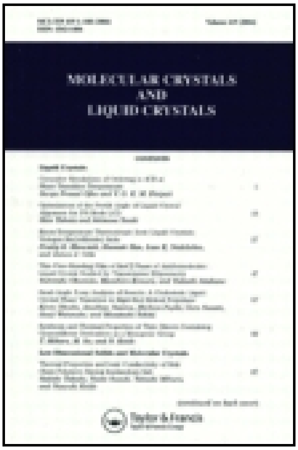

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Transition in 1′, 1′′′-Dihexylbiferrocenium Triiodide Accompanied by a Change In Mixed-Valence State

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Version of record first published: 04 Oct 2006.

To cite this article: Satoru Nakashima, Shinsuke Nakazaki, Hiroshi Sakai, Masanobu Watanabe & Izumi Motoyama (1996): Phase Transition in 1′, 1′′′-Dihexylbiferrocenium Triiodide Accompanied by a Change In Mixed-Valence State, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 59-64

To link to this article: http://dx.doi.org/10.1080/10587259608042265

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 59–64
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Printed in Malaysia

PHASE TRANSITION IN 1',1'''-DIHEXYLBIFERROCENIUM TRIIODIDE ACCOMPANIED BY A CHANGE IN MIXED-VALENCE STATE

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Abstract Two different crystals of 1',1'''-dihexylbiferrocenium triiodide were obtained from the different solution (hexane or dichloromethane). The salt prepared from hexane has a longer interlayer distance and gives trapped-valence state of Fe atoms, while the salt recrystallized from dichloromethane has a shorter interlayer distance and gives typical fusion-type valence detrapping of the mixed-valence state on the ^{57}Fe Mössbauer spectroscopy. By annealed at 323 K the latter changes into the former salt. The X-ray diffraction study of the latter supports the results of the ^{57}Fe Mössbauer spectroscopy.

INTRODUCTION

The mixed-valence state of the binuclear ferrocene derivatives is related to the crystal structure.[1, 2] It is important for both fundamentals and applications to study the relation systematically. Our strategy for systematic design is to use derivatives with a series of long alkyl chains. We have reported an interesting even-odd character in the number of carbon atoms of the alkyl chain.[3, 4]

In the present study ^{57}Fe Mössbauer spectra and X-ray diffraction were measured in order to reveal the relation between the mixed-valence state and the crystal structure in 1',1'''-dihexylbiferrocenium triiodide. It is also studied whether the mixed-valence state changes or not with a transformation of the crystal structure in the solid state.

EXPERIMENTAL

1',1'''-Dihexylbiferrocene was synthesized according to a method reported for the other dialkyl derivatives.[5] It was isolated by column chromatography on alumina and purified by recrystallization from dichloromethane-hexane. M.p.= 32.6°C; ^{1}H NMR($CDCl_3$) δ 0.87, 1.23, 1.36, 2.09, 3.83, 3.86, 4.11, and 4.24 ppm.

The triiodide salts were prepared by adding a stoichiometric amount of I_2 dissolved in hexane to a hexane solution of 1',1'''-dihexylbiferrocene. About one-half of the sample prepared in the above manner was recrystallized from a dichloromethane solution at 273 K [Found for 1',1'''-dihexylbiferrocenium triiodide: (from hexane) C, 42.13; H, 4.63; (from dichloromethane) C, 41.99; H, 4.52. Calc. for $C_{32}H_{42}Fe_2I_3$: C, 41.83; H, 4.57%].

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.

All X-ray powder diffraction patterns were measured by using graphite-monochromated Cu-Kα radiation (Rigaku) at room temperature.

Three-dimensional room-temperature X-ray data for the single crystal of 1',1'''-dihexylbiferrocenium triiodide obtained from dichloromethane at 273 K were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 60.0° on a Rigaku AFC6A four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ=0.71073Å). The data were corrected for Lorentz and polarization effects. Lattice parameters were determined by least-squares fitting of 25 reflections having $21.97 < 2\theta < 24.92°$.[6] The structure was solved by and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final residuals were R=0.082 and R_w=0.095.

RESULTS AND DISCUSSION

X-Ray powder diffraction patterns of 1',1'''-dihexylbiferrocenium triiodide from hexane and dichloromethane solution are shown in Fig. 1. According to the results reported before with longer alkyl chains[3, 4, 7, 8] the first intense diffraction is assumed to be the reflection from interlayer spacing. By the assumption the interlayer distance can be calculated to be 13.3 Å in the salt obtained from hexane (the longer interlayer distance), while it can be calculated to be 10.6 Å in the salt obtained from dichloromethane (the shorter interlayer distance). The result agrees with the reported one[4]; i. e., the analogous salts with even-numbered carbon atoms in the alkyl chain have two crystal forms having the longer and shorter interlayer distances.

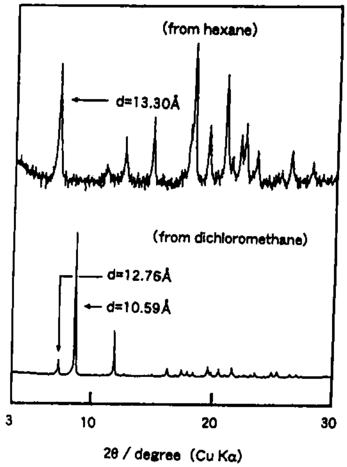

FIGURE 1 X-Ray powder diffraction patterns of 1',1'''-dihexylbiferrocenium triiodide.

The variable-temperature ^{57}Fe Mössbauer spectra of 1',1'''-dihexylbiferrocenium triiodide with the longer interlayer distance are shown in Fig. 2. The spectra consist of an inner and an outer doublet, with a nearly 1:1 ratio in area corresponding to Fe^{III} and Fe^{II}, like the case of typical temperature-independent trapped-valence biferrocenium analogues. The ^{57}Fe Mössbauer spectra of 1',1'''-dihexylbiferrocenium triiodide are already reported and showed the temperature-independent trapped-valence state.[9] It is thought that the reported result corresponds to the salt with longer interlayer distance in the present study. The variable-temperature ^{57}Fe Mössbauer spectra of 1',1'''-dihexylbiferrocenium triiodide with shorter interlayer distance are shown in Fig. 3. This shows a typical fusion-type valence detrapping, where two quadrupole-split doublets observed at low temperatures approach each other at increasing temperature, giving only one doublet ascribed to a valence state averaged over the bi- and ter-valent iron atoms without significant line broadening in the detrapping process. The detrapping temperature is lower than that of other dialkylbiferrocenium triiodides. The present results agree with the reported one[4]; i. e., the crystals with longer interlayer distance show the temperature-independent trapped-valence state, while the crystals with shorter interlayer distance show the fusion-type valence detrapping.

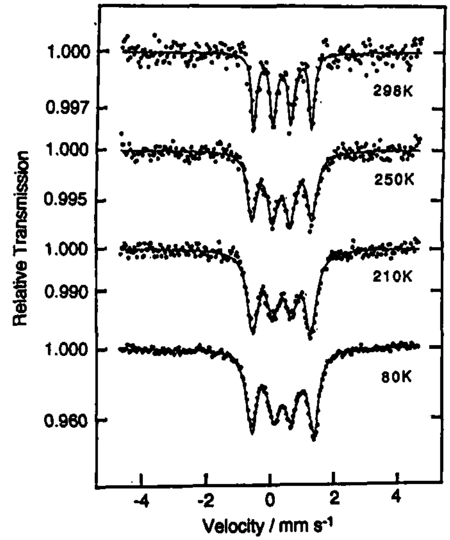

FIGURE 2 Variable-temperature ^{57}Fe Mössbauer spectra of 1',1'''-dihexylbiferrocenium triiodide obtained from hexane.

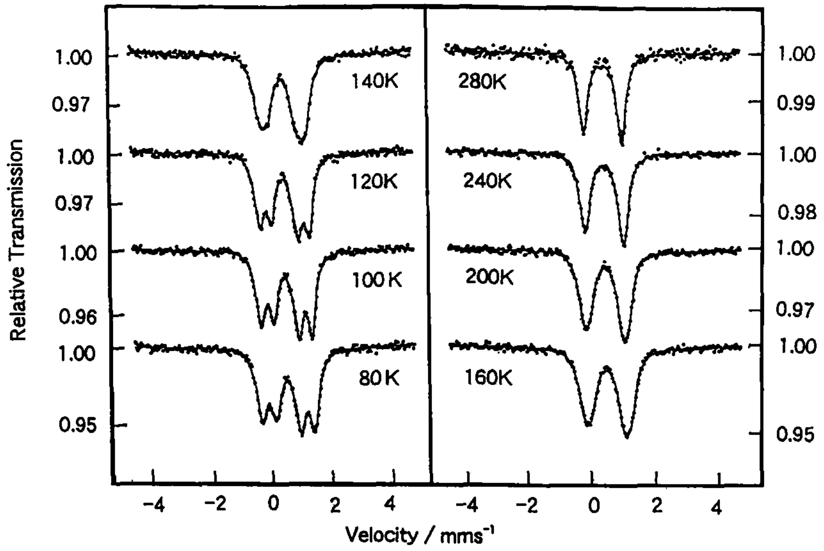

FIGURE 3 Variable-temperature ^{57}Fe Mössbauer spectra of 1',1'''-dihexylbiferrocenium triiodide obtained from dichloromethane.

The crystal structure for 1',1'''-dihexylbiferrocenium triiodide obtained from dichloromethane at 273 K is shown in Fig. 4. The mean Fe-C(ring) distance is found to be 2.068Å, intermediate between the values of 2.045Å for ferrocene[10] and 2.075Å for ferrocenium cation,[11] indicating that the valence state is intermediate between Fe^{II} and Fe^{III}. Both the cation and anion are located at the center of symmetry. The results agree with the salt exhibiting the averaged-valence state at room temperature. The crystal structure of the present study is the same as 1',1'''-bis(dodecyl)biferrocenium triiodide obtained from dichloromethane except for the slight difference of the conformation in the alkyl chain.[4] The results combined with those of the X-ray powder diffraction patterns suggest that the interlayer direction is |010|.

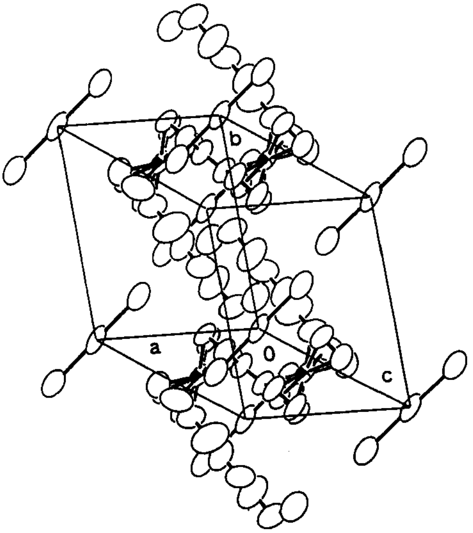

FIGURE 4 Crystal structure of 1',1'''-dihexylbiferrocenium triiodide obtained from dichloromethane.

The salt with the shorter interlayer distance was heated to 323 K for 40 min. The X-ray powder diffraction was measured at room temperature. It was shown that the salt with the shorter interlayer distance changes to one with the longer interlayer distance by annealing at 323 K for 40 min. The present and the reported results[4, 12] show that all salts with shorter interlayer distance change to the salts with longer interlayer distance by annealing at high temperatures. After annealing at 323 K for 40 min we measured the ^{57}Fe Mössbauer spectrum at room temperature. As shown in Fig. 5, the trapped-valence state of Fe atoms are observed for the annealed salt, although the averaged-valence state of Fe atoms is observed for the non-annealed salt (see Fig. 3 at 280 K). This phenomenon is in accord with the change of X-ray diffraction patterns. The results show that the mixed-valence state changes with a transformation of the crystal structure in the solid state. The DTA showed the endothermic peak near the temperature, which shows that the transition is first order one. Some salts returned to the salt with shorter interlayer distance upon standing at 273 K for several days.

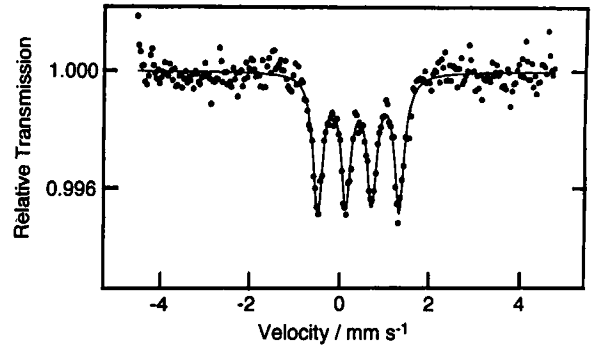

FIGURE 5 ^{57}Fe Mössbauer spectrum at room temperature for annealed crystals of 1',1'''-dihexylbiferrocenium triiodide recrystallized from dichloromethane.

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