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Mössbauer Spectroscopic Study on the Mixed-Valence States of 1′,1‴-Dimethyl-, 1′,1‴-Dipentyl-, 1′,1‴-Dihexyl-, and 1′,1‴-Didecylbiferrocenium Triiodide

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Synopsis. 1′,1‴-Dimethyl-, 1′,1‴-dipentyl-, 1′,1‴-dihexyl-, and 1′,1‴-didecylbiferrocene were synthesized and Mössbauer spectroscopic measurements of their monocation salts were carried out at various temperatures in order to know the mixed-valence states. Effects of alkyl substituent on the valence states of iron atoms in the monocation salts of 1′,1‴-dialkylbiferrocenes are discussed.

Biferrocene derivatives are easily monooxidized to give the corresponding monocation salts, in which iron atoms are in a mixed-valence state. The electronic interaction and the electron-transfer process between the two metal sites in different oxidation states have been extensively investigated by means of Mössbauer spectroscopy. These compounds can be classified into two types of valence states of the iron atoms, a trapped-valence type and an averaged-valence type, by means of Mössbauer spectroscopy.[1)] The former type has different states of iron atoms corresponding to ferrocene-like bivalent and ferricenium-like tervalent iron atoms, while the latter has an equivalent state of iron atom averaged over ferrocene-like bivalent and ferricenium-like tervalent iron atoms.

Iijima et al. first observed an interesting temperature-dependence of the mixed-valence state in 1′,1‴-diethyl- and 1′,1‴-dipropylbiferrocenium triiodide, which are of an averaged-valence type above ca. 200 K but of a trapped-valence type below ca. 200 K.[2)] Similar temperature-dependences were also observed later in one crystal form of 1′,1‴-dibutylbiferrocenium triiodide[3)] and in biferrocenium triiodide.[3,4)]

In the present paper, the triiodide salts of other 1′,1‴-dialkylbiferrocene monocations shown in Fig. 1, such as 1′,1‴-dimethyl- (**1**), 1′,1‴-dipentyl- (**2**), 1′,1‴-dihexyl- (**3**), and 1′,1‴-didecylbiferrocene monocation (**4**), were synthesized and investigated by means of Mössbauer spectroscopy in order to clarify the effect of 1′,1‴-dialkyl substitution on the valence states of iron atoms.

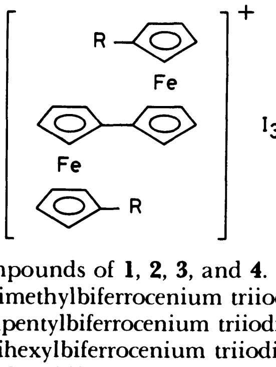

Fig. 1. Compounds of **1**, **2**, **3**, and **4**.
(**1**) 1′,1‴-Dimethylbiferrocenium triiodide (R=CH_3),
(**2**) 1′,1‴-Dipentylbiferrocenium triiodide (R=C_5H_{11}),
(**3**) 1′,1‴-Dihexylbiferrocenium triiodide (R=C_6H_{13}),
(**4**) 1′,1‴-Didecylbiferrocenium triiodide (R=$C_{10}H_{21}$).

Experimental

Materials. 1′,1‴-Dialkylbiferrocenes were prepared by the Ullmann coupling at 110—120 °C for 18 h of 1′-alkyl-1-bromoferrocenes. The triiodide salts were prepared by partial oxidation of the corresponding dialkylbiferrocenes in benzene with a stoichiometric amount of I_2. All the analytical data of the triiodide salts obtained in the present experiment are shown below. Found: C, 30.99; H, 2.71%. Calcd for $C_{22}H_{22}Fe_2I_3$: C, 33.93; H, 2.85%. Found: C, 40.56; H, 4.99%. Calcd for $C_{30}H_{38}Fe_2I_3$: C, 40.44; H, 4.30%. Found: C, 41.84; H, 4.64%. Calcd for $C_{32}H_{42}Fe_2I_3$: C, 41.82; H, 4.61%. Found: C, 47.46; H, 5.83%. Calcd for $C_{40}H_{58}Fe_2I_3$: C, 46.59; H, 5.67%.

Mössbauer Spectroscopic Measurements. A $^{57}Co(Pt)$ source moving in a constant-acceleration mode was used for Mössbauer spectroscopic measurements. The Mössbauer spectra were obtained by using an ELSCINT Mössbauer spectrometer with a proportional counter. The isomer shifts were referred to metallic iron foil. The Mössbauer parameters (isomer shift, *I. S.*, and quadrupole splitting, *Q. S.*) were obtained by least-squares fitting to Lorentzian peaks.

Results and Discussion

The Mössbauer parameters are summarized in Table 1, while typical spectra are shown in Fig. 2. The spectra of 1′,1‴-dimethylbiferrocenium triiodide (**1**) at 78 and 298 K consist of an inner- and an outer-doublet with nearly 1 : 1 ratio in areal intensity, which are

Table 1. Mössbauer Parameters

Compound	Temperature/K	*I. S.*[a)]/ mm s^{-1}	*Q. S.*/ mm s^{-1}
1	298	0.43	1.74
		0.43	0.56
	78	0.49	1.82
		0.47	0.51
2	298	0.45	1.88
		0.44	0.54
	78	0.50	1.94
		0.49	0.55
3	298	0.45	1.80
		0.41	0.64
	78	0.47	1.91
		0.50	0.63
4	253	0.46	1.94
		0.46	0.48
	78	0.52	2.03
		0.52	0.49

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

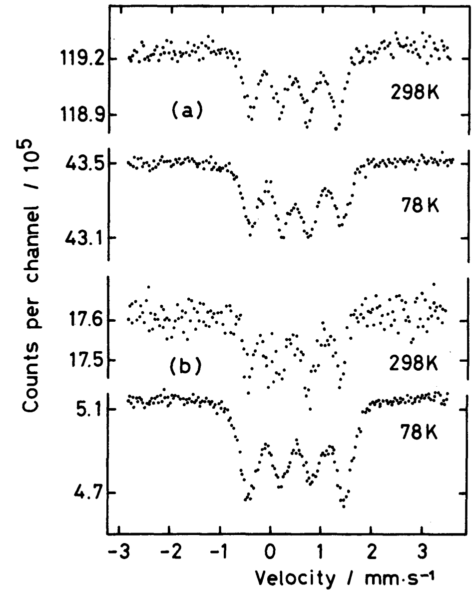

Fig. 2. Typical Mössbauer spectra of (a) 1′,1‴-dimethyl- and (b) 1′,1‴-dihexylbiferrocenium triiodide at 78 and 298 K.

ascribable to ferricenium-like tervalent and ferrocene-like bivalent states, respectively. Compound **1** is of trapped-valence type and temperature-independent. Table 1 shows that 1′,1‴-dipentyl- (**2**), 1′,1‴-dihexyl- (**3**), and 1′,1‴-didecylbiferrocenium triiodide (**4**) are classified into a trapped-valence type and are temperature-independent as well as **1**. The measurements of Mössbauer spectra of compound **4** were unsuccesful at room temperature because of its decreased recoil-free fraction.

The values of *Q. S.* of ferrocene-like bivalent iron atoms in these compounds are smaller than those of biferrocenium picrate (2.141 mm s^{-1} at 78 K and 2.053 mm s^{-1} at 298 K)[5] and biferrocenium triiodide (2.119 mm s^{-1} at 4.2 K and 2.013 mm s^{-1} at 300 K).[6] On the other hand, the values of *Q. S.* of ferricenium-like tervalent for these compounds are larger than those of biferrocenium picrate (0.288 mm s^{-1} at 78 K and 0.302 mm s^{-1} at 298 K)[5] and biferrocenium triiodide (0.381 mm s^{-1} at 4.2 K and 0.400 mm s^{-1} at 300 K).[6] Similar trends have been observed in 1′,1‴-diethyl-, 1′,1‴-dipropyl-, and 1′,1‴-dibutylbiferrocenium triiodide at low temperatures, although this effect seems to decrease in the case of 1′,1‴-didecylbiferrocenium triiodide.

As mentioned in the introduction, the Mössbauer spectra of 1′,1‴-diethyl- and 1′,1‴-dipropylbiferrocenium triiodide, and one crystal form of 1′,1‴-dibutylbiferrocenium triiodide show a remarkable temperature-dependence; i. e., iron atoms are in a trapped-valence state at low temperatures and in an averaged-valence state near room temperature. On the other hand, all the spectra obtained in the present study show the trapped-valence type from 78 K to room temperature. Although the Mössbauer parameters observed for the monocation salts in the present study at 78 K resemble those of 1′,1‴-diethyl-, 1′,1‴-dipropyl-, and 1′,1‴-dibutylbiferrocenium triiodide at 78 K, the temperature-dependences are not observed.

It was suggested that the environment surrounding each cation in a number of mixed-valence compounds in the solid state determines whether or not an intramolecular electron transfer occurs.[3,7] One of the most important factors controlling intramolecular electron transfer can be a symmetric structure of each binuclear mixed-valence cation experiencing weak or moderate electronic coupling between the two metal ions, associated with the positions of each anion. In the case of longer chain alkyl substituents, the possibility to have a center of symmetry for the dialkylbiferrocenium cation will also be reduced because of the increased possibility of having various kinds of conformational arrangements in the substituent.

The results suggest that the length of the chain of the alkyl substituent has an important effect on the mixed-valence states of 1′,1‴-dialkylbiferrocenium triiodides, probably because the alkyl substituents are too long or too short. The terminal atoms of the I_3^- anion will then be situated closer to one of the iron atoms of a given cation, even near room temperature. Detailed crystallographical studies of some of dialkylbiferrocenium triiodides are now being studied.

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