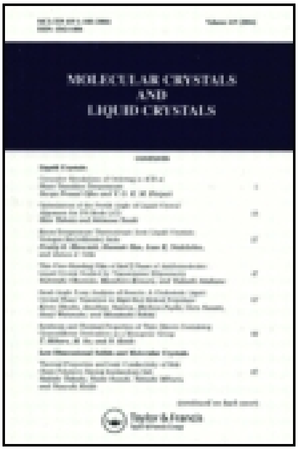

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Effects of Cation Symmetry and its Packing on the Mixed-Valence State of Binuclear Ferrocenes

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The mixed-valence state for (*S*,*S*), (*R*,*R*), and DL samples in 1′,1‴bis(2-phenylbutyl)-1,1″-biferrocenium salt was investigated and compared with that in 1′,1‴-bis(2-methylbutyl)- 1,1″-biferrocenium triiodide. The difference between them was attributed to the effect of benzene ring. It was understood that the packing effect becomes more substantial by introducing the benzene ring in the substituent.

Keywords: mixed-valence state; binuclear ferrocene; asymmetric carbon; ^{57}Fe Mössbauer spectroscopy; cation symmetry; packing effect

INTRODUCTION

The electron transfer between well-separated metal sites in the mixed-valence binuclear ferrocene derivatives has already been discussed in connection with superconduction and biological redox system.[1] The important role of the cation symmetry and its packing in the mixed-valence state has been shown.[2-4] There is a problem, however, in understanding the steric effect; i. e., it is difficult to separate the effect into the contribution of the cation symmetry and that of the packing effect in the crystal. Recently, the present author discussed the effect of the cation symmetry and the packing effect on the mixed-valence state of binuclear ferrocene derivatives on the basis of results of the difference between the DL and (*S*,*S*) samples and that between the salts from hexane and from dichloromethane in 1',1'''-bis(2-methylbutyl)-1,1''-biferrocenium triiodides having asymmetric carbon in substituent.[5] In the present study, in order to know the relation comprehensively between the effect of cation symmetry and packing effect, we investigated the mixed-valence state for the (*S*,*S*), (*R*,*R*), and DL samples in 1',1'''-bis(2-phenylbutyl)-1,1''-biferrocenium salts.

EXPERIMENTAL

Syntheses

1',1'''-Bis(2-phenylbutyl)-1,1''-biferrocenes were synthesized according to the method reported for a series of biferrocenes disubstituted with alkyl substituents.[6] In the acylation, the DL-2-phenylbutyryl chloride, (*S*)-(+)-2-phenylbutyryl chloride, and (*R*)-(-)-2-phenylbutyryl chloride were used for the DL, (*R*,*R*), and (*S*,*S*) samples, respectively. The products were isolated by column chromatography on alumina and purified by recrystallization from dichloromethane-hexane. The purity was checked by ^{1}H NMR. The iodine salts of (*S*,*S*), (*R*,*R*), and DL-1',1'''-bis(2-phenylbutyl)-1,1''-biferrocenes were prepared by adding I_2 dissolved in hexane to a hexane solution of the corresponding 1',1'''-bis(2-phenylbutyl)-1,1''-biferrocenes. Although 3/2 times the amount of I_2 was added, the elemental analyses suggested the presence of $nI_2 \cdot I_3^-$ (n=0.5~1) anion and preliminary X-ray structural analysis suggested the presence of pentaiodide anion. About one-half of the sample prepared in the above manner was recrystallized from a dichloromethane solution.

^{57}Fe Mössbauer spectroscopic measurements

A ^{57}Co(Rh) source moving in a constant-acceleration mode was used for ^{57}Fe Mössbauer spectroscopic measurements. Variable-temperature ^{57}Fe Mössbauer spectra were obtained by using a Toyo Research spectrometer and a continuous-flow cryostat. The Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shift values are referred to metallic iron.

RESULTS AND DISCUSSION

We refer to the binuclear ferrocene derivatives synthesized from DL-2-phenylbutyryl, (*S*)-(+)-2-phenylbutyryl, and (*R*)-(-)-2-phenylbutyryl chlorides for the acylation as DL, (*R,R*), and (*S,S*)-1',1'''-bis(2-phenylbutyl)-1,1''-biferrocene, respectively.

Figure 1 shows the variable-temperature ^{57}Fe Mössbauer spectra of (*R,R*) sample for iodine salt of 1',1'''-bis(2-phenylbutyl)-1,1''-biferrocene from dichloromethane. The ferrocene-like and ferrocenium-like doublets are observed independently at 80 K. The two doublets approach to each other gradually with increasing temperature, but never fuse into one doublet even at 300 K. Significant difference in spectrum was not observed between the salts from hexane and dichloromethane. The (*S,S*) samples also showed the same mixed-valence state as (*R*,*R*) samples, as was to be expected.

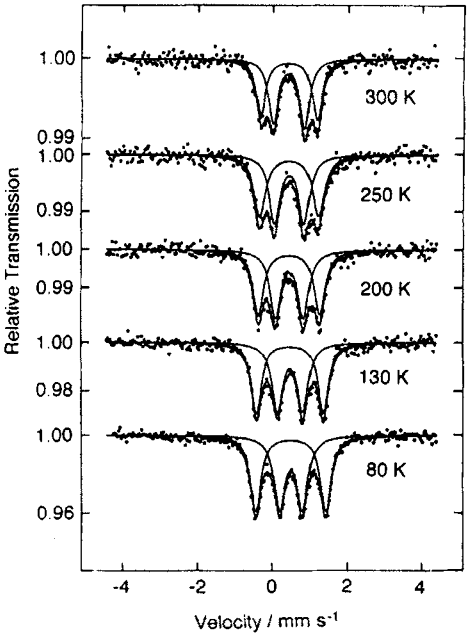

FIGURE 1 Variable-temperature ^{57}Fe Mössbauer spectra of iodine salt of (*R*,*R*)-1',1'''-bis(2-phenylbutyl)-1,1''-biferrocene from dichloromethane.

Figure 2 shows the variable-temperature ^{57}Fe Mössbauer spectra of DL sample for iodine salt of 1',1'''-bis(2-phenylbutyl)-1,1''-biferrocene from dichloromethane. It can easily be seen that the valence state is different from (*S*,*S*) or (*R*,*R*) sample. The spectrum at 80 K consists of three doublets. The Mössbauer parameters indicate that the outer and inner doublets are the ferrocene-like and ferrocenium-like doublets, respectively. The intermediate doublet is the valence detrapped one. Therefore, the trapped-valence and detrapped-valence states coexist.

The area ratio of the detrapped-valence state increases with increasing temperature. The spectrum at room temperature shows only detrapped-valence state. This is a typical coexistent-type valence detrapping. No significant difference in spectrum was observed between the salts from hexane and dichloromethane.

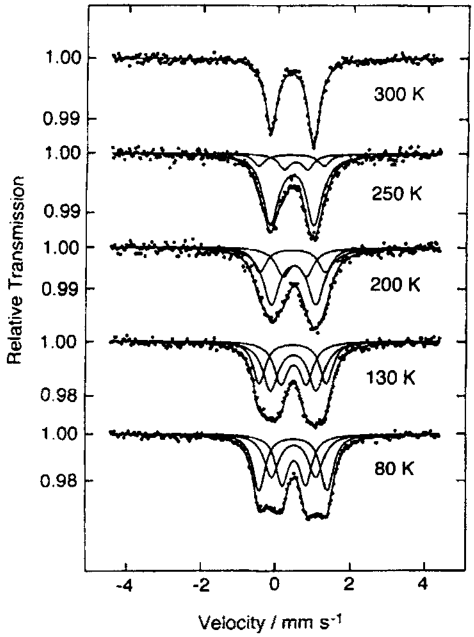

FIGURE 2 Variable-temperature ^{57}Fe Mössbauer spectra of iodine salt of DL-1',1'''-bis(2-phenylbutyl)-1,1''-biferrocene from dichloromethane.

As was discussed, there is not a difference in mixed-valence state between the salts from hexane and dichloromethane in the present 2-phenylbutyl derivative, while there is a difference between them in 2-methylbutyl derivative[5]. The difference in the 2-methylbutyl derivative was attributed to the order or disorder of the rotational isomers of the substituent. It is supposed that the stable phase is easily obtained even from hexane in the present salts, maybe because of the intermolecular interaction via benzene ring. The interesting point is that the DL sample showed a detrapped valence state at room temperature, in which of the DL sample the Mössbauer spectrum is not superposition of (*S,S*), (*R,R*), and (*R,S*) components, suggesting a substantial intermolecular interaction through the benzene ring. This finding is a big contrast to the result of 2-methylbutyl derivative.

The present result reveals that the balance of the two effects (effects of cation symmetry and its packing) is changed by introducing the benzene ring in the substituent. It can be understood that the packing effect becomes more substantial by introducing the benzene ring in the substituent.

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