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Temperature Dependence of the Mixed-Valence States in 1',1'''-Bis(o-methylbenzyl)biferrocenium$^+$ TCNE$^-$

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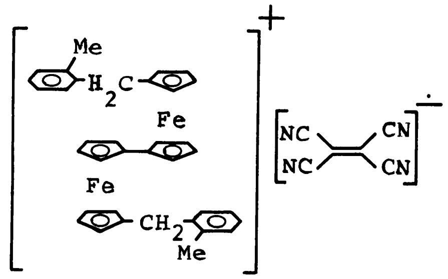
1',1'''-Bis(o-methylbenzyl)biferrocenium$^+$ TCNE$^-$ was synthesized and its mixed-valence state was studied by means of ESR and Mössbauer spectroscopy. It was found from Mössbauer spectra that the trapped- and the averaged-valence states coexist at higher temperatures and the relative areal intensity of the averaged-valence state increases with an increasing temperature. An abrupt increase of the relative areal intensity above 180 K suggests that an intermolecular effect on the mixed-valence state changes at the temperature.



1',1'''-Bis(o-methylbenzyl)-biferrocenium$^+$ TCNE$^-$

Recent studies on the mixed-valence states of binuclear ferrocene derivatives have pointed out that the intermolecular interactions between cation-cation and/or cation-anion play an important role to the mixed-valence states and the valence delocalization.[1-12] For example, the I_2Br^-, IBr_2^-, I_3^-, $CuBr_2^-$, and $FeCl_4^-$ salts of mixed-valence biferrocene derivatives show different valence states, which were attributed to the different interactions between cations and anions.[4-6] It is expected that the way of the packing of cations and anions will be affected by the introduction of aromatic planar species, such as tetracyanoethylene (TCNE), instead of linear trihalide anions. In the present study, an interesting temperature dependence of the mixed-valence state in 1',1'''-bis(o-methylbenzyl)biferrocenium$^+$ TCNE$^-$ is described.

1',1'''-Bis(o-methylbenzyl)biferrocene was prepared according to the procedure reported before.[10] The TCNE salt was obtained by refluxing 1',1'''-bis(o-methylbenzyl)biferrocene with TCNE in acetonitrile for several hours under nitrogen. It was found from the elemental analysis that the product consists of the parent component and TCNE in the molar ratio of 1:1. Found: C, 70.38; H, 4.94; N: 6.30%. Calcd for 1',1'''-bis(o-methylbenzyl)biferrocenium$^+$ TCNE$^-$, $Fe_2C_{42}H_{34}N_4$: C, 71.41; H, 4.85; N, 7.93%. 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 (for the measurements from 78 K to room temperature) and an Austin Science Associates Mössbauer spectrometer (for 4.2 K) 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. An X-band ESR spectrum for a powdered sample was measured at 78 K using a JEOL JES-PE-3X ESR spectrometer.

The Mössbauer parameters, values of I.S., quadrupole splitting (Q.S.), and areal ratios, are summarized in Table 1 and the typical spectra are shown in Fig. 1. Temperature dependence of the mixed-valence states can be seen clearly in Fig. 1. The spectrum at 4.2 K shows a typical trapped-valence state, in which two doublets are observed corresponding to ferrocene-like bivalent and ferrocenium-like tervalent irons. In the spectrum at 78 K, a small amount of new doublet appears in addition to the component of typical trapped-valence state. The Mössbauer parameters (I.S. = 0.59 mm s^{-1} and Q.S. = 1.25 mm s^{-1}) indicate that the new doublet is ascribed to iron atoms in an averaged-valence state, which corresponds to a state averaged over ferrocene-like and ferrocenium-like irons. The areal intensity of the doublet assigned to the averaged-valence state irons relative to the intensity of the total spectral area increases with an increasing temperature. This observation is quite in contrast to the case of its triiodide salt, in which either a trapped-valence state is observed at lower temperatures or an averaged-valence state at higher temperatures but there is no coexistence of both the valence states at any intermediate temperatures.

Table 1. Mössbauer parameters for 1',1'''-bis(o-methylbenzyl)-biferrocenium$^+$ $TCNE^-$

Temperature/K	I.S.[a]/mm s^{-1}	Q.S./mm s^{-1}	$A_{averaged}/A_{total}$
300	0.43	1.15	0.60
	0.40	1.79	
	0.43	0.65	
271	0.47	1.09	0.47
	0.46	1.66	
	0.45	0.61	
240	0.49	1.12	0.41
	0.46	1.68	
	0.46	0.65	
219	0.49	1.13	0.37
	0.48	1.73	
	0.48	0.62	
199	0.53	1.14	0.29
	0.50	1.70	
	0.50	0.62	
180	0.53	1.18	0.21
	0.49	1.77	
	0.50	0.65	
130	0.55	1.17	0.18
	0.53	1.81	
	0.53	0.62	
78	0.59	1.25	0.14
	0.54	1.92	
	0.55	0.55	
4.2	0.53	1.89	0.00
	0.53	0.51	

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

An ESR spectrum of the powdered sample at 78 K is shown in Fig. 2. Although the powder pattern signal for ferrocenium-type ions is observed, no signal for TCNE anion radicals is observed leaving a possibility of antiferromagnetic interaction between the two TCNE anion radicals. It has been suggested that the anisotropy of the g-value of ESR spectra, Δg, has a close connection with the mixed-valence states observed in the Mössbauer spectra of mixed-valence biferrocene derivatives.[3,13] The ESR parameters obtained in the present study are $g_{\parallel}=3.25$, $g_{\perp}=1.94$, and $\Delta g=1.31$. The values are almost the same as the values for 1',1'''-bis(o-methylbenzyl)biferrocenium$^+$ I_3^- ($g_{\parallel}= 3.28$, $g_{\perp}= 1.84$, and $\Delta g= 1.44$) and 1',1'''-bis(p-methylbenzyl)biferrocenium$^+$ I_3^- ($g_{\parallel}= 3.18$, $g_{\perp}= 1.85$, and $\Delta g= 1.33$)[3] and suggest that iron atoms are in a temperature-dependent mixed-valence state.[10]

The temperature dependence of the ratio of areal intensity of the averaged-valence state against the total areal intensity and that of the logarithmic value of the total areal intensity are shown in Figs. 3 and 4, respectively. It is found in Fig. 3 that the valence delocalization starts lower than 78 K completing at a temperature higher than 300 K. However, the dependence of the areal intensity ratio of the averaged-valence state to the total areal intensity seems to become suddenly steeper above 180 K. According to the Debye approximation at high temperatures, the logarithmic values of recoil-free fraction and therefore of total areal intensity of Mössbauer spectrum of their absorber are expected to decrease linearly with increasing temperatures.[14] It is also seen in Fig. 4 that the dependence of the logarithmic value of total areal intensity is decomposed into two straight lines crossing near 180 K, which suggests that the valence delocalization of the TCNE salt is closely related to a phase transition phenomena. DSC measurements, however, did not show any sharp peak near 180 K. The results suggest that the cooperative intermolecular interactions related to a kind of higher-order phase transition in the temperarure region of valence delocalization play an important

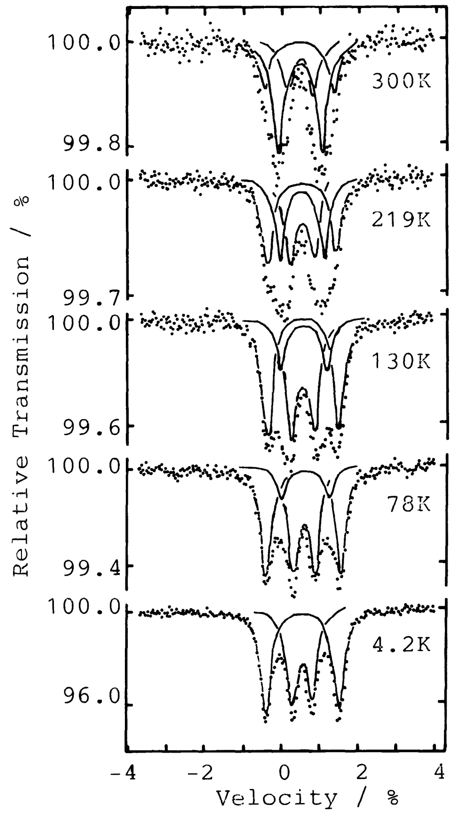


Fig. 1. Mössbauer spectra of 1',1'''-bis(o-methylbenzyl)-biferrocenium$^+$ TCNE$^-$.

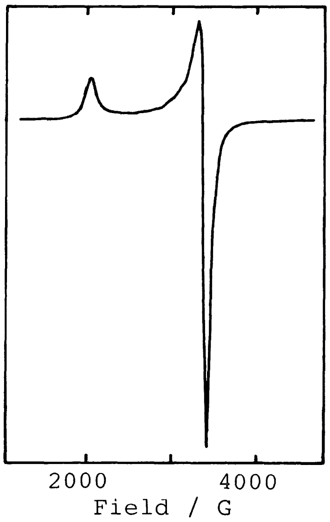


Fig. 2. An ESR spectrum for 1',1'''-bis(o-methylbenzyl)-biferrocenium$^+$ TCNE$^-$ at 78 K.

role in the valence delocalization for the present compound.

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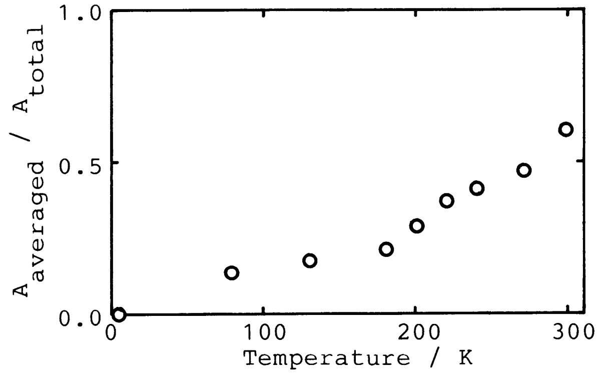

Fig. 3. Temperature dependence of the relative areal intensity of the averaged-valence state in 1',1'''-bis(o-methylbenzyl)biferrocenium$^+$ TCNE$^-$.

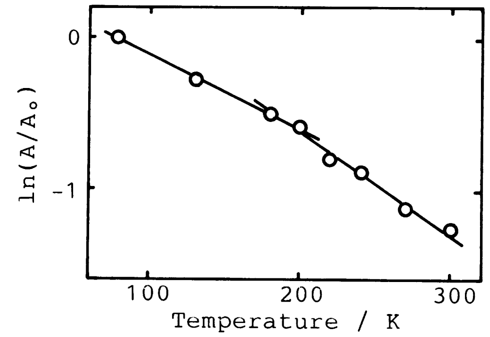

Fig. 4. Temperature dependence of the total areal intensity(A) in the Mössbauer spectra for 1',1'''-bis(o-methylbenzyl)-biferrocenium$^+$ TCNE$^-$. (A) is normalized with respect to the value at 78 K(A_0).

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