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STUDIES ON THE CRYSTAL STRUCTURE AND THE PLASTIC CRYSTALLINE PHASE OF TETRACHLOROFERROCENE

Kumiko SATO,* Michiko KONNO,† and Hirotoshi SANO

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukasawa, Setagaya-ku, Tokyo 158
†The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106

The structure of the ordered room-temperature phase of tetrachloroferrocene was determined by single-crystal X-ray diffraction. The structure is monoclinic, space group $P2_1$ and final $R = 0.038$ for 1129 independent reflections. The chloro groups have a 1,1',2,2' configuration with an average rotation of 2.5° of the rings from the eclipsed configuration. Mössbauer spectra exhibit a line broadening ascribed to fluctuation of the electric field gradient (EFG) caused by the orientational disorder between the x or y and z axes of molecule.

The molecules of ferrocene and its derivatives consisting of an iron atom sandwiched between two pentadienyl rings are known to exhibit various kinds of mesophase. Formylferrocene possesses a plastic crystalline phase between 43.5 °C and its melting point. We have previously reported an investigation of the structure of this plastic phase using single-crystal X-ray diffraction method and Mössbauer spectroscopy. The molecules were shown to be orthorhombic with $a = 11.9$, $b = 16.4$, $c = 7.0$ Å at 50°C in the plastic phase and to have cooperative translation along the a axis at the transition point.

1,1',2,2'-Tetrachloroferrocene and 1,1',2,2',3,3',4,4'-octachloroferrocene were found to exhibit mesophase formation by F. L. Hedberg and H. Rosenberg in 1974.[1] The nature of mesophase appears to be of either the rotationally-freed plastic crystalline state or the translationally-freed liquid crystalline state. The purpose of the studies presented here was to characterize the structure and the nature of the mesophase of 1,1',2,2'-tetrachloroferrocene. The crystal structure was determined at room temperature by X-ray diffraction. Mössbauer spectroscopy was used to measure the recoil-free fraction, the half-width and other parameters over the range from room temperature to the melting point. The thermal behaviour has been examined by using differential scanning calorimetry.

The titled compound was synthesized by following the previous literature.[1] The purification from the isomers was accomplished by repeated sublimations after carrying out a column chromatography on alumina. The purity was confirmed by checking the melting point. Mössbauer spectra were measured according to the previously outlined procedure.[2]

Yellow needle single crystals suitable for X-ray study were obtained by slow

evaporation of a hexane solution. A crystal with an approximate size of 0.30 x 0.25 x 0.20 mm, sealed in a Lindemann-glass tube, was employed for data collection. Intensity data were collected up to $2\theta = 55°$ on a four-circle diffractometer using graphite-monochromated Mo Kα radiations and $\omega - 2\theta$ scan technique. A total of 1129 independent reflections has significant intensities [$|F_o| > 3\sigma(|F_o|)$]. The structure was solved by the heavy-atom method. Refinement of the trial structure was carried out in a block-diagonal least-squares method. The calculations were carried out on a FACOM M160F computer of the Institute with a local version of UNICS.[3)]

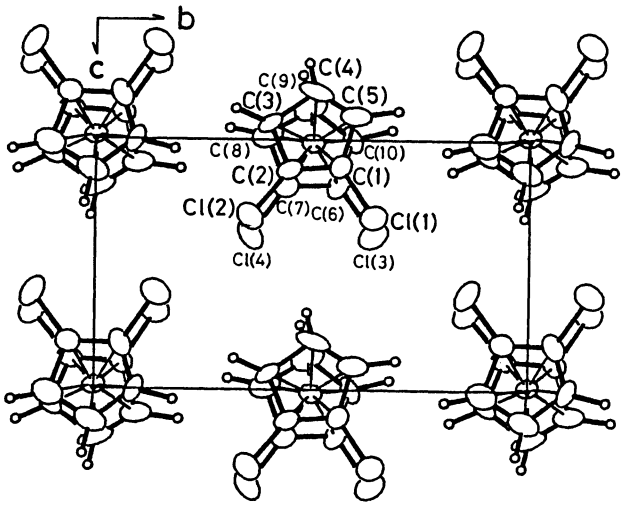

Fig. 1. A view of the molecular structure perpendicular to the bc plane, showing the eclipsed configuration.

Tetrachloroferrocene is monoclinic, space group $P2_1$, with a = 7.137(7), b = 11.974(11), c = 6.956(8) Å, β = 109.26(9)°, U = 560.8(9) Å^3, Z = 2, D_c = 1.917 g cm^{-1}. The average C - C distance in the rings of 1.430 Å is larger than the average value of 1.389 Å reported for ferrocene and is in excellent agreement with the values of 1.426 Å and 1.429 Å, found in diacetylferrocene and ferrocenedicarboxylic acid, respectively. The relative orientation of the two π-cyclopentadienyl systems in $Fe(C_5H_3Cl_2)_2$ is pictured in Fig. 1, from which it can be seen that the ferrocene moiety adopts an almost perfectly eclipsed configuration.

The average C - Cl bond length of 1.716 Å is in good agreement with the standard value for aromatic compounds, 1.70 Å,[4)] but is smaller than the C - Cl distance of 1.76 Å found in bis-[1-(2'-chloroferrocenyl)]. The π-cyclopentadienyl system defined by C(1) - C(2) - C(3) - C(4) - C(5) has a root-mean-square (rms) deviation of 0.0145 Å from the least squares plane, 0.98326X + 0.00860Y + 0.18201Z + 0.85685 = 0.0; the system C(6) - C(7) - C(8) - C(9) - C(10) has a rms deviation of 0.011 Å from the plane, -0.98141X - 0.02850Y - 0.18978Z + 2.43433 = 0.0. The cyclopentadienyl (Cp) rings are planar and nearly in parallel, the angle between the planes being 1°3'. The interannular distances are tabulated in Table 1. Two of the closest interannular distances are C(5) - C(10) of 3.258 Å and C(4) - C(9) of 3.284 Å. Both the Cl-Cl of interannular distances are shorter than the sum of the van der Waals radii, 3.8 Å. The steric repulsion between the interannular chloro groups may explain the slight tilt of the Cp ring.

Table 1. Interannular distances/ Å

C(1) - C(6)	3.296(12)
C(2) - C(7)	3.305(12)
C(3) - C(8)	3.315(14)
C(4) - C(9)	3.284(12)
C(5) - C(10)	3.258(14)
Cl(1) - Cl(3)	3.532(4)
Cl(2) - Cl(4)	3.466(4)

Figure 1 shows a view of the molecular structure perpendicular to the bc plane, in such a way that roughly spherical molecules are most closely packed in a crystal and that the molecules are separated by normal van der Waals distances without unusual intermolecular interactions.

Mössbauer spectra have been measured in the range from room temperature to the melting

point. The values of isomer shift and quadrupole splitting at room temperature (0.44 mm s^{-1} with respect to metallic iron and 2.50 mm s^{-1}, respectively), exhibit the typical values for ferrocene derivatives so far reported. Tetrachloroferrocene undergoes phase transitions from an ordered phase to an unknown disordered phase, PC(I), at 118 °C and is followed by a transition to a PC(II) phase at 133 °C. Figure 2 represents Mössbauer spectra of the ordered phase measured at room temperature and the disordered phases, PC(I) and PC(II). Although there is no serious change in the Mössbauer parameters, a broadening of the absorption lines is observed at high temperatures. Figure 3 gives the temperature dependence of the spectral line-width.

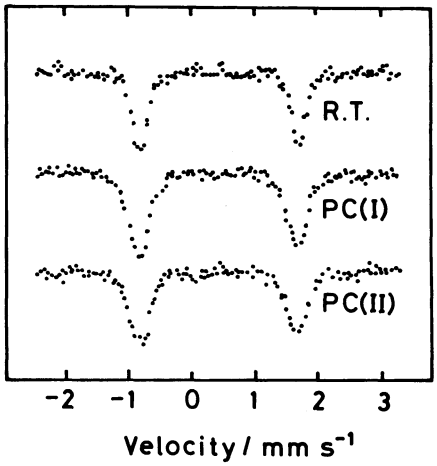

Fig. 2. Temperature dependence of Mössbauer spectra of tetrachloroferrocene.

In general, the decreasing line-width of spectral peaks with increasing temperature is ascribed to the decreasing recoil-free fraction, but for this compound it is found that the line-width increases continuously with the increase of temperature.[5] The behavior of the line-width is interpreted by assuming an initial step of a rotational molecular motion, which is consistent with a relaxation of the EFG. Such behaviour was also observed in acetylferrocene and investigated in detail by X-ray diffraction and Mössbauer spectroscopy. A progressive broadening above room temperature was reported and ascribed to the molecular rotational phase transition.[6]

Mössbauer spectra of tetrachloroferrocene exhibit no discontinuous change at each transition point but a broadening even below the melting point. The data suggest a slow reorientation of the z axis of EFG, which is assumed to coincide with the molecular axis of this compound based on the similar values of the Mössbauer parameters to those of ferrocene. And the barrier for the reorientational motion of molecules in the plastic phase is extremely high owing to the intermolecular hindrance by the interaction with the neighbouring molecules. Figure 4 shows the temperature dependence of mean-square amplitude for iron atoms estimated from the areal intensities in Mössbauer spectra.[2] The mean-square amplitude could be measured near till the melting point. Although the monotonous increase reveals the harmonic lattice vibration from room temperature to the first transition point (T_1), the mean-square amplitude abruptly increases at T_1. As a result of thermal analysis, the entropy change at T_1 is found to be larger than that at the second transition point (T_2), indicating that the molecules acquire a number of degrees of motional freedom at T_1. There exists no discontinuity in the mean-square amplitude at T_2.

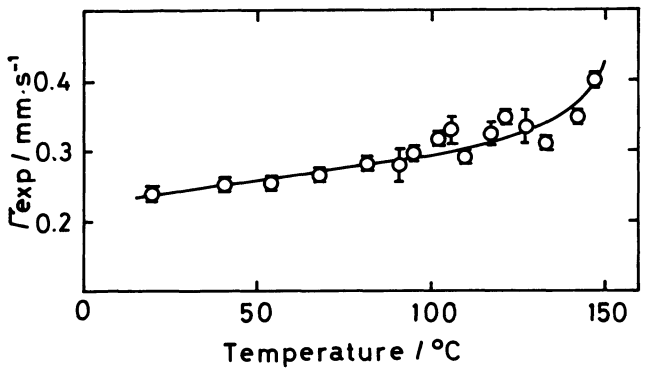

Fig. 3. Temperature dependence of the spectral half-width of tetrachloroferrocene.

It is interesting to compare the molecular motion and structure of tetrachloroferrocene with those of formylferrocene which also has a plastic crystalline phase.[7] The mean-square amplitude of formylferrocene shows a significant deviation from the harmonic lattice vibration near the transition point and abruptly increases at the transition point. However, the mean-square amplitude of tetrachloroferrocene can be detected even near the melting point, and these values are much smaller than that of formylferrocene. By assuming that the molecules of formylferrocene are compelled to cooperatively slide along the a axis at the transition point, the rather large values of mean-square amplitude obtained for formylferrocene are well explained in terms of the translational motion of the molecules. On the other hand, the molecules of tetrachloroferrocene may not need such significant translational motion to the adjacent positions for starting the molecular rotation.

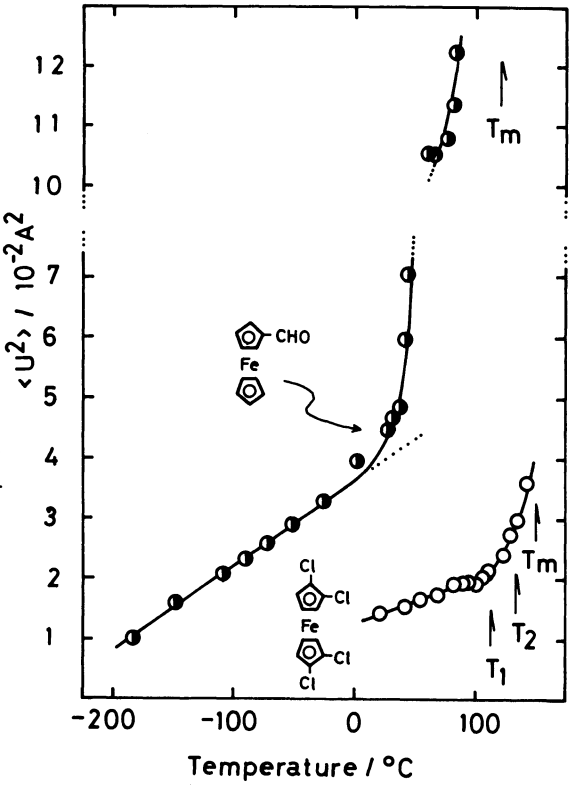

Fig. 4. Mean-square amplitude. Open circles for tetrachloroferrocene and half-filled circles for formylferrocene.

These results seem to have a good correlation with their molecular structures, i.e., the molecular structure of tetrachloroferrocene is almost spherical compared with that of formylferrocene, so that the former can easily start rather isotropic molecular rotational motion associated with a subsidiary isotropic translational motion in the plastic phase.

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