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# Order-disorder phase transition with associated cell-tripling in the (octamethylferrocene)(2,3-dichloro-1,4-naphthoquinone)$_2$ charge-transfer complex

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## Abstract

The structural change associated with the first-order phase transition ($T_C$ = 155.1 K) in a mixed-stack charge-transfer complex (octamethylferrocene)(2,3-dichloro-1,4-naphthoquinone)$_2$ was investigated crystallographically. X-ray structure determination at 90 K revealed that the transition is associated with the order-disorder of the $C_5Me_4H$ ring in octamethylferrocene. In the low temperature phase, tripling of the unit cell occurred, accompanied by a change in spacegroup from $P2_1/c$ to $P-1$, and every third octamethylferrocene molecule twists out of the plane to minimize steric interactions.

*Keywords*: Ferrocene; Phase transition; Disorder; Crystal structure; Charge-transfer complex; Unit cell tripling

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## 1. Introduction

Metallocene-based charge-transfer (CT) complexes composed of metallocene donors (D) and acceptors (A) have attracted considerable attention because of their molecular magnetism and electronic phase transitions [1,2]. Furthermore, molecular motions and order-disorder phenomena of metallocenes in the solid-state have been a topic of interest [3–7]. As part of our continuous investigation into metallocene-based CT complexes [8–10], we prepared a neutral charge-transfer complex (octamethylferrocene)(2,3-dichloro-1,4-naphthoquinone)$_2$ (**1**; Fig. 1). X-ray structure determination at 173 K revealed that **1** exhibits a mixed-stack structure. The $C_5Me_4H$ rings of octamethylferrocene exhibit rotational disorder and the four methyl groups are distributed over five sites with occupancies of 0.8 [11]. Differential scanning calorimetry (DSC) measurements have revealed that a first-order phase transition occurs at 155.1 K on cooling and at 174.6 K on heating ($\Delta T$ = 19.5 K), which is accompanied by an entropy change of 3.8 J $K^{-1}mol^{-1}$ [11]. In this study, although hampered by the combination of twinning and superstructures, we successfully determined the crystal structure below $T_C$. The crystal structure revealed that the phase transition is associated with order-disorder of the $C_5Me_4H$ ring and tripling of the unit cell. Phase transitions in the solid state including order-disorder transitions are often associated with cell-doubling [12], whereas cell tripling is much less common. We compare the structures of the high temperature (HT) and low temperature (LT) phases in detail, and discuss the correlation between the cell tripling and the ring ordering of octamethylferrocene. To our knowledge, this study is the only example of the structure determination of an octamethylferrocene exhibiting rotational ring disorder.

## 2. Results and discussion

Fig. 2 shows the packing diagram of the LT phase of **1** determined at 90 K. The corresponding HT phase unit cell [11] is shown by dashed lines. The unit cell volume is about three times larger in the LT phase than in the HT phase [$V_{173K}$ = 1699.5(3) Å$^3$, $V_{90\ K}$ = 5030(3) Å$^3$] due to a change in spacegroup from $P2_1/c$ (HT phase) to $P{-}1$ (LT phase). In the LT phase, a superlattice is formed, with the repeating unit becoming three times longer with respect to the *a*- and *b*-axes of HT phase. The ADA units are stacked in columns, and layers of donors or acceptors are formed perpendicular to the stacking direction. The unit cell in the HT phase contains two formula units, and half of the donor molecule is crystallographically independent. The ORTEP diagrams of the molecular structures of octamethylferrocene in the HT and LT phases are shown in Figs. 3a and 3b, respectively. In the HT phase, the $C_5Me_4H$ rings are disordered, whereas they are ordered in the LT phase. In the LT phase, two donor molecules (D1 and D3) and two halves of donor molecules (D2 and D4) are crystallographically independent, and the latter are located on the inversion center. D1 and D2 are rotational isomers (Fig. 3b). In D2, the two ring carbons without methyl groups are on opposite sides of a pseudo-symmetry axis including the metal atom and the centers of the two rings, whereas they are on the same side in D1. The arrangements and conformations of D3 and D4 are almost identical to those of D1 and D2, respectively (Figs. S1–S3), except that the orientation of the methyl groups is slightly different. Hence, only the structures of D1 and D2 will be discussed in detail.

The molecular arrangement in the stacking column is shown in Fig. 4. In the HT phase, the repeat unit along the stacking direction is ADA (Fig. 4a), whereas a three-unit repeat is observed in the LT phase (Fig. 4b). The acceptor arrangements are almost unchanged in the HT and LT phases, but the donor arrangement changes due to the ring ordering. In the LT phase, one third of the donors (D2) are tilted away from the stacking axis, while the other donors (D1) are stacked parallel to the stacking axis.

Closer examination of the crystalline environments shows that the change in molecular arrangement is sterically related to the ring ordering. First, we will discuss the relationship between the donor and acceptor. In the HT phase, the methyl groups of the Cp ring and the substituents (oxygen and chlorine) of the adjacent acceptor are in a staggered conformation, as shown in Fig. 4a. The Cp ring and the adjacent acceptor are almost parallel with a dihedral angle of 4.28°. In the LT phase, the relationship between D1 and the adjacent acceptor is similar to that observed in the HT phase, with a staggered orientation that leads to almost parallel molecular planes (dihedral angles: 4.6° and 5.5°). In contrast, the $C_5Me_4H$ rings in D2 exhibit an eclipsed orientation with respect to the adjacent acceptors (Fig. 4b, middle), which leads to the tilting of D2 by 10.4°, owing to the steric interactions between the substituents.

Next, we will discuss the steric relationship between the donors. The closest donor arrangement within the donor layer in the LT phase is shown in Fig. 5. In the HT phase, the donors are located at regular intervals (Fe···Fe distance: 8.168 Å), whereas the repeat unit becomes threefold (D1 D1 D2) in the LT phase (Fig. 5a). The Fe···Fe distances for D1−D1 and D1−D2 are 7.692 Å and 8.462 Å, respectively. As shown in Fig. 5b, the contraction of D1−D1 is due to the interlocked arrangement of the methyl-deficient sites, whereas the expansion of D1–D2 is due to the steric hindrance between the methyl groups. Steric interactions along other directions in the layer are less significant due to longer intermolecular distances.

Rotational disorder of the $C_5Me_5$ rings is observed in decamethylferrocene compounds [13–15], but no rotational disorder has been observed in the crystal structures containing octamethylferrocene [16–19]. To our knowledge, the present case is the sole example of ring disordering in octamethylferrocene structures. The asymmetric $C_5Me_4H$ ring is unlikely to disorder, whereas a two-fold disorder of a $C_5Me_4H$ ring is observed in a salt of octamethylaluminocene [20]. Disordering of the four methyl groups in $C_5Me_4H$ into five sites is accompanied with an entropy change of $\Delta S = 2R \ln 5 = 26.7$ J K$^{-1}$ mol$^{-1}$. However, the transition entropy associated with the order-disorder transition in **1** is only 3.8 J K$^{-1}$ mol$^{-1}$ [11], which is because of compensation due to the difference in the lattice entropy. Ordering of the $C_5Me_4H$ ring that accompanies such a large entropy stabilization is likely to be the origin of the phase transition. It would be interesting whether the disorder in the HT phase is static or dynamic, but solid-state NMR investigations could not be applied due to the very small yield of **1**. A rotator phase often appears at high temperatures in metallocene compounds [3,4], including octamethylferrocene [21] and its salts [22,23], but no such phase was observed in **1** [11].

From the viewpoint of phase transitions, the cell tripling is noteworthy. Phase transitions in the solid state often accompany cell-doubling [12]. Examples of cell tripling are limited, but include: ordering of spins [24] or molecules [25] in triangular or hexagonal lattice; charge ordering of mixed-valence compounds in manganese perovskites [26] and conducting coordination polymers [27]. It is interesting that the origin of the cell tripling in **1** is of steric origin and not electronic, although cell tripling is observed in simple organic molecules [28]. Here, the cell tripling is probably due to optimization of the packing structure that is associated with the ring ordering.

## 3. Conclusion

Structural investigation has revealed the origin of the first-order phase transition ($T_C$ = 155.1 K) in (octamethylferrocene)(2,3-dichloro-1,4-naphthoquinone)$_2$. The transition was found to be associated with the order-disorder of the $C_5Me_4H$ ring in octamethylferrocene, which is likely due to the phase transition. In the low temperature phase, tripling of the unit cell occurred and one in three octamethylferrocene molecules is tilted to avoid steric interactions with the neighboring acceptor. The cell tripling is steric in origin, and is a consequence of the ring ordering.

## 4. Experimental

Single crystals of (octamethylferrocene)(2,3-dichloro-1,4-naphthoquinone)$_2$ were prepared as described previously [11]. X-ray diffraction data were collected on a Bruker SMART APEX II Ultra CCD diffractometer using MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å) at 90 K. The crystal used for data collection was composed of two domains. The two domains were integrated separately for each component and the integrated data were merged and corrected for absorption using TWINABS [29]. Structure refinement was performed with reflections in HKLF 5 format (BASF value: 0.42). The structure was solved by the direct method and refined on $F^2$ using SHELX-97 [30]. The non-hydrogen atoms were refined anisotropically. The packing diagrams were drawn using ORTEP-3 [31]. CCDC 833036 contains the supplementary crystallographic data for this paper.

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## Appendix A. Supplementary material

Supplementary data related to this article can be found online, at doi:10.1016/j.jorganchem.XXXX.XX.XXX.

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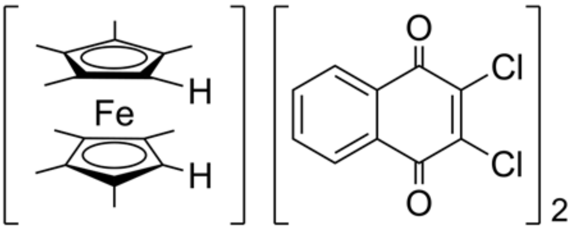

**Fig. 1.** Chemical formula of (octamethylferrocene)(2,3-dichloro-1,4-naphthoquinone)$_2$ (**1**)

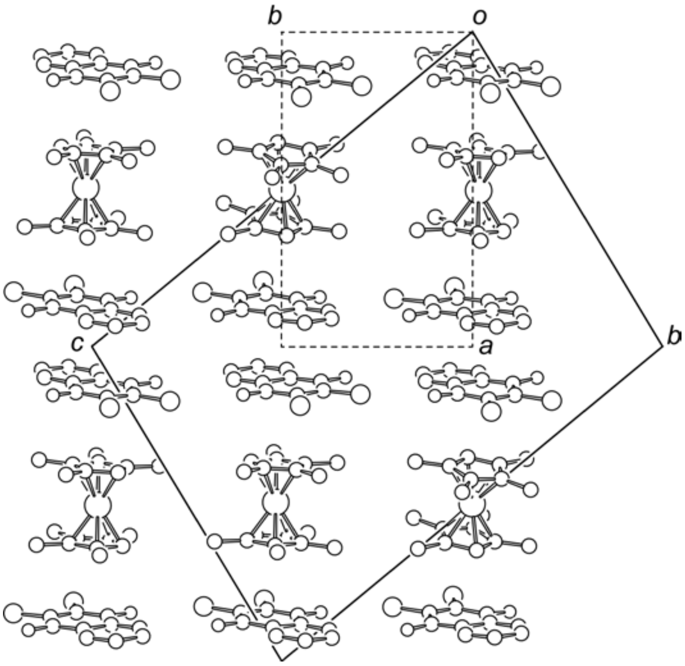

**Fig. 2.** Packing diagram of **1** in the LT phase projected along the *a*-axis. The LT unit cell and the corresponding HT unit cell are shown by solid lines and dashed lines, respectively. Hydrogen atoms are omitted for clarity.

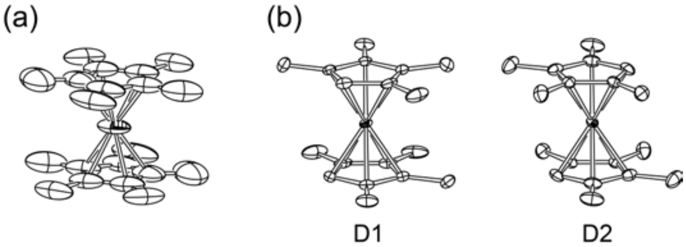

**Fig. 3.** ORTEP diagram of the molecular structures of octamethylferrocene in the (a) HT phase [11] and (b) LT phase. Hydrogen atoms are omitted for clarity.

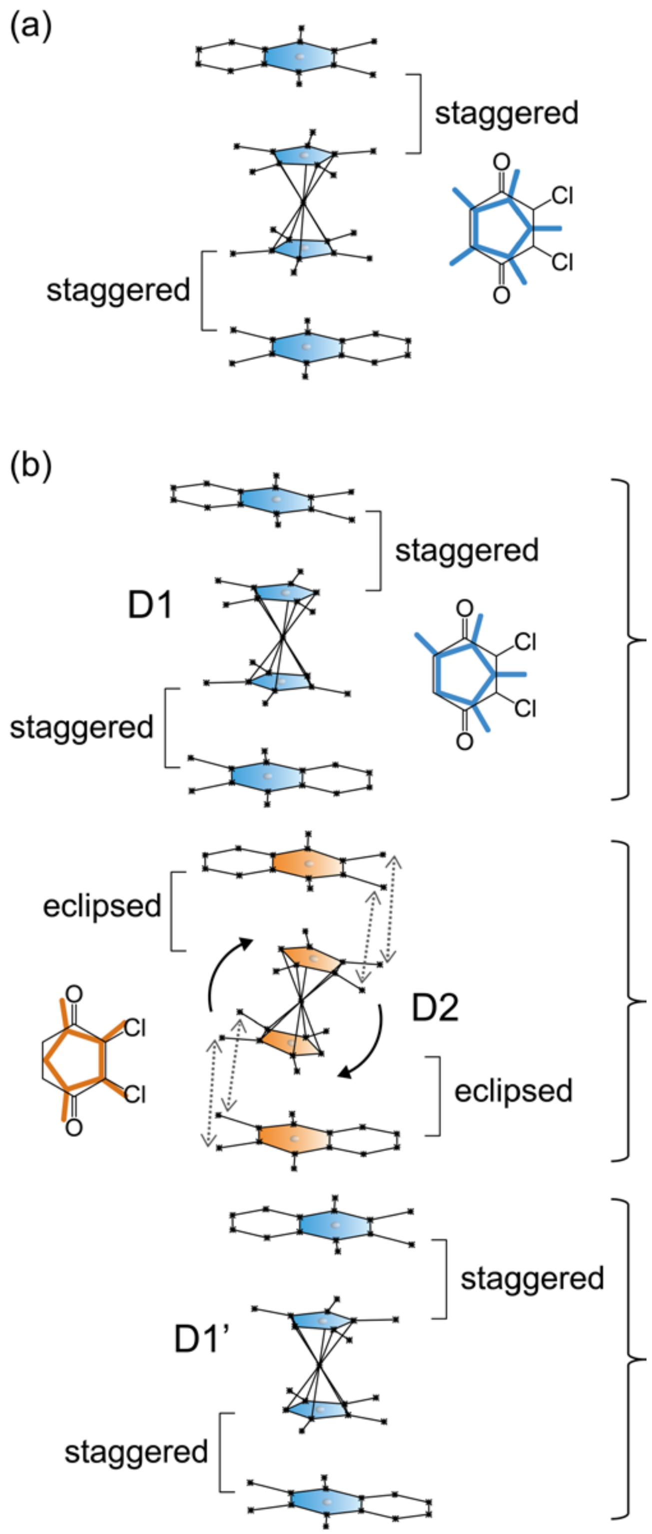

**Fig. 4.** Stacking structure of **1** in the (a) HT phase and (b) LT phase. Tilting of D2 associated with steric interactions is illustrated by arrows. Hydrogen atoms are omitted for clarity. Schematic representations of the relative orientation of the $C_5Me_4H$ ring and the adjacent six membered ring of the acceptor are also shown.

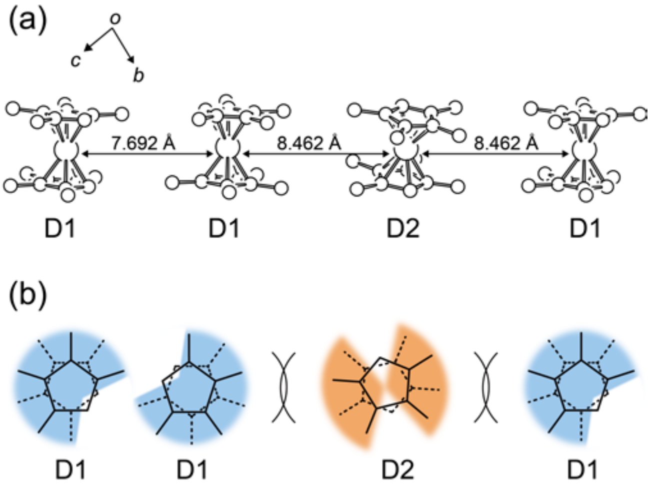

**Fig. 5.** (a) Donor arrangement within the donor layer in the LT phase of **1**. Hydrogen atoms are omitted for clarity. (b) Schematic illustration of the corresponding donor arrangement viewed from the pseudo-symmetric axes of the donors.

**Table 1.**

Crystallographic parameters for **1** at 90 K (LT phase) and 173 K (HT phase).

| | **1** (90 K) | **1** (173 K)[c] |
|---|---|---|
| Formula | $C_{38}H_{34}Cl_4FeO_4$ | |
| Formula weight | 752.3 | |
| $T$ (K) | 90 | 173 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P-1$ | $P2_1/c$ |
| $a$ (Å) | 15.079(5) | 13.8846(3) |
| $b$ (Å) | 15.924(5) | 8.1681(17) |
| $c$ (Å) | 21.344(7) | 15.110(3) |
| $\alpha$ (°) | 81.091(4) | |
| $\beta$ (°) | 85.793(4) | 96.016(2) |
| $\gamma$ (°) | 84.361(4) | |
| $V$ (Å$^3$) | 5030(3) | 1699.5(3) |
| $Z$ | 6 | 2 |
| $D_{\mathrm{calc}}$ (g cm$^{-3}$) | 1.490 | 1.466 |
| $\mu$ (mm$^{-1}$) | 0.810 | 0.799 |
| Reflections collected | 27051 | 9312 |
| Independent reflections | 20098 | 3821 |
| $F(000)$ | 2328 | 772 |
| Parameters | 1298 | 228 |
| Final $R_1$[a], w$R_2$[b] ($I > 2\sigma$) | 0.0307, 00851 | 0.0376, 00988 |
| Final $R_1$[a], w$R_2$[b] (all data) | 0.0373, 0.0919 | 0.0451, 0.1039 |
| Goodness of fit on $F^2$ | 1.026 | 1.048 |

[a] $R_1 = \Sigma \,||F_o| - |F_c|| / \Sigma |F_o|$

[b] $wR_2 = [\,\Sigma\, w(F_o^2 - F_c^2)^2 / \Sigma\, w(F_o^2)^2\,]^{1/2}$

[c] Ref. 11

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