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Endohedral analogs of ferrocene: ab initio theoretical predictions

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Abstract

The problem of the existence of endohedral analogs of ferrocene is discussed. It is shown that radical $CorH_5^{\bullet}$, where Cor is corannulene $C_{20}H_{10}$ and five atoms H are added to the α-positions relative to the five-membered cycle (*pent**) of Cor, can form stable polyhedral dimer D_{2h}-$C_{40}H_{30}$ (D). The ground state of D is triplet. The energy of dimerization of $CorH_5^{\bullet}$ is equal to 175 kcal mol^{-1}. The geometric and electronic structure of hypothetical endohedral complex D_{5d}-2η^5-Fe@D (**1**) and its isomer D_{5d}-2η^5-Fe$(CorH_5)_2$ (**1b**), which is a sandwich complex, are simulated by the ab initio MO LCAO SCF method (HF/3-21G). It is found that the energy of **1** is less than the energy of **1b** by 171 kcal mol^{-1}. The energies of the Fe–*pent** bond in complexes **1** (115 kcal mol^{-1}) and **1b** (111 kcal mol^{-1}) are close to those of the Fe–Cp bond in bis(cyclopentadienyl)iron $FeCp_2$ (110 kcal mol^{-1}). Complex **1** and also complex D_{5d}-2η^5-Fe@$C_{40}H_{10}$ (**2**), carbon skeletons of which have an analogous structure to **1** and with ten H added to the α-positions relative to polar pentagons (*pent**), can be considered as endohedral analogs of ferrocene. Atom Fe in these complexes interacts with atoms of both polar pentagons. The binding energy of the atom Fe with the polyhedral fragment $C_{40}H_{10}$ of **2** is a bit less than in **1** (on 6 kcal mol^{-1}). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Sandwich complexes; Endohedral clusters; Fullerenes; Hydrofullerenes; Atom Fe; Quantum-chemical calculations; Ab initio HF/3-21G method

1. Introduction

In the late 1960s, the following problem was formulated by Professor A.N. Nesmeyanov: to synthesize a polyhedral molecule with a skeleton of the cage consisting of carbon atoms and containing an atom Fe (or any other transition metal) inside, linked by the $\pi(\eta^5)$-bonds with two carbon five-membered cycles of the cage [1]. It would seem that such a polyhedral complex can be produced from ferrocene, if the atoms of two pentagons of this species were connected by five bridges made of groups $(CH)_n$ or $(CH_2)_n$, with the formation of a polyhedral molecule in symmetry D_{5h} or D_{5d}. However in practice, this notion was not a success.

At the same time, attempts to solve the Nesmeyanov task, by theoretical methods, led to the proof of the possibility of the existence of such polyhedral carbon molecules, such as the homoatomic cluster I_h–C_{60} [2]. In 1985, this prediction was confirmed experimentally. Moreover, together with the cluster C_{60}, different polyhedral molecules C_n and also their endohedral complexes were produced: C_{70}, La@C_{60} and other similar species [3,4]. However, polyhedral analogs of ferrocene, in which the atom Fe was bound with two pentagons by the $\pi(\eta^5)$-bonds, were not produced. It was noticed also that the polyhedral saturated hydrocarbon molecule $C_{20}H_{18}Me_2$ of dodecahedral shape was synthesized earlier [5]. However, its size was too small for the atom Fe, and the size of the C_{60} cavity was too large for atom Fe, which cannot simultaneously be bound to two pentagons. Therefore, the polyhedral analog of ferrocene should be searched among species Fe@C_n where $20 < n < 60$.

Recent ab initio calculations by SCF-HF and LDF methods had demonstrated that small fullerene cages C_{28}, C_{32} and C_{40} may form endohedral complexes in which the metal atom is sufficiently strongly bound with atoms of the carbon cage. The empty C_{28} fullerene is found to have a $^5A_2$ open shell ground state and behaves as a sort of hollow superatom, with an effective valence of four, both towards the outside and inside of

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the carbon cage. Ab initio calculations had predicted that C_{28} could be stabilized by inserting a tetravalent atom such as Si, Ge, Sn, Ti, Zr [6a]. Experimental data showed that the strength of the bond M–C_{28} is increased in the sequence $Ti < Zr < Hf < U$ [6b]. However, the complex of Zr was found to be the most stable at theoretical evaluations. Binding of *endo*-atoms such as C, Si, Ge, Sn with the carbon cage was found to be weaker than in the case of transition metals. Theoretical evidence showed that $C_{28}H_4$ and $C_{28}F_4$ in which atoms H and F were added to atoms with the most spin population, should be stable molecules [6c]. The possibility of simultaneous binding from the inside and outside of the C_{28} cage was also shown, based on theoretical results. It was supposed [6c] that mainly electronegativity of the metal atoms (M) determines the stability of the endohedral complexes M@C_{28}.

Complex Ti@C_{32} was found to be the most stable one among the metallofullerenes M@C_{32} [7]. The binding energies M–C_{32} for complexes D_{3h}-K@C_{32} D_{3d}-Cr@C_{32}, D_{3h}-Fe@C_{32} were found to be small. Formation of similar complexes M@C_{32} of Ca, Sc, Y and Zr proved to be energetically unfavorable.

Polyhedral cluster C_{40} has 40 isomers consisting of the five- and six-membered cycles. We shall discuss some properties of the isomers with the T_d and D_{5d} symmetry only. Cluster T_d-C_{40} can be considered as a superatom with an effective valence of four and cluster D_{5d}-C_{40} can be used for the modeling of polyhedral analogs of ferrocene. The ground state of cluster T_d-C_{40} has a multiplicity of five. Two isomers of D_{5d}-C_{40} with the singlet (I) and triplet (II) ground state exist [8a]. Cluster II can be considered a superatom with an effective valence equal to two. These isomers are distinguished by the structure of their polar caps. The polar cap of (I) consists of one pentagon and five hexagons, whereas in the case of II, six pentagons form the polar cap. The energy of cluster I is less than the energies of complexes T_d-C_{40} and II (38 and 364 kcal mol^{-1}, respectively). Cluster T_d-C_{40} can form endohedral complexes with atoms of Group IV of the periodic table. Notice that the stability of cationic complexes T_d-Nb@C_{40}^+ and T_d-Nb@$C_{40}H_4^+$ was proved theoretically in Ref. [8b].

The problem of the existence of endohedral metallofullerenes M@C_n with $n \leq 40$, in which η^5- or $2\eta^5$-bonds are formed, was not considered. Notice that the formation of such complexes of nonsubstituted fullerenes as well as similar exohedral ones is improbable since their π-systems are strongly delocalized and coefficients at AO of atom C in binding MO (at interaction M–C_n) are small ones. However, it was shown that for stabilization of *exo*-η^5-bonds in fullerene with atoms of a selected pentagonal face (*pent**), one can use two ways [9]:

1. to add to atoms C functional groups R (for example R = H, Cl, Br, Ph) to the α-positions relative to *pent** (we denote these atoms C by C^{α});
2. to substitute atoms C^{α} for heteroatoms of Groups III–V of the periodic table.

These theoretical predictions [9a,b] have obtained partial experimental confirmation: η^5-complexes η^5-$C_{60}Ph_5M$, M = Li, In, Tl were synthesized recently [10]. One can suggest that the first way to stabilization will also be useful in the case of endohedral η^5-complexes.

In the present paper, we return to the theoretical aspects of the Nesmeyanov task on the search for and simulation of geometric and electronic structure of polyhedral analogs of ferrocene. One of the ways to solve this problem can be reduced to formal substitution of each cyclopentadienyl radical in ferrocene on the bowl-shaped radical $C_{20}H_{15}^{\bullet}$ of cyclopentadienyl type which is produced from corannulene $C_{20}H_{10}$ (Cor) [11] as a result of addition of five H atoms to the α-positions, relative to its pentagon. If two radicals $CorH_5^{\bullet}$ are arranged so that their carbon skeletons are directed by convexity out, then peripheral C atoms of these bowl-shaped ligands can make up additional bonds, forming endohedral complexes D_{5d}-Fe@D (**1**) or D_{5h}-Fe@D* (**1a**) where D and D* are polyhedral dimers D_{5d}-$(C_{20}H_{15}^{\bullet})_2$ and D_{5h}-$(C_{20}H_{15}^{\bullet})_2$ of radical $C_{20}H_{15}^{\bullet}$, respectively.

In the present paper, results of ab initio calculations of endohedral complexes Fe@$C_{40}H_m$ ($m = 0, 10, 20, 30$) with symmetry D_{5d} (or D_{5h}), which can be considered as polyhedral analogs of ferrocene, constructed on the base of polyhedral dimers of corannulene or its derivatives, are reported and discussed. Classical sandwich complexes $FeCor_2$, $Fe(CorH_5)_2$ and *exo*-cluster D_{5d}-$2\eta^5$-$C_{40}H_{10}(FeCp)_2$ are also investigated.

2. Calculation details

The calculations were carried out by the ab initio HF/3-21G method at the RHF level for molecular systems with closed electron shells and at the ROHF level for radical and triplet states using the GAMESS program package [12] for DEC 3000 Alpha AXP-400X workstation. The analytical gradient method was used for optimization of geometric parameters. Procedures DIRSCF and SHIFT were used for acceleration of calculations.

It is well known that reasonably accurate calculations on organometallics require extended basis sets [13]. However, we are mainly interested in only the qualitative picture of species considered. Besides, complexes Fe@$C_{40}H_n$ contain a sufficiently large number of atoms. This is why we restrict by only the 3-21G basis.

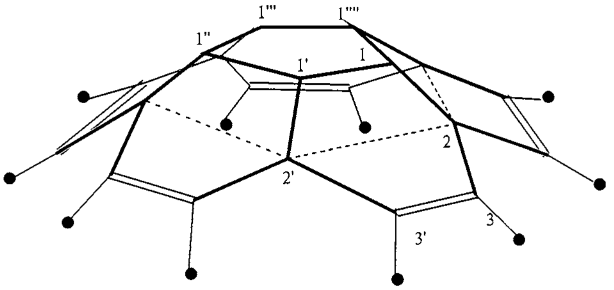


Fig. 1. Geometric structure of $C_{20}H_{10}$(Cor) in C_{5v} symmetry. Here and elsewhere points correspond to atoms H.

3. Results and discussion

3.1. *Corannulene $C_{20}H_{10}$ (Cor, Fig. 1), ions $CorH_5^-$, $CorH_5^+$ (Fig. 2) and radical $CorH_5^\bullet$ (Fig. 3)*

Results of the HF/3-21G calculations of corannulene, anion $CorH_5^-$ and radical $CorH_5$ are listed in Tables 1 and 2 (also see Ref. [14]). It was found that the molecule Cor and anion $CorH_5^-$ have C_{5v} symmetry, and the group symmetry of radical $CorH_5^\bullet$ is C_s. The reduced symmetry of this radical is a consequence of double degeneration of the HOMO level of $CorH_5^-$ (the Jahn–Teller effect).

The spin population of radical $CorH_5$ is localized at its pentagonal face (*pent**). Therefore this radical is a natural analog of cyclopentadienyl-radical (Cp). Besides, its geometric structure must aid the formation of the polyhedral dimer since hexagonal faces of $CorH_5^\bullet$ are bent out (for example dihedral angle $\theta^6 = 1{-}2{-}2'{-}3'$ is equal to 160°; see Table 2 and Fig. 3). Hexagons of Cor are bent in the other direction ($\theta^6 = -169°$). Since the HOMO level of anion $CorH_5^-$ is double degenerate, the ground state of cation $CorH_5^+$ must be triplet. This conclusion is confirmed by calculations (see Tables 1 and 2 and Fig. 2).

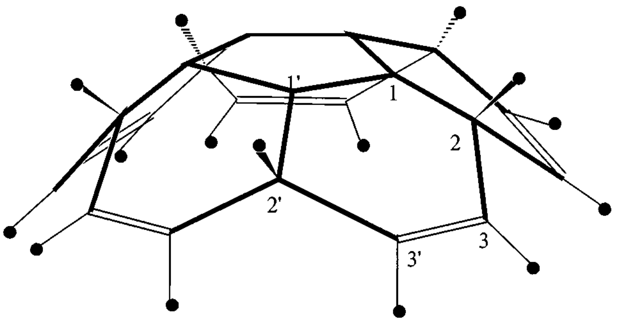


Fig. 2. Geometric structure of ions $CorH_5^-$ and $CorH_5^+$ in C_{5v} symmetry.

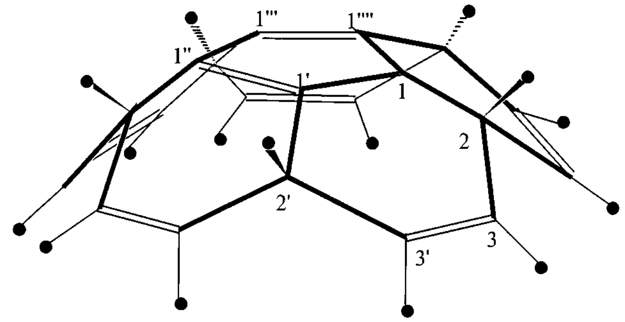
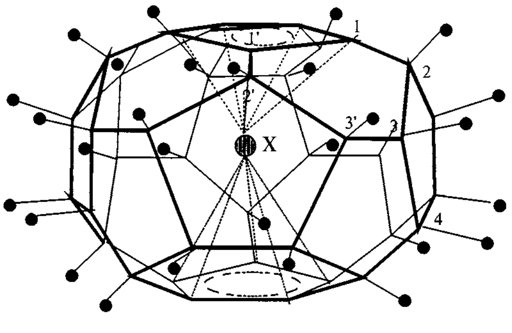


Fig. 3. Geometric structure of radical $CorH_5^\bullet$ in C_s symmetry.

3.2. *Sandwich complexes of atom Fe with radicals $CorH_5^\bullet$*

Local minima on the potential energy surface (PES) of system $[Fe + 2(CorH_5^\bullet)]$ which correspond to species D_{5d}-2η^5-Fe@D (**1**, Fig. 4), D_{5h}-2η^5-Fe@D* (**1a**, Fig. 5), D_{5h}-2η^5-Fe$(CorH_5)_2$ (**1b**, Fig. 6), D_{5d}-2η^5-Fe$(CorH_5)_2$ (**1c**)[1] were found. The first two species can be considered as endohedral complexes of two isomers of hydrofullerene $C_{40}H_{30}$ with symmetry D_{5d} and D_{5h}, respectively; the two other species are typical sandwich complexes. The carbon cage of **1** (fullerene D_{5d}-C_{40}) consists of 12 pentagons and ten hexagons. Fullerene D_{5h}-C_{40} contains two pentagons, 15 hexagons and five tetragons.

Energy characteristics of complexes under consideration are listed in Table 1, and geometric ones are contained in Tables 2 and 3. It follows from Table 1 that the species investigated have closed electron shells. The total energy E_t of **1** is minimal. The energies of the sandwich complexes **1b** and **1c** are practically equal. These complexes are conformers.



1, X =Fe; **3**, X — default

Fig. 4. Geometric structure of endohedral complex D_{5d}-2η^5-Fe@$C_{40}H_{30}$ (**1**) and hydrofullerene C_{2h}-$C_{40}H_{30}$ (**3**). Hydrofullerene **3** (≡D) is a polyhedral dimer of radical $CorH_5^\bullet$.

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[1] The geometric structure of **1c** can be produced from **1b** (Fig. 6) as a result of the rotation of the moiety of $CorH_5$ by an angle 36°, relative to the symmetry axis.

Table 1

Energy characteristics of species considered: total energies (E_t), energies of the Fe–*pent** bonds ($\Delta_{Fe-pent*}$), energies of dimerization (Δ_{dimer}), energies of HOMO (E_{HOMO}) and LUMO (E_{LUMO}) and their symmetry, effective charges (q) and multiplicity (m) of ground state calculated by HF/3-21G level

System	Number	m	Symmetry	$-E_t$ (a.u.)	$\Delta_{Fe-pent*}$ (Δ_{dimer}) (kcal mol^{-1}) [a]	E_{HOMO} (eV)	E_{LUMO} (eV)	q (a.u.)						
								C^1	C^2	C^3	M	H^{α} [b]	H	$-\Sigma q_c$
Cor		1	C_{5v}	758.9082	–	-8.24 e_2	1.82 e_1	0.01	−0.10	−0.20	–	–	0.24	2.44
$CorH_5^{\bullet}$		2	C_s	761.6743	–	-3.22 a'	4.47 a'	0.11^{1} 0.03^{2} 0.07^{2}	-0.47^{1} -0.45^{4}	−0.16	–	0.27^{1} 0.26^{2} 0.27^{2}	0.22	3.52
$CorH_5^-$		1	C_{5v}	761.6868	–	-1.98 e_1	8.39 e_2	0.00	−0.43	−0.16	–	0.20	0.17	3.75
$CorH_5^+$		3	C_{5v}	761.4585	–	-9.01 e_1	1.49 e_2	0.13	−0.47	−0.16	–	0.32	0.28	3.37
Fe–$CorH_5^+$	**4a**	1	C_{5v}	2017.6951	-54.5^{6} 110.4^{2} -59.7^{5} 135.4^{3} 85.5^{1}	-12.49 e_1	-4.63 a_1	−0.14	−0.45	−0.15	1.52	0.27	0.26	4.45
Fe–$CorH_5^{\bullet}$	**4b**	2	C_s	2017.8925	-71.2^{5} 123.8^{3} 73.9^{1}	-1.99 a'	1.65 a'	−0.12	−0.44	−0.16	0.78	0.27	0.22	3.60
Fe@$CorH_5^+$	**5a**	1	C_{5v}	2017.7214	-38.0^{6} 126.9^{2} -43.2^{5} 16.6^{3} -33.4^{1}	-12.79 e_1	-3.23 a_1	−0.13	−0.43	−0.20	1.46	0.32	0.27	4.76
Fe@$CorH_5^{\bullet}$	**5b**	2	C_{5v}	2017.6608	-216.5^{5} -21.4^{3} -71.4^{1}	-1.76 a_1	2.56 e_1	−0.08	−0.42	−0.19	0.71	0.27	0.23	4.30
Fe–$(CorH_5)_2$	**1b**	1	D_{5h}	2779.7427	110.3 19.7^{5} 117.0^{3} 92.1^{1}	-8.18 e''_1	4.19 e'_1	−0.12	−0.45	−0.16	1.78	0.26	0.22	8.82
Fe–$(CorH_5)_2$	**1c**	1	D_{5d}	2779.7433	110.7 19.7^{5} 117.2^{3} 92.3^{1}	-8.20 e_{1g}	4.20 e_{1u}	−0.12	−0.45	−0.16	1.78	0.26	0.22	8.85
Fe@D [c]	**1**	1	D_{5d}	2780.0165	427.2 17.2^{5} 115.2^{3} 90.3^{1}	-7.86 e_{1u}	5.05 a_{1u}	−0.16	–0.30	–0.22	2.36	0.23	0.22	9.02
Fe@D_1 [c]	**6**	1	D_{5d}	2773.7678	-97.4^{5} 0.8^{3} -24.9^{1}	-3.47 a_{1g}	1.29 a_{1u}	−0.16	0.04	−0.25	1.57	–	0.23	4.61

Table 1 (Continued)

System	Number	m	Symmetry	$-E_t$ (a.u.)	$\Delta_{Fe-pent*}$ (Δ_{dimer}) (kcal mol^{-1}) [a]	E_{HOMO} (eV)	E_{LUMO} (eV)	q (a.u.)						
								C^1	C^2	C^3	M	H^{α} [b]	H	$-\Sigma q_c$
Fe@D* [c]	**1a**	1	D_{5h}	2779.4418	–	$5.28\ e''_1$	$1.63\ e'_2$	−0.12	−0.34	−0.21	2.03	0.24	0.22	8.86
Fe@C_{40}	**7**	1	D_{5d}	2761.5127	−128.6	$-7.60\ e_{1g}$	$-0.82\ a_{2u}$	−0.11	−0.04	−0.03	1.96	–	–	1.96
Fe@$C_{40}H_{10}$	**2**	1	D_{5d}	2767.8524	14.5^5	$-6.18\ a_{2u}$	$0.86\ a_{1u}$	−0.12	−0.42	0.03	2.12	0.27	–	4.81
					112.1^3									
					87.1^1									
Cor_2 (D_1)	**6a**	1	D_{5d}	1517.7468	(−43.6)	$-7.26\ e_{1u}$	$2.11\ a_{1u}$	−0.05	0.10	−0.26	–	–	0.24	4.80
$(CorH_5)_2$ (D)	**3**	3	C_{2h}	1523.6283	(175.5)	$-3.15\ b_u$	$4.77\ a_g$	0.11^1	-0.36^1	–0.20	–	0.24^1	0.22^2	6.68
						$-2.35\ a_g$		0.03^2	-0.32^2			0.22		
								0.07^2	-0.34^2			0.23^2		
C_{40}	**7a**	1	D_{5d}	1505.5912	–	$-8.35\ e_{1g}$	$-1.06\ e_{2g}$	0.01	−0.01	–	–	–	–	0.00
$C_{40}H_{10}$	**2a**	3	C_{2h}	1511.4742	–	$-4.09\ b_u$	$0.88\ b_u$	0.13^1	-0.48^1	0.06	–	0.28	–	2.72
						$-4.04\ a_g$		0.05^2	-0.45^2					
								0.09^2	-0.47^2					
Fe–$Cp^{\bullet}$ [d]		2	C_{5v}	1447.3158	-73.9^5	$-2.23\ a_1$	$1.45\ e_1$	−0.40	–	–	0.65	–	0.25	–
					121.1^3									
					71.2^1									
$FeCp_2$ [d]		1	D_{5d}	1638.5937	110.4	$-9.10\ e_{1g}$	$3.37\ e_{1u}$	−0.40	–	–	1.38	–	0.26	3.98
					18.2^5									
					115.7^3									
					90.8^1									
$C_{40}H_{10}(FeCp)_2$	**8**	1	D_{5d}	4405.7342	116.5	$-2.76\ e_{1g}$	$-0.70\ e_{1u}$	−0.12	−0.44	0.05	1.52	0.26	–	4.58

[a] The superscript denotes the multiplicity of the electron state of Fe or Fe^+ in Eq. (1) for sandwich complexes and in equations $\Delta E = E_t({}^m Fe) + E_t(C_{20}H_n^+) - E_t(FeC_{20}H_n^+)$ or $\Delta E = E_t({}^m Fe^q) + E_t(C_{20}H_n) - E_t(C_{20}H_n^q)$ in half-sandwich complexes.

[b] Atoms H^{α} are added to atoms C in the α-positions relative to one (or two) face *pent**.

[c] D is a polyhedral dimer of $CorH_5^{\bullet}$ in symmetry D_{5d}, D_1 is a polyhedral dimer of Cor in symmetry D_{5d}, D* is a polyhedral dimer of $CorH_5^{\bullet}$ in symmetry D_{5h}. Note: total energies E_t of the atom Fe and the cation Fe^+ in level HF/3-21G are equal to (a.u.): −1256.1003 (^{1}Fe), −1256.0207 (^{3}Fe), −1256.3318 (^{5}Fe), −1255.8447 ($^2Fe^+$), −1256.1077 ($^6Fe^+$).

[d] Data from [15].

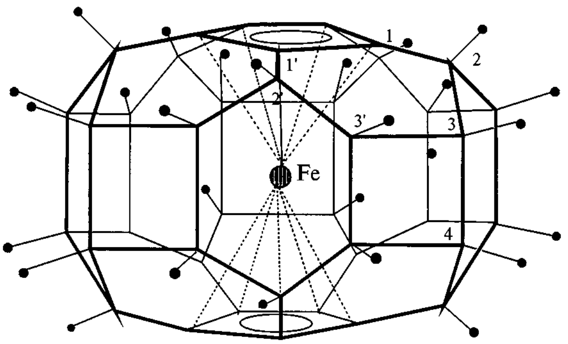
Table 2

Distances (d/Å), bond order (W/a.u.), angles between bond C(1)–C(2) and plane of *pent** (φ), dihedral angles C(1)–C(2)–C(2′)–C(3′) in hexagons (θ^6) of species calculated by HF/3-21G level

System	C^1–$C^{1'}$		C^1–C^2		C^2–C^3		C^3–$C^{3'}$		Fe–C^1		Fe–*pent**		φ (°)	θ^6 (°)
	d [a]	W	d	W	d [a]	W	d	W	d	W	d	W		
Cor	1.415	1.187	1.359	1.392	1.449	1.180	1.368	1.655	–	–	–	–	23	−169
$\mathrm{CorH}_5^{\bullet}$	1.442^2	1.150	1.491^1	0.921	1.528	0.905	1.320	1.920	–	–	–	–	10^1	161
	1.341^2	1.655	1.494^2	0.919									7^2	
	1.470^1	1.116	1.491^2	0.916									6^2	
CorH_5^-	1.396	1.388	1.497	0.925	1.528	0.905	1.321	1.924	–	–	–	–	18	161
CorH_5^+	1.411	1.233	1.485	0.904	1.530	0.900	1.319	1.916	–	–	–	–	17	160
Fe–CorH_5.	1.405	1.265	1.491	0.933	1.526	0.909	1.319	1.924	2.196	0.205	1.841	1.025	17	160
Fe–CorH_5^+	1.412	1.211	1.494	0.923	1.526	0.906	1.318	1.922	2.120	0.295	1.747	1.475	18	160
Fe@$\mathrm{CorH}_5^{\bullet}$	1.401	1.323	1.492	0.913	1.534	0.910	1.329	1.880	2.434	0.091	2.202	0.455	16	159
Fe@CorH_5^+	1.413	1.247	1.493	0.898	1.528	0.902	1.328	1.849	2.099	0.205	1.721	1.025	17	160
D_{5d}-Fe–$(\mathrm{CorH}_5)_2$	1.404	1.275	1.491	0.941	1.527	0.910	1.320	1.924	2.182	0.167	1.828	0.835	18	160
D_{5h}-Fe–$(\mathrm{CorH}_5)_2$	1.404	1.275	1.491	0.942	1.527	0.910	1.320	1.923	2.184	0.167	1.828	0.835	18	160
D_{5d}-Fe@D	1.404	1.254	1.468	0.908	1.565	0.912	1.592	0.924	2.099	0.157	1.726	0.785	6	151
D_{5h}-Fe@D*	1.421	1.276	1.502	0.937	1.558	0.910	1.585	0.917	2.254	0.107	1.902	0.535	12	159
Fe@D_1	1.487	1.008	1.344	1.611	1.513	0.934	1.559	0.906	2.462	–	2.112	–	35	165
Fe@C_{40}	1.455	1.109	1.391	1.317	1.447	1.150	1.374	1.434	2.403	0.124	2.060	0.620	24	168
Fe@$\mathrm{C}_{40}\mathrm{H}_{10}$	1.419	1.273	1.524	0.839	1.534	0.925	1.468	1.092	2.200	0.145	1.834	0.725	9	142
Cor_2 (D_1)	1.478	1.020	1.312	1.825	1.514	0.931	1.577	0.904	–	–	–	–	26	−176
$(\mathrm{CorH}_5)_2$ (D) triplet	1.424^2	1.174	1.461^1	0.902	1.588	0.916	1.563	0.886	–	–	–	–	12	151
	1.338^2	1.625	1.469^2	0.899										
	1.456^1	1.134	1.466^2	0.899										
$\mathrm{C}_{40}\mathrm{H}_{10}$ triplet	1.457^2	1.144	1.523^1	0.850^1	1.530	0.909	1.456	1.094	–	–	–	–	13	145
	1.352^2	1.653	1.530^2	0.848^2										
	1.493^1	1.108	1.528^2	0.845^2										
C_{40}	1.471	1.118	1.381	1.480	1.452	1.111	1.339	1.545	–	–	–	–	31	176
$\mathrm{C}_{40}\mathrm{H}_{10}(\mathrm{FeCp})_2$ [b]	1.426	1.220	1.529	0.887	1.531	0.898	1.326	1.717	2.153	0.214	1.778	1.070		
	(1.418)	(1.256)							(2.298)	(0.176)	(1.956)	(0.880)	3	150

[a] The superscript denotes the number of bonds (or angles) of the given length (or deg).

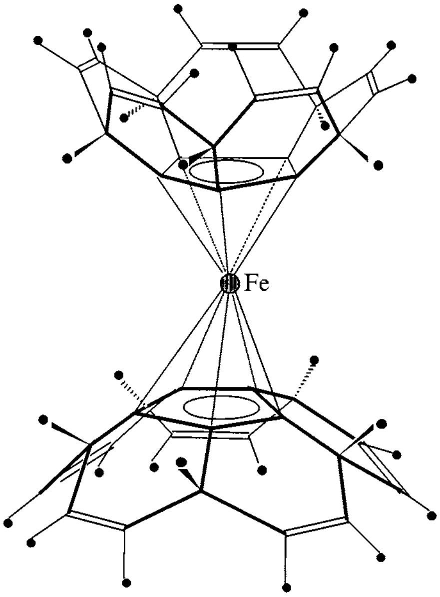
[b] Data in brackets are related to Cp–ligand.



1a

Fig. 5. Geometric structure of endohedral complex D_{5h}-2η^5-Fe@C$_{40}$H$_{30}$ (**1a**). Here hydrofullerene D_{5h}-C$_{40}$H$_{30}$ (≡ D*) is an isomer of **3**.

The energy E_t of **1b** exceeds the energy of the endohedral complex **1** by 172 kcal mol^{-1}. This is a consequence of the formation of the closed polyhedral structure **1**. The total energy of **1a** exceeds the energy of **1** by 360 kcal mol^{-1}. This is a consequence of the great strain of bonds in the tetragons of **1a** (see Fig. 5). Vertical ionization potentials of complexes **1** and **1b**,**c** are sufficiently high ($-E_{\mathrm{HOMOs}} \approx 8$ eV). Energies of the HOMO and LUMO of each of these complexes are distinguished by more than 12 eV. Based on the results mentioned above, it can be affirmed that complexes **1** and **1b**,**c** are kinetically stable systems.



1b

Fig. 6. Geometric structure of sandwich complex D_{5h}-2η^5-Fe(CorH$_5$)$_2$ (**1b**). The structure of the **1c** can be produced from **1b** as a result of rotation of a moiety CorH$_5^{\bullet}$ relative to the symmetry axis of angle 36°.

Calculations of half-sandwich complexes (Fe–CorH$_5$)^q and (Fe@CorH$_5$)^q at charges $q = 0$, 1, and also of polyhedral fragment C$_{40}$H$_{30}$ of complex **1**, were carried out for estimations of the strength of the Fe–*pent** bonds. Here we have used the symbol @ to designate the inner arrangement of atom Fe relative to carbon skeleton of Cor.

Results of calculation of the electronic and geometric structure of cation Fe–CorH$_5^+$ (**4a**) and radical Fe–CorH$_5^{\bullet}$ (**4b**) are listed in Table 1 and Fig. 2 (see Fig. 7). It is found that the electron shell of cation **4a** is closed and the symmetry group of **4a** and **4b** is C_{5v}. The energy of dissociation of **4a** on cation ^{2}Fe$^+$ (with multiplicity 2) and radical CorH$_5^{\bullet}$ is equal to 110.4 kcal mol^{-1}, whereas the heat of reaction **4a** → ^{3}Fe + CorH$_5^+$ amounts to 135.4 kcal mol^{-1}. The spin population of CorH$_5^{\bullet}$ is localized at atoms of the pentagon. Therefore it would seem that the coordination of atom Fe with the inner side of Cor is impossible. However, we found complexes Fe@CorH$_5^+$ (**5a**, Fig. 8) and Fe@CorH$_5^{\bullet}$ (**5b**, Fig. 8), which are by isomers of **4a** and **4b** accordingly (see Fig. 7), with similar arrangement of atoms Fe. Complexes **5a** and **5b** have C_{5v} symmetry. It follows from Table 1 that cluster **5a** is more stable than its isomer **4a** by 16.5 kcal mol^{-1} and the distance Fe–*pent** in **5a** is less than **4a** (0.026 Å). This is the consequence of the additional interaction of atom Fe with atoms of carbon skeleton.

The ground state of the polyhedral hydrocarbon molecule C$_{40}$H$_{30}$ (**3**, see Fig. 4) is triplet and the symmetry of **3** is $C_{2h} = i \times C_s$. Cluster **3** is a polyhedral dimer D of radical CorH$_5^{\bullet}$. The energy of dimerization is equal to 175.5 kcal mol^{-1}. The spin population in this biradical is localized on atoms of polar pentagon (*pent**) and differs little for each such *pent** from the spin population in cyclopentadienyl radical and CorH$_5^{\bullet}$. Similarly to ferrocene and complexes **1b**,**c**, atom Fe in **1** is coordinated at η^5-type with two polar five-membered faces of molecule **3**. Energy dissociation of **1** on radicals **5a** and CorH$_5^{\bullet}$ is equal to 427 kcal mol^{-1}. Therefore complex **1** must be a thermodynamically stable species. The energy ΔE of Fe–*pent** binding for complex **1** is determined by

$$2\Delta E = E_t(^m\mathrm{Fe}) + E_t(\mathrm{C}_{40}\mathrm{H}_n) - E_t(\mathrm{Fe@C}_{40}\mathrm{H}_n) \qquad (1)$$

where m is the multiplicity of Fe. For the ground state ^{5}Fe and $n = 30$, this energy is equal to 17.2 kcal mol^{-1}. If it is assumed that the multiplicity of the valence state of atom Fe is equal to three, an analogous value amounts to 115.2 kcal mol^{-1}. Distances Fe–C(1) and Fe–*pent** in **1** are shorter than in complex **1c** (see values R^1 in Table 3).

It is noticed that the effective charge on atom Fe in the classical sandwich complex **1c** is equal to 1.87 a.u. and its value is determined by a_{1g} and e_{1g} MOs and three lone pairs mainly localized on d$_z$2, d$_x$2$_{-y}$2, d$_{xy}$

Table 3
Bond lengths (d/Å), bond orders (W/a.u.), distances from atoms C^i up to center of cluster (R^i/Å), height of carbon skeleton (H/Å) and its diameter (D/Å), dihedral angles C(2)–C(3″)–C(3′)–C(4) in side pentagonal face (θ^5) of polyhedral species calculated by HF/3-21G level

System	C^3–C^4		R^1	R^2	R^3	H	D	θ^5 (°)
	d	W						
D_{5d}–Fe@D	1.572	0.894	2.462	2.720	3.345	4.223	6.691	138
D_{5d}–Fe@D$_1$	1.566	0.892	2.099	3.082	3.416	3.452	6.831	158
D_{5h}–Fe@D*	1.589	0.905	2.254	3.108	3.447	3.804	6.894	–
D_{5d}–Fe@C$_{40}$	1.487	1.056	2.403	2.916	3.105	3.538	6.210	167
D_{5d}–Fe@C$_{40}$H$_{10}$	1.347	1.642	2.200	3.146	3.171	3.679	6.342	177
D triplet	1.563	0.885	2.090	3.054	3.393	3.44	6.786	157
D$_1$	1.578	0.881	2.300	2.793	3.382	3.853	6.765	140
D_{5d}–C$_{40}$H$_{10}$ triplet	1.347	1.508	2.279	3.130	3.126	3.84	6.259	178
D_{5d}–C$_{40}$	1.512	1.006	2.569	2.870	3.057	4.120	6.114	166
D_{5d}–C$_{40}$H$_{10}$(FeCp)$_2$	1.478	1.043	2.476	3.143	3.059	4.318	6.118	178

AO. The effective charge on atom Fe in endohedral complex **1** amounts to 2.36 a.u. since the lone electron pairs transfer partial electron density to the carbon cage (see value $\Sigma\, q_c$ in Table 1).

3.3. Endohedral sandwich complex D_{5d}-2η^5-Fe@C$_{40}$H$_{10}$ (2)

Complex **2**, with the polyhedral carbon skeleton C$_{40}$ (Fig. 9), can also be considered as another cage analog of ferrocene. All ten H atoms in complex **2** are added to the atom C^α connected with the corresponding polar pentagons. A local minimum of energy for complex **2** was found. The ground state of this species has a closed electron shell; the HOMO–LUMO energy gap amounts to 3.0 eV. Therefore it can be affirmed that complex **2** is a kinetically stable system. Distance Fe···*pent** amounts to 1.726 Å (polar *pent** faces are strongly drawn together with atom Fe). Bond order Fe–*pent**, calculated as a sum of the bond orders of atom Fe with all atoms C forming the face *pent**, is equal to 0.79 a.u. This value is significantly more than those for complex **1**. However, the effective charge at atom Fe ($q = +2.15$ a.u.) in complex **2** is slightly smaller than in complex **1**. Notice also that bonds of C(3)–C(4) in cluster **2** and the symmetry equivalent to them are the shortest ones among analogous ones for complexes under consideration (see Table 3).

Hydrofullerene C$_{40}$H$_{10}$ (**2a**, see Fig. 9) contains a higher number of π-electrons than C$_{40}$H$_{30}$. The conjugated system of polyhedral molecule **2a** is separated into three isolated subsystems: two conjugated subsystems are localized on polar faces *pent**, atoms of cycle C$_{20}$ form the third conjugated system consisting of atoms disposed close to equator (see the Schlegel diagram of **2a** on Fig. 10). The spin population is also localized on polar faces (see Table 4).

The ground state of molecule **2a** has C_{2h} symmetry. The multiplicity of the ground electronic state of this species is equal to three. The vertical ionization potential amounts to 3.7 eV, the HOMO–LUMO energy gap is equal to 4.1 eV. It can be affirmed that the biradical **2a** is a stable system.

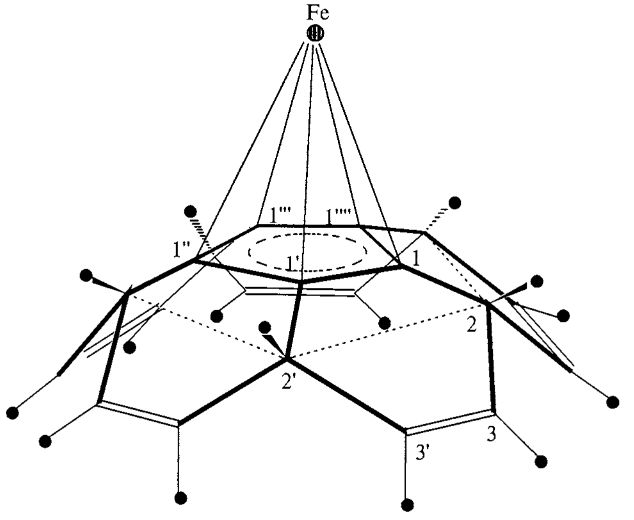


Fig. 7. Geometric structure of half-sandwich complexes η^5-Fe–CorH$_5^+$ (**4a**) and η^5-Fe–CorH$_5^\bullet$ (**4b**) in C_{5v} symmetry.

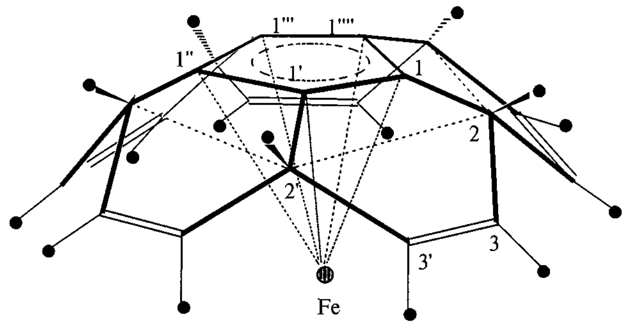
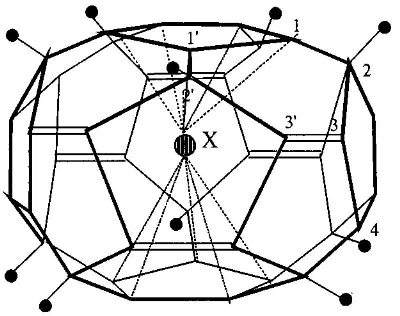


Fig. 8. Geometric structure of half-sandwich complexes η^5-Fe@CorH$_5^+$ (**5a**) and η^5-Fe@CorH$_5^\bullet$ (**5b**) in C_{5v} symmetry.



2, X =Fe; **2a**, X — default

Fig. 9. Geometric structures of endohedral complex D_{5d}-2η^5-Fe@$C_{40}H_{10}$ (**2**) and hydrofullerene D_{5d}-$C_{40}H_{10}$ (**2a**).

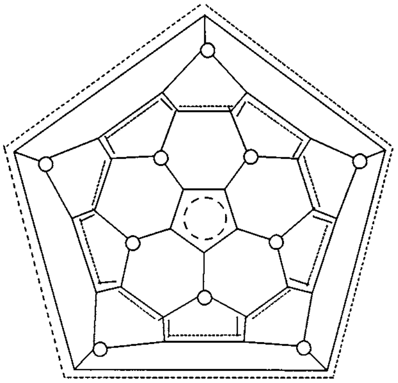


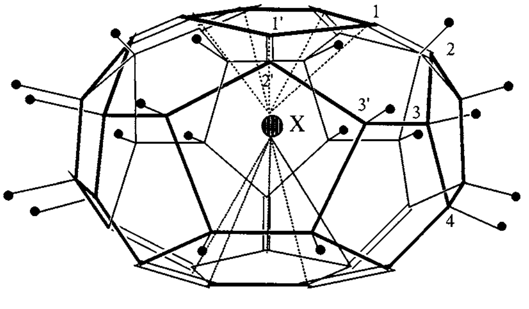
Fig. 10. Two-dimensional Schlegel diagram for hydrofullerene D_{5d}-$C_{40}H_{10}$; circles correspond to group CH, dotted lines conform to three independent conjugated systems.

3.4. Sandwich complex of atom Fe with polyhedral dimer of corannulene

The influence of H atoms added to atoms C^{α} on the stability of the polyhedral analog of ferrocene was also investigated by example of complex D_{5d}-Fe@D_1 (**6**, Fig. 11) where D_1 is the polyhedral dimer of corannulene–hydrofullerene D_{5d}-$C_{40}H_{20}$ (**6a**, see Fig. 11). It was found that complex **6** has a closed electron shell. However, it is necessary to expend energy for formation of **6** from the atom Fe and the two molecules Cor (see Table 1). In contradistinction to the case of dimer D, formation of **6a** requests expense of energy (43.6 Kcal mol^{-1}).

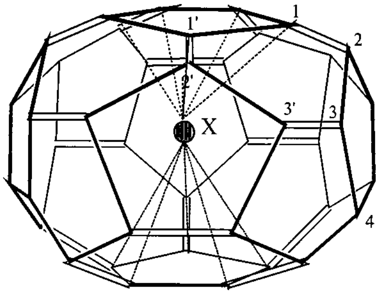
Table 4
Spin populations (ρ) at atoms in radicals calculated by HF/3-21G level

Radical or biradical	ρ (a.u.)			
	C(1)	C(1′)	C(1″)	Fe
$CorH_5^{\bullet}$	0.62	0.02	0.15	–
$(CorH_5)2^{\bullet\bullet}$ (D)	0.56	0.02	0.17	–
$C_{40}H_{10}^{\bullet\bullet}$	0.62	0.02	0.15	–
Fe–$CorH_5^{\bullet}$	0.00	0.00	0.00	0.98
Fe@$CorH_5^{\bullet}$	0.002	0.002	0.002	0.96



6, X =Fe; **6a**, X — default

Fig. 11. Geometric structure of endohedral complex D_{5d}-2η^5-Fe@D_1 (**6**) where D_1 is a polyhedral dimer D_{5d}-$C_{40}H_{20}$ (**6a**) of corannulene.



7, X =Fe; **7a**, X — default

Fig. 12. Geometric structure of endohedral complex D_{5d}-2η^5-Fe@C_{40} (**7**) and fullerene D_{5d}-C_{40} (**7a**).

3.5. Endohedral complex D_{5d}-Fe@C_{40}

The optimal geometrical structures of complex D_{5d}-Fe@C_{40} (**7**) and fullerene D_{5d}-C_{40}. (**7a**, Fig. 12) were also calculated. It was found that these molecules have closed electron shells in the ground states. Their vertical ionization potentials are more than 7 eV. The HOMO–LUMO energy gaps exceed 8 eV. However, the formation of **7** from atom Fe and **7a** is not favorable and the energy expense is equal to 129 kcal mol^{-1}.

Thus, coordination of atom Fe relative to two polar pentagons of the polyhedral cluster C_{40} without the addition of atoms H (or other functional groups) to atoms C^{α} is improbable.

3.6. Exo-complex D_{5d}-2η^5-$C_{40}H_{10}(FeCp)_2$ (**8**)

We also simulated the geometric and electronic structure of complex D_{5d}-2η^5-$C_{40}H_{10}(FeCp)_2$ (**8**). Both ligands FeCp in this complex are located outside the carbon cage $C_{40}H_{10}$ (Fig. 13) and coordinated with atoms of polar five-membered cycles (*pent**). It was found that the electron shell of **8** is closed; the energy of

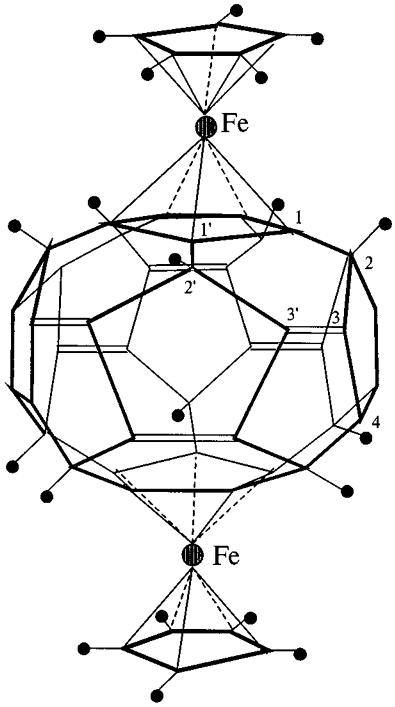


Fig. 13. Geometric structure of exohedral complex D_{5d}-2η^5-$C_{40}H_{10}(FeCp)_2$ (**8**).

the Fe–*pent** bond is equal to 116 kcal mol^{-1}. This value is slightly distinguished from the energy of the Fe–Cp bond in ferrocene (110 kcal mol^{-1}) and the energy of the Fe–*pent** *endo*-bond in complex **2** (112 kcal mol^{-1}). The distance Fe–*pent** is less than the distance Fe–Cp (see Tables 1 and 2).

4. Conclusions

Thus, only two complexes D_{5d}-Fe@$C_{40}H_{30}$ and D_{5d}-Fe@$C_{40}H_{10}$ among endohedral hydrofullerenes considered can be interpreted as polyhedral analogs of ferrocene. The energy of the Fe–*pent** bond in complex D_{5d}-Fe@$C_{40}H_{30}$ is equal to 115 kcal mol^{-1} and close to the energy of the Fe–Cp bond in the classical bis(cyclopentadienyl)iron $FeCp_2$ (110 kcal mol^{-1}) [15]. Complex D_{5d}-Fe@$C_{40}H_{10}$ must be slightly less stable than complex D_{5d}-Fe@$C_{40}H_{30}$ (energy of Fe–*pent** bond in this species is equal to 112 kcal mol^{-1}).

Acknowledgements

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