ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2020, Vol. 46, No. 1, pp. 53–57. © Pleiades Publishing, Ltd., 2020.
Russian Text © The Author(s), 2020, published in Koordinatsionnaya Khimiya, 2020, Vol. 46, No. 1, pp. 56–61.

Crystal Structure of 1,2,4,1',2',4'-Hexamethylferrocene

N. Z. Ibrahimova[a, *, **], **G. M. Jafarov**[a], **D. B. Taghiev**[a], **and I. U. Lyatifov**[a]
[a] *Institute of Catalysis and Inorganic Chemistry, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan*
**e-mail: iltifatl@mail.ru*
***e-mail: nigar-ibrahimova93@mail.ru*

Received February 12, 2019; revised March 15, 2019; accepted April 10, 2019

Abstract—The crystal structure of 1,2,4,1',2',4'-hexamethylferrocene ($\mathrm{Me_6Fc_{sym}}$) was determined by X-ray diffraction. In the $\mathrm{Me_6Fc_{sym}}$ molecule, the C_5 rings occur in the staggered conformation. The Fe–(C_5 ring center) bond length tends to increase in the series $\mathrm{Me_2Fc_{sym}}$, $\mathrm{Me_6Fc_{sym}}$, $\mathrm{Me_8Fc_{sym}}$, and $\mathrm{Me_{10}Fc_{sym}}$. The relative conformations of the vicinal Me groups in the $\mathrm{Me_6Fc_{sym}}$, $\mathrm{Me_8Fc_{sym}}$, and $\mathrm{Me_{10}Fc_{sym}}$ molecules and the pattern of variation of the ^{1}H and ^{13}C NMR signals of the Me groups in the series of polymethylferrocenes $\mathrm{Me}_n\mathrm{Fc_{sym}}$ (n = 2, 4, 6, 8, 10) compared with the methylbenzene analogues indicates that Me groups in symmetric polymethylferrocenes are not coupled, but are relatively free to rotate around the C(C_5 ring)–C(Me) bond (CIF file CCDC no. 1436882).

Keywords: 1,2,4,1',2',4'-hexamethylferrocene, steric interaction, conformation, X-ray diffraction

DOI: 10.1134/S1070328420010029

INTRODUCTION

The chemical stability and diversity of ferrocene derivatives, along with their various potential applications [1], account for intensive research of these chemical systems during the last 60 years. Our interest in the ferrocene derivatives is related to the possibility to develop reversible electrochemical reference electrodes for non-aqueous media based on polymethylferrocenes and the corresponding polymethylferricinium cations [2].

Due to the lack of stability of the ferricinium cation in some solvents and dependence of the redox potential of the ferrocene–ferricinium system on the nature of the organic solvent [3], polymethylferrocenes and the corresponding polymethylferricinium cations are currently considered as more promising systems for the fabrication of reference electrodes [2]. Therefore, we chose 1,2,4,1',2',4'-hexamethylferrocene ($\mathrm{Me_6Fc_{sym}}$) and 1,2,4,1',2',4'-hexamethylferricinium hexafluorophosphate ($\mathrm{Me_6Fc^+PF^-_{6\,sym}}$) as research objects. A ^{1}H NMR spectroscopic study of the homogeneous $\mathrm{Me_6Fc_{sym}}$–$\mathrm{Me_6Fc^+PF^-_{6\,sym}}$ system in deuteroacetone demonstrated [4, 5] that electron exchange in this system is ~3–4 times faster than that in the ferrocene–ferricinium system. Therefore, this system meets the reversibility condition, which is one of requirements imposed on reference electrodes [6] by the IUPAC.

In order to find out whether the $\mathrm{Me_6Fc_{sym}}$–$\mathrm{Me_6Fc^+PF^-_{6\,sym}}$ redox system meets other IUPAC requirements to reference electrodes and to apply the recently upgraded Marcus equation [7] to the electron exchange in this system, we studied the crystal structures of these two complexes.

This paper addresses the crystal structure details for the $\mathrm{Me_6Fc_{sym}}$ molecule.

EXPERIMENTAL

The compound $\mathrm{Me_6Fc_{sym}}$ was synthesized according to procedure described in [8]. Single crystals of $\mathrm{Me_6Fc_{sym}}$ with 0.16 × 0.13 × 0.11 mm dimensions were grown in hexane at –10°C.

X-ray diffraction study of $\mathrm{Me_6Fc_{sym}}$ was carried out on a Bruker SMART APEX-II CCD three-circle automated diffractometer with an array detector (T = 150 K, MoK_α-radiation, λ = 0.71073 Å, graphite monochromator, φ- and ω-scan modes). The absorption corrections were applied by the SADABS program [9]. The structure was solved by the direct methods and refined by full-matrix least-squares method on F^2 in the anisotropic approximation for non-hydrogen atoms. The hydrogen atom positions were calculated geometrically and included in the refinement according to the riding model with fixed isotropic parameters ($U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{equiv}}(\mathrm{C})$ for CH_3 groups and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{equiv}}(\mathrm{C})$ for all other groups). All calculations were performed using the SHELXTL software package [10]. The main experimental details and the unit cell parameters are summarized in

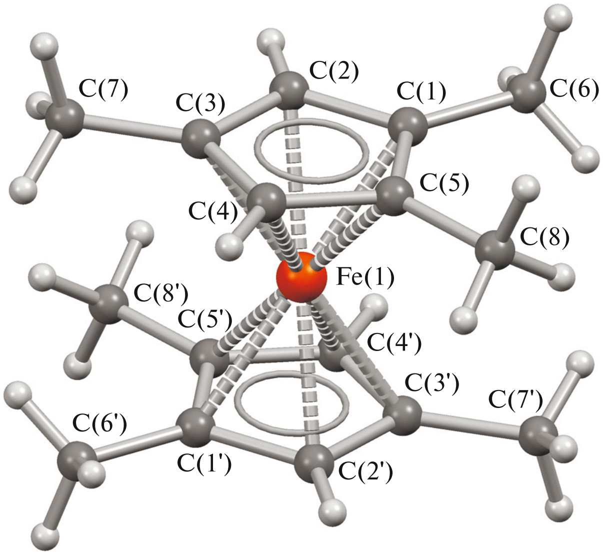

Fig. 1. General view of the Me_6Fc_{sym} molecule and carbon atom numbering.

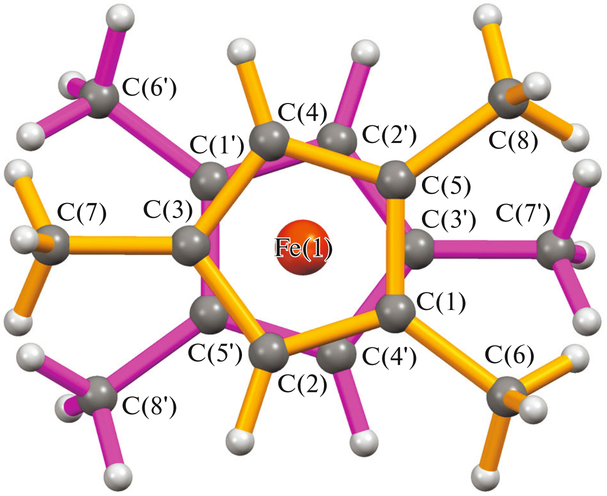

Fig. 2. Staggered conformation of the C_5 rings of the Me_6Fc_{sym} molecule.

Table 1 and selected bond lengths and bond angles are given in Table 2.

The atomic coordinates, bond lengths, bond and torsion angles, and anisotropic displacement parameters for Me_6Fc_{sym} are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1861054; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The geometry of the Me_6Fc_{sym} molecule is shown in Figs. 1 and 2. As can be seen from Fig. 2, the C_5 rings in Me_6Fc_{sym} have a staggered conformation (φ = 35.67°); the same is true for Me_8Fc_{sym} [11] and $Me_{10}Fc_{sym}$ [12]. Since in the Me_2Fc_{sym} molecule in the solid state [13, 14], the C_5 rings are in the eclipsed conformation, the conformational change in the three above-listed polymethylferrocene molecules can reasonably be attributed to steric interactions between the Me groups of different rings or to crystal packing forces.

The C_5 ring in the Me_6Fc_{sym} molecule is planar, with the greatest deviation from the plane being 0.003(5) Å. The C_5 rings are parallel. The angle through the centers of the C_5 rings and the iron atom is 180(16)°. The distance between the ring centers is 3.298 Å.

In the Me_6Fc_{sym} molecule, all C(C_5 ring)–C(C_5 ring) distances are equal to within the experimental error. Their average value of 1.422(7) Å is close to the corresponding distances in the Me_8Fc_{sym} (1.428(4) Å) [11] and $Me_{10}Fc_{sym}$ (1.419(2) Å) molecules [12]. The average C(C_5 ring)–C(Me) distance, 1.502(7) Å, corresponds to the usual C(sp^2)–C(sp^3) bond length [15]. The average Fe–C(C_5 ring) bond length, 2.045(5) Å, is also consistent with the Fe–C(C_5 ring) bond lengths in Me_8Fc_{sym} (2.054(3) [11], 2.048(6) [16]) and $Me_{10}Fc_{sym}$ (2.053(2) [17], 2.050(2) Å [12]).

A number of weak intermolecular non-covalent contacts are present in the Me_6Fc_{sym} structure. Many of them are formed between the C_5 ring (electron donor) of one molecule and a hydrogen atom (electron acceptor) of the C_5 ring of another molecule. These contacts actually connect organometallic chains into a 3D supramolecular framework, thus extending the structure in the x, y, and z directions [18–20].

Table 2 presents selected bond lengths and bond angles for the Me_6Fc_{sym} molecule, in which the Me groups deviate from the C_5 ring plane (away from the Fe atom). The single Me group deviates by 2.49° (C(7)) and the vicinal Me groups deviate by 0.87° (C(8)) and 1.64° (C(6)). A deviation of Me groups from the C_5 ring plane (away from the Fe atom) in methyl-substituted ferrocene molecules was found for the first time in [11] for the crystal structures of Me_8Fc_{sym} and $Me_{10}Fc_{sym}$, which were studied in order to elucidate the cause for the additive upfield shift of the resonance signals of Me group carbon in the ^{13}C NMR spectra of Me_nFc_{sym} (n = 2, 4, 6, 8, 10) [21]. Despite the fact that the shortest nonvalence C···C contacts of the Me groups of different rings (3.79–3.85 Å) were shorter than twice the van der Waals radius of the Me group (4 Å), the authors did not attribute the Me group deviation from the C_5 ring plane [11] to the steric interactions between the Me groups of different C_5 rings, since a similar Me group deviation was observed in $Me_5C_5Fe(CO)_2SO_2CH_2$–CH=CH–

Table 1. Crystallographic data and X-ray experiment and structure refinement details for Me_6Fc_{sym}

Parameter	Value
M	270.18
System	Monoclinic
Space group	$P2_1/c$
Unit cell parameters:	
a, Å	8.685(6)
b, Å	10.871(7)
c, Å	7.513(5)
β, deg	109.894(14)
V, Å^3	667.1(7)
Z	2
ρ(calcd.), g/cm^3	1.345
μ, mm^{-1}	1.106
F(000)	288
Crystal size, mm	0.16 × 0.13 × 0.11
θ Range, deg	3.120–24.964
Ranges of indices h, k, l	$-10 \le h \le 8$, $-12 \le k \le 12$, $-8 \le l \le 8$
Total number of reflections	4197
Number of unique reflections (R_{int})	1166 (0.1150)
GOOF for F^2	1.022
R-factor ($I > 2\sigma(I)$)	$R_1 = 0.0579$, $wR_2 = 0.0893$
R-factor (all reflections)	$R_1 = 0.1374$, $wR_2 = 0.1155$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.370/–0.487

Table 2. Selected bond lengths and bond angles in the Me_6Fc_{sym} molecule

Bond	d, Å	Bond	d, Å	Angle	ω, deg
Fe(1)–C(4)	2.037(5)	C(1)–C(5)	1.420(7)	C(5)C(1)C(2)	107.8(4)
Fe(1)–C(2)	2.043(5)	C(1)–C(2)	1.425(7)	C(1)C(2)C(3)	108.7(5)
Fe(1)–C(1)	2.045(5)	C(2)–C(3)	1.430(7)	C(4)C(3)C(2)	106.5(5)
Fe(1)–C(5)	2.049(5)	C(3)–C(4)	1.416(7)	C(3)C(4)C(5)	109.6(5)
Fe(1)–C(3)	2.051(5)	C(4)–C(5)	1.420(6)	C(1)C(5)C(4)	107.5(5)
Average	2.045(5)	Average	1.422(7)		
C(1)–C(6)	1.504(7)			C(5)C(1)C(6)	126.8(5)
C(3)–C(7)	1.499(7)			C(2)C(1)C(6)	125.4(5)
C(5)–C(8)	1.503(6)			C(1)C(5)C(8)	126.2(5)
Average	1.502(7)			C(4)C(5)C(8)	126.3(5)

Table 3. $^1H(CH_3)$ and $^{13}C(CH_3)$ NMR chemical shifts for the methyl groups (in CS_2 and CH_2Cl_2, respectively) in the symmetrical polymethylferrocenes Me_nFc_{sym} (n = 2, 4, 6, 8, 10)* referred to TMS

Me_nFc_{sym}	n				
	2	4	6	8	10
$^1H(CH_3)$	1.92	1.88	1.79(1) 1.76(2)	1.72 1.66	1.61
$^{13}C(CH_3)$	14.32	14.19	13.67(1) 11.85	11.59 9.64	9.48

* The numerals in parentheses are the numbers of methyl groups.

C_6H_5 [22], where no second methyl-substituted ring is present [11].

In the subsequent studies of the ^{13}C NMR spectra of unsymmetrical polymethylferrocenes, the above-noted steric interactions between the Me groups located in different rings of symmetrical polymethylferrocenes were revealed and estimated as ~0.4–0.5 ppm, which is approximately 3 times lower than the steric interaction between the vicinal Me groups (~1.5 ppm) [8, 23].

The Me group deviation from the Fe atom of $Me_{10}Fc_{sym}$ was attributed [11, 12] only to the steric interaction between vicinal Me groups located in the same C_5 ring.

In polymethylferrocene molecules, the non-valence H···H contacts of vicinal Me groups are the shortest among all H···H contacts. Indeed, the H···H contacts are 2.38 Å in Me_6Fc_{sym}; 2.23 and 2.26 Å in Me_8Fc_{sym} [11]; and, on average, 2.4 Å in $Me_{10}Fc_{sym}$ [11, 12]. If the Me group deviation from the Fe atom is due only to the interaction of vicinal Me groups within the same ring, some of the methyl groups in polymethylferrocenes would be expected to deviate from the ring plane towards the iron atom. In the fully substituted benzene-derived Me_6C_6 molecule, the steric overcrowding of vicinal methyl groups is resolved by alternating deviation of the methyl groups up and down from the benzene ring plane [24, 25] and concerted (coupled) rotation of the methyl groups around the $C(C_6)$–C(Me) bond [26, 27].

In the homologous series of polymethylferrocenes, unlike that of methylbenzenes, the $Me_mC_5H_{5-m}M$ moiety bonded to the considered methyl-substituted C_5 ring precludes the deviation of the methyl groups from the C_5 ring plane in both directions, that is, also towards the Fe atom. Also, because of the large angle (72°) between the vicinal Me groups of the Me_5C_5 ring (in comparison with the corresponding angle of 60° in Me_6C_6), the steric interaction between them is weaker than that in Me_6C_6. Under the action of these two factors, the successively increasing steric strain of the methylferrocene series, is not resolved in the $Me_{10}Fc_{sym}$ complex as in Me_6C_6, but is retained. All Me groups deviate from the C_5-ring plane in the same direction (away from Fe), and the vicinal Me groups are not in the coupled state (in 2 : 1 or 1 : 2 conformation) but are in the 2 : 2 conformation. Indeed, the 2 : 2 (or nearly 2 : 2) conformation is observed for vicinal Me groups in Me_6Fc, all Me groups in Me_8Fc_{sym} [11], and six out of ten Me groups in $Me_{10}Fc_{sym}$ [12].

The different structural consequences of steric overcrowding in the methyl homologues of ferrocene and benzene also account for the distinctive feature of their ^1H and ^{13}C NMR spectra [21, 27]. Indeed, the monotonically increasing steric interaction of vicinal Me groups in the series Me_2Fc_{sym}, 1,3,1',3'-Me_4Fc_{sym}, Me_6Fc_{sym}, Me_8Fc_{sym}, and $Me_{10}Fc_{sym}$ is manifested as regular and additive upfield shifts of the ^1H and ^{13}C NMR signals of the Me groups (Table 3).

In the series of methyl-, 1,2-dimethyl-, 1,3,5-trimethyl-, 1,2,4,5-tetramethyl-, pentamethyl-, and hexamethylbenzenes, the ^1H and ^{13}C NMR signals of the Me groups also regularly shift upfield in the additive manner up to Me_5C_6H inclusive [27]. On going from pentamethylbenzene to hexamethylbenzene, this trend in the variation of ^1H and ^{13}C NMR chemical shifts is broken and the ^1H and ^{13}C NMR signals of the Me groups shift downfield, indicating weakening of the steric interaction between the vicinal Me groups in the Me_6C_6 molecule. According to [24, 25], weakening of the steric interaction in Me_6C_6 is due to the alternating up and down deviation from the benzene ring plane and concerted rotation [26, 27]. Neither of these two structural changes takes place in symmetrical polymethylferrocenes. Therefore, the cause for the deviation of the Me groups from the C_5 ring plane away from the Fe atom in polymethylferrocenes is still an open question.

Comparison of the Fe–(C_5 ring center) bond length in Me_6Fc_{sym} (1.649(5) Å) with those in the complexes Me_2Fc_{sym} (1.647 [28], 1.6447(10) and 1.6487(10) [13], 1.649(6) [14]), Me_8Fc_{sym} (1.653 [16], 1.655(8) [11]) and $Me_{10}Fc_{sym}$ (1.6568(8) [11], 1.651 Å [28]) suggests that the Fe–(C_5 ring center) bond generally tends to elongate along the homologous series. Although this elongation over the series of methyl-substituted ferrocene homologues is within 2–3σ, this is in line with the steric interaction between the Me groups located in different rings manifested in the ^{13}C NMR spectra of Me$_n$Fc$_{sym}$ as ~0.4–0.5 ppm upfield shifts [8, 23].

Thus, the considered crystal structure details of Me$_6$Fc$_{sym}$ molecules can mainly be explained by steric interactions of the vicinal methyl group, both with one another (within one Me$_m$C$_5$H$_{5-m}$ ligand) and with the Me groups of another Me$_m$C$_5$H$_{5-m}$ ligand of the molecule.

A comparative analysis of X-ray diffraction data for the crystal structures of Me$_6$Fc$_{sym}$ and its 1,2,4,1',2',4'-hexamethylferricinium cation (in the form of symmetrical hexamethylferricinium hexafluorophosphate) will be presented in the next publication.

REFERENCES

1. Astruc, D., *Eur. J. Inorg. Chem.*, 2017, vol. 1, p. 6.
2. Bartlett, P.N. and Branch, J., *Electroanal. Chem. Interfacial Electrochem.*, 2016, vol. 780, p. 282.
3. Nielson, R.M., McManis, G.E., Safford, L.K., and Weaver, M.J., *J. Phys. Chem.*, 1989, vol. 93, p. 2152.
4. Ibrahimova, N.Z., Mamedov, I.G., Jafarov, G.M., et al., *Chem. Problems*, 2017, no 1, p. 51.
5. Ibrahimova, N.Z., Jafarov, G.M., Taghiyev, D.B., and Lyatifov, I.U., *Chem. Problems*, 2019, no. 2, p. 310.
6. Gritzner, G. and Kuta, J., *Pure Appl. Chem.*, 1984, vol. 56, no. 4, p. 461.
7. Li Xiang-Yuan, *Intern. J. Quantum Chem*, 2015, vol. 115, p. 700.
8. Lyatifov, I.R., *Doctoral Thesis* (*Chemistry*), Leningrad: Leningrad Technol. Inst., 1990.
9. Sheldrick, G.M., *SADABS. Version 2.03, Bruker/Siemens Area Detector Absorption Correction Program*, Madison: Bruker AXS Inc., 2003.
10. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*: 2015, vol. 71, p. 3.
11. Struchkov, Yu.T., Andrianov, V.G., Sal'nikova, T.N., et al., *J. Organomet. Chem.*, 1978, vol. 145, p. 213.
12. Freyberg, D.P., Robbins, J.L., Raymond, K.N., and Smart, J.C., *J. Am. Chem. Soc.*, 1979, vol. 101, p. 892.
13. Lousada, C.M., Pinto, S.S., Canongia Lopes, J.N., et al., *J. Phys. Chem. A*, 2008, vol. 112, p. 2977.
14. Foucher, D.A., Honeyman, Ch.H., Lough, A.J., et al., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, vol. 51, p. 1795.
15. *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959*, Sutton, L.E., Ed., London: Chemical Society, 1965.
16. Schmitz, D., Fleischhauer, J., Meier, U., et al., *J. Organomet. Chem.*, 1981, vol. 205, p. 381.
17. Arrais, A., Diana, E., Gobetto, R., et al., *Eur. J. Inorg. Chem.*, 2003, p. 1186.
18. Gurbanov, A.V., Mahmoudi, G., Guedes da Silva, M.F.C., et al., *Inorg. Chim. Acta*, 2018, vol. 471, p. 130.
19. Hazra, S., Martins, N.M.R., Mahmudov, K.T., et al., *J. Organomet. Chem.*, 2018, vol. 867, p. 193.
20. Kvyatkovskaya, E.A., Zaytsev, V.P., Zubkov, F.I., et al., *Acta Crystallogr. Sect. E: Crystallogr. Commun.*, 2017, vol. 73, no. 4, p. 515.
21. Materikova, R.B., Babin, V.N., Lyatifov, I.R., et al., *J. Organomet. Chem.*, 1977, vol. 142, p. 81.
22. Churchill, M.R. and Wormald, J., *Inorg. Chem.*, 1971, vol. 10, no. 3, p. 572.
23. Mamedov, I.G., Orudzheva, A.B., Kalimov, R.M., et al., *Vestn. BGU,* 2013, no. 3, p. 5.
24. Stride, J., *Acta Crystallogr, Sect. B: Struct. Sci.*, 2005, vol. 61, p. 200.
25. Le Maguéres, P., Lindeman, S.V., and Kochi, J.K., *Organometallics*, 2001, vol. 20, p. 115.
26. Wolfoenden, W.R. and Grant, D.M., *J. Am. Chem. Soc.*, 1966, vol. 88, p. 1496.
27. Cheney, B.V. and Grant, D.M., *J. Am. Chem. Soc.*, 1967, vol. 89, p. 5319.
28. Makal, A.M., Plazuk, D., Zakrzewski, J., et al., *Inorg. Chem.*, 2010, vol. 49, p. 4046.

Translated by Z. Svitanko