HYDROGEN BOND IN CRYSTAL STRUCTURE OF SALTS OF SYMMETRIC POLYMETHYLFERRICINUM CATIONS (SYM: [(CH₃)ₙC₅H₅⁻]ₙFe⁺X⁻, n =3,4,5 or MeₙFc⁺X⁻, n = 6, 8, 10; X⁻ = PF₆⁻, BF₄⁻, Br₃⁻)

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Abstract: The article explains reasons of elongation (0.019 Å) of the bond between iron–cyclopentadienyl ring in the 1,2,4,1’,2’,4’-hexamethylferricinium (sym. Me₆Fc⁺) cation formed due to the one-electron oxidation of iron atom of sym.1,2,4,1’,2’,4’-hexamethylferrocene (sym. Me₆Fc) molecule which is 2-2.5 times smaller (0.04–0.05 Å) than that observed in pairs of ferrocene/ferricinium (Fc/Fc⁺), sym. octamethylferrocene/sym.octamethylferricinium (Me₈Fc/Me₈Fc⁺) and decamethylferrocene/decamethylferricinium (Me₁₀Fc/Me₁₀Fc⁺). For this purpose, X-ray structural parameters characterizing the interaction between cation and anion in the sym.Me₆Fc⁺PF₆⁻ complex was compared with appropriate parameters in Me₆Fc⁺BF₄⁻, Me₆Fc⁺Br₃ and Me₆Fc⁺PF₆ complexes; and it was mooted that there is an F⁻–H type hydrogen bond in this complex taking into account the length of the non-valent F⁻–H contact (bond) in the sym. Me₆Fc⁺PF₆ complex. The lengths of P–F bonds and F–P–F angles of the PF₆ anion in the listed 4 sandwich complexes were compared with appropriate parameters in the PF₆ anion of the LiPF₆ crystal. It has been unequivocally proved that F⁻–H hydrogen bonds exist in the sym.Me₆Fc⁺PF₆⁻ complex.

Keywords: sym. 1,2,4,1’,2’,4’-hexamethylferrocene, sym. 1,2,4,1’,2’,4’-hexamethylferricinium-hexafluorophosphate, hydrogen bond, Van der Waals radius of the atom

Introduction

The properties of the spatial and electronic structure of sym. polymethylferrocenes and their one-electron oxidation products – sym. polymethylferricinium cations (a) with a sandwich structure made it possible to use them in various fields such as drugs, catalysts, sensors, inhibitors, nanomaterials, reference electrodes, etc. [1-6].

\[
\text{Me}_n\text{Fc} \leftrightarrow \text{Me}_n\text{Fc}^+ + e^- \quad (a)
\]

Fig. 1. Crystal structures of the sym. Me₆Fc (b) and sym. Me₆Fc⁺PF₆⁻ (c) complexes
Our interest in these complexes is related to the development of an electrochemical reference electrode based on sym. polymethylferrocene/sym. polymethylferricinium (Me₈Fc/Me₈Fc⁺, n = 6, 8, 10) redox systems [7-11]. It created a need to comparatively study the crystal structures of the sym. hexamethyleriferrocene (sym.Me₆Fc) molecule (b) and sym. hexamethyleriferrocinium-hexafluorophosphate salt (sym. Me₆Fc⁺PF₆⁻) (c) in the research carried out in this direction. In the course of the research, we faced a problem of whether there is a hydrogen bond between the cation and the anion in the salt. This article is aimed at studying the presence of F⋯H hydrogen bonds in sym. Me₆Fc⁺PF₆⁻ salt.

**Experimental part**

Single crystals of sym. Me₆Fc⁺PF₆⁻ with 0.170 x 0.140 x 0.120 mm dimensions were grown in acetone at –10° C.

**X-ray diffraction** study of sym. Me₆Fc⁺PF₆⁻ was carried out on a Bruker SMART APEX-II CCD three-circle automated diffractometer with an array detector (T = 150 K, MoKα-radiation, λ = 0.71073 Å, graphite monochromator, ϕ- and ω-scan modes). The absorption corrections were applied by the SADABS program [12]. The structure was solved by the direct methods and refined by full-matrix least-squares method on F² in the anisotropic approximation for nonhydrogen atoms. The hydrogen atom positions were calculated geometrically and included in the refinement in accord with the riding model with fixed isotropic parameters (Ti_so(H) = 1.5Fequiv(C) for CH₃ groups and &i_so(H) = 1.2Fg EQUIV(C) for all other groups). All calculations were performed using the SHELXTL software package [13]. The main experimental details and the unit cell parameters are summarized in Table 1.

The conditions of growing single crystals of sym. Me₆Fc complex and the conducted experiment and obtained structural data by the method of X-ray structural analysis are reflected in our previous works [7, 8]. At the same time, supplementary materials on the crystal structures of sym. Me₈Fc⁺BF₄⁻ and Me₁₀Fc⁺PF₆⁻ complexes were also analyzed in order to confirm unambiguously the obtained results on these structures.

**Table 1. Crystallographic data on X-ray experiment and structure refinement details for sym. Me₆Fc⁺PF₆⁻**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>M, g/mol</td>
<td>415.15</td>
<td>Crystal size, mm</td>
<td>0.170 x 0.140 x 0.120</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>150(2)</td>
<td>θ range, deg.</td>
<td>3.305 – 25.686</td>
</tr>
<tr>
<td>λ, Å</td>
<td>0.71073</td>
<td>Ranges of indices h, k, l</td>
<td>–8≤h≤5, –18≤k≤16, –20≤l≤20</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Space group</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Unit cell parameters:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a, Å</td>
<td>6.7313(10)</td>
<td>Total number of reflections</td>
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</tr>
<tr>
<td>b, Å</td>
<td>15.331(2)</td>
<td>Number of unique reflections (Rn)</td>
<td>1622 [Rn = 0.0490]</td>
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<tr>
<td>c, Å</td>
<td>16.7169(19)</td>
<td>GOOF for F²</td>
<td>1.135</td>
</tr>
<tr>
<td>β, deg.</td>
<td>90.097(5)</td>
<td>R-factor (I &gt; 2σ(I))</td>
<td>R₁ = 0.0623, wR₂ = 0.1629</td>
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<tr>
<td>V, Å³</td>
<td>1725.1(4)</td>
<td>R-factor (all ref lections)</td>
<td>R₁ = 0.0718, wR₂ = 0.1670</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>Δρ max/Δρ min, e Å³</td>
<td>0.968/-0.750</td>
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<tr>
<td>ρ(calcld.), g/cm³</td>
<td>1.598</td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ, mm⁻¹</td>
<td>1.022</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(000)</td>
<td>852</td>
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</tr>
</tbody>
</table>
Results and discussion

The parameters of the crystal structures of sym. hexamethyferrocene (sym. Me₆Fc) molecule and sym. hexamethylferricinium-hexafluorophosphate salt (sym. Me₆Fc⁺PF₆⁻) obtained by us [7, 8] were analyzed comparatively with the appropriate structural parameters of the salts of octa- and decamethylferricinium cations ([Me₈Fc⁺X⁻, n = 8, 10; X⁻ = PF₆⁻, BF₄⁻, Br⁻] known from references to investigate the presence of hydrogen bonds in the sym. Me₆Fc⁺PF₆⁻ complex.

Results of the analysis are indicative that the elongation (Δl) of the bond between the iron-cyclopentadienyl ring (Fe–A) (A is the center of the cyclopentadienyl ring) in the ferricinium (Fc⁺), octamethylferricinium (sym. Me₈Fc⁺) and decamethylferricinium (Me₆Fc⁺) cations formed as a result of one-electron oxidation of iron atom in ferrocene (Fc), octamethylferrocene (sym. Me₈Fc) and decamethylferrocene (Me₁₀Fc) molecules is in the order of 0.04–0.05 Å, whereas this difference (elongation of Fe–A bonding, Δl) in our studied sym. Me₆Fc and sym. Me₆Fc⁺PF₆⁻ complexes is 0.019 Å, namely, is 2–2.5 times less [8].

\[ \Delta l = l(\text{Fe}–\text{A})_{\text{Me}_6\text{Fc}^+} – l(\text{Fe}–\text{A})_{\text{Me}_6\text{Fc}} = 0.019 \text{ Å} \]

Fig. 2. Elongation (Δl) of Fe–A bond during one-electron oxidation of sym. Me₆Fc molecule (The H atoms were not shown for the sake of simplicity)

This indicates that the ring in the sym. Me₆Fc⁺ cation formed as a result of oxidation cannot move far from the iron atom due to some reason. It cannot be explained by the fact that the Fe–A bond in the Me₆Fc⁺ cation is stronger than in the Me₁₀Fc⁺ cation, because the number of electron-donating methyl groups in the Me₁₀Fc⁺ cation is more. In other words, theoretically, the Fe–A bond in the Me₆Fc⁺ cation should be weaker than that in the Me₁₀Fc⁺ cation.

The research on the length of non-valent contacts (bonds) in the crystal structure of the sym. Me₆Fc⁺PF₆⁻ complex showed that the reason for the slight elongation of the Fe–A bond in this complex may be due to the FH hydrogen bond that can form between the cation and the anion. It is known that, according to the mechanism of intermolecular hydrogen bond formation, this type of bond is usually formed between one F, O, sometimes Cl, N, Br atom particle and another H atom (H⁺) particle with partial positive charge. Therefore, at the first glance, the hydrogen bonding through the H atoms bonded to the sp3-hybridized C atom in methyl homologues of sandwich complexes formed through weakly polarized chemical bonds was not very convincing. However, the analysis of literature data in this aspect shows that it has been proved both by theoretical calculations [14] and experimentally [15] that F atoms of PF₆⁻ and BF₄⁻ anions are able to form hydrogen bonds with H atoms bonded with sp2- and sp3-hybridized C atoms. Taking this into account, the structural parameters of sandwich complexes (sym. Me₆Fc⁺PF₆⁻, sym. Me₈Fc⁺BF₄⁻, Me₁₀Fc⁺PF₆⁻, Me₁₀Fc⁺Br₃⁻) were comparatively and carefully investigated in respect of the aspect whether there are hydrogen bonds or not.

This study showed that the F...H hydrogen bond was observed in polymethylferricinium salts for the first time in the structure of the Me₈Fc⁺BF₄⁻ complex [15]. However, since the purpose of the research topic discussed in the article [15] is dedicated to another problem, the authors haven't studied the effect of the F...H type hydrogen bond on the structure of the sym. Me₈Fc⁺ cation, for example, the “staggered” conformation (d) of the cyclopentadienyl ligands relative to each other and the length of the Fe–A bond.
Fig. 3. Staggered (d) and eclipsed (e) conformation of ferrocene [16]

The study also showed that unlike the sym. \( \text{Me}_8 \text{Fc}^+ \text{BF}_4^- \) complex, the article on the structure of the completely methylated \( \text{Me}_{10} \text{Fc}^+ \text{PF}_6^- \) complex of the ferricinium cation [17] does not provide any specific information about the F⋯H type-hydrogen bond. Therefore, we obtained the supplementary material for this article and analyzed the appropriate structural data in order to completely determine whether there are F⋯H hydrogen bonds in the \( \text{Me}_{10} \text{Fc}^+ \text{PF}_6^- \) complex [17] or not.

The analysis showed that the lengths of the P1–F1, P1–F2 and P1–F3 bonds are 1.6085 Å, 1.603 Å, and 1.601 Å, respectively [17] in the PF\(_6^-\) anion of the \( \text{Me}_{10} \text{Fc}^+ \text{PF}_6^- \) complex with a "staggered" conformation. The lengths of these bonds are practically the same as the length of the P–F bond (1.603 (1) Å) [18] observed in the anion of the pure \( \text{LiPF}_6 \) crystal (that is, in the state of absence of F⋯H type-hydrogen bond). From this, we come to the conclusion that the F atoms of the PF\(_6^-\) anion in the \( \text{Me}_{10} \text{Fc}^+ \text{PF}_6^- \) complex do not form F⋯H type-hydrogen bonds in the crystal state, and the fact that the cyclopentadienyl rings of the \( \text{Me}_{10} \text{Fc}^+ \) cation are in the "staggered" conformation is related to the crystal forces in the crystal lattice. Because, if there were F⋯H hydrogen bonds in the \( \text{Me}_{10} \text{Fc}^+ \text{PF}_6^- \) complex, the length of P–F bond would be significantly different from 1.603 (1) Å.

It ought to be noted that according to the authors [19], "there is no also interconnecting bond between tribromide \( \text{Br}_3^- \) anion and \( \text{Me}_{10} \text{Fc}^+ \) cation" in the \( \text{Me}_{10} \text{Fc}^+ \text{Br}_3^- \) complex. Therefore, in our opinion, the "eclipsed" conformation (e) observed in the \( \text{Me}_{10} \text{Fc}^+ \text{Br}_3^- \) complex was formed by the crystal packing effect of the crystal, just like the conformation (d) of the \( \text{Me}_{10} \text{Fc}^+ \text{PF}_6^- \) complex.

Fig. 4. Scheme of F⋯H hydrogen bonds in the sym. \( \text{Me}_6 \text{Fc}^+ \text{PF}_6^- \) complex

Unlike the 3 complexes discussed above (sym. \( \text{Me}_8 \text{Fc}^+ \text{BF}_4^- \), \( \text{Me}_{10} \text{Fc}^+ \text{PF}_6^- \), \( \text{Me}_{10} \text{Fc}^+ \text{Br}_3^- \)), the structure of sym.\( \text{Me}_6 \text{Fc}^+ \text{PF}_6^- \) complex clearly reflects the sym. F⋯H type-hydrogen bond. Thus, the
sum of the Van der Waals radii of the fluorine and hydrogen atoms is 2.67 Å [20], while the lengths of F1…H(8)B(C8)* and F2…H4(C4)* non-valent bonds are 2.053 Å and 2.527 Å, which is significantly smaller than 2.67 Å. The fact that the lengths of the hydrogen bonds are smaller than the sum of the Van der Waals radii (less than 2.67 Å) indicates the presence of F⋯H hydrogen bonds in the sym.Me6Fc+PF6− complex.

At the same time, the presence of F⋯H type hydrogen bond is also confirmed by the values of the P–F bond lengths and F–P–F angles of the PF6− anion in the sym.Me6Fc+PF6− complex. Thus, the length of the P1–F1, P1–F2 and P1–F3 bonds in PF6− anion are 1.570 Å, 1.590 Å, and 1.576 Å, respectively; in other words, when F⋯H hydrogen bonds are formed in the investigated sandwich complexes, the P–F bonds in the PF6− anion should get shorter and significantly differ from the value (1.603 (1) Å) observed in the PF6− anion of the LiPF6 crystal [18] (table 1).

Table 2. Reference of bond lengths and bond angles (ζ) of sym. Me6Fc+PF6−, Me10Fc+PF6− and Li+PF6− coordination compounds in PF6− anion

<table>
<thead>
<tr>
<th>Coordination compounds</th>
<th>PF6−</th>
</tr>
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<tr>
<td></td>
<td>P–F1</td>
</tr>
<tr>
<td>Me6Fc+PF6−</td>
<td>1.570 Å</td>
</tr>
<tr>
<td>Me10Fc+PF6−</td>
<td>1.6085 Å</td>
</tr>
<tr>
<td>Li+PF6−</td>
<td>1.603 Å</td>
</tr>
</tbody>
</table>

Fig. 5. “Staggered” configuration of Cs-rings in the sym. Me6Fc+ cation

So, the comparative study of the crystal structure of the sym. Me6Fc+PF6− complex unambiguously proves that there is an F⋯H type hydrogen bond in the sym.Me6Fc+PF6− complex.

It should be noted that the hydrogen bonds shown in the sym. Me6Fc+PF6− complex are oriented in space in such a way that, on the one hand, they prevent the elongation of the Fe–A bond (see Fig. 4, hydrogen bonds F2…H and F1…H), and on the other hand, lead to the arrangement of two Me3C5H2 rings relative to each other in the sym. Me6Fc+ cation, as shown in Fig. 5 (“staggered” configuration).

Conclusion

The comparative analysis of crystal structures of sym. Me6Fc+PF6−, sym. Me6Fc+BF4−, Me10Fc+Br3 and Me10Fc+PF6− complexes shows that slight charging of the sym. Me6Fc+ cation with Me groups as compared to Me2Fc+ and Me10Fc+ cations gives the PF6− anion the opportunity to get very close to an iron atom and, as a result, form F1…H(8)B(C8) and F2…H4(C4) type hydrogen bonds with H atoms of the Me groups and ring. Since F1…H(8)B(C8) and F2…H4(C4) hydrogen bonds are formed between different rings of the same cation, these bonds do not allow the rings to
move away from each other (i.e. from the iron atom). As a result, during oxidation of the neutral sym. \(\text{Me}_6\text{Fc}\) molecule to the sym.\(\text{Me}_6\text{Fc}^+\) cation, the elongation of the metal-ring bond (0.019 Å) is 2–2.5 times smaller than that observed in other \(\text{Me}_n\text{Fc}/\text{Me}_n\text{Fc}^+\) \((n = 0, 8, 10)\) redox couples (from 0.04–0.05 Å).

References


ВОДОРОДНАЯ СВЯЗЬ В КРИСТАЛЛИЧЕСКОЙ СТРУКТУРЕ СОЛЕЙ СИМ. КАТИНОВ ПОЛИМЕТИЛФЕРРИЦИНИЯ [сим.((CH₃)m CsH₅-n]²Fe⁺X⁻, m=3,4,5 или Me₆Fs⁺X⁻, n = 6, 8, 10; X⁻ = PF₆⁻, BF₄⁻, Br₃⁻]

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Аннотация: В статье интерпретированы причины 2–2.5-кратного уменьшения разности длин связи железо–циклопентадиенильное кольцо при однозарядном окислении молекулы сим. 1,2,4,1',2',4'-гексаметилферрироцен и гексаметилферрициния (сим. Me₆Fs⁺) в катион сим. 1,2,4,1',2',4'-гексаметилферрироцен (сим. Me₆Fs⁺; Δl=0,019Å) по сравнению с этой же разностью в парах ферроцен–феррициний (Fs–Fs⁺), сим. октаметилферрироцен–симв. октаметилферрицинии (сим. Me₄Fs–симв. Me₄Fs⁺) и декаметилферрироцен–декаметилферрицинии (Me₁₀Fs–Me₁₀Fs⁺) (Δl=0,04–0,05Å). Для этого были сравнены структурные параметры, характеризующие взаимодействие катиона и аниона комплекса сим. Me₆Fs⁺PF₆⁻ с соответствующими параметрами комплексов сим. Me₆Fs⁺BF₄⁻, Me₁₀Fs⁺Br₃⁻ и Me₁₀Fs⁺PF₆⁻ и учитывая длины непривлекательных F⁻–H контактов (связей) высказано идея о наличии водородных связей типа F⁻–H в комплексе сим. Me₆Fs⁺PF₆⁻. Сравнение длин P–F связей и величины углов F–P–F аниона PF₆⁻ в 4-х вышеперечисленных сдвоенных комплексах (сим. Me₆Fs⁺PF₆⁻, сим. Me₆Fs⁺BF₄⁻, Me₁₀Fs⁺Br₃⁻ и Me₁₀Fs⁺PF₆⁻) с соответствующими параметрами аниона PF₆⁻ в кристалле LiPF₆ позвоило однозначно доказать существование водородной связи типа F⁻–H в комплексе Me₆Fs⁺PF₆⁻.

Ключевые слова: 1,2,4,1',2',4'-сим. гексаметилферроцен, гексафторфосфат-сим. 1,2,4,1',2',4'-гексаметилферрициния, водородная связь, ван-дер-Ваальсовый радиус атома

**SİMMETRİK QURULUŞLU POLİMETİLFERRİSİNIUM KATİONLARIN DUZLARININ (SİM. [(CH₃)m CsH₅-n]²Fe⁺X⁻, m=3,4,5 və ya Me₆Fs⁺X⁻, n = 6, 8, 10) KRİSTAL QURULUŞUNDA HİDROGEN RABİTƏSİ**

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Xülasə: Məqalədə sim. 1,2,4,1',2',4'-heksametilferrozen (sim. Me₆Fs⁺) molekülunda dəmir atomunun birelektronlu oksidəşməsi nəticəsində omda gələn sim. 1,2,4,1',2',4'-heksametilferrisinium (sim. Me₆Fs⁺)
Kationunda dəmir–tsiklopentadiil halqası arəsində rəbitin uzanmasının (0.019 Å) ferrosen-ferrisinium (Fs-Fs⁺), sim. oktametilferrosen-sim. oktametilferrisinium (sim. Me₈Fs–sim. MeFs⁺) və dekametilferrosen-dekametilferrisinium (Me₁₀Fs–Me₁₀Fs⁺) cütlərində müşahidə olunandan (0.04–0.05 Å) 2–2.5 dəfə kiçik olmasının səbəbi izah olunmuşdur. Bunun üçün sim. Me₈Fs⁺PF₆⁻ kompleksində kationla anion arəsində qarşılıqlı təsiri xarakterizə edən rentgenquruluş parametrər sim. Me₈Fs⁺BF₄⁻, Me₁₀Fs⁺Br₃ və Me₁₀Fs⁺PF₆⁻ komplekslərində müvafiq parametrərlə müqayisə edilmiş və sim. Me₈Fs⁺PF₆⁻ kompleksində qeyri-valent F⁻H kontaktın (rəbitinin) uzunluğunu nəzərə alaraq bu kompleksdə F⁻H tipli hidrogen rəbitəsinin mövcudluğunu həqiqətən fikir ilə sürətmüşdür. Sadalanan 4 sendviç kompleksin tərkibindəki PF₆⁻ anionun P–F rəbitərinin uzunluqları və F–P–F bucaqları LiPF₆ kristalinin PF₆⁻ anionundaki uyğun parametrələ müqayisə edilərək sim. Me₈Fs⁺PF₆⁻ kompleksində F⁻H hidrogen rəbitəsinin olduğu birünəği səbət edilmişdir.

Açar sözlar: sim. 1,2,4,1’,2’,4’-heksametilferrosen, sim. 1,2,4,1’,2’,4’-heksametilferrisinium-heksafluorfosfat, hidrogen rəbitəsi, atomun van-der-Vaals radiusu