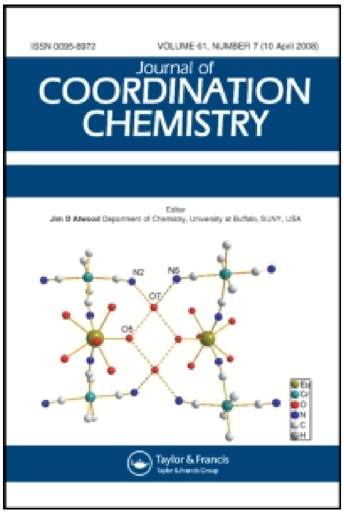

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Packing Effect on Mixed-Valence States of 1',1'''-Dialkyl- and 1',1'''-Bis(Methylbenzyl)Biferrocenium Triiodides

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PACKING EFFECT ON MIXED-VALENCE STATES OF 1',1'''-DIALKYL- AND 1',1'''-BIS(METHYLBENZYL)BIFERROCENIUM TRIIODIDES

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Abstract A remarkable packing effect on the mixed-valence state was observed in 1',1'''-diisobutylbiferrocenium triiodide. The effect was also observed for a series of 1',1'''-dialkyl- and 1',1'''-bis(methylbenzyl)biferrocenium triiodides by means of ESR spectroscopy.

Keywords: Packing effect, ESR spectroscopy, mixed-valence state

INTRODUCTION

Two crystal forms of 1',1'''-dibutylbiferrocenium triiodide were obtained, which show different temperature-dependence of mixed-valence state.[1] Remarkable counter anion effect has also been observed, probably due to the crystal packing.[2]

In the present study the mixed-valence states of 1',1'''-dialkyl- and 1',1'''-bis(methylbenzyl)biferrocenium triiodides dispersed in polymer were investigated by means of Moessbauer and ESR spectroscopy and were compared with the results in crystalline state.

MOESSBAUER SPECTRA

Figure 1 shows the ^{57}Fe-Moessbauer spectra of 1',1'''-diisobutylbiferrocenium triiodide in a dispersed state. The Moessbauer spectra consist of two doublets, indicating two types of iron atoms (trapped-valence state). They show no temperature-dependence of the mixed-valence state. The mixed-valence state in a crystalline form, on the other hand, is temperature-dependent, and the spectra near room temperature show an averaged-valence state.[1]

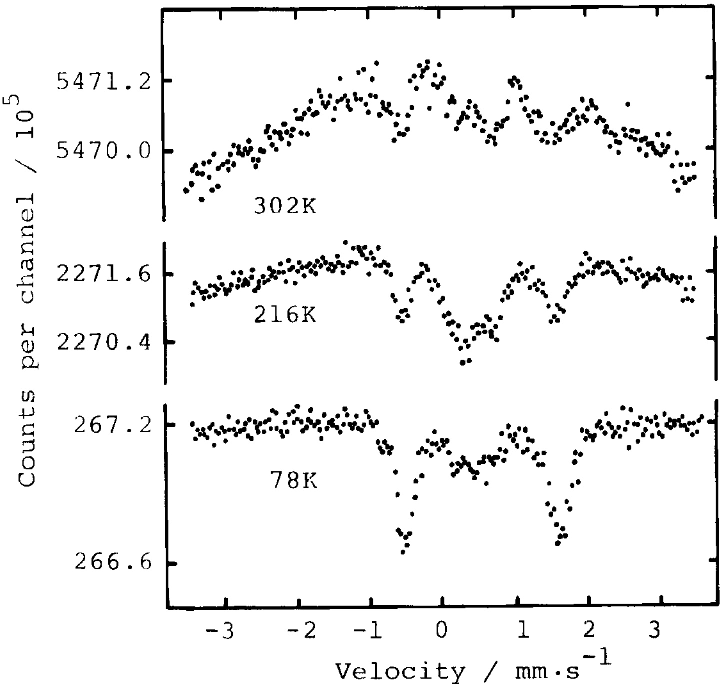

Fig. 1 Moessbauer spectra of 1',1'''-diisobutylbiferrocenium triiodide dispersed in poly(methyl methacrylate) from 78 K to room temperature.

ESR SPECTRA

It has been known that g-tensor anisotropy has a close connection with the mixed-valence states of biferrocene derivatives observed by the method of Moessbauer spectroscopy.[1-5] Figure 2 shows the summary of ESR parameters in crystalline and dispersed state at 78 K. The Δg values show a characteristic feature; i. e., the values for the samples whose valence state changes depending on temperature are smaller than those for the samples which show only a trapped-valence state. These results indicate that the decrease in the Δg values has a relationship with the nature of the electron exchange between the bivalent and tervalent iron atoms in the biferrocenium derivatives. This consideration is reasonable for explaining the appreciably small Δg values of the 1',1'''-diiodo- and 1',1'''-dibromobiferrocenium triiodide whose Moessbauer spectra show an averaged-valence state with only one doublet even at 4.2 K.[5] The difference of the ESR parameters ,$g_{\parallel}$, $g_{\perp}$, and Δg, among the various kinds of 1',1'''-dialkyl and 1',1'''-bis(methylbenzyl) derivatives in their crystalline state is reduced in the dispersed

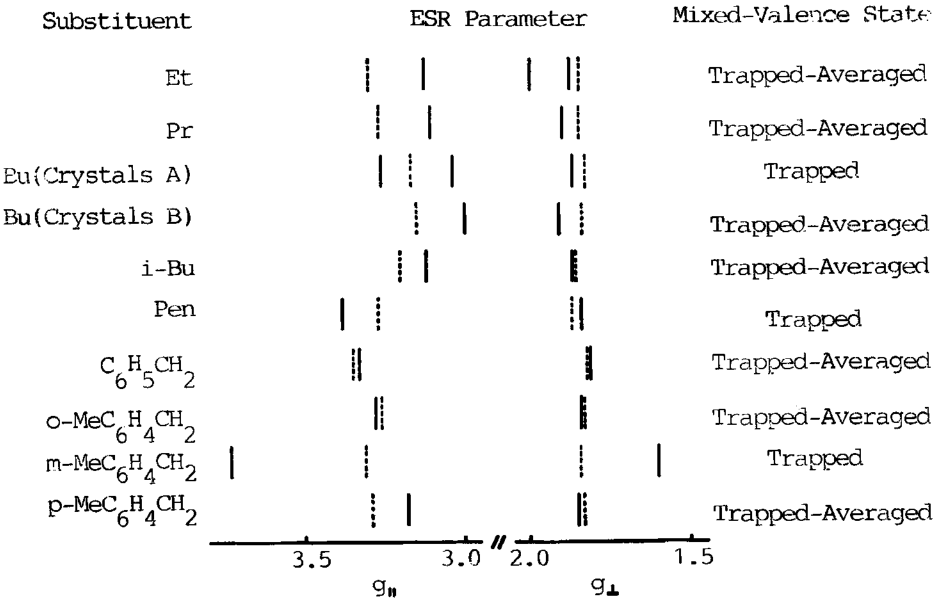

Fig. 2 Summary of ESR parameters in crystalline state(——) and dispersed state(·····) at 78 K for 1',1'''-dialkyl- and 1',1'''-bis(methylbenzyl)biferrocenium triiodides. "Trapped-Averaged" shows a trapped-valence state at low temperatures and an averaged-valence state near room temperature. "Trapped" shows only the trapped-valence state from a low temperature to room temperature.

state. The difference in ESR parameters in crystalline samples should be attributed not only to intramolecular effects of the alkyl or methylbenzyl substituent but also to intermolecular effects.

CONCLUSION

The results obtained in the present study indicate that the packing effect of the biferrocenium cations and their counter anions influences the electronic structures of the two iron atoms.

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