Simulation of the molecular and electronic structure of C_{60} fullerene π-complex with twelve half-sandwich species FeC_5H_5

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The problem of existence of η^5-π-complexes of fullerenes and their derivatives is discussed. The stability of the η^5-π-complex $C_{60}(FeCp)_{12}$ (*viz.*, icosahedral C_{60} fullerene "coated" with twelve FeCp groups, each coordinated to its "own" pentagonal face of the fullerene cage) was first estimated in the framework of density functional approach (PBE approximation). The molecular and electronic structure of a biradical complex of C_{60} fullerene with ten FeCp groups, $C_{60}(FeCp)_{10}$ (D_{5d} symmetry), and a $2\eta^5$-π-complex of substituted fullerene $H_{10}C_{60}$, $H_{10}C_{60}(FeCp)_2$ (D_{5d} symmetry) in which hydrogen atoms are attached to the C atoms in the α-positions relative to the atoms of the polar five-membered cycles, was simulated. According to calculations, the "coated" complex, I_h-$C_{60}(FeCp)_{12}$, should be much more stable than the complex of "naked" fullerene with one or two polarly located FeCp groups and only slightly less stable than the ferrocene molecule $FeCp_2$. The existence of $C_{60}(FeCp)_{12}$ and $H_{10}C_{60}(FeCp)_2$ complexes was suggested.

Key words: C_{60} fullerene, ferrocene, C_{60} fullerene π-complexes, "coated" fullerenes, nonempirical quantum-chemical calculations, density functional theory, PBE approximation, Fe—C_{60} bond energy.

The term "coated" fullerenes is usually referred to exohedral fullerene complexes M_nC_m in which the carbon cage is surrounded by a rather large number of metal atoms (M) that form either single-layer or multilayer polyhedral clusters M_n.[1] The complexes M_nC_m are synthesized in the vapor phase and their chemical composition is analyzed by mass spectroscopy. The "coated" complexes $Li_{12}C_{60}$ and $Ba_{32}C_{60}$ were detected.[2,3] The results of calculations of "coated" fullerenes, which confirm the assumption that such systems can exist in the gas phase have been reported.[4—8] For instance, the $C_{60}Li_n$ complexes (n = 1—14) have been studied.[4,5] The molecular and electronic structures of the "coated" C_{60} fullerene complexes with Ti, Cr, Au, La, and In atoms have been simulated.[6] The molecular structures of $C_{60}M_n$ (M = Be, Mg, Al; n = 12, 20, 32) complexes were calculated and their heats of formation were estimated.[7] The $In_{12}C_{60}$ complex has been studied.[9]

It should be noted that the fullerene complexes "coated" with metal atoms should be highly reactive due to the presence of unsaturated valences at the outside M atoms. Therefore, the isolation of such species as kinetically stable chemical compounds seems to be highly improbable. However, the "coated" fullerenes can be made much less reactive by "coating" them with functional groups comprised of metal atoms and organic ligands.

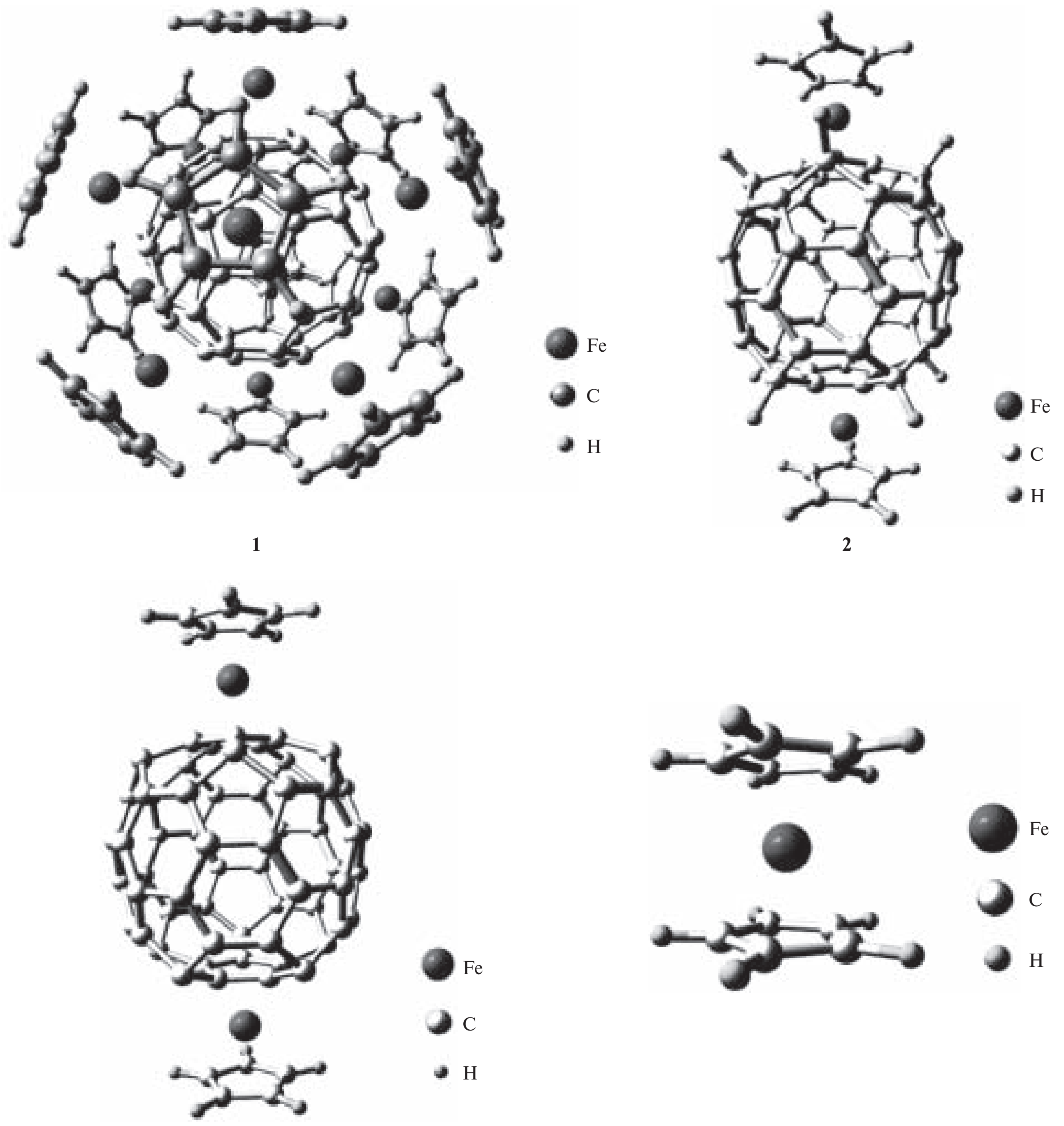
Recently,[10] we proved the possibility of existence of thermodynamically and kinetically stable exohedral complexes $C_{60}H_5XCp$ (X = Fe, Si; Cp is the cyclopentadienyl radical) based on the results of Hartree—Fock (HF/3-21G) calculations. In these complexes, hydrogen atoms are attached to the C atoms of C_{60} fullerene in the α-positions relative to the five-membered cycle involved in the η^5-π-interaction with the XCp species. This type of attachment of H atoms to the fullerene cage leads to division of extended conjugated system of the C_{60} fullerene into two independent subsystems one of which is localized on the five-membered cycle. This favors substantial stabilization of $C_{60}H_5XCp$ η^5-complexes compared to η^5-π-C_{60}XCp complexes. Our PM3 calculations of a C_{60} fullerene complex with twelve XCp (X = Si, Ge, Sn) species, each being η^5-coordinated to the atoms of one five-membered cycle, led to analogous results.[11]

In this work, we report the results of simulation of the molecular and electronic structure of a C_{60} fullerene complex with twelve half-sandwich species FeCp, $12\eta^5$-π-$C_{60}(FeCp)_{12}$ (**1**). In addition, calculations of complexes $C_{60}(FeCp)_{10}$ (**1a**), $C_{60}H_{10}(FeCp)_2$ (**2**), and $C_{60}(FeCp)_2$ (**3**) and the hydrocarbon biradical $C_{60}H_{10}$ (**2a**) were carried out. The structures of complexes **1—3** are shown in Fig. 1.

Calculation Procedure

Calculations of local energy minima for systems **1**, **1a**, **2**, **2a**, and **3** were carried out with full geometry optimiza-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 709—712, May, 2002.



1 **2** **3** **4**

Fig. 1. Molecular structures of the complexes $C_{60}(FeCp)_{12}$ (**1**), $H_{10}C_{60}(FeCp)_2$ (**2**), $C_{60}(FeCp)_2$ (**3**), and ferrocene molecule $FeCp_2$ (**4**).

tion using the density functional (DFT) approach with the Perdew—Burke—Ernzerhof (PBE) exchange-correlation potential[12] and the TZ (for Fe) and DZ (for C and H) basis sets using the PRIRODA program.[13] This program allows calculations of open-shell systems in the Kohn—Sham approximation. Calculations of complex **1** on a PC with a 700 MHz CPU took 28 h. The results of calculations were used for assessing the possibility of existence of complexes **1—3**.

Results and Discussion

Table 1 lists the energy characteristics and selected geometric parameters of η^5-π-complexes **1**, **2**, **3**, and the ferrocene molecule $FeCp_2$ (**4**) (see Fig. 1) and their fragments **1a**, **2a**, FeCp (**4a**), and $Cp^{\bullet}$ (**4b**). Biradical **1a** can be formed by elimination of two polar species FeCp

Table 1. Energy characteristics and geometric parameters of η^5-π-complexes **1—4** and their fragments **1a—4a** and **2b** obtained from DFT-PBE calculations with the TZ (for Fe) and DZ (for C and H) basis sets

Compound	m^a	Symmetry	$-E_t{}^b$ (au)	E(Fe—pent*)^c /kcal mol^{-1}	R/Å			
					C—C_{pent}	C—C_{Cp}	Fe—C_{pent}	Fe—C_{Cp}
$C_{60}(FeCp)_{12}$ (**1**)	1	I_h	19766.2452	103.8	1.454	1.439	2.110	2.065
$C_{60}(FeCp)_{10}$(**1a**)	3	D_{5d}	16852.4329	—	1.447—1.452	1.439	2.120—2.195	2.082—2.085
$H_{10}C_{60}(FeCp)_2$ (**2**)	1	D_{5d}	5203.5112	134.1	1.432	1.437	2.088—2.089	2.067
$H_{10}C_{60}$ (**2a**)	3	S_2	2289.6023	—	1.382—1.477	—	—	—
$H_{10}C_{60}$ (**2a′**)	1	C_{2h}	2289.5923	—	1.383—1.466	—	—	—
$H_{10}C_{60}{}^{2-}$ (**2b**)	1	D_{5d}	2289.7131	—	1.423	—	—	—
$C_{60}(FeCp)_2$ (**3**)	1	D_{2h}	5197.4060	66.1	1.462—1.471	1.437—1.441	2.120—2.137	2.053—2.059
C_{60} (**3a**)	1	I_h	2283.7138	—	1.458	—	—	—
$FeCp_2$ (**4**)	1	D_{5h}	1650.1657	142.6	—	1.438	—	2.065
FeCp (**4a**)	2	C_1	1456.7406	—	—	1.456	—	—
$Cp^\bullet$ (**4b**)	2	C_{2v}	193.1976	—	—	1.425—1.450	—	—

[a] Multiplicity.

[b] Total energy.

[c] Energy of the Fe—pent* bond calculated for complexes **1**, **2**, **3**, and **4** using the energy parameters of reactions (3), (2), (1), and formula (4), respectively.

from **1**. Biradical **2a** can be produced by attaching H atoms to all C atoms of C_{60} fullerene (**3a**) in the α-positions relative to two polar five-membered cycles specified by the fifth-fold symmetry axis. According to calculations, system **2a** has a triplet ground state. This molecule has a S_2 symmetry and its energy is 6.1 kcal mol^{-1} lower than that of the singlet state with C_{2h} symmetry (see Table 1, system **2a**´).

Attachment of ten H atoms to the C_{60} molecule to give derivative **2a** leads to the situation where two five-membered cycles are no longer involved in the overall spherical conjugated system and have high spin populations (0.79 au on each pentagon). Therefore, such biradical derivatives of C_{60} fullerene must more prone to formation of η^5-π-complexes than "naked" C_{60} cluster. An analogous effect is also predicted for C_{60} fullerene π-complexes with FeCp species. In this case, the attachment of each FeCp group to one five-membered cycle has the same feature, namely, the cycle is no longer involved in the overall conjugated system, thus leading to its reduction. For instance, each polar five-membered cycle in biradical complex **1a** and in complex **2a** with triplet ground state is characterized by a spin population of 0.28 au. This qualitative reasoning is confirmed by the results of calculations of systems **1—3** (see below).

Geometric parameters. We will denote each five-membered cycle in the C_{60} fullerene molecule, to which one half-sandwich species FeCp (**4a**) is coordinated, as pent*. From the data listed in Table 1 it can be seen that the Fe...C_{pent*} distance is the shortest in complex **2** (2.088 Å) and the longest in complex **3** (2.137 Å). The Fe...C_{Cp} distances lie between 2.052 Å (**3**) and 2.067 Å (**2**). The bond lengths in the cyclopentadienyl fragments Cp virtually coincide with those in the ferrocene molecule, $FeCp_2$ (**4**). The C—C bond lengths in the pent* fragments are close to 1.45 Å.

Calculations of complexes **1**, **1a**, **2**, and **3** with full geometry optimization led to I_h symmetry for **1** and to D_{5d} symmetry for **1a**, **2**, and **3**. In complex **1**, the radius of the carbon cage of the C_{60} fragment, R_C, is 3.605 Å and the distance between the Fe atoms and the center of symmetry, R_{Fe}, is 5.097 Å. The diameter of this molecule estimated from the longest distance between H atoms is 14.212 Å.

In biradical complex **1a**, the Fe atoms also lie on a sphere of radius R_{Fe} = 5.097 Å. The C—C bond lengths in the polar five-membered (uncoordinated) cycles are 1.449 Å. The R_{Fe} value is 4.980 Å for complex **2** and 5.090 Å for complex **3**.

In complexes **1—3**, the FeCp species are coordinated to the pent* faces in such a manner that the Cp—Fe—pent* fragments are characterized by eclipsed configuration of C atoms (the same as in molecule **4**). Distances from the Fe atom to the C atoms of the coordinated face in these complexes are shortened in the order **3** > **1** > **2**, which indicates strengthening of the Fe—pent* bond in this series of compounds (see Table 1).

It should be noted that the DFT-PBE method reproduces the Fe...C distances much more correctly than the HF method (even with extended basis sets). For instance, the Fe...C distance in the ferrocene molecule **4** was found to be 2.20 (HF) and 2.065 Å (DFT-PBE); the latter value virtually coincides with the experimental result, 2.064(3) Å.[14] The ground-state structure of molecule **4** has a D_{5h} symmetry. The structure with D_{5d} symmetry corresponds to the transition state of rotation about the principal axis with a potential barrier of 0.9 kcal mol^{-1}.

Energy characteristics. Let us denote the dissociation energy of the Fe—pent* bond in a complex with the ordinal number ***i*** as $E(\boldsymbol{i},\text{Fe—pent*})$. For complex **3**, this energy was estimated using the halved value of the heat of the reaction

$$\mathbf{3} \rightarrow 2\ \text{FeCp} + C_{60}. \qquad (1)$$

We found that $E(\mathbf{3},\text{Fe—pent*}) = 66.1$ kcal mol^{-1} (see Table 1).

For complex **2**, taking into account the heat of the reaction,

$$\mathbf{2} \rightarrow 2\ \text{FeCp} + H_{10}C_{60} \qquad (2)$$

we found that $E(\mathbf{2},\text{Fe—pent*}) = 134.1$ kcal mol^{-1}.

By analogy, the strength of the Fe—pent* bond in complex **1** was estimated using the halved value of the heat of the reaction

$$\mathbf{1} \rightarrow 2\ \text{FeCp} + \mathbf{1a} \qquad (3)$$

and it was found that $E(\mathbf{1},\text{Fe—pent*}) = 103.8$ kcal mol^{-1}.

The energy of the Fe—Cp bond, E(Fe—Cp), in the ferrocene molecule **4** (142.6 kcal mol^{-1}) calculated in the same approximation by the formula

$$E(\text{Fe—Cp}) = E_t(\text{FeCp}^\bullet) + E_t(\text{Cp}^\bullet) - E_t(\mathbf{4}) \qquad (4)$$

(hereafter, E_t(M) is the total energy of species M) was used as the reference strength of the η^5-bond.

However, this value of E(Fe—Cp) is much higher than the average energy, E_a(Fe—Cp), determined using the formula

$$2E_a(\text{Fe—Cp}) = 2E_t(\text{Cp}^\bullet) + E_t(^m\text{Fe}) - E_t(\mathbf{4}),$$

where m is the multiplicity.

If E_a(Fe—Cp) is calculated using the $E_t(^5\text{Fe})$ energy of the ground state of the Fe atom with the multiplicity 5 ($E_t(^5\text{Fe}) = -1263.4397$ au), one gets E_a(Fe—Cp) = 103.7 kcal mol^{-1}. An analogous estimate made with $E_t(^3\text{Fe}) = -1263.3619$ au (in this case, the spin is conserved) led to E_a(Fe—Cp) = 128.2 kcal mol^{-1}. If we compare the calculated and experimental[15] values, it is easily seen that the DFT-PBE method overestimates the average bond energy in the ferrocene molecule by more than 30 kcal mol^{-1} in the basis set used. On going to the TZ basis set for all atoms this difference decreases by ~10 kcal mol^{-1}.

Comparison of the energies of the Fe—pent* bond in complexes **1—3** and the energy of the Fe—Cp bond, E(Fe—Cp), in the ferrocene molecule **4** shows that these values increase in the order **3** < **1** < **2** < **4**. This pattern of changes in the bond energy is consistent with the above-mentioned shortening of the Fe—C_{Cp} distance in complexes **1—4**.

Thus, the results of our calculations showed that complex **2**, with the bis(cyclopentadienyl) derivative **2a** of C_{60} fullerene as a ligand, should be the most stable among systems **1—3**. Complex **3** with the "naked" C_{60} cluster is the least stable, while complex **1** is intermediate in stability. However, the energy of the Fe—pent* bond in "coated" complex **1** is rather high, which suggests the existence of this complex. Closed electron shell and rather large energy difference between the lowest unoccupied and highest occupied MOs (2.14 eV) are additional arguments in favor of kinetic stability of this complex.

The authors express their gratitude to D. N. Laikov for providing acfcess to the PRIRODA program. We estimated this program at our true worth.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-33216), the Russian Federation Ministry of Industry, Science, and Technology (Project No. 9.4.06), the Russian Federation State Scientific and Technical Program "Condensed Matter Physics" (investigation line "Fullerenes and Atomic Clusters"), and the INTAS (Grant 00-237).

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Received October 8, 2001;
in revised form December 3, 2001