May, 1987] *Bull. Chem. Soc. Jpn.,* ***60****, 1673—1680 (1987)* 1673

Mössbauer and ESR Spectroscopic Studies on the Mixed-Valence States of 1',1'''-Dialkyl- and 1',1'''-Bis(methylbenzyl)biferrocenium Triiodides in Crystalline and Dispersed State

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(Received October 24, 1986)

Iron atoms in the two different crystal forms of 1',1'''-dibutylbiferrocenium triiodide showed different temperature-depending mixed-valence states; i.e., an averaged-valence state at higher temperatures and a trapped-valence state at lower temperatures in one crystal form but only a trapped-valence state from 78 K to room temperature in the other crystal form. The temperature-depending mixed-valence states were observed in 1',1'''-diisobutylbiferrocenium triiodide, whereas only a trapped-valence state was found in 1',1'''-dipentylbiferrocenium triiodide. Both the 1',1'''-dibutyl- and 1',1'''-diisobutylbiferrocenium triiodide showed Mössbauer spectra that were different from those of their crystalline states in a dispersed state. A good correlation of the anisotropy of g-values with the mixed-valence states was observed in the ESR spectra for a series of 1',1'''-dialkyl- and 1',1'''-bis(methylbenzyl)biferrocenium triiodides. The difference in the ESR parameters between these compounds in the crystalline state was reduced in the dispersed state.

It has been known that biferrocene derivatives are easily mono-oxidized to give mixed-valence cations. Those mixed-valence biferrocene compounds can be classified into two types of valence states of iron atoms; a trapped-valence type and an averaged-valence type, by means of Mössbauer spectroscopy.1) Different states of iron atoms corresponding to ferrocene-like bivalent and ferricenium-like tervalent iron atoms are found in the former, while only an equivalent state of iron atoms is found over the Mössbauer time scale (ca. 10^{-7} s) in the latter.

In studies of bridged biferrocene derivatives it was concluded that the presence of conjugated π-systems between the two ferrocene moieties was necessary to have an interaction between the two metal atoms in well-separated mixed-valence compounds.2—4) Recently, it has been found that an introduction of a substituent to biferrocenium cations influences the mixed-valence states; e.g., a monocationic salt of 1',1'''-dichlorobiferrocene5) shows a trapped-valence state from 4.2 K to room temperature, while monocationic salts of 1',1'''-diiodo-6) and 1',1'''-dibromobiferrocene5) show an averaged-valence state over the Mössbauer time scale in the same temperature range. Studies by XANES and XPS show that the electron-transfer rate between the two iron atoms in dibromo derivative is lower than ca. 10^{16} s^{-1}.7) A trapped-valene state of iron atoms in 1',1'''-diethyl- and 1',1'''-dipropylbiferrocenium triiodide are known to change into an averaged-valence state at high temperatures.8)

Similar temperature dependences of the valence state were recently reported for the triiodide salts of monocationic 1',1'''-dibutyl-,9) 1',1'''-dibenzyl-,9) 1',1'''-bis(*o*-methylbenzyl)-,10) and 1',1'''-bis(*p*-methylbenzyl)biferrocene.10) It has been found that a trapped-valence state and an averaged-valence state coexist in 1',1'''-dibutyl-,9) 1',1'''-dibenzyl-,9) and 1',1'''-bis(*p*-methylbenzyl)biferrocenium triiodide.10) In these studies, it has been suggested that the environment surrounding each cation in the solid state should determine the mixed-valence state. The studies on the effects of counter anions were carried out to elucidate the mechanism of the intramolecular electron transfer.11—15)

It has been suggested that the anisotropy of the *g*-value, $\Delta g = g_{\parallel} - g_{\perp}$, has a close connection with those mixed-valence states obtained from Mössbauer spectra in the studies of mixed-valence biferrocene derivatives.16) In the present study, the mixed-valence states of 1',1'''-diisobutyl- and 1',1'''-dipentylbiferrocenium triiodide and two crystal forms of the 1',1'''-dibutyl derivative were investigated in a crystalline state and in a state dispersed in poly(methyl methacrylate) by using Mössbauer spectroscopy. The mixed-valence states for a series of 1',1'''- dialkyl- and 1',1'''-bis(methylbenzyl)biferrocenium triiodides are also investigated in a crystalline and in a dispersed state by using ESR spectroscopy.

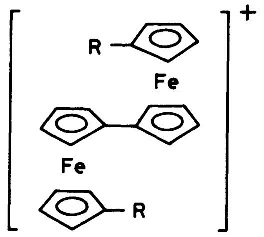

Fig. 1. 1',1'''-Disubstituted biferrocenium triiodides used in the present studies (R=ethyl, propyl, butyl, isobutyl, pentyl, benzyl, *o*-methylbenzyl, *m*-methylbenzyl, and *p*-methylbenzyl).

Experimental

Materials. 1′,1‴-Dialkyl- and 1′,1‴-bis(methylbenzyl)biferrocenes were prepared by the Ullmann coupling of 1-bromo-1′-alkylferrocenes and 1-bromo-1′-(methylbenzyl)ferrocenes at 100—110 °C for 18 h, respectively. The products were identified by using ^{1}H NMR and elemental analysis. Data of the elemental analysis and melting points for the new compounds, 1′,1‴-diisobutyl- and 1′,1‴-dipentylbiferrocene, are shown below, respectively: Found: C, 68.69; H, 7.66%. Calcd for $C_{28}H_{34}Fe_2$: C, 69.73; H, 7.11%. mp: 62 °C. Found: C, 69.67; H, 8.27%. Calcd for $C_{30}H_{38}Fe_2$: C, 70.61; H, 7.51%. mp: 36 °C.

The triiodide salts were prepared by a partial oxidation of the corresponding 1′,1‴-dialkyl- and 1′,1‴-bis(methylbenzyl)biferrocenes in benzene with a stoichiometric amount of I_2. The products were recrystallized from CH_2Cl_2 and identified by using elemental analysis. Data of the elemental analysis for the new mixed-valence compounds, 1′,1‴-diisobutyl- and 1′,1‴-dipentylbiferrocenium triiodide, are shown below, respectively: Found: C, 36.86; H, 4.31%. Calcd for $C_{28}H_{34}Fe_2I_3$: C, 38.97; H, 3.97%. Found: C, 40.56; H, 4.99%. Calcd for $C_{30}H_{38}Fe_2I_3$: C, 40.44; H, 4.30%.

1′,1‴-Dibutylbiferrocenium triiodide recrystallized from CH_2Cl_2 gave two kinds of crystal forms. One is needle-like crystals (crystals A), and the other is plate-like crystals (crystals B). Data of elemental analysis for these two crystal forms are shown below. Found for crystals A: C, 39.31; H, 4.14%. Found for crystals B: C, 39.20; H, 4.20%. Calcd for $C_{28}H_{34}Fe_2I_3$: C, 38.97; H, 3.97%.

The samples dispersed in polymer were obtained by evaporating a CH_2Cl_2 solution of poly(methyl methacrylate) containing 1—4% of each triiodide salt.

Mössbauer Spectroscopic Measurements. A ^{57}Co(Rh) source moving in a constant-acceleration mode was used for Mössbauer spectroscopic measurements. Mössbauer spectra were obtained by using an ELSCINT Mössbauer spectrometer and a proportional counter. Isomer shifts were referred to metallic iron foil. Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks.

ESR Measurements. X-band ESR spectra for powdered crystalline samples and dispersed samples were determined at 78 K using a JEOL JES-PE-3X ESR spectrometer.

Results and Discussion

Mössbauer Spectra. The biferrocene derivatives used in the present studies are shown in Fig. 1. Mössbauer spectrum for crystals obtained by the diffusion of hexane into a CH_2Cl_2 solution of 1′,1‴-dibutylbiferrocenium triiodide at room temperature shows only a single doublet which corresponds to a valence state averaged over ferrocene-like bivalent and ferricenium-like tervalent state. On the other hand,

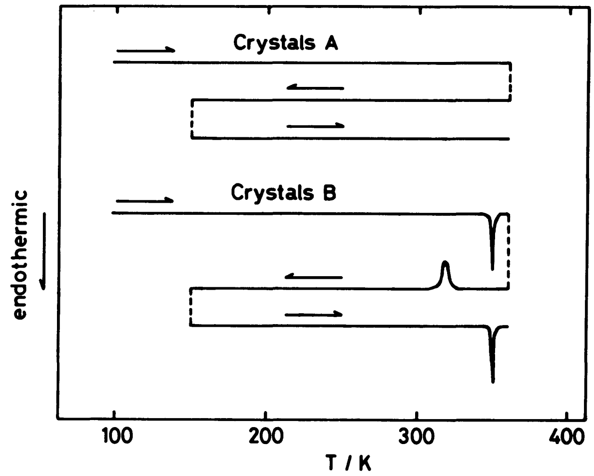

Fig. 3. Differential scanning calorimetric curves for two crystal forms of 1′,1‴-dibutylbiferrocenium triiodide at scanning rate, 5 K min^{-1}.

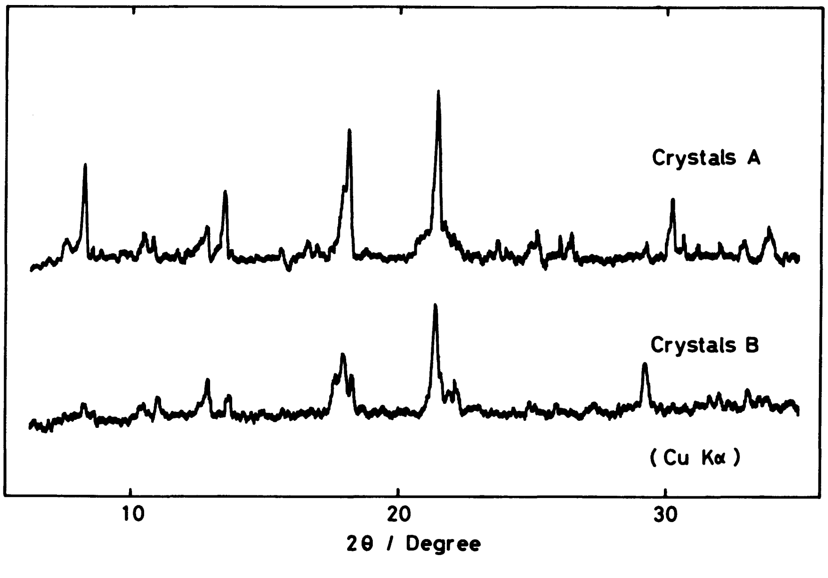

Fig. 2. X-Ray powder patterns for two crystal forms of 1′,1‴-dibutylbiferrocenium triiodide at room temperature.

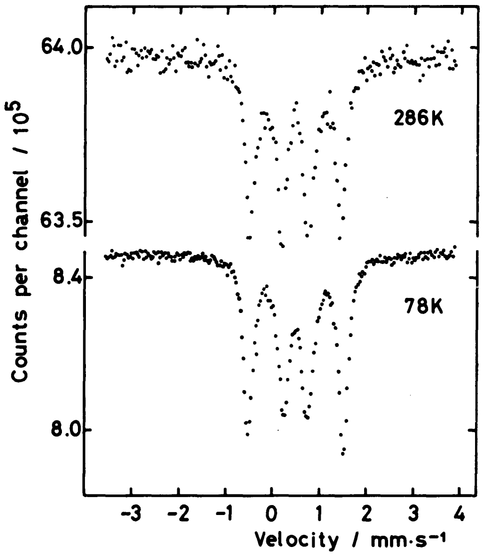

Fig. 4. Mössbauer spectra for crystals A of 1′,1‴-dibutylbiferrocenium triiodide at 78 and 286 K.

the microcrystals obtained by adding a benzene solution of I_2 to a benzene solution of 1′,1‴-dibutylbiferrocene give three doublets in the Mössbauer spectrum, which consist of two doublets corresponding to ferrocene-like bivalent and ferricenium-like tervalent iron atoms and of one doublet of a valence state averaged over the two valence states.[9]

Crystals A and crystals B of 1′,1‴-dibutylbiferrocenium triiodide give different X-ray powder patterns (Fig. 2) and different DSC (differential scanning calorimetry) curves (Fig. 3). An endothermic peak can be observed at 349 K in crystals B under a heating rate of 5 K min^{-1} but not observed in crystals A under the same heating rate. These results suggest that both crystals A and B have crystal structures different from each other.

The Mössbauer spectra in the two crystal forms are shown in Figs. 4 and 5. The Mössbauer spectroscopic data are summarized in Table 1. In crystals A, the spectra at 78 and 286 K consist of an inner- and an outer-doublet with a nearly 1:1 ratio in the areal intensity; these are ascribable to a ferricenium-like tervalent and ferrocene-like bivalent iron, respectively.

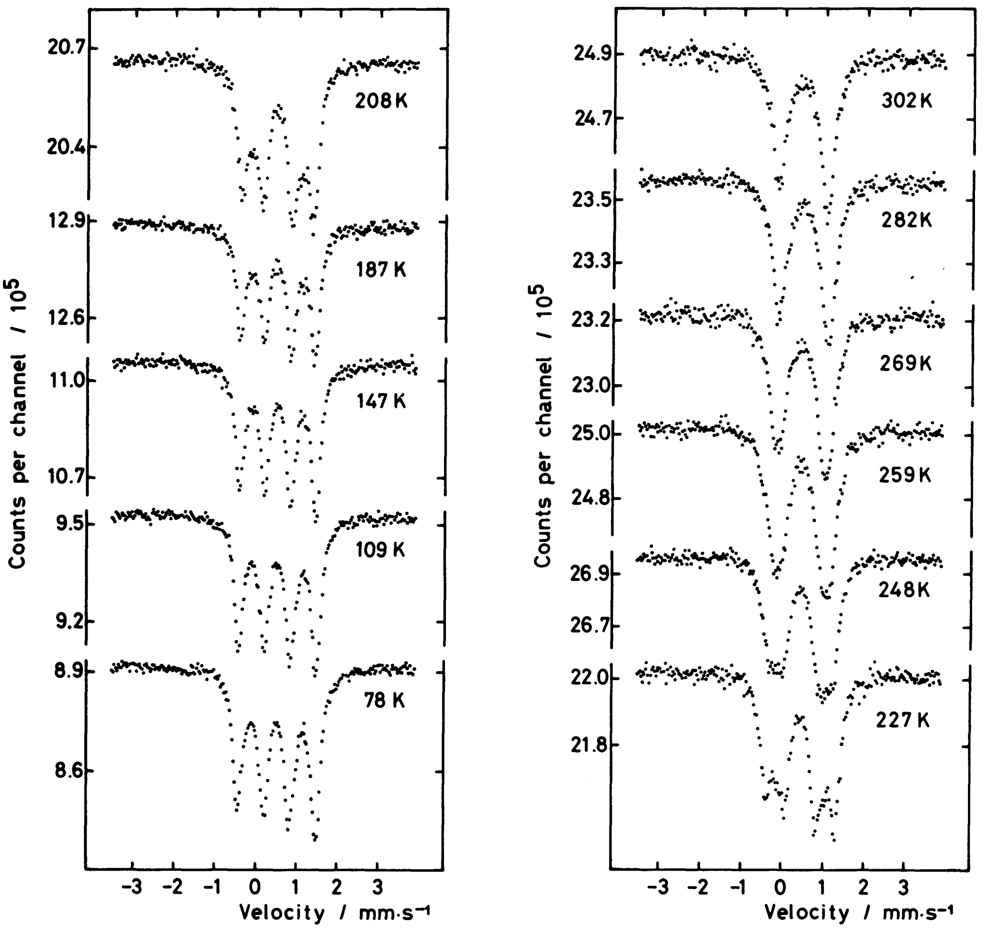

Fig. 5. Mössbauer spectra for crystals B of 1′,1‴-dibutylbiferrocenium triiodide from 78 K to room temperature.

It is clearly concluded that crystals A are of the trapped-valence type from 78 K to room temperature. On the contrary, the spectra of crystals B consist of one doublet ascribed to a state averaged over ferrocene-like and ferricenium-like states near room temperature, but of two doublets below ca. 250 K; i.e., crystals B show temperature-dependent mixed-valence states. The results indicate that the electron-transfer rate between the two iron atoms is dependent on the crystal structure.

The quadrupole splitting, ΔE_q, for the outer doublet ascribed to ferrocene-like iron atoms found in crystals B is a little smaller than that found in crystals A, while the ΔE_q value of the inner-doublet corresponding to ferricenium-like iron atoms is a little larger in crystals B than in crystals A (both at 78 K). This suggests that the interaction between Fe(II) and Fe(III) in crystals B is a little stronger than that in crystals A (even at 78 K).

Figures 6 and 7 show the Mössbauer spectra of 1′,1‴-diisobutyl- and 1′,1‴-dipentylbiferrocenium triiodide. The Mössbauer spectroscopic data are summarized in Table 2. A spectral change from two doublets (trapped-valence state) to one doublet (averaged-valence state) with increased temperatures is observed in 1′,1‴-diisobutylbiferrocenium triiodide, as in the case of crystals B of 1′,1‴-dibutylbiferrocenium triiodide. However, the transition tem-

Table 1. Mössbauer Parameters for 1′,1‴-Dibutylbiferrocenium Triiodide

Species	Temperature/K	$\delta^{a)}$/mm s^{-1}	ΔE_q/mm s^{-1}
Crystals A	286	0.44	1.88
		0.44	0.56
	78	0.50	2.03
		0.50	0.51
Crystals B	302	0.43	1.18
	282	0.44	1.19
	269	0.45	1.18
	259	0.45	1.20
	248	0.46	1.51
		0.46	0.91
	227	0.47	1.65
		0.46	0.80
	208	0.47	1.73
		0.47	0.75
	187	0.48	1.81
		0.48	0.66
	147	0.50	1.86
		0.50	0.64
	109	0.51	1.89
		0.51	0.64
	78	0.52	1.90
		0.52	0.64

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

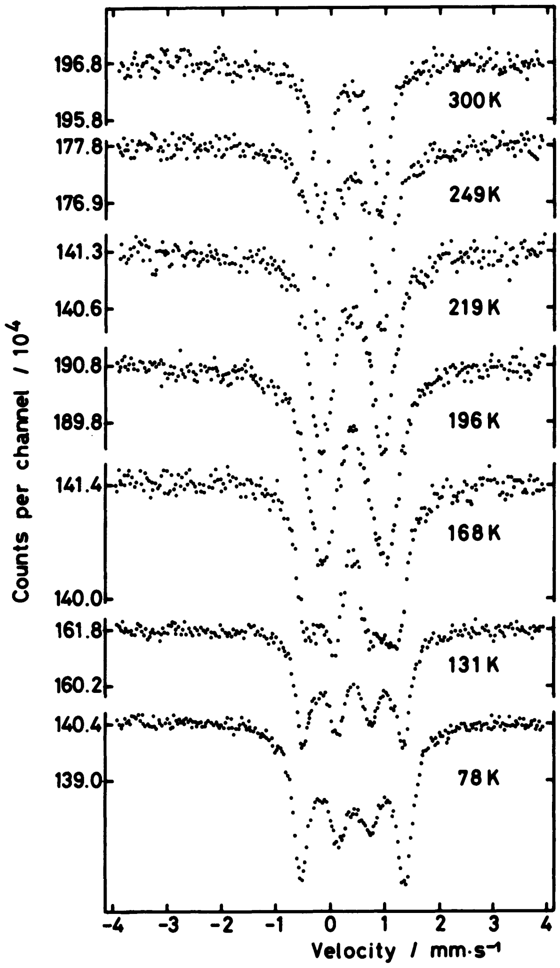

Fig. 6. Mössbauer spectra of 1′,1‴-diisobutylbiferrocenium triiodide from 78 K to room temperature.

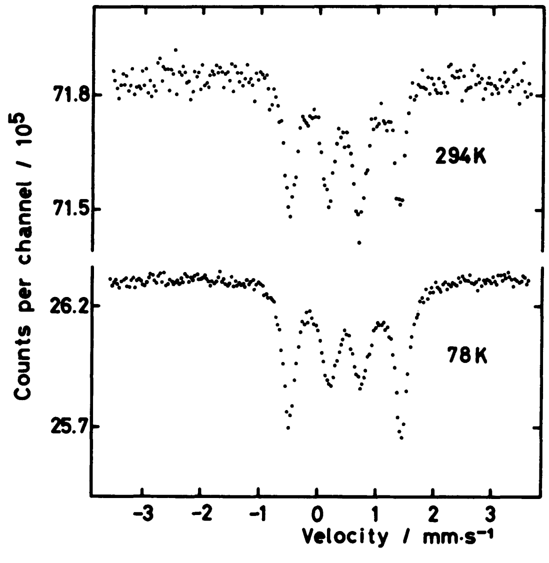

Fig. 7. Mössbauer spectra of 1′,1‴-dipentylbiferrocenium triiodide at 78 and 294 K.

perature, where the valence state changes from a trapped- to an averaged-valence state, is found to be lower in the isobutyl derivative than in crystals B of the butyl derivative. On the other hand, the Mössbauer spectra of the pentyl derivative show only a trapped-valence state from 78 K to room temperature.

It has already been reported that 1′,1‴-dibutylbiferrocenium cations take a trans conformation with respect to a planar fulvalene ligand in structual studies of their needle form triiodide salt (crystals A).[9,17] There are two structural features that also indicate that the structure of the cation is unsymmetric; the carbon-atom framework of one of the butyl groups lies essentially parallel to the Cp ring to which the butyl group is attached; whereas a part of the carbon-atom framework of the other butyl group is folded perpendicular to the Cp ring, and the I$_3^-$ ion has an unsymmetric structure being disposed unequally to the two iron atoms in the cation, putting more negative charge on one terminal iodine atom than the other terminal iodine atom. It is interesting to note that the more negative iodine atom is situated closer to the Fe(III) atom than the other iron atom, Fe(II). It may be concluded that the conformation of the butyl substituents influences the positioning of the I$_3^-$ ion.

Table 2. Mössbauer Parameters for 1′,1‴-Diisobutyl- and 1′,1‴-Dipentylbiferrocenium Triiodide

Compound	Temperature/K	$\delta^{a)}$/mm s^{-1}	ΔE_q/mm s^{-1}
1′,1‴-Diisobutyl-	300	0.45	1.09
biferrocenium	249	0.48	1.13
triiodide	219	0.48	1.14
	196	0.50	1.16
	168	0.50	1.59
		0.51	0.71
	131	0.51	1.82
		0.52	0.64
	78	0.53	1.91
		0.54	0.59
1′,1‴-Dipentyl-	294	0.45	1.88
biferrocenium		0.44	0.54
triiodide	78	0.50	1.94
		0.49	0.55

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

Figure 8 shows the Mössbauer spectra of 1′,1‴-dibutylbiferrocenium triiodide dispersed in poly(methyl methacrylate). The Mössbauer spectroscopic data are summarized in Table 3. The Mössbauer spectra in the dispersed state show two doublets; i. e., a definite trapped-valence state below 196 K and an insufficiently averaged state at 300 K. The collapse of the two doublets of the Mössbauer spectra begins at a higher temperature in the dispersed state than in crystals B, while that is not observed in the temperature range from 78 K to room temperature in crystals A. The Mössbauer spectra and those parameters of 1′,1‴-diisobutylbiferrocenium triiodide dispersed in poly(methyl methacrylate) are shown in Fig. 9 and in Table 3, respectively. Two doublets are found in the Mössbauer spectra for the dispersed state in the temperature range of 78—302 K, whereas an averaged-valence state is observed above ca. 210 K in the crystalline state.

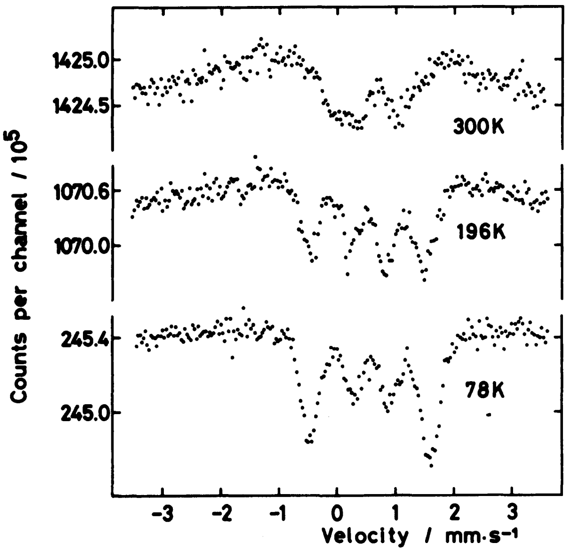

Fig. 8. Mössbauer spectra of 1′,1‴-dibutylbiferrocenium triiodide dispersed in poly(methyl methacrylate) from 78 K to room temperature. See footnote b) in Table 3.

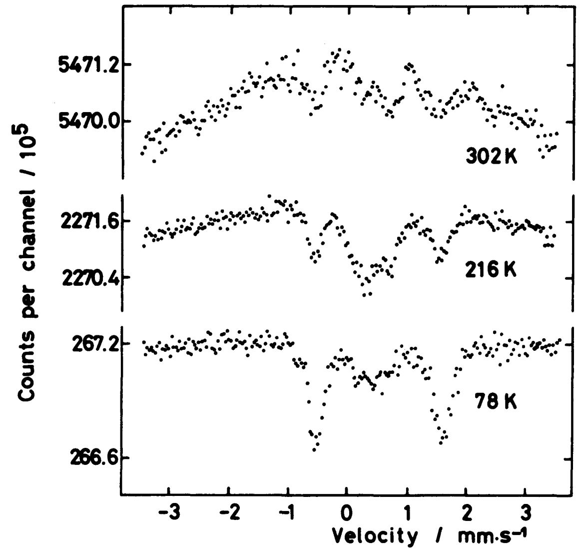

Fig. 9. Mössbauer spectra of 1′,1‴-dibutylbiferrocenium triiodide dispersed in poly(methyl methacrylate) from 78 K to room temperature.

Table 3. Mössbauer Parameters for 1′,1‴-Dibutyl- and 1′,1‴-Diisobutylbiferrocenium Triiodide Dispersed in Poly(methyl methacrylate)

Compound	Temperature K	δ[a)] mm s^{-1}	ΔE_q mm s^{-1}
1′,1‴-Dibutylbiferrocenium triiodide dispersed in poly(methyl methacrylate)[b)]	300	0.49	1.04
	196	0.50	1.94
		0.51	0.61
	78	0.54	2.06
		0.55	0.60
1′,1‴-Diisobutylbiferrocenium triiodide dispersed in poly(methyl methacrylate)	302	0.47	2.08
		0.44	0.45
	216	0.50	2.13
		0.43	0.41
	78	0.53	2.15
		0.44	0.36

a) Isomer-shift data are reported with respect to metallic iron foil. b) The mixture of the crystals A and B was used for the Mössbauer spectroscopic measurement in the dispersed system, because the observed ESR parameters were close to each other in the crystals A and B dispersed in poly(methyl methacrylate).

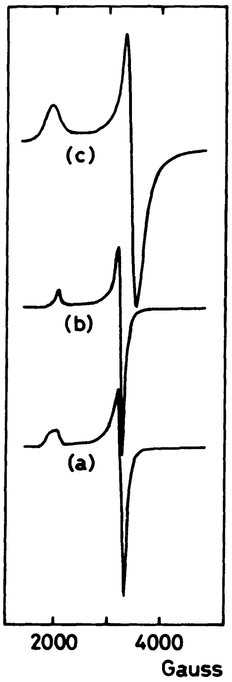

Fig. 10. ESR spectra for (a) crystals A, (b) crystals B, and (c) dispersed state of 1′,1‴-dibutylbiferrocenium triiodide at 78 K.

The difference in the valence state between the dispersed and the crystalline state is also reflected on the quadrupole splittings, ΔE_q, of the 1′,1‴-dibutyl and 1′,1‴-diisobutyl derivatives. For example, the values of ΔE_q for the outer and inner doublet for 1′,1‴-diisobutylbiferrocenium triiodide in the dispersed state are a little larger and smaller than those crystalline state, respectively. This suggests that the interaction between Fe(II) and Fe(III) atoms in dispersed state is a little weaker than that in crystalline state in 1′,1‴-diisobutylbiferrocenium triiodide even at 78 K and that the trapped-valence state remains at higher temperatures in the dispersed state. The same relationship between the valence state and the ΔE_q value is also observed in the dispersed and crystalline (A and B) states in the dibutyl derivative. The results of the valence state reflected on the quadrupole splittings in the dispersed and the crystalline state also indicate that the interaction between the triiodide anions and the biferrocenium monocations plays an important role in the intramolecular electron exchange between the two iron atoms.

ESR Spectra. It has been known that *g*-tensor anisotropy has a close connection with the mixed-valence states of biferrocene derivatives observed by the method of Mössbauer spectroscopy.[16)] Figure 10 shows the ESR spectra of 1′,1‴-dibutylbiferrocenium triiodide (crystals A, crystals B, and a dispersed sample) at 78 K. The $g_{\parallel}$ and $g_{\perp}$ values were found in crystals B to be 3.00 and 1.91, respectively. These *g*-values are in a good agreement with those previously reported ($g_{\parallel}$=2.98 and $g_{\perp}$=1.92 at 4.2 K);[11)] they were obtained by diffusing hexane into a CH_2Cl_2 solution of the triiodide salt. As mentioned above, the Mössbauer spectra of the present crystals B and the crystals obtained by the diffusion method satisfactorily coincide with each other from 78 K to room temperature. These two kinds of crystals obtained by the different methods are considered to have the same crystal structure. The spectral features of the ESR for crystals A are different from those for crystals B. The difference is remarkable in the signal corresponding to $g_{\parallel}$ component; i.e., the sharp signal ($g_{\parallel}$=3.00) was observed for crystals B, while the signal corresponding to $g_{\parallel}$ was observed as a superposition of two kinds of $g_{\parallel}$ values ($g_{\parallel}$=3.04 and 3.26) in crystals A. These differences in the ESR spectra between crystals A and B are in accordance with the results of the Mössbauer spectra.

An intermediate $g_{\parallel}$ value (3.17) in the crystals (3.26 and 3.04) is observed for butyl derivative dispersed in poly(methyl methacrylate).

The ESR parameters of the other dialkylbiferrocenium derivatives in crystalline and dispersed states at 78 K are also shown in Fig. 11 and in Table 4. ESR parameters for 1′,1‴-diethylbiferrocenium triiodide observed in the present experiment ($g_{\parallel}$=3.13 and $g_{\perp}$=2.00 and 1.88) are consistent with those previously reported ($g_{\parallel}$=3.02 and $g_{\perp}$=2.01 and 1.89 at 3.3 K).[11)] As discussed above, the Mössbauer spectra of 1′,1‴-diethyl-, 1′,1‴-dipropyl-, 1′,1‴dibutyl-(crystals B), and 1′,1‴-diisobutylbiferrocenium triiodide show an av-

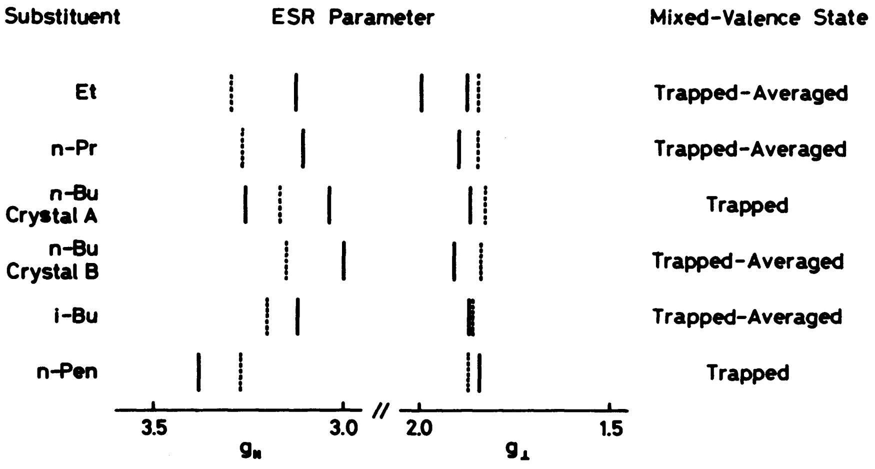

Fig. 11. Summary of ESR parameters in crystalline state (——) and dispersed state (------) at 78 K with those mixed-valence states in crystalline state for 1′,1‴-dialkylbiferrocenium triiodides. "Trapped-Averaged" shows a trapped-valence state at low temperatures and an averaged-valence state near room temperature. "Trapped" shows only the trapped-valence state from low temperature to room temperature.

Table 4. ESR Parameters for 1′,1‴-Dialkylbiferrocenium Triiodide at 78 K

Substituent	State	$g_\parallel$	$g_\perp$	Δg[a]
Ethyl-	Crystalline	3.13	2.00	1.19
			1.88	
	Glassy	3.30	1.85	1.45
Propyl-	Crystalline	3.11	1.90	1.21
	Glassy	3.27	1.85	1.42
Butyl-	Crystalline	3.26	1.87	1.39
(Crystals A)		3.04		1.17
	Glassy[b]	3.17	1.83	1.34
Butyl-	Crystalline	3.00	1.91	1.09
(Crystals B)	Glassy[c]	3.15	1.84	1.31
Isobutyl-	Crystalline	3.12	1.87	1.25
	Glassy	3.20	1.86	1.34
Pentyl-	Crystalline	3.38	1.84	1.54
	Glassy	3.27	1.87	1.40

a) This is the g-tensor anisotropy defined as $\Delta g = g_\parallel - g_\perp$. When a rhombic signal is seen, an average of two $g_\perp$ values is used for $g_\perp$. b) Crystals A were dispersed in poly(methyl methacrylate). c) Crystals B were dispersed in poly(methyl methacrylate).

eraged-valence state near room temperature; they change into those for a trapped-valence state with decreasing temperature while only trapped-valence states are observed for 1′,1‴-dibutyl- (crystals A) and 1′,1‴-dipentylbiferrocenium triiodide from 78 K to room temperature. For the above two groups (classified based on the difference of the temperature dependence of the valence states), the Δg value for each group shows a characteristic feature; i.e., the Δg values (Δg=1.09—1.25) for the former group, whose valence state changes from 78 K to room temperature, are smaller than those (Δg=1.39—1.54) for the latter group, whose valence state shows only a trapped-valence state.

As mentioned in the Introduction, 1′,1‴-dibenzyl-, 1′,1‴-bis(*o*-methylbenzyl)- and 1′,1‴-bis(*p*-methylbenzyl)biferrocenium triiodide show temperature-dependences of the mixed-valence state similar to those observed in 1′,1‴-dipropylbiferrocenium triiodide. On the other hand, 1′,1‴-bis(*m*-methylbenzyl)biferrocenium triiodide shows a trapped-valence state from low temperature to room temperature.

Figure 12 and Table 5 summarize the results of ESR spectra for the compounds in crystalline and dispersed states. ESR parameters for 1′,1‴-dibenzylbiferrocenium triiodide observed in the present experiment ($g_\parallel$=3.33 and $g_\perp$=1.81) are consistent with those previously reported ($g_\parallel$=3.42 and $_\perp$=1.80 at 4.2 K).[11] In 1′,1‴-bis(methylbenzyl)biferrocenium triiodides, the Δg values also show a characteristic feature; i.e., Δg=1.33—1.52 for the samples whose valence state changes from 78 K to room temperature. The Δg values are much smaller than the value (Δg=2.13) for the sample which shows only a trapped-valence state.

These results indicate that the decrease in the Δg values has a relationship with the nature of the electron exchange between the bivalent and tervalent iron atoms in the biferrocenium derivatives. This consideration is reasonable for explaining the appreciably small Δg values of the 1′,1‴-diiodo- and 1′,1‴-dibromobiferrocenium triiodide whose Mössbauer spectra show an averaged-valence state (only one

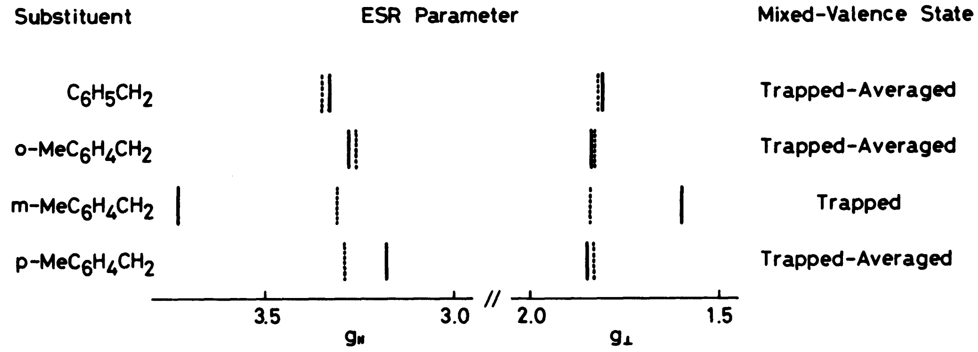

Fig. 12 Summary of ESR parameters in crystalline state (——) and dispersed state (------) at 78 K with those mixed-valence states in crystalline state for 1′,1‴-bis(methylbenzyl)biferrocenium triiodides. "Trapped-Averaged" shows a trapped-valence state at low temperatures and an averaged-valence state near room temperature. "Trapped" shows only the trapped-valence state from low temperature to room temperature.

Table 5. ESR Parameters for 1′,1‴-Bis(methylbenzyl)-biferrocenium Triiodide at 78 K

Substituent	State	$g_{\parallel}$	$g_{\perp}$	Δg[a]
Benzyl-	Crystalline	3.33	1.81	1.52
	Glassy	3.35	1.82	1.53
o-Methylbenzyl-	Crystalline	3.28	1.84	1.44
	Glassy	3.26	1.83	1.43
m-Methylbenzyl-	Crystalline	3.73	1.60	2.13
	Glassy	3.31	1.84	1.47
p-Methylbenzyl-	Crystalline	3.18	1.85	1.33
	Glassy	3.29	1.83	1.46

a) This is the *g*-tensor anisotropy defined as $\Delta g = g_{\parallel} - g_{\perp}$.

doublet), even at 4.2 K.[11]

The difference of the ESR parameters ($g_{\parallel}$, $g_{\perp}$, and Δg) among the various kinds of 1′,1‴-dialkyl and 1′,1‴-bis(methylbenzyl) derivatives in their crystalline state is reduced in the dispersed state. These differences in the ESR parameters between the crystalline and dispersed state also correspond to the differences in the valence state between both the states observed in the Mössbauer spectra for the derivatives (see the previous section). The difference in ESR parameters in crystalline samples should be attributed not only to intramolecular effects of the alkyl or methylbenzyl substituent but also to intermolecular effects. The results obtained in the present studies indicate that the packing effect of the biferrocenium cations and their counter anions influences the electronic structures and the intramolecular electron transfer rates between the two iron atoms.

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