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Mixed-Valence States in TCNQ Salts of 1′,1‴-Dibutyl-, 1′,1‴-Dipentylbiferrocene and Their Mixed Crystals

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Synopsis. Mixed-valence states in TCNQ salts of 1′,1‴-dibutyl-, 1′,1‴-dipentylbiferrocene and their mixed crystals were investigated by Mössbauer spectroscopy. It was found that a valence delocalization of the mixed crystals was affected by the host lattice.

It is known that mixed-valence states of biferrocene derivatives are affected by counter anions,[1,2] and that intermolecular interactions play an important role in the mixed-valence states. It is also known that introduction of aromatic planar molecules as counter anions provides an interesting series of mixed-valence biferrocene derivatives.[3,4] In the present study, mixed-valence states in 7,7,8,8-tetracyanoquinodimethane (TCNQ) salts of 1′,1‴-dibutyl-, 1′,1‴-dipentylbiferrocene and their mixed crystals were inverstigated by means of Mössbauer spectroscopy.

Experimental

Materials. 1′,1‴-Dibutyl-,[5] 1′,1‴-dipentylbiferrocene,[6] and their TCNQ salts[3] were prepared according to the method previously reported. It was found from elemental analysis that the TCNQ salts consist of binuclear ferrocene and TCNQ in a molar ratio of 1:3. Found: C, 70.13; H, 4.25; N, 14.92%. Calcd for 1′,1‴-dibutylbiferrocenium$^+$(TCNQ)$_3^-$, $\mathrm{Fe_2C_{64}H_{46}N_{12}}$: C, 70.21; H, 4.24; N, 15.35%. Found: C, 70.71; H, 4.69; N, 14.95%. Calcd for 1′,1‴-dipentylbiferrocenium$^+$(TCNQ)$_3^-$, $\mathrm{Fe_2C_{66}H_{50}N_{12}}$: C, 70.60; H, 4.49; N, 14.97%. Mixed crystals were obtained by the following method. A mixture of 1′,1‴-dipentylbiferrocene (40.1 mg, 7.86×10^{-5} mol), and TCNQ (98.6 mg. 4.83×10^{-4} mol) was refluxed for 5 hours in 50 ml of acetonitrile under nitrogen and kept in a freezer for one night. Precipitates were filtered and collected as mixed crystals **1**. The filtrate was kept in the freezer for one night. Precipitates were filtered and collected as mixed crystals **2**. Found for mixed crystals **1**: C, 69.99; H, 4.34; N. 15.44%. Found for mixed crystals **2**: C, 70.12; H, 4.46; N, 15.24%. Calcd for 1:1 mixed crystals, $\mathrm{(Fe_2C_{28}H_{34})_{0.5}(Fe_2C_{30}H_{38})_{0.5}(C_{12}H_4H_4)_3{=}Fe_2C_{65}H_{48}N_{12}}$: C, 70.41; H, 4.36; N, 15.16%. It is found that the products consist of the sum of two kinds of binuclear ferrocenes (1′,1‴-dibutylbiferrocene+1′,1‴-dipentylbiferrocene) and TCNQ in the molar ratio of (ca. 0.5+ ca. 0.5): 3. It is difficult to determine definitely the ratio of 1′,1‴-dibutylbiferrocene to 1′,1‴-dipentylbiferrocene in the mixed crystals **1** and **2** from the elemental analysis data, because the difference between the butyl substituent and the pentyl substituent is small in the salts which have large molecular weight. X-Ray diffraction patterns of 1′,1‴-dipentylbiferrocenium$^+$(TCNQ)$_3^-$ shown in Fig. 1 are similar as a whole, suggesting that the salts are isomorphous and make a mixed crystal. The slight difference observed between them can be attributed to the difference of the alkyl group in their cations. The patterns of the mixed crystals **1** are more similar to 1′,1‴-dibutylbiferrocenium$^+$(TCNQ)$_3^-$, while those of mixed crystals **2** to 1′,1‴-dipentylbiferrocenium$^+$(TCNQ)$_3^-$, showing that mixed crystals **1** contain more 1′,1‴-dibutylbiferrocenium than dipentylbiferrocenium and mixed crystals **2** more 1′,1″-dipentylbiferrocenium than dibutylbiferrocenium than dibutylbiferrocenium. The possibility to be a mixture but not to be mixed crystals is also rejected, based on the results on the Mössbauer spectra measurements (see Results and Discussion).

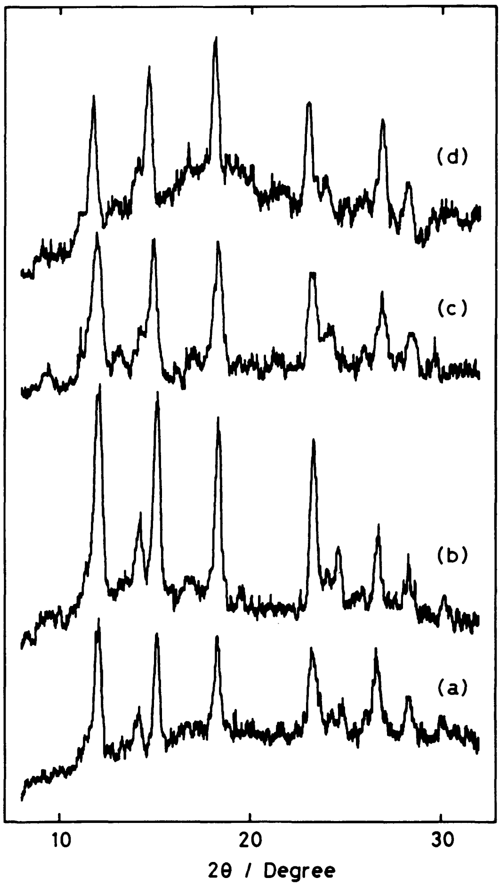

Fig. 1. X-Ray powder patterns (Cu K$_\alpha$) for (a) 1′,1‴-dibutylbiferrocenium$^+$ (TCNQ)$_3^-$, (b) mixed crystals **1**, (c) mixed crystals **2**, and (d) 1′1‴-dipentylbiferrocenium$^+$ (TCNQ)$_3^-$.

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 Austin Science Associates Mössbauer spectrometer and a proportional counter. Isomer shift values were referred to metallic iron foil. Mössbauer parameters were obtained by least-squares fitting to Lorentian peaks.

Results and Discussion

Mössbauer spectra of 1′,1‴-dibutyl- and 1′,1‴-dipentylbiferrocenium$^+$(TCNQ)$_3^-$ are shown in Figs. 2 and 3, respectively. The Mössbauer spectrum of 1′,1‴-dibutylbiferrocenium$^+$(TCNQ)$_3^-$ at 5 K shows a

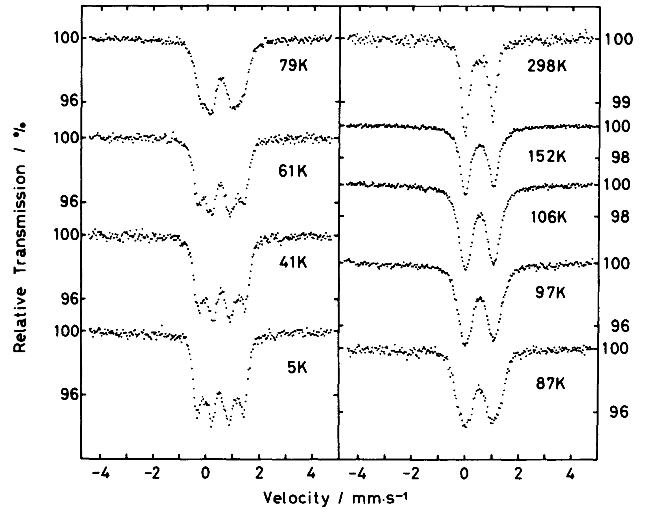

Fig. 2. Mössbauer spectra of 1′,1‴-dibutylbiferrocenium$^+$ $(TCNQ)_3^-$.

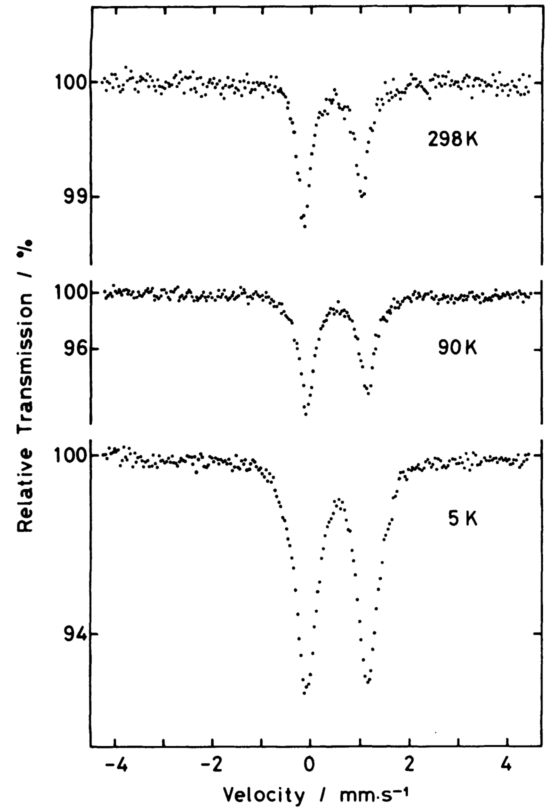

Fig. 3. Mössbauer spectra of 1′,1‴-dipentylbiferrocenium$^+$ $(TCNQ)_3^-$.

main component ascribed to a trapped-valence state together with a small component of averaged-valence state. The relative intensity of the doublet for the averaged-valence state increases with increasing temperature, as observed in 1′,1‴-bis(*o*-methylbenzyl)biferrocenium$^+$ TCNE$^-$ (TCNE=tetracyanoethylene).[4] 1′,1‴-Dipentylbiferrocenium$^+$ $(TCNQ)_3^-$ shows only the component of averaged-valence state in the whole temperature range from 5 to 298 K.

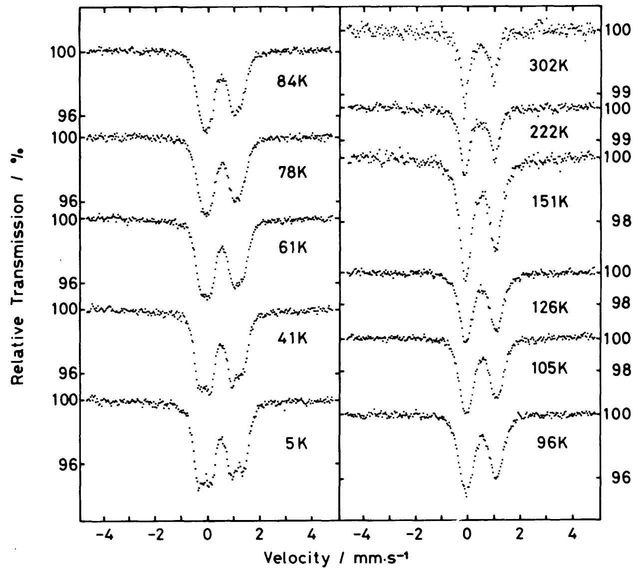

Fig. 4. Mössbauer spectra of mixed crystals **1**.

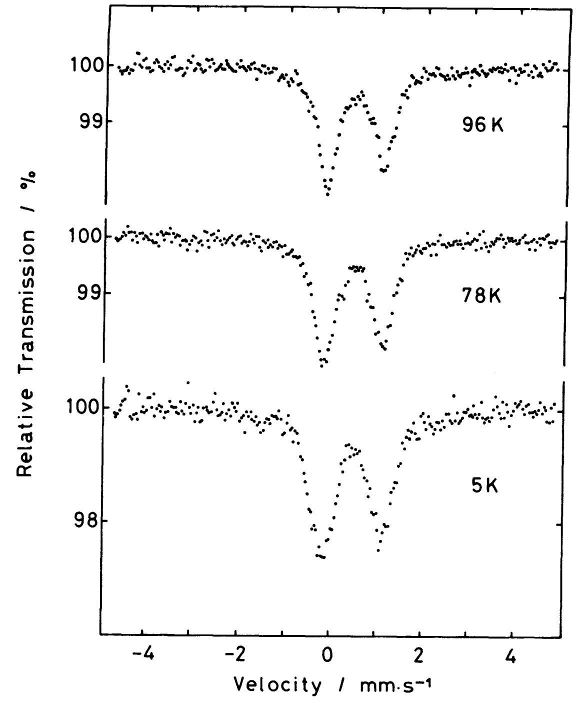

Fig. 5. Mössbauer spectra of mixed crystals **2**.

Mössbauer spectra of mixed crystals **1** and **2** are shown in Figs. 4 and 5, respectively, and the quadrupole splitting (Q. S.) values of all the salts studied in the present study are summarized in Fig. 6. Although the temperature dependence of the mixed-valence states in mixed crystals **1** is classified into a so-called coexisting type, as in the case of 1′,1‴-dibutylbiferrocenium$^+$$(TCNQ)_3^-$. The Q. S. value at 5 K (0.74 mm s^{-1}) of mixed crystals **1** is different from the value (0.55 mm s^{-1}) of 1′,1‴-dibutylbiferrocenium$^+$ $(TCNQ)_3^-$ at 5 K. In the coexisting region of the trapped- and averaged-valence state (at 5—126 K) in 1′,1‴-dibutylbiferrocenium$^+$$(TCNQ)_3^-$, the Q. S. val-

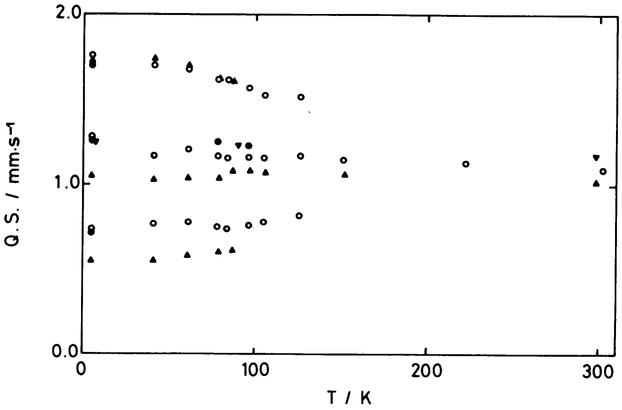

Fig. 6. Temperature dependences in the Q. S. values of 1′,1‴-dibutylbiferrocenium⁺ $(TCNQ)_3^-$ (Δ), 1′,1‴-dipentylbiferrocenium⁺ $(TCNQ)_3^-$ (∇), mixed crystals **1** (○), and mixed crystals **2** (●).

ues of the iron atoms in the averaged-valence state are close to an averaged value of the Q. S. values for the ferrocene-like doublet and ferrocenium-like doublet of their trapped-valence state and almost equal to the value at 302 K. The Q. S. values of the iron atoms in the averaged-valence state for mixed crystals **1** (e.g., 1.09 mm s^{-1} at 302 K) show averaged values of the values of 1′,1‴-dibutylbiferrocenium⁺ $(TCNQ)_4^-$ (e.g., 1.02 mm s^{-1} at 298 K) and 1′,1‴-dipentylbiferrocenium⁺ $(TCNQ)_3^-$ (e.g., 1.17 mm s^{-1} at 298 K) as expected for mixed crystals. The results reject the possibility of a mixture of the two salts obtained for the mixed crystals **1** because no line-broadening is found at higher temperatures. Mixed-valence states in mixed crystals **2** are similar to those in 1′,1‴-dipentylbiferrocenium⁺$(TCNQ)_3^-$, although a small component assigned to the trapped-valence state coexists at 5 K. The Q. S. values of the trappped-valence state (1.79 mm s^{-1} and 0.72 mm s^{-1} at 5 K) are similar to those of mixed crystals **1** and are different from those of 1′,1‴-dibutylbiferrocenium⁺$(TCNQ)_3^-$. The results found in the mixed crystals **2** also reject the possibility of a mixture of the component salts.

The results obtained in the present study indicate that the valence delocalization is affected by the crystal lattice, which is predominantly under the control of the host component, 1′,1‴-dibutylbiferrocenium⁺ $(TCNQ)_3^-$ in mixed crystals **1** and of 1′,1‴-dipentylbiferrocenium⁺$(TCNQ)_3^-$ in mixed crystals **2**.

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