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Note

Structural investigation of the phase transition in decamethylferrocene–acenaphthenequinone charge-transfer complex

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ABSTRACT

An X-ray structural determination of decamethylferrocene–acenaphthenequinone charge-transfer complex at 293 K and 193 K revealed that the first-order phase transition at 257 K is associated with ordering of the disordered pentamethylcyclopentadienyl rings in decamethylferrocene. The pentamethylcyclopentadienyl rings exhibit two-fold rotational disorder in the room temperature phase, where the dominant form is an eclipsed conformation. In the low temperature phase, the molecular structure is ordered with a staggered conformation. The space groups were determined to be *Cmcm* and *Pnma* in the respective phases.

1. Introduction

Metallocene-based charge-transfer (CT) complexes have attracted special attention from the viewpoint of molecular magnetism [1,2]. In the course of our continuous investigation into metallocene-based CT complexes [3–5], we prepared a charge-transfer complex composed of decamethylferrocene and acenaphthenequinone (Fig. 1) [6]. Decamethylferrocene is a strong donor, while acenaphthenequinone is a weak acceptor. They form a neutral complex with a 1:1 stoichiometry that exhibits a first-order phase transition at 257 K. Molecular motions of metallocenes in the solid state have been a topic of interest [7–10]. Thus, we were curious about the nature of the phase transition, suspecting that it is correlated with some dynamical motion of the donor. Kuwahara has performed microscopic investigations of the phase transition by solid-state NMR spectroscopy, and a model of the phase transition has been proposed based on the analysis of ^{1}H spin-diffusion rates as well as ^{13}C and ^{1}H NMR spectra [6]. Our previous attempt to determine the crystal structure was not fully successful. However, we could collect better data recently, and here we report the crystal structures of the complex both in the room temperature (RT) phase and in the low temperature (LT) phase. It was revealed that the phase transition is associated with order–disorder of the pentamethylcyclopentadienyl (Cp*) rings in decamethylferrocene as well as a molecular rearrangement, which is accompanied by a change of the space group. Comparison of the crystal structures with the structure proposed based on NMR investigations is discussed. Rotational disorder of Cp* rings is seen in some metallocenium charge-transfer salts [11], and correlation of the order–disorder with phase transitions is important also from the viewpoint of physical properties [12].

2. Results and discussion

2.1. Crystal structures of decamethylferrocene–acenaphthenequinone

Crystallographic parameters at 193 and 293 K are listed in Table 1. The crystal system is orthorhombic in both phases, while the space group changes from *Pnma* in the LT phase to *Cmcm* in the RT phase. The unit cells are almost the same ($Z = 4$), with a slight reduction of the volume at low temperature.

The molecular structures of the donors at each temperature are shown in Fig. 2. In the LT phase, the donor exhibits a staggered conformation (Fig. 2a), with the C_5 axis located on the mirror plane and half of the molecule crystallographically independent. In the RT phase, a rotational disorder was observed (Fig. 2b). The Cp* rings exhibit two-fold disorder with an occupancy ratio of 0.627:0.373.

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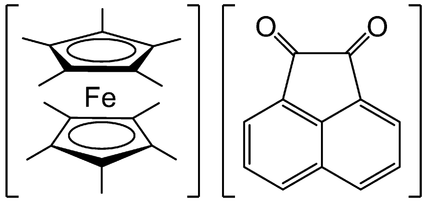

Fig. 1. Structural formula of decamethylferrocene–acenaphthenequinone complex.

The dominant component is an eclipsed conformation, and one quarter of the molecule is crystallographically independent. In both phases, the acceptor exhibits C_{2v} symmetry, and half of the molecule is crystallographically independent. The intramolecular bond lengths of the donor and the acceptor were determined to be typical values in both phases.

The packing diagram of the complex in the LT phase is shown in Fig. 3. The donors and acceptors are stacked alternately in both phases, forming a canted columnar structure. Perpendicular to the stacking direction, the donors and acceptors form layers. The structure of these layers is slightly different in each phase. In the LT phase, the acceptors are shifted with respect to each other, lying above and below the plane (Fig. 4a), while in the RT phase they lie in the plane (Fig. 4b). This applies to the donor arrangements as well.

The local structure of the complex within the column in the LT phase is shown in Fig. 5. The acceptor faces the adjacent donor at the five-membered ring portion of the Cp* group, which results in the canted stacking structure. In this phase, the donor adopts the staggered conformation, and thus the orientation of the adjacent Cp* rings above and below the acceptor are different: one is staggered and the other is eclipsed. The steric hindrance is smaller for the former interaction, where the two carbonyl groups of the acceptor are located just between three methyl groups of the donor. Between the Cp* ring of the donor and the five-membered ring of the acceptor, the centroid distances are 3.44 Å and 3.61 Å and the tilt angles 7.7° and 7.1° for the staggered and eclipsed orientations, respectively. The smaller angle for the latter, *i.e.* more parallel donor–acceptor arrangement, is consistent with the steric hindrance.

Table 1
Crystallographic parameters for decamethylferrocene–acenaphthenequinone complex.

	at 173 K	at 293 K
Empirical formula	C_{32} H_{36} Fe O_2	
Formula weight (g mol^{-1})	508.46	
Crystal system	Orthorhombic	Orthorhombic
Space group	*P* nma (No. 62)	*C* mcm (No. 63)
Crystal size (mm^3)	0.15 × 0.20 × 0.35	
a (Å)	20.390(3)	15.0066(13)
b (Å)	14.583(2)	8.6813(8)
c (Å)	8.5677(14)	20.4088(18)
Volume (Å^3)	2547.6(7)	2658.8(4)
Z	4	4
$d_{calcd.}$ (g cm^{-3})	1.3257(4)	1.270
μ (mm^{-1})	0.62	0.59
Reflections collected	13191	9066
Independent reflections	2349 (R_{int} = 3.80%)	1627 (R_{int} = 2.20%)
F(000)	1080	
R_1[a], wR_2[b] ($I > 2\sigma$(I))	$R_1 = 0.0983$, $wR_2 = 0.2260$	$R_1 = 0.0511$, $wR_2 = 0.1444$
R_1[a], wR_2[b] (all data)	$R_1 = 0.1048$, $wR_2 = 0.2293$	$R_1 = 0.0630$, $wR_2 = 0.1567$
Goodness-of-fit on F^2	1.141	1.075
Parameters	169	146
Largest diff. peak and hole (e Å^{-3})	1.52 and −1.02	0.49 and −0.34

[a] $R_1 = \Sigma \,||F_o| - |F_c|| / \Sigma \,|F_o|$.
[b] $wR_2 = [\, \Sigma\, w(F_o^2 - F_c^2)^2 / \Sigma\, w(F_o^2)^2 \,]^{1/2}$

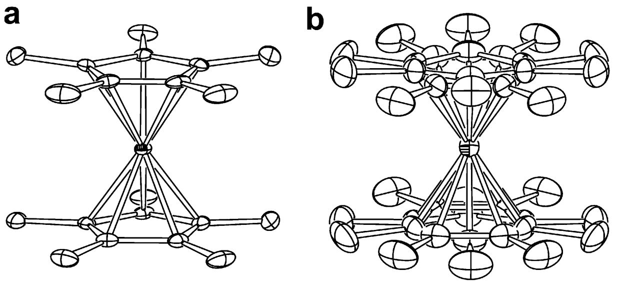

Fig. 2. ORTEP [15] drawing of the molecular structures of decamethylferrocene in the complex (a) at 193 K and (b) at 293 K. Thermal ellipsoids are shown at the probability level of 20%, respectively. Hydrogen atoms are omitted for clarity.

In the RT phase, the dominant component of the Cp* ring exhibits the staggered orientation with respect to the five-membered ring of the acceptor, with an intermolecular centroid–centroid distance between them of 3.53 Å and an angle of 10.5°. The minor component exhibits the eclipsed orientation, which is energetically unfavorable due to steric interactions. The minor component of the Cp* ring is also tilted with respect to the adjacent acceptor (angle of 3.7°), but to a lesser degree than the major component.

2.2. Comparison of the observed structure with the proposed structure based on NMR

The observed structure of decamethylferrocene–acenaphthenequinone was compared with the predicted structure based on NMR data. From the ^{1}H spin-diffusion

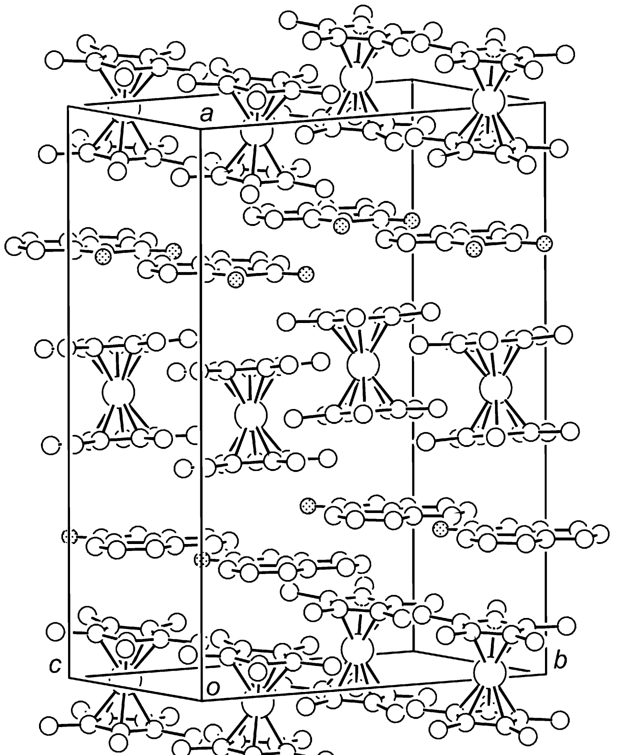

Fig. 3. Packing diagram of the complex at 193 K. Hydrogen atoms are omitted for clarity.

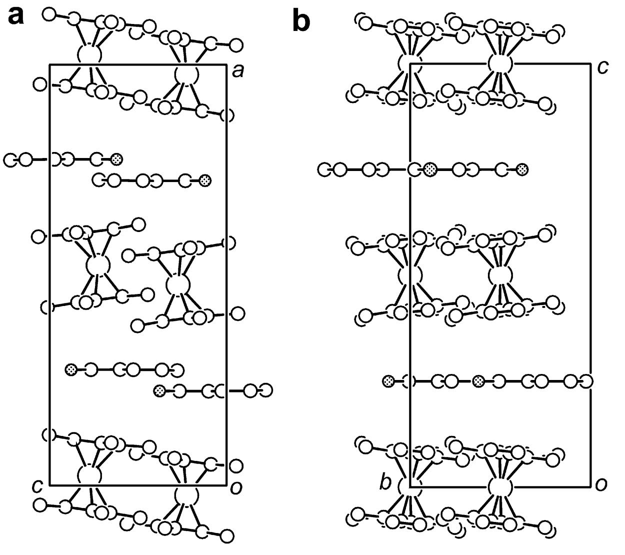

Fig. 4. Packing diagrams of the complex (a) at 193 K and (b) at 293 K. Hydrogen atoms are omitted for clarity.

rates, the shortest C(Me)$_{\mathrm{donor}}$–H$_{\mathrm{acceptor}}$ distance at −27.7 °C (LT phase) was estimated to be shorter by 0.4 Å than that at 20 °C (RT phase) [6]. The corresponding distances determined crystallographically are 3.64 Å at 193 K, as indicated in Fig. 5, and 3.88 Å at 293 K. The observed contraction was slightly less than but in general agreement with the NMR prediction. The shortening is attributed to the local geometrical change associated with the phase transition and not to thermal contraction; the stacking axis lengths are comparable at 20.390(3) Å and 20.409(2) Å in the respective phases. We noted that the corresponding distance in the RT phase is even shorter for the minor component (3.54 Å), but its effect on the NMR experiments may be small due to its smaller occupancy.

High-resolution ^{13}C and ^{1}H NMR spectroscopy suggested that inclination of the acceptor with respect to the donor occurs in the LT phase, based on the site splitting of ^{13}C signals of the acceptor [6]. In the crystal, however, the acceptor was shown to lie on the C_{2v} axis in the LT phase. We noted that the thermal ellipsoids for the acceptor were somewhat elongated, and this is possibly an averaged structure; slight disorder of the acceptor with respect to the C_{2v} axis may occur. Splitting of the methyl ^{1}H signals in the LT phase may be attributed to the ordering of the Cp* ring.

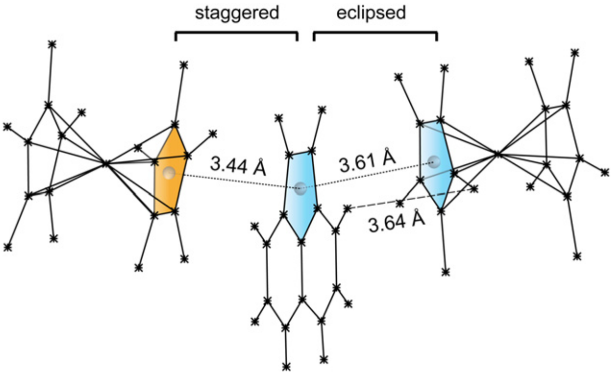

Fig. 5. Local structure of the complex within the column at 193 K. Hydrogen atoms of decamethylferrocenes are omitted. The dotted lines represent distances between the centroids of the five-membered rings. The dashed line represents the shortest C(Me)$_{\mathrm{donor}}$–H$_{\mathrm{acceptor}}$ distance.

2.3. *Phase transition entropy of decamethylferrocene–acenaphthenequinone*

The disorder as shown crystallographically is consistent with the phase transition entropy of $\Delta S = 7.4\ \mathrm{JK^{-1}mol^{-1}}$ observed by DSC measurement [6]. For the ordering of two-fold disorder with an occupancy of 0.63:0.37, the phase transition entropy is calculated to be 5.5 $\mathrm{JK^{-1}mol^{-1}}$ using the equation $\Delta S = -R\,(0.63\ \ln 0.63 + 0.37\ \ln 0.37)$, where R is the Boltzmann constant. The higher observed value is ascribable to differences in the entropy of the lattice.

3. Conclusion

The first-order phase transition in decamethylferrocene–acenaphthenequinone charge-transfer complex was characterized crystallographically. Ordering of the disordered Cp* ring was found, which also accounts for the observed entropy change. Shortening of the intermolecular distance between the donors and acceptors in the low temperature phase, which was suggested by NMR investigations, was confirmed. Rotational disorder of Cp* rings is often seen in metallocenium salts, but this charge-transfer complex is a clear case where the ordering of the disorder was shown to occur associated with a phase transition.

4. Experimental

Single crystals of decamethylferrocene–acenaphthenequinone charge-transfer complex were prepared as described previously [6]. X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer using MoKα radiation ($\lambda = 0.71073$ Å) at 293 K and 173 K. The structures were solved by the direct method and refined on F^2 by using SHELX-97 [13]. Empirical absorption correction was applied (SADABS [14]). The non-hydrogen atoms were refined anisotropically.

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Appendix A. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as a supplementary publication CCDC-765319 (173 K) and 765320 (293 K). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.jorganchem.2010.03.034

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