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FEATURES OF CRYSTAL STRUCTURES OF SYMMETRIC  
POLYMETHYLFERROCENES

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**Abstract:** Features of the crystal structure of the sym.  $Me_6Fc$  molecule are compared with features of crystal structures of sym.  $Me_nFc$  ( $n = 2, 8, 10$ ) and nonsymmetrical pentamethylferrocene  $(Me_5C_5)FeC_5H_5$ . The intra-ring and off-ring valence angles of the  $1,2,4-Me_3C_5H_2$  ligand in the complex sym.  $Me_6Fc$  are interpreted by the steric interactions of the vicinal methyl groups with each other, as well as with a single Me-group of the second  $1,2,4-Me_3C_5H_2$  ligand of the molecule. It found that in spite of the fact that changes in the Fe-( $C_5$  ring center) bond length in a series sym.  $Me_nFc$  ( $n = 2, 6, 8, 10$ ) correspond to an increase in steric effects between methyl groups of different rings, there is also an electronic effect of methyl groups which does not emanate from superior steric effects in the sym. polymethylferrocenes. (CIF file CCDC No. 1436882).

**Keywords:**  $1,2,4,1',2',4'$ -hexamethylferrocene, steric effect, electronic effect

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### Introduction

The feasible applied aspects [1] of ferrocene derivatives and the features of their electronic structure [2, 3] make these compounds one of the most intensively studied chemical systems in the last half a century. Our interest in ferrocene derivatives is related to the possibility of developing reversible electrochemical reference electrodes based on polymethylferrocene and polymethylferricenium cations in non-aqueous medium [4], as well as to the specialty of their crystal and electronic structures [5-8].

One of the factors affecting the energetic characteristics of the electron transfer reaction in a system of polymethylferrocene/polymethylferricenium cation mentioned in the work on reference electrodes are changes in the inner-sphere reorganization energy in the course

of electron transfer. This composite was directly determined by magnitude of changes in the bond length of the iron atom-center of the cyclopentadienyl ring Fe-( $C_5$  ring center) during the oxidation of the polymethylferrocene molecule. Therefore, first at all, we focused on the influence of steric and electronic effects of the substituents on the bond length Fe-( $C_5$  ring center) in initial sym.  $Me_6Fc$  molecule.

In the previous article [7], we revealed specific features of the crystal structure of  $1,2,4,1',2',4'$ -hexamethylferrocene molecule (sym.  $Me_6Fc$ ). In this article, these structural features are compared with appropriate parameters of other members of a homologous series of symmetric polymethylferrocene and non-symmetric pentamethylferrocene  $(Me_5C_5)FeC_5H_5$  [9].

### Experimental part

$Me_6Fc$  was synthesized in accordance with the procedure described in [10].

0.16x0.13x0.11 mm of  $Me_6Fc$  monocrystals were grown in hexane at a temperature of 10°C.

X-ray structural analysis of  $Me_6Fc$  was carried out on an automatic three-circle diffractometer with a two-coordinate detector - Bruker SMART APEX-II CCD ( $T = 150$  K,  $\lambda MoK_{\alpha}$ -radiation,  $\lambda = 0.71073$  Å, graphite

monochromator, graphite monochromator,  $\varphi$  and  $\omega$ -scanning). For the obtained data, calculation of X-ray absorption was made using the SADABS program [11]. The structure was deciphered by direct methods and refined by full-matrix least square method (LSM) referring to  $F^2$  with approach to anisotropic approximation for non-hydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and included in the precision

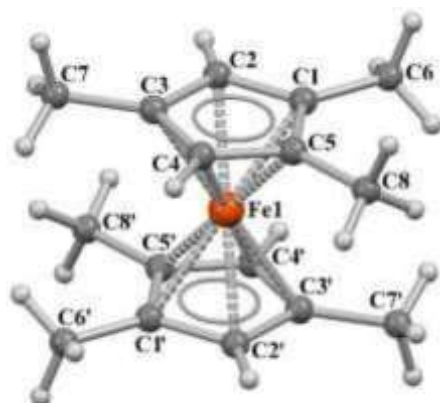
according to the "rider model" with fixed isotropic displacement parameters ( $U_{iso}(H) = 1.5U_{eq}(C)$  for  $CH_3$ -groups and  $U_{iso}(H) = 1.2U_{eq}(C)$  for all other groups). All calculations were performed using the SHELXTL software package [12].

Tables of atom coordinates, bond lengths, valence and torsion angles, and anisotropic displacement parameters (ADPs) for sym.  $Me_6Fc$  were deposited in the Cambridge bank with structural data: CCDC 1861054.

### Results and discussion

The geometry of sym.  $Me_6Fc$  molecule was shown in Fig. 1; and Table 1 shows the lengths of the Fe-(C<sub>5</sub> ring center) in a series of

sym.  $Me_nFc$  polymethylferrocenes ( $n = 2, 6, 8, 10$ ).



**Fig. 1.** General view of sym.  $Me_6Fc$  molecule and scheme of numbering the carbon atoms

**Table 1.** Changes in bond length of Fe-(C<sub>5</sub> ring center) in a series of  $Me_nFc$  ( $n = 2, 6, 8, 10$ )

$Me_nFc$	$n = 2$	$n = 6$	$n = 8$	$n = 10$
<b>Fe-C(<math>Me_mC_5H_{5-m}</math>), Å</b>	1.647 (100 K) [13] 1.649 (173 K) [6]	1.649 (150 K)	1.653 (100 K) [14] 1.655 (298 K) [15]	1.6568 (296 K) [15] 1.651 (90 K) [13]

\*— values in parenthesis are temperatures at which the X-ray structural analysis of monocrystal was carried out.

As can be seen from Table 1, the Fe-C distance ( $Me_3C_5H_2$ ) (1.649 Å) in the symmetric  $Me_6Fc$  molecule is situated between respective distances in the sym.  $Me_2Fc$  (1.647 Å) [13] and sym.  $Me_8Fc$  (1.653 Å) [14] and (1.655 Å) [15]. This means that in symmetric methyl homologues of ferrocene with increasing the number of Me-groups, the distance of Fe-(C<sub>5</sub> ring center) tends to increase (Table 1), which does not correspond to the electron-donor

properties of Me-substituents.

Most likely, this discrepancy must be related to the steric effect of two substituted  $Me_mC_5H_{5-m}$  rings ( $m$  - is the number of methyl groups in the ligand) in sym.  $Me_nFc$  molecules. Mutual electrostatic repulsion of the substituted  $Me_mC_5H_{5-m}$  rings, preventing the shortening of Fe-(C<sub>5</sub> ring center) bond, veiled the electronic properties of Me-groups.

However, during configuring the structure

of nonsymmetric polymethylferrocene, in particular, of nonsymmetric pentamethylferrocene ( $\text{Me}_5\text{C}_5$ ) $\text{FeC}_5\text{H}_5$ , due to the absence (or decrease) of the aforementioned steric repulsion, the electron-donor properties of the Me-groups are clearly appeared: the distance between iron and the substituted ring shortens (1.640 Å [9] and 1.642 Å [16]), but the distance between iron and unsubstituted ring, on the contrary, gets longer (1.653 Å [9], 1.658 Å [16]), (compared with ferrocene (1.654 Å) [17]).

The elongation of the Fe-C<sub>5</sub>H<sub>5</sub> bond (as

compared with ferrocene) is most likely due to the antibonding effect of the Fe-C<sub>5</sub>Me<sub>5</sub> bond, on which the electron density is composed of five methyl groups.

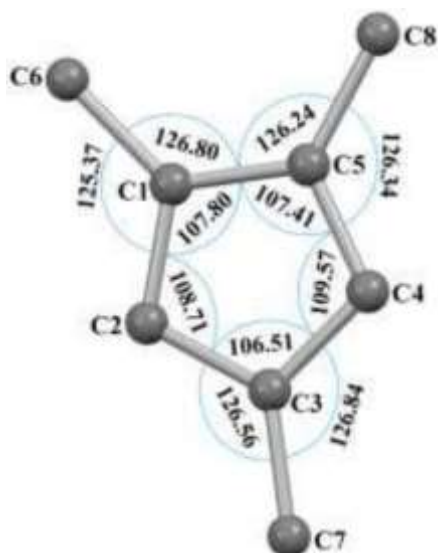
In changes in the bond lengths between Fe atom and carbon atoms of the C<sub>5</sub>-ring of the molecule sym. Me<sub>6</sub>Fc, the following tendency is observed: the distance from the Fe atom to the ring substituted carbon atoms (Fe-C<sub>substituted</sub>) is longer than distance from this Fe to the unsubstituted carbon atoms (Table 2):

**Table 2.** Bond length between Fe atom and carbon atoms of the C<sub>5</sub>-ring of the sym. Me<sub>6</sub>Fc molecule

Fe-C <sub>substituted</sub> (C <sub>5</sub> -ring)	Å	FeC <sub>unsubstituted</sub> (C <sub>5</sub> -ring)	Å
Fe-C(1)	2.045	Fe-C(2)	2.043
Fe-C(3)	2.051	Fe-C(4)	2.037
Fe-C(5)	2.049		

A similar picture is observed in the crystal structures of sym. Me<sub>8</sub>Fc [14, 15], Me<sub>2</sub>Fc [6] and in triple-decker sandwich complexes containing tetramethyl-cyclopentadienyl ring [18]. It is accounted that one of the reasons of elongation of these bonds may be the deviation of the Me- group in the plane of the C<sub>5</sub>-ring away from the Fe atom [18].

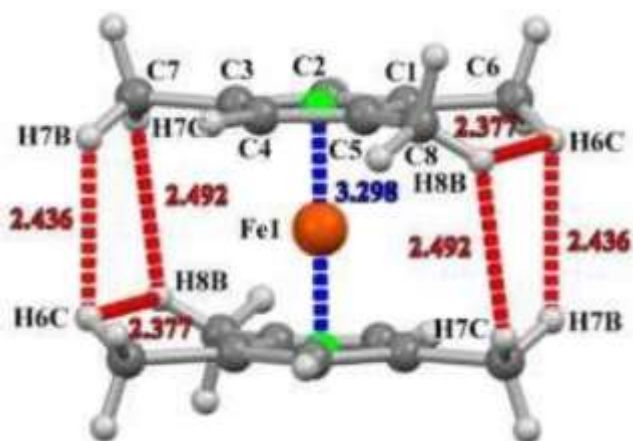
The nature of changes in the intra- and inter-ring valence angles of the 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligand allows us to identify these changes as steric effects of the vicinal methyl groups with each other, as well as with the single Me-group of the second 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligand bonding with an iron atom.



**Fig. 2.** Intra- and inter-ring valence angles of 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligand in sym. Me<sub>6</sub>Fc molecule

Fig. 2 shows that the steric effect of vicinal Me-groups (nearest H ... H contacts in the crystal are 2.377 Å) leads to a slight increase in the angles  $\angle C1C5C8$  ( $126.2^\circ$ ) and  $\angle C5C1C6$  ( $126.8^\circ$ ) from the ideal value ( $126^\circ$ ).

Differences in the values of these angles ( $126.2^\circ$  and  $126.8^\circ$ ), as well as of the adjacent  $\angle C4C5C8$  ( $126.3^\circ$ ) and  $\angle C2C1C6$  ( $125.4^\circ$ ) angles indicate that either the steric effect of the H8A atom (Me at C5) with the H4 atom (hydrogen at C4) is stronger than the steric effect of the H6C atom (Me at C1) with the H2 atom (hydrogen at C2), or these differences are due to the interaction of vicinal Me-groups with a single Me-group located in the second C<sub>5</sub>-ring



of the molecule. (The capital letters A, B, and C are used to distinguish the hydrogen atoms of the mentioned methyl group. Hydrogen A is located almost perpendicular to the plane of the C<sub>5</sub>-ring and away from the iron atom). However, the distances H8A (Me at C5) ... H4 and H6C (Me at C1) ... H2 are greater than the sum of the van der Waals radii of the hydrogen atom. Therefore, the observed difference between two pairs of adjacent angles is most likely explained by a stronger steric effect between H6C and H7B atoms (2.436 Å), which opening the  $\angle C5C1C6$  ( $126.8^\circ$ ) angle, leads to a decrease in the  $\angle C2C1C6$  ( $125.4^\circ$ ) angle.

**Fig. 3.** H...H unbonded contacts between vicinal Me-groups of the 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligand, as well as between vicinal Me-groups and the single Me group of different 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligands of the Me<sub>6</sub>Fc molecule

The steric effect between vicinal Me-groups within C<sub>5</sub>-ring, as well as their interaction with a single Me-group of the second C<sub>5</sub>-ring, in turn, led the decrease of intra-ring angles  $\angle C4C5C1$  ( $107.8^\circ$ ),  $\angle C2C1C5$  ( $107.5^\circ$ ) and  $\angle C2C3C4$  ( $106.5^\circ$ ), as compared with their ideal value ( $108^\circ$ ).

Since, the C<sub>5</sub>-ring of the Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligand has a flat structure; a slight decrease in the angles ( $\angle C4C5C1$  and  $\angle C2C1C5$ ) is also rounded on intra-ring angles at the unsubstituted carbon atoms of the ring -  $\angle C5C4C3$  and  $\angle C1C2C3$ : the latter increased ( $108.7$  and  $109.4^\circ$ ) relative to the ideal value ( $108^\circ$ ).

The unbounded lengths between the Me-groups of different C<sub>5</sub>-rings (Fig. 3) also explain differences between deviating angles of Me-groups from the plane of the C<sub>5</sub>-ring. So, from two vicinal Me-groups (C6 and C8), the group (C6) that has the smallest unbounded

contact with a single Me-group of the other C<sub>5</sub> ring (2.436 Å between the H6C and H7B atoms) deviates more from the plane of the C<sub>5</sub>-ring ( $1.64^\circ$ ) than the Me group (C8), which has a slightly elongated unbounded contact (2.492 Å between the H8B and H7C atoms) ( $0.87^\circ$ ). In turn, a single Me-group (C7), spatially interacting with both vicinal Me-groups (C6 and C8) of the other C<sub>5</sub>-ring, deviates even more from the plane of the C<sub>5</sub>-ring ( $2.49^\circ$ ) than each of the vicinal Me-groups.

Thus, the features of the crystal structure of the sym-Me<sub>6</sub>Fc molecule determined in limit of the Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligand can be interpreted by steric effects between vicinal methyl groups, and also between latter and Me-groups located in another Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligand. The tendency of change the bond length of Fe-(C<sub>5</sub> ring center) in the series of sym. Me<sub>n</sub>Fc ( $n = 2,6,8,10$ ) also corresponds to an increase in steric effect between methyl groups of different rings.

However, a comparison of these results with respect to bond lengths of Fe-(C<sub>5</sub>H<sub>5</sub> ring center) and Fe-(C<sub>5</sub>Me<sub>5</sub> ring center) in the nonsymmetric pentamethylferrocene indicates that a change in the bond lengths of the Fe-(C<sub>5</sub>

ring center) in sym. polymethylferrocenes also occurs under the influence of electron-donor properties of methyl groups, which do not appear in symmetric polymethylferrocenes due to the predominance of steric effects.

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### SİMMETRİK POLİMETİL FERROSEN LƏRİN KRİSTAL QURULUŞLARININ XÜSUSİYYƏTLƏRİ

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*Sim. Me<sub>6</sub>Fc* molekulunun kristal quruluşunun xüsusiyyətləri sim. polimetilferrosenlərin Me<sub>n</sub>Fc (n = 2, 8, 10) və qeyri-sim. pentametilferrosenin (Me<sub>5</sub>C<sub>5</sub>)FeC<sub>5</sub>H<sub>5</sub> kristal quruluşlarının xüsusiyyətləri ilə müqayisə edilir. Sim. Me<sub>6</sub>Fc kompleksində 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligandının daxili və xarici valent bucaqları molekulda visinal metil qruplarının həm bir-biri ilə, həm də ikinci 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> ligandında yerləşmiş tək Me qrupu ilə fəza qarşılıqlı təsiri ilə izah olunur. Göstərilir ki, sim. Me<sub>n</sub>Fc (n = 2, 6, 8, 10) sırasında metil qruplarının fəza qarşılıqlı təsiri onların elektron qarşılıqlı təsirindən güclü olduğu üçün Fe-C(Me<sub>m</sub>C<sub>5</sub>H<sub>5-m</sub>) rabitəsinin uzunluğunda müşahidə olunan dəyişiklik metil qruplarının halqalar arasındakı fəza qarşılıqlı təsirinin artması ilə əlaqədardır. (CIF file CCDC No. 1436882).

**Äçar sözlər:** 1,2,4,1',2',4'-heksametilferrosen, fəza qarşılıqlı təsir, elektron qarşılıqlı təsir

### ОСОБЕННОСТИ КРИСТАЛЛИЧЕСКИХ СТРУКТУР СИМЕТРИЧНЫХ ПОЛИМЕТИЛФЕРРОЦЕНОВ

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Особенности кристаллической структуры молекулы сим. MeF<sub>6</sub> сравниваются с особенностями кристаллических структур сим. Me<sub>n</sub>F<sub>6</sub> (n=2,8,10) и несим. пентаметилферроцена (Me<sub>5</sub>C<sub>5</sub>)FeC<sub>5</sub>H<sub>5</sub>. Внутри- и внекольцевые валентные углы 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> лиганда в комплексе сим. MeF<sub>6</sub> интерпретированы стерическими взаимодействиями вицинальных метильных групп как между собой, так и с одиночной Me группой второго 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub> лиганда молекулы. Показано, что, хотя изменение длины связи Fe-C(Me<sub>m</sub>C<sub>5</sub>H<sub>5-m</sub>) в ряду сим. Me<sub>n</sub>F<sub>6</sub> (n=2,6,8,10) и соответствует росту стерического взаимодействия между метильными группами разных колец, однако, в симметричных полиметилферроценах имеет место и электронное влияние метильных групп, которое не проявляется из-за преобладания стерических взаимодействий. (CIF file CCDC No. 1436882).

**Ключевые слова:** 1,2,4,1',2',4'-гексаметилферроцен, стерическое взаимодействие, электронное взаимодействие