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**HYDROGEN BOND IN CRYSTAL STRUCTURE OF SALTS OF SYMMETRIC
POLYMETHYLFERRICINIUM CATIONS (SYM. $[(CH_3)_mC_5H_{5-m}]_2Fe^+X^-$, $m=3,4,5$ or
 $Me_nFc^+X^-$, $n = 6, 8, 10$; $X^- = PF_6^-, BF_4^-, Br_3^-$)**

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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. Me_6Fc^+) cation formed due to the one-electron oxidation of iron atom of sym.1,2,4,1',2',4'-hexamethylferrocene (sym. Me_6Fc) 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 (Me_8Fc/Me_8Fc^+) and decamethylferrocene/decamethylferricinium ($Me_{10}Fc/Me_{10}Fc^+$). For this purpose, X-ray structural parameters characterizing the interaction between cation and anion in the sym. $Me_6Fc^+PF_6^-$ complex was compared with appropriate parameters in $Me_8Fc^+BF_4^-$, $Me_{10}Fc^+Br_3^-$ and $Me_{10}Fc^+PF_6^-$ complexes; and it was mooted that there is an $F^{\cdots}H$ type hydrogen bond in this complex taking into account the length of the non-valent $F^{\cdots}H$ contact (bond) in the sym. $Me_6Fc^+PF_6^-$ complex. The lengths of P–F bonds and F–P–F angles of the PF_6^- anion in the listed 4 sandwich complexes were compared with appropriate parameters in the PF_6^- anion of the $LiPF_6$ crystal. It has been unequivocally proved that $F^{\cdots}H$ hydrogen bonds exist in the sym. $Me_6Fc^+PF_6^-$ 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

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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].



Our interest in these complexes is related to the development of an electrochemical reference electrode based on sym. polymethylferrocene/sym. polymethylferricinium (Me_nFc/Me_nFc^+ , $n = 6, 8, 10$) redox systems [7-11]. It created a need to comparatively study the crystal structures of the sym. hexamethylferrocene (sym. Me_6Fc)

molecule (**b**) and sym. hexamethylferricinium-hexafluorophosphate salt (sym. $Me_6Fc^+PF_6^-$) (**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 $F^{\cdots}H$ hydrogen bonds in sym. $Me_6Fc^+PF_6^-$ salt.

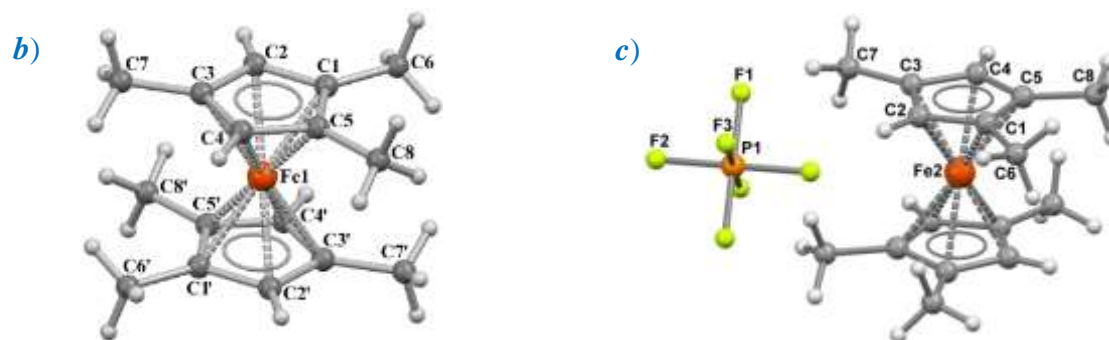


Fig. 1. Crystal structures of the sym. Me_6Fc (b) and sym. $\text{Me}_6\text{Fc}^+\text{PF}_6^-$ (c) complexes

Experimental part

Single crystals of sym. $\text{Me}_6\text{Fc}^+\text{PF}_6^-$ with 0.170 x 0.140 x 0.120 mm dimensions were grown in acetone at -10°C .

X-ray diffraction study of sym. $\text{Me}_6\text{Fc}^+\text{PF}_6^-$ was carried out on a Bruker SMART APEX-II CCD three-circle automated diffractometer with an array detector ($T = 150\text{ K}$, MoK_α -radiation, $\lambda = 0.71073\text{ \AA}$, 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 F^2 in the anisotropic approximation for nonhydrogen atoms. The hydrogen atom positions were calculated geometrically and included in the refinement in accord to the riding model with fixed isotropic parameters ($T_{\text{iso}}(\text{H}) = 1.5F_{\text{equiv}}(\text{C})$ for CH_3 groups and $i_{\text{iso}}(\text{H}) = 1.2F_{\text{equiv}}(\text{C})$ 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.

Table 1. Crystallographic data on X-ray experiment and structure refinement details for sym. $\text{Me}_6\text{Fc}^+\text{PF}_6^-$

Parameter	Value	Parameter	Value
M, g/mol	415.15	Crystal size, mm	0.170 x 0.140 x 0.120
Temperature, K	150(2)	θ range, deg.	3.305 – 25.686
λ , \AA	0.71073	Ranges of indices h, k, l	$-8 \leq h \leq 5$, $-18 \leq k \leq 16$, $-20 \leq l \leq 20$
System	Monoclinic		
Space group	C2/c		
Unit cell parameters:		Total number of reflections	5247
a, \AA	6.7313(10)	Number of unique reflections (R_{int})	1622 [$R_{\text{int}} = 0.0490$]
b, \AA	15.331(2)	GOOF for F_2	1.135
c, \AA	16.7169(19)	R -factor ($I > 2\sigma(I)$)	$R_1 = 0.0623$, $wR_2 = 0.1629$
β , deg.	90.097(5)		
V, \AA^3	1725.1(4)	R -factor (all reflections)	$R_1 = 0.0718$, $wR_2 = 0.1670$
Z	4		
ρ (calcd.), g/cm^3	1.598	$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e \AA^{-3}	0.968/–0.750
μ , mm^{-1}	1.022		
F(000)	852		

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].

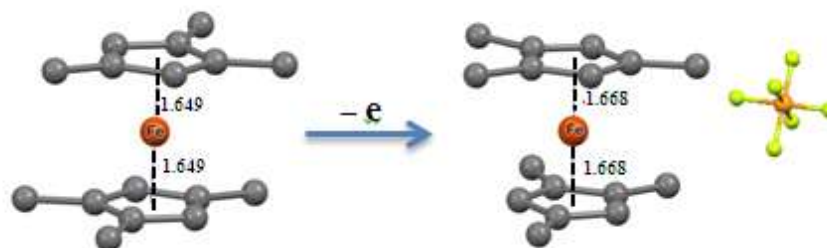
Results and discussion

The parameters of the crystal structures of sym. hexamethylferrocene (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 ([Me_nFc⁺X⁻, n = 8, 10; X⁻ = PF₆⁻, BF₄⁻, Br₃⁻] 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

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.

iron-cyclopentadienyl ring (Fe–A) (A is the center of the cyclopentadienyl ring) in the ferricinium (Fc⁺), octamethylferricinium (sym. Me₈Fc⁺) and decamethylferricinium (Me₁₀Fc⁺) 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 the our studied sym.Me₆Fc and sym. Me₆Fc⁺PF₆⁻ complexes is 0.019 Å, namely, is 2–2.5 times less [8].



$$\Delta l = l(\text{Fe-A})_{\text{Me}_6\text{Fc}^+} - l(\text{Fe-A})_{\text{Me}_6\text{Fc}} = \mathbf{0.019 \text{ \AA}}$$

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^{+δ}) 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 PF_6^- and BF_4^- anions are able to form hydrogen bonds with H atoms bonded with sp^2 - and sp^3 -hybridized C atoms. Taking this into account, the structural parameters of sandwich complexes (sym. $\text{Me}_6\text{Fc}^+\text{PF}_6^-$, sym. $\text{Me}_8\text{Fc}^+\text{BF}_4^-$, $\text{Me}_{10}\text{Fc}^+\text{PF}_6^-$, $\text{Me}_{10}\text{Fc}^+\text{Br}_3^-$) were comparatively and carefully investigated in respect of the aspect whether there are hydrogen bonds or not.

This study showed that the $\text{F}\cdots\text{H}$ hydrogen bond was observed in polymethylferricinium salts for the first time in the structure of the $\text{Me}_8\text{Fc}^+\text{BF}_4^-$ 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 $\text{F}\cdots\text{H}$ type hydrogen bond on the structure of the sym. Me_8Fc^+ cation, for example, the "staggered" conformation (*d*) of the cyclopentadienyl ligands relative to each other and the length of the Fe–A bond.

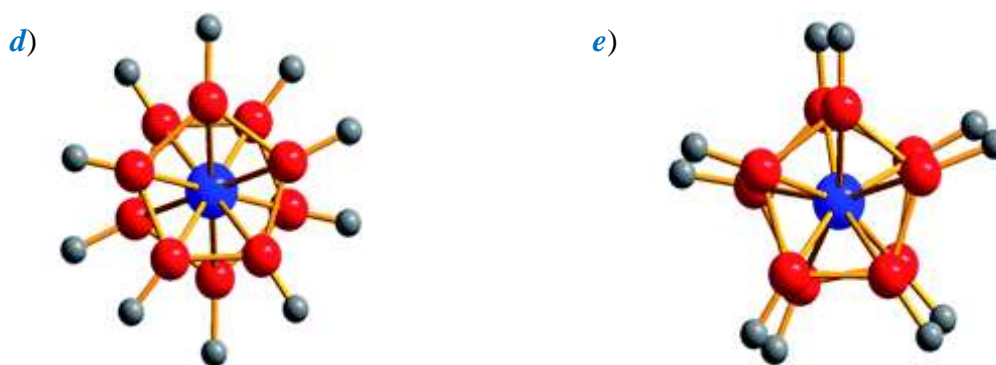


Fig. 3. Staggered (*d*) and eclipsed (*e*) conformation of ferrocene [16]

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 $\text{F}\cdots\text{H}$ 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 $\text{F}\cdots\text{H}$ 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 LiPF_6 crystal (that is, in the state of absence of $\text{F}\cdots\text{H}$ 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 $\text{F}\cdots\text{H}$ 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 $\text{F}\cdots\text{H}$ 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 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.

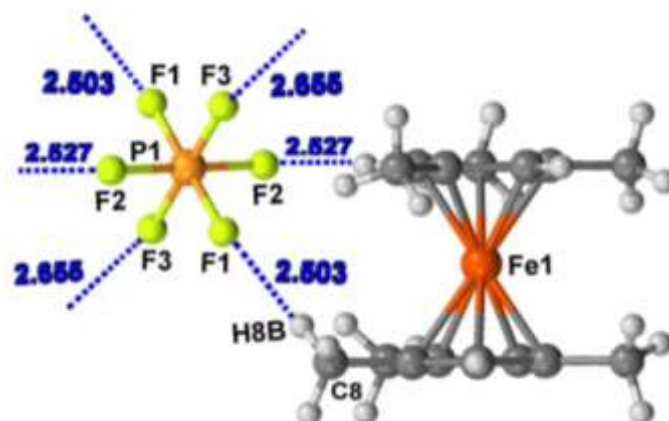


Fig. 4. Scheme of F \cdots H hydrogen bonds in the sym. Me₆Fc⁺PF₆⁻ complex

Unlike the 3 complexes discussed above (sym. Me₈Fc⁺BF₄⁻, Me₁₀Fc⁺PF₆⁻, Me₁₀Fc⁺Br₃⁻), the structure of sym.Me₆Fc⁺PF₆⁻ complex clearly reflects the sym. F \cdots 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 \cdots H hydrogen bonds in the sym.Me₆Fc⁺PF₆⁻ complex.

At the same time, the presence of F \cdots 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 \cdots 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 2).

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

Coordination compounds	PF ₆ ⁻					
	P–F1	P–F2	P–F3	\angle F1PF2	\angle F1PF3	\angle F3PF2
Me ₆ Fc ⁺ PF ₆ ⁻	1.570 Å	1.590 Å	1.576 Å	89.7°	91.5°	89.4°
Me ₁₀ Fc ⁺ PF ₆ ⁻	1.6085 Å	1.603 Å	1.601 Å	90°	90°	90°
Li ⁺ PF ₆ ⁻	1.603 Å	1.603 Å	1.603 Å	90°	90°	90°

So, the comparative study of the crystal structure of the sym. Me₆Fc⁺PF₆⁻ complex unambiguously proves that there is an F \cdots 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).

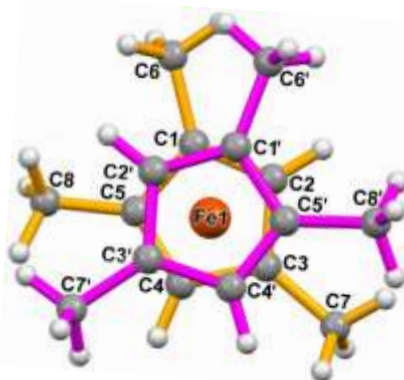


Fig. 5. “Staggered” configuration of C₅-rings in the sym. Me₆Fc⁺ cation

Conclusion

The comparative analysis of crystal structures of sym. Me₆Fc⁺PF₆⁻, sym. Me₈Fc⁺BF₄⁻, Me₁₀Fc⁺Br₃ and Me₁₀Fc⁺PF₆⁻ complexes shows that slight charging of the sym. Me₆Fc⁺ cation with Me groups as compared to Me₈Fc⁺ 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. Me₆Fc molecule to the sym. Me₆Fc⁺ cation, the elongation of the metal-ring bond (0.019 Å) is 2–2.5 times smaller than that observed in other Me_nFc/Me_nFc⁺ (n = 0, 8, 10) redox couples (from 0.04–0.05 Å).

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ВОДОРОДНАЯ СВЯЗЬ В КРИСТАЛЛИЧЕСКОЙ СТРУКТУРЕ СОЛЕЙ СИМ. КАТИОНОВ ПОЛИМЕТИЛФЕРРИЦИНИЯ [сим.(CH₃)_mC₅H_{5-m}]₂Fe⁺X⁻, m=3,4,5 или Me_nFs⁺X⁻, n = 6, 8, 10; X⁻ = PF₆⁻, BF₄⁻, Br₃⁻)

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Аннотация: В статье интерпретированы причины 2–2.5-кратного уменьшения разности длины связи железо–циклопентадиенильное кольцо при одноэлектронном окислении молекулы сим. 1,2,4,1',2',4'-гексаметилферроцена (сим. Me₆Fs) в катион сим. 1,2,4,1',2',4'-гексаметилферрициния (сим. Me₆Fs⁺; Δl=0,019Å) по сравнению с этой же разностью в парах ферроцен-феррициний (Fs-Fs⁺), сим. октаметилферроцен-сим. октаметилферрициний (сим. Me₈Fs-сим. Me₈Fs⁺) и декаметилферроцен-декаметилферрициний (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. Me₈Fs⁺BF₄⁻, Me₁₀Fs⁺Br₃ и Me₁₀Fs⁺PF₆⁻ и учитывая длины невалентных F...H контактов (связей) высказана идея о наличии водородных связей типа F...H в

комплексе сим. $\text{Me}_6\text{Fs}^+\text{PF}_6^-$. Сравнение длин P–F связей и величин углов F–P–F аниона PF_6^- в 4-х вышеперечисленных сэндвичевых комплексах (сим. $\text{Me}_6\text{Fs}^+\text{PF}_6^-$, сим. $\text{Me}_8\text{Fs}^+\text{BF}_4^-$, $\text{Me}_{10}\text{Fs}^+\text{Br}_3$ и $\text{Me}_{10}\text{Fs}^+\text{PF}_6^-$) с соответствующими параметрами аниона PF_6^- в кристалле LiPF_6 позволило однозначно доказать существование водородной связи типа F...H в комплексе $\text{Me}_6\text{Fs}^+\text{PF}_6^-$.

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 POLİMETİLFERRİSİNİUM KATIONLARIN DUZLARININ (SİM. $[(\text{CH}_3)_m\text{C}_5\text{H}_{5-m}]_2\text{Fe}^+\text{X}^-$, $m=3,4,5$ və ya $\text{Me}_n\text{Fs}^+\text{X}^-$, $n=6, 8, 10$); $\text{X}^- = \text{PF}_6^-$, BF_4^- , Br_3^-) KRİSTAL QURULUŞUNDA HİDROGEN RABİTƏSİ

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Xülasə: Məqalədə sim. 1,2,4,1',2',4'-heksametilferrosen (sim. Me_6Fs) molekulunda dəmir atomunun birelektronlu oksidləşməsi nəticəsində əmələ gələn sim. 1,2,4,1',2',4'-heksametilferrisinium (sim. Me_6Fs^+) kationunda dəmir–tsiklopentadienil halqası arasındakı rəbitənin uzanmasının (0.019 Å) ferrosen-ferrisinium (Fs-Fs^+), sim. oktametilferrosen-sim. oktametilferrisinium (sim. Me_8Fs -sim. MeFs^+) və dekametilferrosen-dekametilferrisinium (Me_{10}Fs - $\text{Me}_{10}\text{Fs}^+$) cütlərində müşahidə olunandan (0.04–0.05 Å) 2–2.5 dəfə kiçik olmasının səbəbi izah olunmuşdur. Bunun üçün sim. $\text{Me}_6\text{Fs}^+\text{PF}_6^-$ kompleksində kationla anion arasında qarşılıqlı təsiri xarakterizə edən rentgenquruluş parametrlər sim. $\text{Me}_8\text{Fs}^+\text{BF}_4^-$, $\text{Me}_{10}\text{Fs}^+\text{Br}_3$ və $\text{Me}_{10}\text{Fs}^+\text{PF}_6^-$ komplekslərində müvafiq parametrlərlə müqayisə edilmiş və sim. $\text{Me}_6\text{Fs}^+\text{PF}_6^-$ kompleksində qeyri-valent F...H kontaktın (rəbitənin) uzunluğunu nəzərə alaraq bu kompleksdə F...H tipli hidrogen rəbitəsinin mövcudluğu haqqında fikir irəli sürülmüşdür. Sadalanan 4 sendviç kompleksin tərkibindəki PF_6^- anionun P–F rəbitələrinin uzunluqları və F–P–F bucaqları LiPF_6 kristalının PF_6^- anionundakı uyğun parametrlərlə müqayisə edilərək sim. $\text{Me}_6\text{Fs}^+\text{PF}_6^-$ kompleksində F...H hidrogen rəbitəsinin olduğu birmənalı sübut edilmişdir.

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