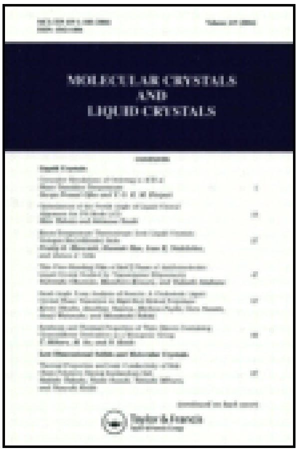

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Structure and Magnetic Properties of a Charge Transfer Salt of a Ferrocene-based Diradical, (1,3-Diferrocenylbenzene) (F 4 -TCNQ) 2 (chlorobenzene) 2

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To cite this article: Tomoyuki Mochida, Shinya Suzuki & Hiroshi Moriyama (2002): Structure and Magnetic Properties of a Charge Transfer Salt of a Ferrocene-based Diradical, (1,3-Diferrocenylbenzene) (F 4 -TCNQ) 2 (chlorobenzene) 2, Molecular Crystals and Liquid Crystals, 376:1, 295-300

To link to this article: http://dx.doi.org/10.1080/10587250210804

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 295-300
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1058-725X/02 $12.00 + .00

Structure and Magnetic Properties of a Charge Transfer Salt of a Ferrocene-based Diradical, (1,3-Diferrocenylbenzene) (F_4-TCNQ)$_2$(chlorobenzene)$_2$

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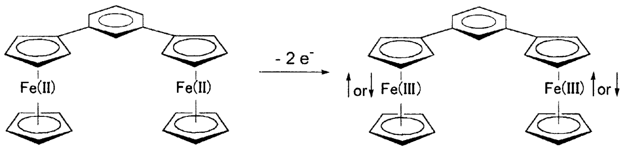
The charge transfer complex of 1,3-diferrocenylbenzene and F_4-TCNQ, (1,3-diferrocenylbenzene)(F_4-TCNQ)$_2$(chlorobenzene)$_2$, has been prepared. The compound consists of a diferrocenylbenzene diradical and dimerized anion radicals, exhibiting a segregated-stack structure. The paramagnetic susceptibility, showing a weak antiferromagnetic interaction (Weiss constant $\theta = -3$ K), is dominated by the contribution of the diradical.

Keywords Diferrocenylbenzene; Diradical; F_4-TCNQ; Charge transfer complex; Magnetism

INTRODUCTION

A number of ferrocene-based charge transfer complexes have been reported so far, from the viewpoint of ferromagnetic molecular assembly [1]. On the other hand, construction of high spin molecules can be achieved by joining organic diradicals through the *m*-phenylene group [2]. One may consider that a combination of these two approaches should be promising in raising the ferromagnetic T_C. An interesting example is an iron-based complex, in which the two spin sources (*i.e.*, Fe atoms) are covalently joined through an *m*-diethynylbenezene group, exhibiting a strong intramolecular ferromagnetic interaction [3], though there are only a few reports on diradicals composed of ferrocenium cations. In this respect, the magnetic properties of ferrocenium diradicals joined by an *m*-phenylene moiety are of interest. Here we focus on diferrocenylbenzenes as the donor constituent of charge transfer salts, since formation of the desired diradical is expected by combining the donor with strong acceptors. The synthesis and electrochemical properties are known for some diferrocenylbenzenes [4, 5], for which the intramolecular interactions between the ferrocene moieties are discussed in detail [4]. Among various combinations of diferrocenylbenzenes with organic acceptors, we could obtain single crystals of (1,3-diferrocenylbenzene)(F_4-TCNQ)$_2$(chlorobenzene)$_2$ (**1**). In this paper, we report the structure and magnetic properties of **1**, consisting of a diradical carrying ferrocenium cations at the *m*-positions of the phenyl group.



EXPERIMENTAL

1,3-Diferrocenylbenzene was synthesized by the method reported in the literature [5]. F_4-TCNQ was purchased from Tokyo Kasei Kogyo Co., Ltd. The charge transfer complexes were obtained as black needle crystals by a diffusion method in chlorobenzene solutions. Magnetic susceptibilities of polycrystals of **1** were measured using a SQUID magnetometer in the temperature range between 2 and 300 K at a magnetic field of 5000 G. The core diamagnetic component was corrected by calculation from Pascal's constants. The crystal structure of **1** was solved by four-circle X-ray analysis using a Rigaku AFC-7R diffractometer with Mo*K*α radiation at 296 K. Crystallographic parameters for **1**: Formula $C_{62}H_{32}N_8F_8Fe_2Cl_2$, space group *Cc*, $Z = 4$, $a = 7.119(3)$ Å, $b = 24.438(8)$ Å, $c = 30.518(4)$ Å, $\beta = 90.54(3)^\circ$, $V = 5309(2)$ Å^3. All calculations were performed using the teXsan [6] software package. The structure was solved by the direct method (SHELXS-97 [7]) and refined by using 3698 independent reflections with $|Fo| > 3\sigma(Fo)$ in the 2θ range of $4^\circ < 2\theta < 55^\circ$. The final values of $R = 0.083$ and $Rw = 0.086$. The crystallographic data have been deposited at Cambridge Crystallographic Data Centre (CCDC). Although combinations of 1,3- and 1,4-diferrocenylbenzenes, and 1,3,5-triferrocenylbenzene with various electron acceptors were investigated in various solvents, only very strong acceptors, such as F_4-TCNQ and DDQ, afforded charge transfer complexes, which are powders except for combination **1**.

RESULTS AND DISCUSSION

Figure 1 shows the ORTEP drawing of the molecular structure of the dication in **1**. Figure 2(a) shows the crystal structure of **1** viewed along the stacking direction. The donor and acceptor molecules form segregated stack arrangements. The *b*-axis projection, showing the stacking structure, is depicted in Figure 2(b). The acceptor molecules are strongly dimerized. The C-N infrared stretching frequencies of 2196 and 2179 cm^{-1} as well as the intramolecular geometry for F_4-TCNQ demonstrates that the acceptor molecule has a formal charge of –1. On the other hand, the donor

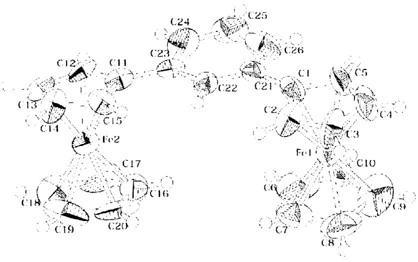


FIGURE 1 An ORTEP drawing of the dication in **1**.

molecule is in a two-electron oxidation state, which is a diradical containing two Fe(III) atoms. The average Fe-C(Cp) distances are 2.08 Å and 2.07 Å for Fe(1) and Fe(2), respectively, which are the normal ones for ferrocenium cations [8]. The oxidation state is also consistent with the 1:2 stoichiometry. The two Cp rings in each ferrocene unit have an eclipsed conformation. Both of the ferrocenyl groups are oriented to the same direction with respect to the benzene ring. The Cp rings of the two ferrocenyl groups are nearly parallel to the benzene ring; the angles between the Cp and benzene planes are 5.6° and 7.6° for Cp(Fe(1)) and Cp(Fe(2)), respectively. The molecular conformation makes a striking contrast with those in 5-cyano- and 5-chloro-derivatives of 1,3-diferrocenyl benzene [4]. In these neutral crystals, one ferrocene group is above and the other below the benzene ring. Thus, we point out that the stable conformation may be different for the neutral and the oxidized species, which should be taken into account when discussing the interaction between the ferrocenyl moieties in bridged compounds.

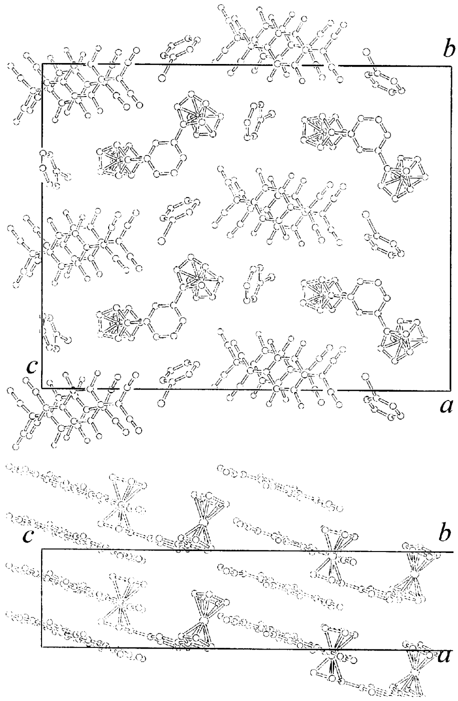


FIGURE 2 Projection of the crystal packing of **1** along the *a*-axis (top), and along the *b*-axis (bottom).

Figure 3 shows the temperature dependence of the magnetic susceptibility of **1**. The paramagnetic susceptibility obeys a Curie-Weiss law, showing a weak antiferromagnetic interaction with a Weiss constant of $\theta = -3$ K. The response is dominated by the 1,3-diferrocenylbenzene diradicals, while the acceptor radicals form singlet pairs due to the strong dimerization. The susceptibility is attributed to the contribution of a ferrocenium cation with an effective magnetic moment *ca* 2.4 μ_B per one ferrocenium site. This value, deviating from the spin only value of 1.73 μ_B by the orbital contribution, is quite common to ferrocenium salts [10]. The complex is electrically insulating despite the segregated-stack structure, in accordance with the above structural feature and the non-mixed valent nature. In conclusion, we have constructed a charge transfer complex containing a 1,3-diferrocenylbenzene diradical, which may be considered as the ferrocene-based analogue of *m*-phenylene diradicals. The small difference in the first and the second oxidation potentials of 0.09 V [4] in 1,3-diferrocenylbenzene, reflecting the weakness of the interactions between the ferrocenium moieties, may lead to the difficulty in obtaining mixed-valent salts. This may be consistent with the fact that 1,3-diferrocenylbenzene afforded charge transfer salts only with very strong acceptors.

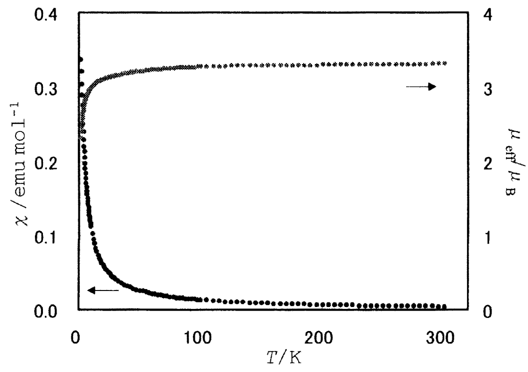


FIGURE 3 Temperature dependence of the molar magnetic susceptibility χ of **1**. The χT *vs* T plot is also shown.

Acknowledgments

We are grateful to Dr. Hatsumi Mori (ISTEC) for SQUID measurements.

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