Indium-containing heterofullerenes and their η^5-π-complexes

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The molecular and electronic structure of hypothetical metallofullerenes In_5C_{55} (**1a**) and $In_{10}C_{60}$ (**2a**) were simulated by the MNDO/PM3 method. Formally, heterofullerene **1a** is obtained from the C_{60} cluster by replacement of the carbon atoms at α-positions relative to one of the pentagons by In atoms, and cluster **2a** is obtained from the C_{70} cluster by replacement of the carbon atoms framing the polar pentagons of this fullerene by In atoms. Along with clusters **1a** and **2a**, their η^5-π-complexes In(η^5-**1a**) (**1b**) and $In_2(2\eta^5$-**2a**) (**2b**) with one (**1b**) and two (**2b**) exohedral In atoms coordinated to the pentagons (*pent**) isolated by In atoms were also studied. The energies of the In—*pent** bonds in **1b** and **2b** are approximately equal to 104 kcal mol^{-1}.

Key words: fullerenes, metallofullerenes, indium, η^5-π-complexes; MNDO/PM3 method.

The possibility of existence of η^5-π-complexes of fullerene C_{60} has been discussed in a number of papers.[1–6] It has been shown[1] that complexes of such a type formed by the unsubstituted C_{60} cluster must be much less stable than their classical analogs. For this reason, it seems problematic that η^5-π-complexes of C_{60} can exist. At the same time it was established[2–6] that attachment of five functional groups R to the α-positions relative to one of the pentagons of fullerene C_{60} results in the formation of cluster R_5C_{60} whose delocalized 55-electron π-system can be divided into two parts consisting of 5 and 50 π-electrons and that the first of them has a cyclopentadienyl character. This must favor stabilization of η^5-π-complexes of the R_5C_{60} cluster formed upon coordination of an appropriate species (for instance, FeCp, *etc.*) to the pentagon (*pent**) isolated by functional groups R. Recently,[7] this hypothesis, theoretically substantiated earlier,[2–6] has been confirmed experimentally by the synthesis of the first representatives of pentahaptocyclopentadienyl complexes $MC_{60}R_5$ (M = K, Tl, and Li; R = Ph).

In a cage molecule (for instance, in cluster C_{60}), the cyclopentadienyl fragment can also be isolated in another fashion, namely, by replacement of carbon atoms at the α-positions relative to one of the pentagons by appropriate heteroatoms, which results in the formation of a polyhedral molecule (or radical) $C_{55}X_5$ (**1a**). Such an approach was used for X = Si, Ge, Sn, N, P, B, and Al.[8] In particular, it was shown that the insertion of these atoms into the carbon framework considerably stabilizes the η^5-π-complexes of **1a** with the Li atom. Analogously, replacement of carbon atoms at the α-positions relative to the polar pentagons of C_{70} by one of the atoms mentioned above (*i.e.*, when going to complex $X_{10}C_{60}$ (**2a**)) results in the formation of a system characterized by increased ability to form η^5-π-complexes as compared to C_{70}.[9]

In this work we investigate fullerenes **1a** and **2a** with X = In. Along with these systems, whose existence is of particular interest since the In—C σ-bonds are formed in these fullerenes, we also studied their half-sandwich η^5-π-complexes In(η^5-**1a**) (**1b**) and $In_2(2\eta^5$-**2a**) (**2b**).

Calculation Procedure

The calculations were performed by the MNDO/PM3 method[10,11] on a DEC 3000 AXP-400X workstation using the MOPAC 5.10 and GAMESS programs[12] in the RHF approximation for complexes **1b** and **2b** and in the ROHF approximation for radicals **1a** and **2a**.

Results and Discussion

Systems In_5C_{55} (1a) and In(η^5-In_5C_{55}) (1b). The results of calculations for systems **1a** and **1b** (Fig. 1) are shown in Table 1. Radical **1a** was calculated with full geometry optimization. Molecule **1b** was calculated assuming that its C_{5v} symmetry is conserved. Note that the highest occupied energy level of radical **1a** is degenerate in the case of C_{5v} symmetry. Due to the Jahn—Teller effect, the symmetry of cluster **1a** is reduced to C_s, which first of all manifests itself in the nonequivalence of the C—C bond lengths in the isolated pentagon (see Table 1). Their values lie within the 1.38 to 1.46 Å interval, whereas the lengths of the In(1)—C bonds differ slightly and are close to 2.1 Å. The In(1)—C bond orders (according to Wiberg) are approximately equal to 1.0. The highest occupied MO is localized on the *pent** fragment and the moduli of the coefficients at the p_z-AOs are rather large (greater than 0.4). In cluster **1a**,

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Table 1. Energy and structural characteristics of polyhedral systems **1**, **2** calculated by the MNDO/PM3 method: ΔH_f is the heat of formation; E_{HOMO} and E_{LUMO} are the energies of the highest occupied and lowest unoccupied levels, respectively; d is the bond length

System	Multiplicity	ΔH_f /kcal mol^{-1}	$-E_{HOMO}{}^a$	$-E_{LUMO}$	d/Å^b					
			eV		C(1)—C(1′)	C(1)—In(1)	In(1)—C(2)	C(2)—C(2′)	In(2)—C(1)	In(2)—*pent**
1a	Doublet	939	7.26^1	4.60	1.444^2 1.380^2 1.463^1	2.061^1 2.055^2 2.058^2	2.097	1.353	—	—
1b	Singlet	893	9.19^2	4.21	1.429	2.049	2.102	1.352	2.810	2.534
2a	Singlet	1190	9.25^1	6.17	1.422	2.040	2.102	1.340	—	—
	Triplet	1164	7.07^1	4.65	1.422	2.037	2.105	1.357	—	—
2b	Singlet	1062	8.35^2	4.16	1.430	2.053	2.095	1.345	2.810	2.533

Note: ΔH_f(In) = 58 kcal mol^{-1}.

[a] The subscript denotes the multiplicity of filling the corresponding level.

[b] Numbering of the atoms is shown in Figs. 1 and 2; the subscript denotes the number of bonds of the given length; the nearest symmetry-equivalent atoms are shown by primes.

the electron density is shifted to the In atoms (to −0.17 au) which can be considered as acceptors towards the bonded carbon atoms.

In π-complex **1b**, the lengths of the C—C bonds in the *pent** fragment are equal to 1.43 Å, the exohedral In atom is on the five-fold axis, and the In—*pent** distance is close to 2.5 Å. If the symmetry restrictions are removed, then the geometry of molecule **1b** remains unchanged. The $E_{HOMO} - E_{LUMO}$ energy gap is equal to ~5 eV, which points to the kinetic stability of complex **1b**.

The charges on the In atoms inserted into the carbon framework change slightly as compared to those of cluster **1a**, and a partial charge transfer from the exohedral In atom to the pentagon occurs. This is just the fact that determines the stability of complex **1b** (the energy of the In—*pent** bond is equal to 104 kcal mol^{-1} and the Wiberg index of this bond is equal to 0.88). Note that the In atom in molecule **1a** is univalent.

Systems $In_{10}C_{60}$ (2a) and $In_2(2\eta^5\text{-}In_{10}C_{60})$ (2b). Calculations for complex **2a** (Fig. 2) were performed for the singlet state under the assumption that the D_{5h} symmetry is conserved and for the triplet state with full geometry optimization. The triplet state (see Table 1), in which the electron densities of the unpaired electrons are localized on the polar pentagons, appeared to have the lower energy. The geometric parameters of molecule **2a** in the singlet and triplet states are close; the C—C bond lengths in the polar five-membered cycles are equal to 1.42 Å, while the lengths of the In(1)—C bonds

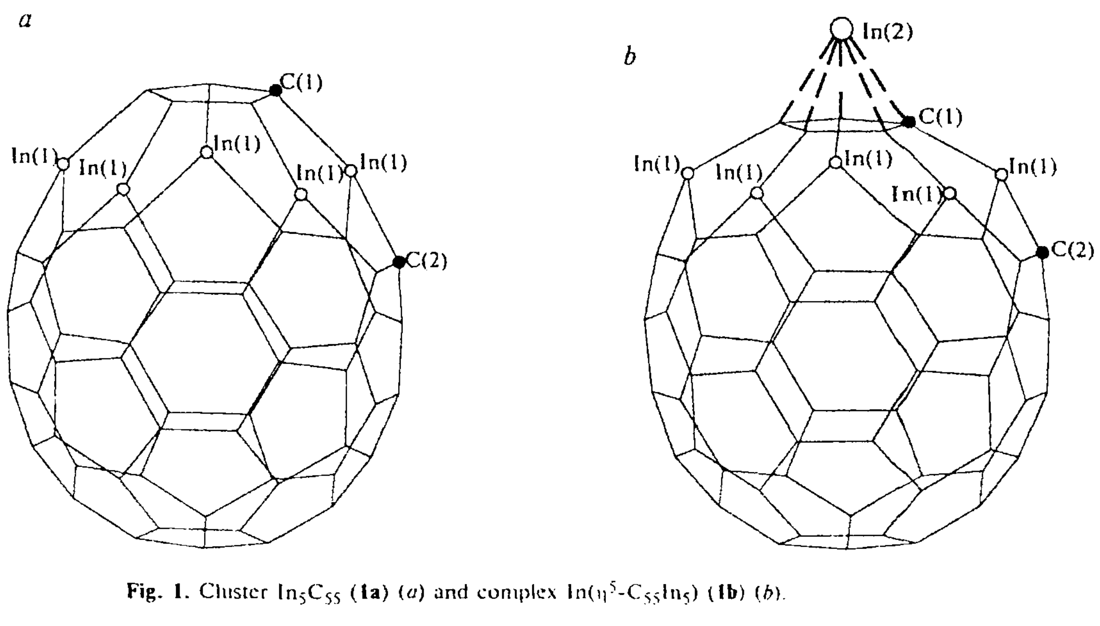

Fig. 1. Cluster In_5C_{55} (**1a**) (*a*) and complex $In(\eta^5\text{-}C_{55}In_5)$ (**1b**) (*b*).

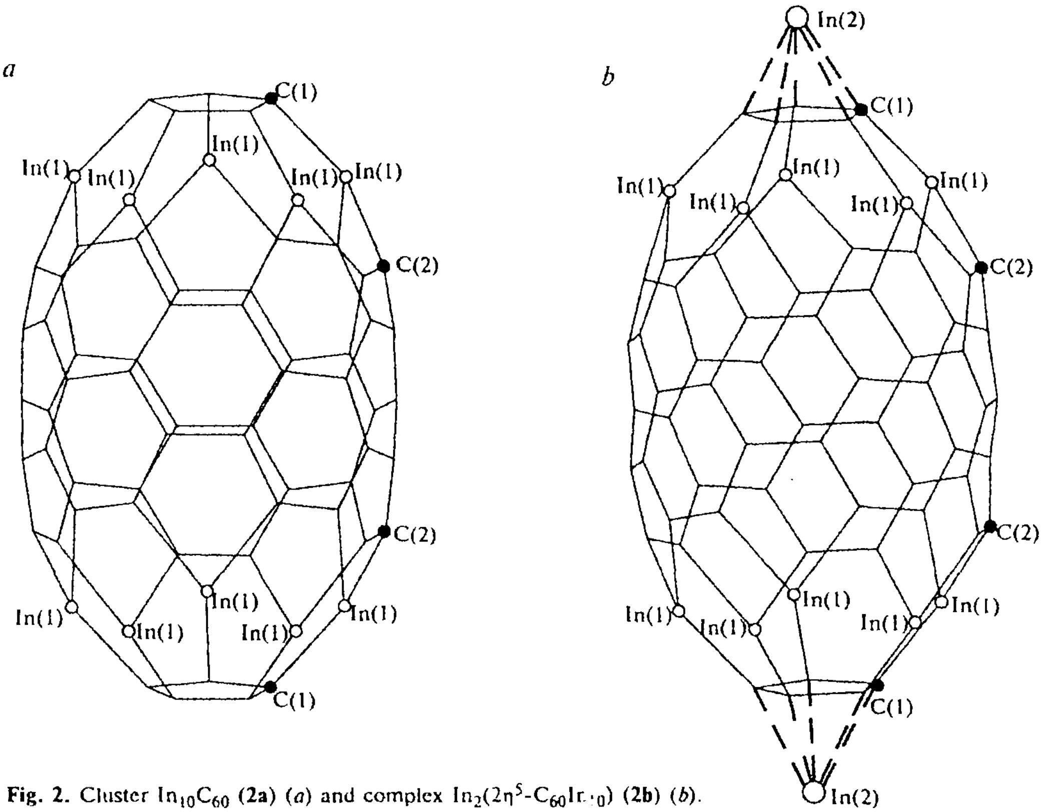

Fig. 2. Cluster In$_{10}$C$_{60}$ (**2a**) (*a*) and complex In$_2$(2η^5-C$_{60}$In$_{10}$) (**2b**) (*b*).

lie in the 2.03 to 2.11 Å interval; the charges on the In atoms differ slightly ($q_{\mathrm{In}} \approx -0.19$ au).

In complex **2b** (see Fig. 2), the C—C bonds in the polar cycles and the In(1)—C(1) bonds are lengthened by about 0.01 Å as compared to analogous values for the triplet state of cluster **2a**. The distances between the exohedral In atoms and *pent** planes are equal to 2.53 Å, which is in agreement with the results of our calculations of complex **1b** and systems In(η^5-C$_{60}$H$_5$) (**3**) and In(η^5-C$_{60}$Ph$_5$) (**4**) studied previously[6] by the MNDO/PM3 method. The charges on the In atoms inserted into the carbon framework of complex **2b** are close to those on the analogous atoms in system **2a** (q_{In} = 0.20 au). However, a partial charge transfer from the exohedral In atoms to the polar pentagonal faces occurs, which determines the stability of this system (the energy of the In—*pent** bond is also equal to ~104 kcal mol^{-1}).

The calculated values of the energy of the In—*pent** bond in complexes **1b** and **2b** are higher than the energies of the In—*pent** bonds in systems **3** and **4** (47.5 and 42.3 kcal mol^{-1}, respectively) also obtained by the MNDO/PM3 method.[6] This indicates that replacement of carbon atoms at the α-positions relative to one of the pentagons by the In atoms results in the higher stabilization of the η^5-π-complexes formed as compared to the case in which H atoms or Ph groups are attached to the α-C atoms. The same effect is also observed for the cyclopentadienyllithium complexes Li(η^5-C$_{60}$H$_5$) (**5**), Li(η^5-B$_5$C$_{55}$) (**6**), and Li(η^5-Al$_5$C$_{55}$) (**7**): the energies of the Li—*pent** bonds in systems **6** and **7** are higher than the energy of the Li—*pent** bond in molecule **5** (see Ref. 8). It is likely that analogous conclusions will also be valid for complexes Tl(η^5-R$_5$C$_{60}$), Tl(η^5-Tl$_5$C$_{55}$), and Tl$_2$(2η^5-Tl$_{10}$C$_{60}$).

In conclusion, it should be noted that the distances between the nearest In atoms in systems **1a**, **2a**, **1b**, and **2b** are equal to ~3.15 Å, which is less than twice the atomic radius of indium (r_{In} = 1.66 Å).[13] However, the Wiberg index of the In—In bond is only equal to 0.04. Therefore, the In—In interaction can be considered as a weak bonding.

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