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Dependence of the Mixed-Valence States on Crystal Form in 1',1'''-Ditetradecylbiferrocenium Triiodide

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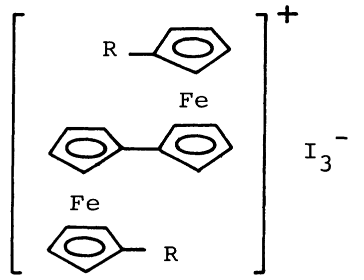
Remarkable dependence of the mixed-valence states on crystal form was observed in 1',1'''-ditetradecylbiferrocenium triiodide. One crystal form showed a temperature-independent trapped-valence state, while the other was found to be a temperature-dependent valence state in which a trapped-valence state at lower temperatures and an averaged-valence state at higher temperatures are observed.

It has been pointed out that mixed-valence states of binuclear ferrocene derivatives are affected by intermolecular interactions between cation and cation and/or between cation and anion.1-3) We have reported the results of 1',1'''-dibutylbiferrocenium triiodide as a peculiar case, in which two kinds of crystals are prepared, one showing a temperature-independent trapped-valence state and the other a temperature-dependent mixed-valence state.3) It is known that the derivatives having a long alkyl substituent are easy to construct a layer structure. Recent study on mixed-valence trinuclear iron stearate having a longer alkyl chain, which shows a layer structure, has revealed that the valence delocalization is not always associated with the motion of solvate molecule.4) The results suggest that an introduction of long alkyl substituent to biferrocene is expected to construct a layer structure, providing a new series of binuclear ferrocene derivatives to investigate the correlation between the mixed-valence states and their crystal structures. In the present study, the dependence of the mixed-valence states is described in connection with the crystal forms of 1',1'''-ditetradecylbiferrocenium triiodide.



1',1'''-Ditetradecylbiferrocenium triiodide ($R=C_{14}H_{29}$)

1',1'''-Ditetradecylbiferrocene was prepared according to the procedure used for synthesizing 1',1'''-dialkylbiferrocenes.5) Mp 66 °C. ^1H NMR($CDCl_3$) δ : 0.88(6H, t), 1.26(48H, s), 2.08(4H, t), 3.83(4H, t), 3.86(4H, t), 4.11(4H, t), and 4.23(4H, t). Found: C, 74.91; H, 9.75%. Calcd for 1',1'''-ditetradecylbiferrocene, $Fe_2C_{48}H_{74}$: C, 75.58; H, 9.78%. The triiodide salt was prepared by partial oxidation in n-hexane with a stoichiometric amount of I_2. Precipitates were filtered and collected as sample 1. Sample 1 was recrystallized from CH_2Cl_2

and collected as sample 2. Found for sample 1: C, 50.06; H, 6.65%. Found for sample 2: C, 50.41; H, 6.77%. Calcd for 1',1'''-ditetradecylbiferrocenium triiodide, $Fe_2C_{48}H_{74}I_3$: C, 50.42; H, 6.52%. A $^{57}Co(Rh)$ source moving in a constant acceleration mode was used for Mössbauer spectroscopic measurements. Mössbauer spectra were obtained by using an Austin Science Associates Mössbauer spectrometer and a proportional counter. The isomer shift (I.S.) values were referred to metallic iron foil. The Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. X-ray powder patterns were determined by using Cu Kα radiation at room temperature.

X-Ray powder patterns of samples 1 and 2 are shown in Fig. 1. The most remarkable feature of them is that the marked reflections appear with an equal interval in the small angle region, showing a layer structure. The inter-layer lengths are estimated to be 18.8 Å in sample 1 and 16.0 Å in sample 2. Other reflections are relatively similar to each other. The line shapes for sample 2, however, are sharper than those for sample 1. Similar patterns are observed in 1',1'''-dihexadecyl-and1',1'''-dioctadecylbiferrocenium triiodide.

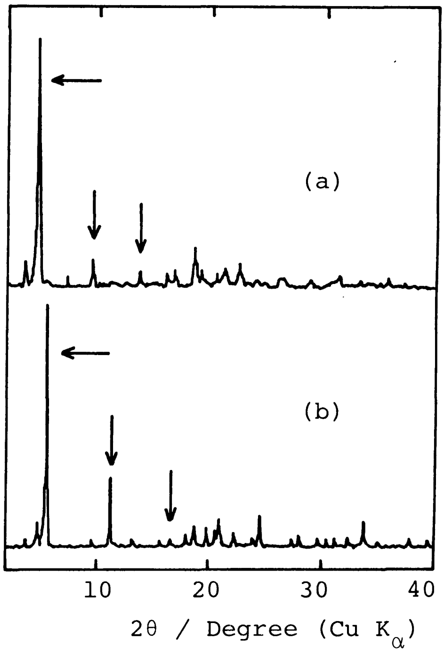


Fig. 1. X-Ray powder patterns for (a) sample 1 and (b) sample 2.

Table 1. Mössbauer parameters for 1',1'''-ditetradecylbiferrocenium triiodide

Sample	Temperature/K	I.S.$^{a)}$/mm·s^{-1}	Q.S./mm·s^{-1}	ln(A/A_{80})$^{b)}$
Sample 1	204	0.48	1.97	-0.94
		0.46	0.58	
	80	0.52	2.01	0.00
		0.51	0.54	
Sample 2	204	0.50	1.17	-0.84
	199	0.50	1.42	-0.83
		0.50	0.94	
	194	0.49	1.53	-0.77
		0.50	0.86	
	175	0.50	1.71	-0.61
		0.50	0.74	
	155	0.49	1.80	-0.42
		0.50	0.69	
	107	0.50	1.89	-0.18
		0.50	0.63	
	80	0.51	1.90	0.00
		0.51	0.62	

a) Isomer-shift data are reported with respect to metallic iron foil.
b) The total areal intensity (A) is normalized with respect to the value at 80 K (A_{80}).

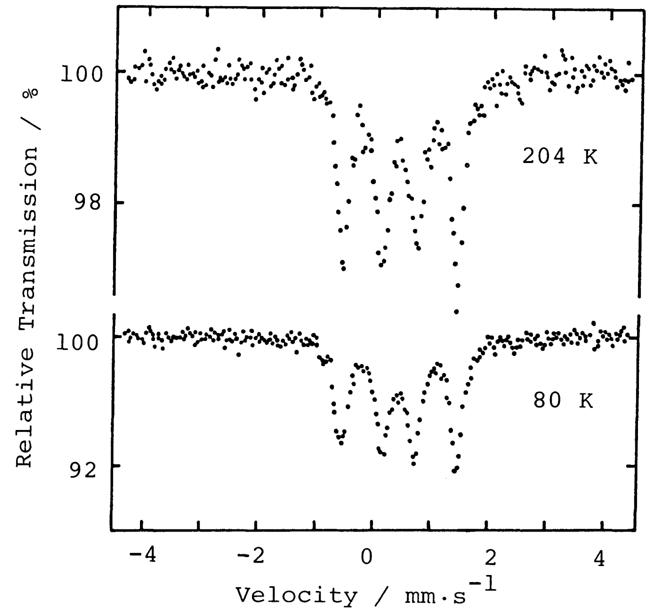


Fig. 2. Mössbauer spectra of sample 1.

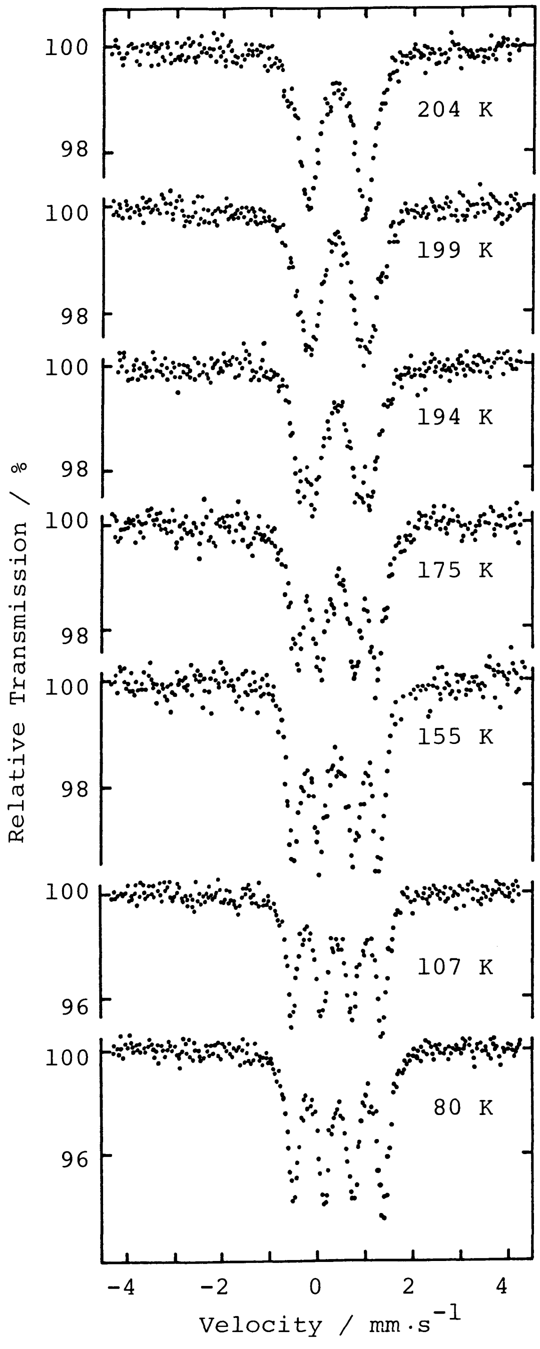


Fig. 3. Mössbauer spectra of sample 2.

Shortening of the inter-layer length by recrystallization from CH_2Cl_2 is also observed in 1',1'''-dihexadecyl derivative (20.2 Å→17.2 Å), while the difference in 1',1'''-dioctadecyl derivative is not observed (21.1 Å→20.9 Å). Lengthening alkyl chain tends to increase inter-layer length, which also confirms that 1',1'''-ditetradecylbiferrocenium triiodide has a layer structure.

Mössbauer spectra of sample 1 and sample 2 are shown in Figs. 2 and 3, respectively. The Mössbauer parameters are summarized in Table 1. Mössbauer spectra were not successfully determined at room temperature because of their decreased recoil-free fraction. The spectra of sample 1 both at 80 and 204 K show a typical trapped-valence state, in which two doublets corresponding to ferrocene-like bivalent and ferrocenium-like tervalent irons are observed. On the other hand, the temperature dependence of the mixed-valence states is clearly seen in sample 2. The two doublets observed at 80 K approach to each other with an increase of temperature to converge into one doublet which is ascribed to an averaged-valence state. The valence averaging temperature is lower than those of other 1',1'''-dialkylbiferrocenium triiodides, such as diethyl-,[6] dipropyl-,[6] and dibutylbiferrocenium triiodide.[3] The averaging process does not seem to be the coexisting type in which the trapped-valence state and the averaged-valence state coexist and the ratio of the latter increases with an increase of temperature. As mentioned in the introduction, it has been pointed out that the mixed-valence states are differently dependent on the crystal form of the same compound.[3] The results obtained in the present study also prove the fact that the crystal structure affects the mixed-valence states and show that the valence delocalization is closely connected with the inter-layer length.

According to the Debye approximation at high temperature, the logarithmic value of recoil-free fraction of Mössbauer spectrum of samples 1 and 2 is expected to decrease linearly with increasing temperatures.[7] The temperature dependence of recoil free fraction used for the estimation of force constant, i. e., intermolecular interaction is expected to be greater when the dependence is smaller. It can be seen from Table 1 that the temperature dependence is larger in sample 1 than that of sample 2, suggesting that the crystal structure for the former is less packed than the latter. Taking into account of the results of X-ray powder patterns, it is suggested that the intermolecular interaction is weaker in the case of larger inter-molecular separation. The present results suggest that an adequate intermolecular interaction in sample 2 affects the delocalization of mixed-valence states, although the intermolecular interaction has been tentatively assumed to be isotropic.

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