Physical Chemistry

Cyclopentadienyl type η^5-π-complexes of C_{60} fullerene derivatives with indium and thallium: simulation of molecular and electronic structure by the MNDO/PM3 method

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The results of MNDO/PM3 calculations of η^5-π-$C_{60}R_5M$ complexes (R = H and Ph; M = Tl and In) are reported. Local energy minima and geometric parameters as well as the heats of formation and ionization potentials were determined for all systems in question. The nature of chemical M—*pent* bonding (*pent* is the pentagonal face) is discussed. The results of calculations are compared with experimental data that confirm our predictions about the possibility of existence of stable cyclopentadienyl type η^5-π-complexes of C_{60} fullerene derivatives. The stability of the $C_{60}In_{12}$ complex with the I_h symmetry, in which the In atoms are coordinated to each of 12 pentagonal faces of C_{60} fullerene, was estimated. The energy of the In—*pent* bond (62.4 kcal mol^{-1}) is close to that in $C_{60}H_5In$ (64.5 kcal mol^{-1}).

Key words: fullerene, π-complexes, thallium, indium; quantum-chemical calculation, MNDO/PM3 method.

The problem of existence of η^5- and η^6-π-complexes of fullerene C_{60} is of great scientific interest and is the subject of wide speculation in the chemical literature. In the first theoretical work[1] concerning this problem, the η^5-$C_{60}Li^+$ and η^6-$C_{60}Li^+$ systems were studied by the MNDO method. It has been found that the energy of the Li^+—C_{60} bond in these complexes is ~50 kcal mol^{-1}. However, taking into account that MNDO calculations overestimate the energy of the Li—C bond by ~30 kcal mol^{-1} (see Ref. 2), the results reported in Ref. 1 make it possible to conclude that the stability of the η^5-$C_{60}Li^+$ and η^6-$C_{60}Li^+$ complexes is low. This conclusion has also been confirmed by the *ab initio* MO LCAO SCF calculations of such a type of system in the DZ + P basis set (see Ref. 3), indicating that the Li^+—C_{60} bond is rather unstable.

The possibility of existence of η^5- and η^6-π-complexes of C_{60} fullerene with such ligands as MCp, MBz, *etc.* (M is the atom of a transition metal) was discussed in Refs. 4—8. It was established that such type π-complexes must be much less stable than their classical analogs. Since the strong delocalization of π-electrons over the polyhedron surface in C_{60} has a destabilizing effect on the strength of the C_{60} bonds with η^5- and η^6-ligands,[7] we proposed and theoretically substantiated a procedure of stabilization of η^5-complexes of C_{60}[8] analogous to that proposed earlier[9] for bowl-shaped hydrocarbon molecules, possible precursors of

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fullerenes. This procedure involves attachment of univalent functional R groups to the α-positions relative to one of the five-membered cycles of the molecules in question and can also be applied to corannulene whose carbon framework coincides with a representative fragment of the C_{60} fullerene (see Ref. 10). An analogous stabilizing effect can be obtained by replacement of carbon atoms at the same α-positions by the atoms of Group IV elements or by those of Group III and V elements.[11] The above procedure makes it possible to separate in the polyhedral cluster a conjugated subsystem similar to the cyclopentadienyl system and thus to reduce the problem of stability of η^5-π-complexes of C_{60} to an analogous problem for cyclopentadienyl type derivatives of C_{60}.

The fruitfulness of this approach has been confirmed by the results reported in Ref. 12, in which first stable cyclopentadienyl type complexes of C_{60} fullerene derivatives, η^5-π-$C_{60}R_5ML_k$ (R = Ph; ML_k = Li, K, Tl, and Cu · PEt_3), were synthesized and the complex with Tl was characterized by the X-ray method. It is of interest to investigate the nature of chemical binding in the systems in question and to estimate whether semiempirical methods can be used to calculate geometric parameters of fullerene complexes with In and Tl. The results of analogous investigations of η^5-π-$C_{60}R_5Li$ systems (R = H and Ph) by the MNDO method have been reported in Ref. 11.

In this work, the molecular and electronic structure of η^5-π-$C_{60}R_5M$ complexes (M = In, Tl; R = H, Ph) as well as that of $[C_{60}R_5]^-$ anions and $[C_{60}R_5]^{\cdot}$ radicals were simulated by the MNDO/PM3 method[13] using parameters for the In and Tl atoms.[14] In the case of M = Tl and R = Ph, the results obtained are compared with experimental data.[12] The structure of the $C_{60}In_{12}$ complex with I_h symmetry was also simulated. The calculations were performed in the RHF (for systems with even number of electrons) and the ROHF (for radicals) approximations using the MOPAC 5.10 and GAMESS[15] programs adapted for the DEC 3000 Model 400X AXP Alpha workstation.

Results and Discussion

Anions $[C_{60}R_5]^-$ (**1a**, R = H; **1b**, R = Ph, Fig. 1). Previously,[8] we calculated anion **1a** assuming that it has C_{5v} symmetry (the results of calculations are included in Tables 1 and 2). The geometry of anion **1b** was optimized assuming that it has C_5 symmetry. The structure shown in Fig. 2 corresponds to the local minimum found on the potential energy surface (PES) of compound **1b**. It should be noted that the phenyl rings in this system are rotated by an angle θ relative to the meridian plane passing through the C(2) atom (see Table 2).

Anion **1b** has a closed electron shell. Its energetic characteristics are listed in Table 1, while the bond lengths and the Wiberg indices mostly differing from the analogous parameters for the unsubstituted (I_h)-C_{60} fullerene are listed in Table 2. Reasonably high ionization potentials of anions **1a,b** estimated using the Koopmans theorem and differences between the energies of the frontier MOs ($\delta = E_{LUMO} - E_{HOMO}$) are evidence of the kinetic stability of these systems. The total effective charge on the C atoms of the separate pentagonal face in compounds **1a,b** is close to −1 (−0.86 a.u. in both cases). The C(1)—C(1′) bonds in the upper pentagonal cycle are markedly shortened as compared to their analogs in C_{60}, whereas the C(1)—C(2) and C(2)—C(3) type bonds are lengthened and the C(3)—C(3′) bonds are only slightly shortened.

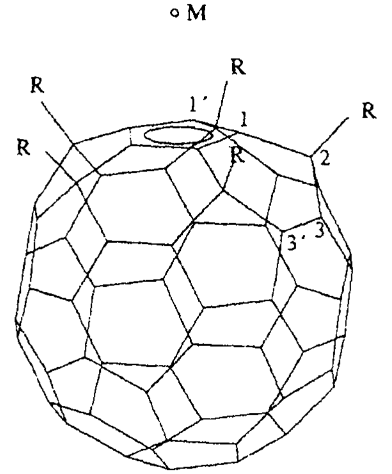

Fig. 1. The structure of systems **1a,b**—**4a,b**: the equivalent atoms differ in primes.

R = H (**a**), Ph (**b**)

Compound	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
M	—	—	—	—	In	In	Tl	Tl

The degenerate HOMOs of each of the anions (**1a** or **1b**) belong to the e_1 irreducible representation of the C_{5v} (C_5) symmetry group. The contributions of p_z-atomic orbitals (AOs) of the C atoms of the upper ("framed") five-membered cycle dominate in these orbitals, *i.e.*, the HOMOs are π-orbitals. Note also that the energy of the π-MO with the a_1 symmetry, localized on the upper pentagonal face, differs from the HOMO energy to a lesser extent than that in the separated Cp^-. Therefore, this MO can also participate in stabilizing η^5-π-complexes.

Radicals $C_{60}R_5^{\cdot}$ (**2a**, R = H; **2b**, R = Ph). Calculations of radicals **2a** and **2b** performed with full optimization of geometry resulted in structures with C_s and C_1 symmetry, respectively. The lower symmetry as compared to anions **1a,b** is due to the Jahn—Teller effect, since the highest occupied energy level in **1a,b** is doubly degenerate. As a whole, the results of calculations of

Table 1. Heats of formation (ΔH_f°/kcal mol^{-1}), one-electron energies E_{HOMO} and E_{LUMO}, energy gaps $\delta = E_{LUMO} - E_{HOMO}$, energies of abstraction of M atom (ΔE(M)) and M$^+$ cation (ΔE(M$^+$)), and effective charges on the atoms (q) in the molecules, ions, and complexes calculated by the MNDO/PM3 method

System		Symmetry	ΔH_f	E_{HOMO}	E_{LUMO}	δ/eV	ΔE(M)	ΔE(M$^+$)	*q*/au				
				eV			kcal mol^{-1}		C(1)	C(2)	C(3)	R	M
Cp$^-$		C_{5v}	15.9	-2.33^2	8.05^2	10.4	—	—	−0.26	—	—	—	—
Cp$^\cdot$		C_s	61.2	-5.34^1	0.52^1	5.8	—	—	0.00^1 -0.20^2 -0.09^2	—	—	—	—
CpIn		C_{5v}	39.5	-8.82^2	-1.03^2	7.8	79.7	176.9	−0.18	—	—	—	0.26
CpTl		C_{5v}	115.6	-7.84^1	-2.47^1	5.4	−10.9	105.4	-0.19^1 -0.21^2 -0.23^2	—	—	—	
C_{60}		I_h	811.7	-9.48^5	-2.89^3	6.6	—	—	0.00	0.00	0.00	—	—
$[C_{60}H_5]^-$	**(1a)**	C_{5v}	642.5	-4.49^2	-0.38^2	4.1	—	—	−0.20	0.13	−0.05	0.08	—
$[C_{60}Ph_5]^-$	**(1b)**	C_{5v}	791.5	-5.10^2	0.12^2	5.2	—	—	−0.19	0.20	−0.03	−0.13	—
$[C_{60}H_5]^\cdot$	**(2a)**	C_s	723.6	-6.10^1	-2.37^1	3.7	—	—	0.02^1 -0.15^2 -0.05^2	0.11	−0.11	0.11	—
$[C_{60}Ph_5]^\cdot$	**(2b)**	C_s	880.9	-6.185^1	-2.331^1	3.9	—	—	-0.15^2 -0.05^2 -0.04^5	0.19^2 0.17^2 0.16^1	0.04^1 0.00^5	—	—
$C_{60}H_5In$	**(3a)**	C_{5v}	717.1	-8.86^1	-2.17^2	6.7	64.5	125.9	−0.14	0.11	−0.06	0.10	0.36
$C_{60}Ph_5In$	**(3b)**	C_{5v}	896.6	-8.83^1	-2.15^2	6.7	42.3	95.4	−0.14	0.20	−0.04	−0.01	0.33
$C_{60}H_5Tl$	**(4a)**	C_{5v}	761.8	-8.77^1	-2.08^2	6.7	6.3	85.8	−0.14	0.11	−0.06	0.09	0.39
$C_{60}Ph_5Tl$	**(4b)**	C_{5v}	957.5	-8.77^2	-2.09^2	6.7	−33.1	39.1	−0.13	0.20	−0.05	−0.03	0.43
$C_{60}In_{12}$	**(5a)**	I_h	940.8	-6.34^3	-1.15^5	5.2	62.4	—	−0.05	−0.05	−0.05	—	0.23
$[C_{60}In_{11}]^\cdot$	**(5b)**	C_s	945.2	-6.19^1	-4.32^1	2.2	—	—	-0.04^2 -0.05^3	−0.05	−0.05	—	0.23^6 0.25^5

Note. The upper index means the multiplicity of the given value; see the numbering of atoms in Fig. 1. The heats of formation of atoms and cations/kcal mol^{-1}: 58.0 (In), 43.5 (Tl), 200.5 (In$^+$), and 205.1 (Tl$^+$).

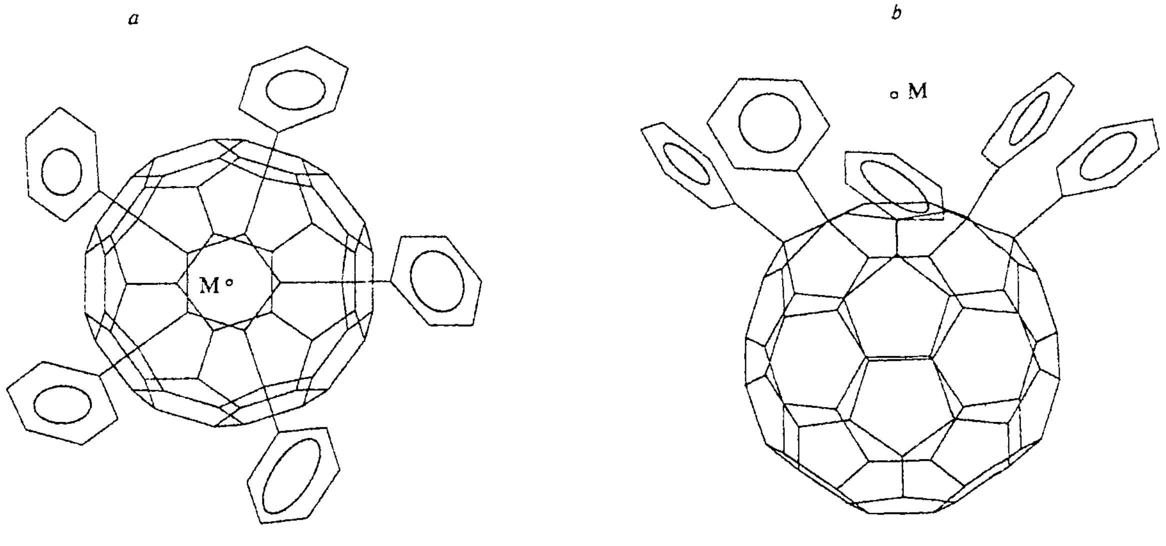

Fig. 2. The structure of anion **1b**, radical **2b**, and complexes **3b** and **4b**: view along the *z* (top view) (*a*) and *y* (*b*) axes.

radical **2a** are in agreement with those of the MNDO/PM3 calculations carried out earlier;[16] however, the heat of formation we obtained appeared to be 1.4 kcal mol^{-1} lower than that reported in Ref. 16.

The most significant changes in the geometry (as compared to the anions) only occurred in the bonds of the atoms of the upper five-membered cycle with their neighbors. The C—C bonds in this cycle are shortened,

Table 2. Bond lengths (*d*), C(1)—C(2)—R bond angles (φ), angles of rotation of phenyl rings (θ), and Wiberg indices (*W*) calculated by the MNDO/PM3 method

System	*d*/Å (*W*/au)							Angle/deg	
	C(1)—C(1′)	C(1)—C(2)	C(2)—C(3)	C(3—C(3′)	C(2)—R	M—*pent*	M—C	φ	θ
Cp^-	1.409 (1.396)	—	—	—	—	—	—	—	—
$Cp^{\cdot}$	1.445^2 1.367^2 1.473^1	—	—	—	—	—	—	—	—
CpIn	1.427 1.427^a	—	—	—	—	2.490 (1.285)	2.770 (0.257) 2.621^a	—	—
C_{60}	1.456 (1.120)	1.386 (1.477)	1.456 (1.120)	1.386 (1.477)	—	—	—	—	—
$[C_{60}H_5]^-$ (**1a**)	1.414 (1.359)	1.487 (0.980)	1.529 (0.960)	1.372 (1.600)	1.111 (0.947)	—	—	113.3	—
$[C_{60}Ph_5]^-$ (**1b**)	1.414 (1.358)	1.493 (0.974)	1.540 (0.943)	1.372 (1.612)	1.504 (0.956)	—	—	114.5	25
$[C_{60}H_5]^{\cdot}$ (**2a**)	1.452^2 1.374^2 1.475^1	1.494^1 1.500^2 1.499^2	1.529 1.371 1.112	—	—	113.1	—		
$[C_{60}Ph_5]^{\cdot}$ (**2b**)	1.452^2 1.374^2 1.475^1	1.494^1 1.500^2 1.499^2	1.538 1.501^4	1.370	1.502^1	—	—	115.1	12
$C_{60}H_5In$ (**3a**)	1.434 (1.274)	1.501 (0.970)	1.526 (0.966)	1.368 (1.621)	1.112 (0.948)	2.546 (1.140)	2.823 (0.228)	113.0	—
$C_{60}Ph_5In$ (**3b**)	1.436 (1.283)	1.512 (0.964)	1.538 (0.946)	1.365 (1.631)	1.504 (0.958)	2.571 (0.950)	2.847 (0.190)	117.0	29
$C_{60}H_5Tl$ (**4a**)	1.435 (1.274)	1.502 (0.970)	1.526 (0.966)	1.368 (1.621)	1.112 (0.949)	2.550 (1.085)	2.827 (0.217)	113.1	—
$C_{60}Ph_5Tl$ (**4b**)	1.443 (1.279) 1.34 $\div 1.45^b$	1.523 (0.958)	1.537 (0.949)	1.363 (1.633)	1.508 (0.957)	2.618 (0.995) 2.60	2.891 (0.199) 2.83 $\div 2.90^b$	118.2	65
$C_{60}In_{12}$ (**5a**)	1.448 (1.198)	1.445 (1.084)	—	—	—	2.523 (1.210)	2.808 (0.242)	—	—
$[C_{60}In_{11}]^{\cdot}$ (**5b**)	1.466^2 1.411^2 1.449^1	1.43	1.451	1.444	—	2.52	2.81		—

Note. The upper index means the multiplicity of the given value; see the numbering of atoms in Fig. 1.

[a] Experimental values taken from Ref. 7.

[b] Experimental values taken from Ref. 12.

in particular the two bonds close in lengths to the double bonds (see Table 2). The spin density is localized almost completely on the upper five-membered cycle.

Complex CpIn. The structure of the frontier MOs of anions **1a—b** described above makes it possible to qualitatively estimate the capability of these MOs to participate in the formation of η^5-π-complexes. Before we begin discussing this issue, let us analyze the structure of the MO of the half-sandwich CpIn complex with the C_{5v} symmetry.[17] To qualitatively elucidate the nature of the Cp—In bond, let us take into account five π-electrons of the Cp ring and three electrons of the In atom.

The correlation diagram corresponding to the formation of the CpIn complex according to the reaction

$$Cp^- + In^+ \longrightarrow CpIn$$

is presented in Fig. 3. On the basis of this diagram and the analysis of the MOs of the CpIn complex found

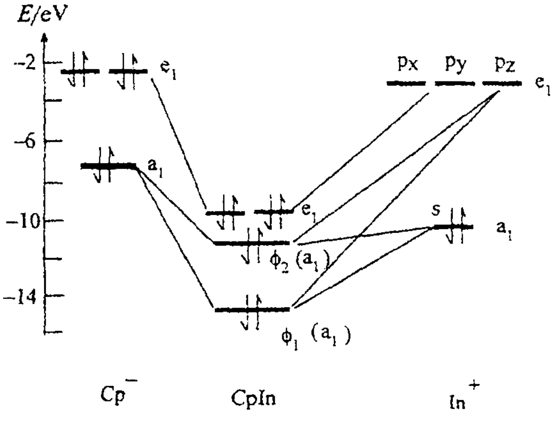

Fig. 3. The correlation diagram of complex CpIn.

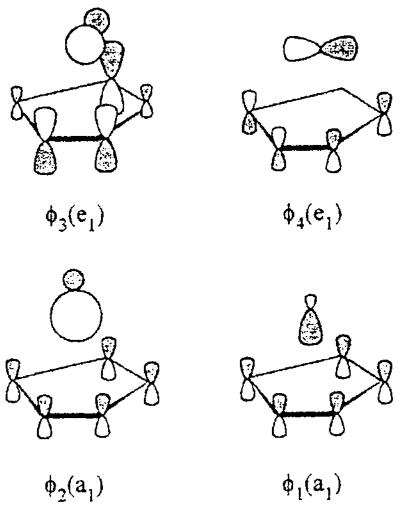

Fig. 4. Molecular orbitals participating in the formation of the In—Cp bond.

when optimizing its geometry (Fig. 4), it can be argued that there are three bonding MOs [$\phi_1(a_1)$, $\phi_3(e_1)$, and $\phi_4(e_1)$] completely filled with six electrons in this complex. The $\phi_2(a_1)$ orbital is an antibonding orbital and should be considered as an orbital of the lone electron pair of the In atom with dominant contribution from the s-AO:

$$\phi_2(a_1) = -0.28\,\Sigma_{i=1}^{5}\,p_z(C^i) + 0.71\,s(In) + 0.30\,p_z(In).$$

Complexes $C_{60}R_5In$ (**3a**, R = H; **3b**, R = Ph). The geometry of complexes **3a,b** was optimized assuming C_{5v} and C_5 symmetry for **3a** and **3b**, respectively. The structures obtained correspond to local minima on the PES. It should be noted that the angle of rotation of the phenyl groups (θ) in complex **3b** shown in Fig. 2 is larger than those in anion **1b** and radical **2b** because of coordination of the metal atom (see Table 2). Additional variations of all geometric parameters characterizing the position of the In atom show that this atom lies on the five-fold symmetry axis.

An analysis of energetic characteristics (see Table 1) makes it possible to conclude that complexes **3a,b** must be stable since their ionization potentials (IPs) are comparable with that of cyclopentadiene and somewhat lower than the IP of C_{60} fullerene; additionally, the δ differences between the LUMO and HOMO energies are considerable. The electron density is transferred from the In atom to the upper pentagonal face to nearly the same degree as in CpIn (see Table 1).

Chemical M—*pent* bonds in complexes **3a—b** have the same nature as those in the half-sandwich CpIn complex, since the interaction between the In atom and the atoms outside the upper pentagonal face can be neglected. The correlation diagrams of reactions $C_{60}R_5^- + In^+ \longrightarrow C_{60}R_5In$ (R = H, Ph) have the same character as that shown in Fig. 3, while the structure of the HOMOs is shown in Fig. 4. The energies of homolytic ΔE(M) and heterolytic $\Delta E(M^+)$ cleavage of the M—*pent* bond are listed in Table 1. Their analysis shows that the energy of the M—*pent* bond in complex **3a** (64.5 kcal mol^{-1}) is lower than that in CpIn and higher than that in **3b** (79.7 and 42.5 kcal mol^{-1}, respectively).

The lengths of the M—*pent* bonds (and the M—C distances) correlate with the ΔE(M) values: the stronger the bond, the shorter it (and the higher its Wiberg index) is. Table 2 makes it possible to trace the most significant changes in the bond lengths close to the upper face. In the case of the formation of the M—*pent* bond, the electron density is transferred from the atom of transition metal M to the upper face; the degree of transfer in complex **3a** is larger than that in **3b** (*cf.* q_M values in Table 1).

Complexes $C_{60}R_5Tl$ (**4a**, R = H; **4b**, R = Ph). The geometry of these structures was optimized with the same symmetry restrictions as for systems **3a** and **3b**. The results of calculations are listed in Tables 1 and 2. The calculated values of geometric characteristics of complex **4b** are close to the experimental data[12] (see Fig. 2 and Table 2). We also note that the angle of deviation of the C(1)—C(2) bond from the plane of the upper face is only 0.6 deg less than its experimental value (22 deg).

Unlike compound **3b**, the angle of rotation of phenyl groups (θ) for **4b** is appreciably larger, which corresponds to increasing the effective size of the Tl atom as compared to the In atom. Large IPs and δ values are evidence of the kinetic stability of systems **4a,b**; however, formation of the Tl—*pent* bonds appeared to be energetically unfavorable for both **4b** and CpTl, though these systems are experimentally observable. It is likely that this fact indicates that the heats of formation of the Tl compounds considered are poorly reproduced in calculations using parameters of the MNDO/PM3 method.

Complex (I_h)-$C_{60}In_{12}$ (5a). By analogy with a hypothetical (I_h)-$C_{60}Li_{12}$ system,[18,19] we investigated the possibility of existence of complex **5a**, in which the In atoms are coordinated to all 12 pentagonal faces of fullerene C_{60}. Optimization of its geometry performed assuming I_h symmetry resulted in a compound with closed electron shell. Reasonably high IP and δ values of complex **5a** are evidence of its stability. The whole π-system of fullerene C_{60} participates in the formation of the bonds with the In atoms. The energy of the In—*pent* bond ($-\Delta E$(In), see Table 1) is close to that obtained for structure **3a**, while the *d*(In—*pent*) and *d*(In—C) distances are even shorter than those in **3a** (and the corresponding Wiberg indices are higher than those in **3a**).

The degree of transfer of the electron density from the In atoms in complex **5a** is somewhat less than that in complexes **3a,b**; however, the carbon framework has the negative charge of 2.77e. Note also that the average value of the energy of abstraction of the In atom from system **5a** ($\Delta_1 E(\mathrm{In})$ = 47 kcal mol^{-1}) calculated by the formula

$$\Delta H_f^\circ(C_{60}) + 12\,\Delta H_f^\circ(\mathrm{In}) - \Delta H_f^\circ(\mathbf{5a}) = 12\,\Delta_1 E(\mathrm{In}),$$

appeared to be rather high. This fact is also evidence in favor of the stability of compound **5a**. It should be noted that we failed to find a local minimum for analogous (I_h)-$C_{60}Tl_{12}$ complex.

Radical [(C_{5v})-$C_{60}In_{11}$]$^\cdot$ (5b). This system is distinguished from **5a** by the absence of the In atom coordinated to the upper pentagonal face and was investigated to determine the energy of its abstraction ($\Delta E(\mathrm{In})$). Full optimization of the geometry of radical **5b** resulted in a structure with C_s symmetry with pronounced deviations from the C_{5v} symmetry only for the upper pentagonal face (see Table 2). The spin density in this radical is mainly localized on the atoms of the upper face (~0.6). The effective charges on the In atoms of the upper hemisphere are somewhat larger than those on the remaining atoms, which have nearly the same charges as in complex **5a**.

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The experimental data[12] and our calculations of η^5-$InC_{60}R_5$ and η^5-$TlC_{60}R_5$ complexes showed once again that the separation of the conjugated cycle from a rather extended π-electron system of C_{60} fullerene is an approach of considerable promise for synthesizing η^5-structures with polyhedral fullerene framework. Analogous stabilization of η^5-complexes of C_{60} can also be achieved in the case of coordination of 12 ligands (ML_k) to all 12 pentagons of C_{60}, when the entire π-system of the fullerene participates in binding with the metal atoms. This effect was first established using the (I_h)-$C_{60}Li_{12}$ cluster as an example.[18]

Unlike complex (I_h)-$C_{60}Tl_{12}$, our calculations of complex (I_h)-$C_{60}In_{12}$ with the analogous structure showed that it can exist. It also follows that the Tl—*pent* bond in complex **4a** is weak while this bond is not formed at all in **4b**. It is likely that this is a result of a poor parametrization for the Tl atom. A comparison of the orders of the In—*pent* and Tl—*pent* bonds in the systems considered (see Table 2) shows that complexes with Tl must not be less stable than those with In. This conclusion is also confirmed by short d(Tl—C) distances and large q_{Tl} values in structures **4a–b** (see Table 1). Therefore it seems probable that complex (I_h)-$C_{60}Tl_{12}$ also exists. Additionally, one can conclude that analogous complexes (I_h)-$C_{60}(ML_k)_{12}$ with the atoms of transition metals (M) appear to be stable, since the M—*pent* interaction has in principle the same character. In this case the overlap of the p_z(C)-AO with the d_{xz}(M)-AO and the d_{yz}(M)-AO must be larger than that with the p_x(M)- and p_y(M)-AO having the same e_1 symmetry (notations are given in the local coordinate system for each pentagonal face with the z axis perpendicular to its plane). It should also be noted that in the case of η^5-$MC_{60}R_5$ complexes (R = H, Ph) the energies of abstraction of M atom ($\Delta E(\mathrm{M})$) for M = In, Tl (calculated in this work), and Li[11] for η^5-$MC_{60}H_5$ are higher than those for η^5-$MC_{60}Ph_5$.

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