having a series of long alkyl chain substituents by means of ^{57}Fe Mössbauer spectroscopy and X-ray diffraction to determine the packing effect on the mixed-valence state.[3–6] Systematic study of the relationship between the mixed-valence state and the crystal structure has revealed an interesting even–odd character in the number of carbon atoms of the alkyl chain in the triiodide salts of binuclear ferrocene derivatives with long alkyl substituents.

In the present study the correlation of the mixed-valence state and crystal structure of 1′,1‴-didecyl- and 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodide is investigated by means of ^{57}Fe Mössbauer spectroscopy and X-ray powder diffraction. The electronic state of the counter anion is also investigated by ^{129}I Mössbauer spectroscopy.

Experimental

1′,1‴-Didecyl- and 1′,1‴-bis(undecyl)-1,1″-biferrocenes were synthesized according to a method reported for a series of biferrocenes disubstituted with long alkyl chains.[3–6] The products were isolated by column chromatography on alumina and purified by recrystallization from dichloromethane–hexane. 1′,1‴-Didecyl-1,1″-biferrocene: m.p. = 60.9–62.0 °C, ^{1}H NMR ($CDCl_3$) δ 0.88, 1.25, 2.08, 3.82, 3.86, 4.11 and 4.23. 1′,1‴-Bis(undecyl)-1,1″-biferrocene: m.p. = 56.5–57.5 °C, ^{1}H NMR ($CDCl_3$) δ 0.88, 1.25, 2.07, 3.83, 3.87, 4.11 and 4.24. The ^{57}Fe Mössbauer spectra at room temperature show only one doublet ascribed to ferrocene-like iron(II) [isomer shift (δ) = 0.45 mm s^{-1} with respect to metallic iron and quadrupole splitting (ΔE_q) = 2.32–2.33 mm s^{-1}]. There are no significant differences between the present products and biferrocene derivatives with other long alkyl substituents.[6]

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″-biferrocene. About one half of each sample prepared in the above manner was recrystallized from a dichloromethane solution at 0 °C [Found for 1′,1‴-didecyl-1,1″-biferrocenium triiodide: (from hexane) C, 46.55; H, 5.70; (from dichloromethane) C, 46.85; H, 5.65. Calc. for $C_{40}H_{58}Fe_2I_3$: C, 46.55; H, 5.65. Found for 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodide: (from hexane) C, 47.85; H, 6.00; (from dichloromethane) C, 47.80; H, 5.85. Calc. for $C_{42}H_{62}Fe_2I_3$: C, 47.60; H, 5.90%]. The triiodide salts for the measurement of ^{129}I Mössbauer spectra were prepared as below. About 30 wt.% of Na^{129}I and 70 wt.% of Na^{127}I in Na_2SO_3 aqueous solution was oxidized by using 3 mol dm^{-3} H_2SO_4 and 10% H_2O_2 and extracted with hexane. The sample from hexane was obtained by adding this solution to a hexane solution of the corresponding binuclear ferrocene derivative. The sample from dichloromethane was obtained by recrystallization from dichloromethane at 0 °C. An annealed sample was obtained by standing at 40 °C for 1 h.



R = $(CH_2)_nCH_3$ n = 9 or 10

Variable-temperature ^{57}Fe Mössbauer spectra were obtained according to the method described before.[6] The ^{129}I Mössbauer measurements were carried out in the transmission geometry by cooling a ^{66}Zn^{129}Te source and the samples to 16 K with a closed-cycle helium refrigerator. The Mössbauer source was prepared by irradiation of 150 mg ^{66}Zn^{128}Te at a thermal neutron fluence rate of 2 × 10^{13} n cm^{-2} s^{-1} for 1 h in the Kyoto University Reactor. The source activity produced by the ^{128}Te(n,γ)^{129}Te reaction was initially about 3.7 × 10^8 Bq, sufficient to obtain a reasonable spectrum in 3–4 h of data collection. The source was used repeatedly. The 27.8 keV Mössbauer γ-rays were detected with a 1 mm thick NaI(Tl) scintillation counter. The Mössbauer spectrometer was calibrated with the well known six-line spectrum of iron foil. Details of the instruments have been described elsewhere.[7] The Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks.

Table 1 Iron-57 Mössbauer parameters for 1′,1‴-didecyl- and 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodides

Substituent	Solvent	T/K	δ*/mm s^{-1}	ΔE_q/mm s^{-1}
Decyl	Hexane	298	0.44	1.90
			0.45	0.49
		203	0.48	1.97
			0.50	0.50
		80	0.52	2.02
			0.54	0.45
	CH_2Cl_2	298	0.44	1.16
		213	0.48	1.19
		203	0.49	1.46
			0.50	0.97
		193	0.50	1.52
			0.50	0.83
		173	0.51	1.65
			0.51	0.75
		153	0.50	1.73
			0.50	0.71
		133	0.51	1.78
			0.52	0.68
		93	0.52	1.83
			0.53	0.63
		80	0.51	1.92
			0.51	0.57
Undecyl	Hexane	298	0.45	1.95
			0.44	0.51
		203	0.50	1.96
			0.51	0.46
		80	0.53	1.98
			0.54	0.40
	CH_2Cl_2	298	0.45	1.95
			0.46	0.49
		203	0.48	1.97
			0.52	0.41
		80	0.53	1.99
			0.54	0.54

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

All X-ray powder diffraction patterns were measured by using graphite-monochromated Cu-Kα radiation (Rigaku) at room temperature. Thermal analyses were performed by using a hand-made DTA (differential thermal analysis) instrument.

Results and Discussion

Mixed-valence states and phase transitions

Recrystallization of 1′,1‴-didecyl- and 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodides from dichloromethane was performed at 0 °C, because it had been established that the crystal structure of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide depends on the recrystallization temperature, *i.e.* the salt obtained at 0 °C from dichloromethane solution has a shorter interlayer distance than that obtained at 30 °C from the same solution.[6] The present salts showed similar behaviour to that found earlier. Namely, both the crystals obtained from hexane have longer interlayer distances. As regards the crystals from dichloromethane, 1′,1‴-didecyl-1,1″-biferrocenium triiodide with an even number of carbon atoms in the alkyl chain has a shorter interlayer distance, while 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodide with an odd number of carbon atoms has a longer interlayer distance.

The ^{57}Fe Mössbauer parameters for the present salts are summarized in Table 1. The present results are in accord with the previous ones in that the samples with longer interlayer distances show a temperature-independent trapped-valence state and those with shorter interlayer distances show 'fusion type' valence detrapping with increasing temperature. For the temperature-independent trapped-valence state, two quadrupole-split doublets ascribed to ferrocene-like bivalent (Fe^{II}) and ferrocenium-like tervalent irons (Fe^{III}) are observed at all temperatures. For the 'fusion type' valence detrapping, two quadrupole-split doublets observed at low temperatures converge with increasing temperature to give one doublet without significant line broadening. The detrapping temperature of 1′,1‴-didecyl-1,1″-biferrocenium triiodide having the shorter interlayer distance is about 220 K, similar to those for 1′,1‴-bis(dodecyl)- (≈230 K),[6] 1′,1‴-bis(tetradecyl)-(≈205 K)[3] and 1′,1‴-bis(hexadecyl)-1,1″-biferrocenium triiodide (≈220 K).[4] 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 (≈280 K),[8,9] propyl (≈270 K)[8] and butyl (≈280 K).[10,11]

Recently, we first reported an interesting valence trapping of the mixed-valence state with increasing temperature, accompanied by a phase transition from shorter to longer interlayer distance in 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide in the solid state.[6] We thus investigated whether the valence trapping occurs in other salts with increasing temperature. 1′,1‴-Didecyl-1,1″-biferrocenium triiodide with the shorter interlayer distance was heated to 30 and 40 °C in turn every 20 min and then cooled to 0 °C for 1 d. The X-ray powder diffractions measured at room temperature showed that the interlayer distance becomes longer upon annealing at 40 °C for 20 min. The transition temperature in the present sample is lower than that in 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide. Some of the 1′,1‴-didecyl-1,1″-biferrocenium salt returns to the former form in the solid state upon standing at 0 °C for 1 d. On the other hand, almost all of the 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide returns to the phase with the shorter interlayer distance. At 40 °C the ^{57}Fe Mössbauer spectrum of 1′,1‴-didecyl-1,1″-biferrocenium triiodide, which shows the averaged-valence state at room temperature, indicated two sets of quadrupole doublets. This is consistent with the change in X-ray diffraction patterns. The intensity ratio of Fe^{II} to Fe^{III} deviates from 1 : 1, as also observed in 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide.[6] This 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 second example of valence trapping with increasing temperature.

1′,1‴-Bis(tetradecyl)-1,1″-biferrocenium triiodide with the shorter interlayer distance was heated to 40, 50 and 60 °C in turn every 20 min and then cooled to 0 °C for 1 d. The X-ray powder diffractions measured at room temperature are shown in Fig. 1. It can be seen that a change to a longer interlayer distance occurs upon annealing at 60 °C for 20 min. 1′,1‴-Bis(hexadecyl)-1,1″-biferrocenium triiodide with shorter interlayer distance was also heated to 40, 50, 60 and 70 °C in turn every 20 min and then cooled to 0 °C for 1 d. The X-ray powder diffraction patterns measured at room temperature are shown in Fig. 2. A change to a longer interlayer distance occurs upon annealing at 70 °C for 20 min. Some salts return to the former state in the solid state upon standing at 0 °C for 1 d. There is a tendency for the transition temperature to rise with increasing number of carbon atoms in the alkyl chain.

Typical DTA curves are shown in Fig. 3. 1′,1‴-Bis(tetradecyl)-1,1″-biferrocenium triiodide obtained from dichloromethane shows an endothermic peak at 328 K, while the salt from hexane does not show the phase transition at the same temperature. The transition temperature is almost the same as that of the change in X-ray diffraction pattern. Although the temperature at which the Mössbauer spectrum is measured is slightly lower than 328 K, it is thought that the phase transition is achieved by standing at that temperature for several hours. Thus the phase transition between the salts with

Table 2 Iodine-129 Mössbauer parameters for 1′,1‴-didecyl- and 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodides

Compound	Site	δ^a/mm s^{-1}	e^2Qq^b/MHz	U_p	h_p
1′,1‴-Didecyl-1,1″-biferrocenium triiodide from hexane	I_A	1.19	−2404	1.15	1.05
	I_{B_2}	0.20	−1350	0.49	0.59
	I_{B_1}	0.09	−1054	0.42	0.46
from dichloromethane	I_A	1.35	−2434	1.26	1.06
	I_B	0.09	−1216	0.42	0.53
from dichloromethane annealed at 40 °C	I_A	1.26	−2415	1.20	1.05
	I_{B_2}	0.16	−1358	0.47	0.59
	I_{B_1}	−0.04	−1035	0.33	0.45
1′,1‴-Bis(undecyl)-1,1″-biferrocenium triiodide from hexane	I_A	1.26	−2499	1.20	1.09
	I_{B_2}	0.29	−1370	0.55	0.60
	I_{B_1}	0.05	−1082	0.39	0.47
from dichloromethane	I_A	1.28	−2485	1.21	1.08
	I_{B_2}	0.29	−1347	0.55	0.59
	I_{B_1}	0.05	−1082	0.39	0.47

[a] Relative to the ZnTe source. [b] Transformed to ^{127}I.

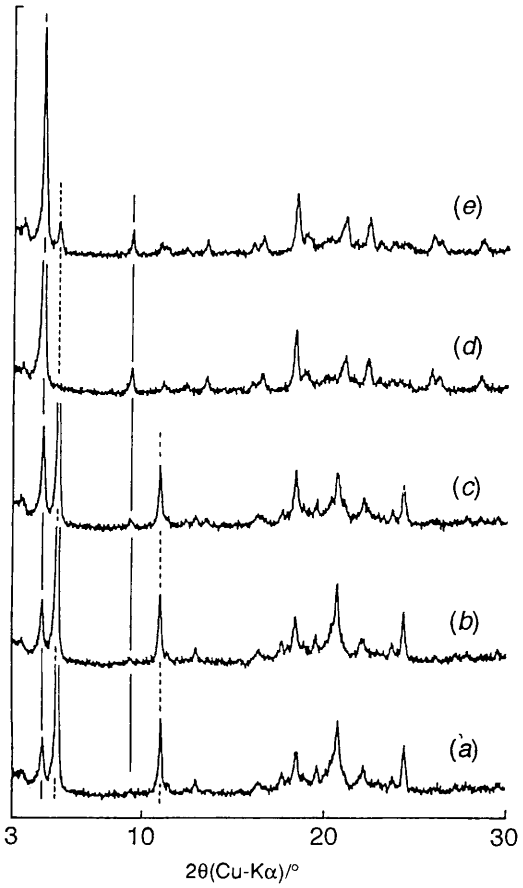


Fig. 1 X-Ray powder diffraction patterns of 1′,1‴-bis(tetradecyl)-1,1″-biferrocenium triiodide measured at room temperature: (*a*) fresh sample obtained from dichloromethane; (*b*) annealed at 40 °C for 20 min; (*c*) annealed at 50 °C for 20 min; (*d*) annealed at 60 °C for 20 min; (*e*) sample of (*d*) at 0 °C for 1 d

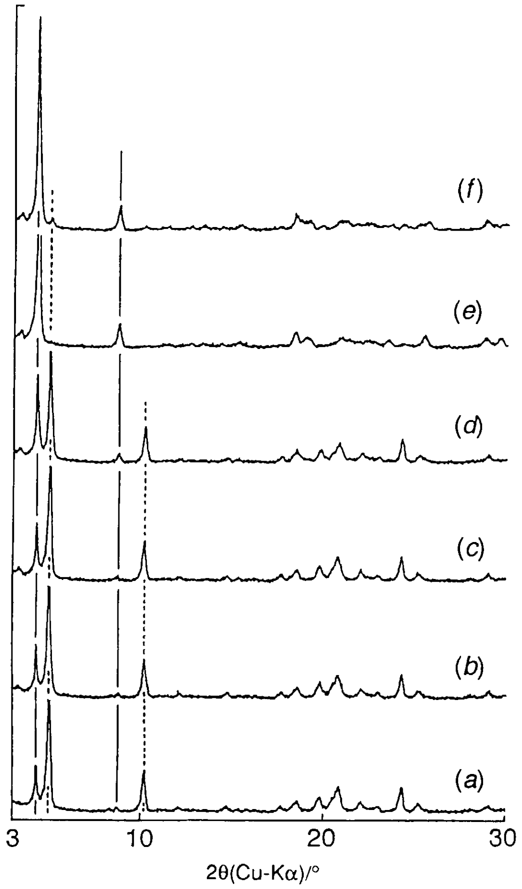


Fig. 2 X-Ray powder diffraction patterns of 1′,1‴-bis(hexadecyl)-1,1″-biferrocenium triiodide measured at room temperature: (*a*)–(*d*) as in Fig. 1; (*e*) annealed at 70 °C for 20 min; (*f*) sample of (*e*) at 0 °C for 1 d

longer and shorter interlayer distances is a first-order one. On the other hand, the valence detrapping is coupled with a second-order phase transition.[12] X-Ray structural analysis of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide shows that the dodecyl substituent has an all-*trans* conformation, which is the most thermodynamically stable.[6] It is thought that all salts with shorter interlayer distances have the same structure as that of 1′,1‴-bis(dodecyl)-1,1″-biferrocenium triiodide. The phase transition from the shorter to longer interlayer distance may be regarded as a partial melting of the long alkyl chain.

^{129}I Mössbauer spectroscopic study of the change in electronic state of the counter anion

Iodine-129 Mössbauer spectroscopy was applied to determine the electronic state of the triiodide anion, also to see whether the

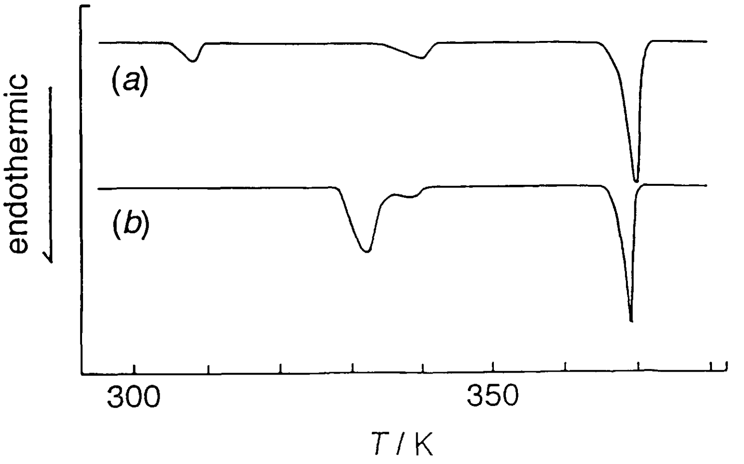


Fig. 3 The DTA curves for 1′,1‴-bis(tetradecyl)-1,1″-biferrocenium triiodide obtained from (*a*) hexane and (*b*) dichloromethane

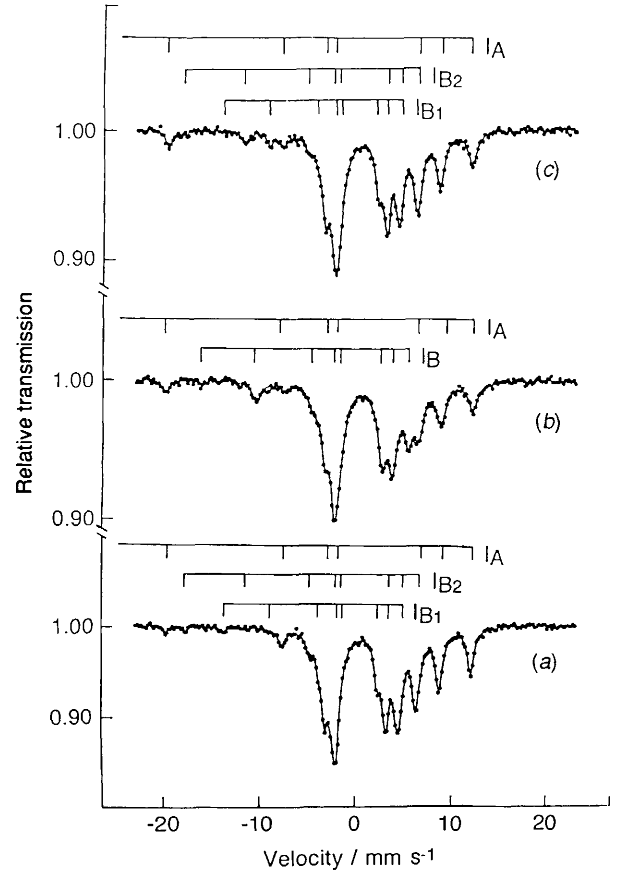


Fig. 4 The ^{129}I Mössbauer spectra at 16 K of 1′,1‴-didecyl-1,1″-biferrocenium triiodide obtained (*a*) from hexane, (*b*) from dichloromethane at 0 °C and (*c*) annealed at 40 °C for 1 h

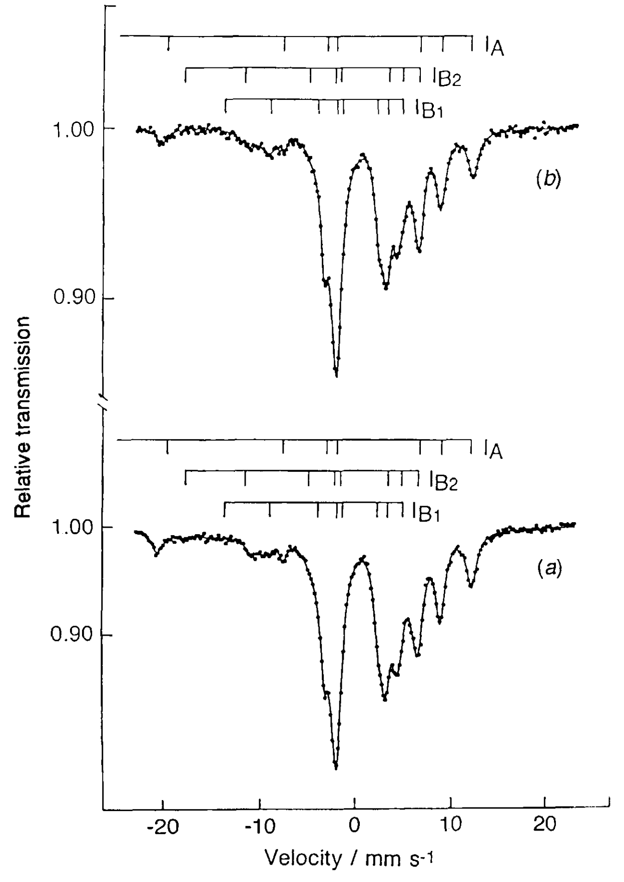


Fig. 5 The ^{129}I Mössbauer spectra at 16 K of 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodide obtained (*a*) from hexane and (*b*) from dichloromethane at 0 °C

electronic state varied with the phase transition. Spectra of 1′,1‴-didecyl- and 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodide are shown in Figs. 4 and 5, respectively, and the corresponding parameters are summarized in Table 2. The quadrupole octet corresponds to a nuclear transition between the ground state (nuclear spin $I_g = \frac{7}{2}$) and the excited state ($I_e = \frac{5}{2}$) of ^{129}I, where the transitions with $\Delta I_z = 0$ and ± 1 are allowed due to the nature of the magnetic dipole transition. The intensities of the eight peaks depend on the square of the Clebsch–Gordan coefficient and, therefore, the spectrum is asymmetric. The sign of the electric field gradient is easily determined based on its asymmetry. The stick diagrams show the peak positions for each of the different kinds of iodine atoms.

It can be seen from Fig. 5 that 1′,1‴-bis(undecyl)-1,1″-biferrocenium triiodide obtained from hexane and dichloromethane show the same spectrum, consisting of the superposition of three different quadrupole octets, indicating the presence of three distinct iodine atoms. The area ratio of each component is about 1 : 1 : 1 for $I_A : I_{B_1} : I_{B_2}$. The asymmetry parameter, η, is 0. From the number of unbalanced p electrons (U_p) and 5p holes (h_p), the charge density localized on I_{B_1} is estimated to be slightly greater than that of I_{B_2}. It is thought that the triiodide anion is asymmetric, $[I_{B_2}–I_A \cdots I_{B_1}]^-$, although the three iodines align in a straight line. The ^{129}I Mössbauer spectrum of 1′,1‴-didecyl-1,1″-biferrocenium triiodide obtained from hexane also shows the presence of three distinct iodine atoms. On the other hand, the spectrum of this salt recrystallized from dichloromethane is similar to those of 1,1″-biferrocenium, 1′,1‴-dibromo- and 1′,1‴-diiodo-1,1″-biferrocenium triiodides.[13] The spectrum consists of two kinds of quadrupole octets (I_A and I_B) with 1:2 intensity ratio. The components I_A and I_B correspond to the central and terminal iodine atoms of linear I_3^- ions, respectively, judging from the values of δ, e^2Qq, the area ratio, and asymmetry parameter ($\eta = 0$). From U_p and h_p, the charge densities localized on the central and terminal iodine atoms are estimated to be slightly positive and about -0.5, respectively. It is thought that the triiodide anion is symmetric, $[I_B{-}I_A{-}I_B]^-$. The negative signs of e^2Qq imply that the V_{zz} principal axis is along the molecular axis of the linear I_3^- ion. The ^{129}I Mössbauer spectrum of 1′,1‴-didecyl-1,1″-biferrocenium triiodide annealed at 40 °C for 1 h consists of three kinds of quadrupole octets (I_A, I_{B_1} and I_{B_2}), indicating that I_3^- is asymmetric. This spectrum differs from that of the recrystallized sample and is similar to that of the sample obtained from hexane. This change is in accord with the ^{57}Fe Mössbauer spectra and X-ray powder diffraction patterns. It is clear that the salt which shows a temperature-independent trapped-valence state possesses an asymmetric triiodide anion, while that which shows valence detrapping has a symmetric triiodide anion.

The present study shows that in the case of the structure with the longer interlayer distance the monocation and the triiodide anion are asymmetric and the interaction between the two is asymmetric, therefore the energy of either of the states $Fe_A^{II}Fe_B^{III}$ 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 monocation and the triiodide anion are symmetric, the interaction between them is symmetric and the averaged-valence state is observed at room temperature. All salts with the shorter interlayer distance undergo a first-order phase transition to salts with the longer interlayer distance and valence trapping occurs, which is accompanied by a change in symmetry of the triiodide anion.

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