Quantum Chemical Modelling of the Scandium Sub-Group Metal Endofullerenes

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Abstract

Endofullerenes with one or several metal atoms inside the carbon cage (metallofullerenes) are of considerable practical interest as promising basic materials for creating highly effective contrasting agents for magnetic resonance imaging (MRI) as well as antioxidant and anticancer drugs. These compounds can also be used in spintronics to build nanoscale electronic devices. In the framework of the density functional theory, this work presents a calculation of the structural, electronic, and thermodynamic characteristics of scandium sub-group metal endofullerenes with the number of encapsulated atoms from one to seven in the gaseous phase. The stable structures with symmetries C_s, C_2, C_3, and C_i, were described. They correspond to the positions of the metal atoms inside the fullerene cage. The theoretical limit for the number of metal atoms at which the endofullerene structure remains stable is six atoms for scandium, four for yttrium, and three for lanthanum. The calculations showed that the most stable structures are the ones with two and three encapsulated atoms. The relationship between the number of encapsulated atoms and the nature of electron density distribution were described. The total charge on the encapsulated metal cluster is positive for $Me@C_{60} - Me_3@C_{60}$ compounds, weakly positive for $Me_4@C_{60}$ (some of the atoms have negative charge), and negative for $Me_5C_{60} - Me_6@C_{60}$ compounds. The spin leakage effect was described for the structures with a doublet spin state. As for the endofullerenes with three and more encapsulated atoms, this effect is insignificant, which makes the creation of contrasting agents for MRI based on them impractical.

Keywords: endofullerenes, metallofullerenes, quantum chemical calculations, density functional theory, molecular symmetry, spin leakage.

1. Introduction

Discovered in 1985, during experiments dedicated to the study of circumstellar space [1], fullerenes have greatly influenced the development of materials science, nanotechnologies, and instrument engineering, as well as biology and medicine. The interest in these compounds has brought together such different areas of natural science as pharmaceutical and medicinal chemistry, solid-state physics, organic chemistry, and geology. By the beginning of the 1990s, only 5 years after the discovery of these nanomaterials, a large amount of data was collected on structural, chemical, and physicochemical properties of fullerenes, and the methods of their synthesis, fractionation, and purification were developed [2].

Unique chemical properties of fullerenes offer great opportunities for obtaining new compounds and materials based on them through chemical modification of the carbon cage. There are methods of obtaining heterofullerenes,

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products of substitution of one or several carbon atoms for heteroatoms, and exofullerenes, formed by chemical functionalisation of the carbon cage. A separate group in the large family of derivatives of fullerenes is comprised by endofullerenes containing separate atoms or atom clusters inside the carbon cage. Molecules of paramagnetic endofullerenes (as a rule, the structures containing encapsulated metal atoms) are characterised by preferential localisation of unpaired electrons on the atoms of carbon as part of the fullerene cage. This phenomenon, first theoretically predicted by A. L. Buchachenko [3] and later experimentally discovered for La@C_{82} [4], is called spin leakage. It allows such compounds to be considered as promising candidates for the creation of contrasting agents for NMR tomography as well as the creation of nanoscale electronic devices.

To date, a large amount of experimental data has been accumulated on the chemistry and physics of endohedral derivatives of fullerene C_{82}, while derivatives with a C_{60} cage have not been thoroughly studied due to the lack of sufficiently reliable methods of macroscale synthesis of such structures [5]. For this reason, the theoretical study of these compounds using the methods of quantum chemistry is especially valuable. *Ab initio* calculations can not only supplement and interpret the results of experimental research, but also provide fundamentally new information on the structural, spectral, and spin characteristics of endohedral cage structures.

2. Experimental

Modelling of scandium sub-group metal endofullerenes was performed within the framework of the density functional theory (DFT) using the programmes *Gaussian* 09 [6], *Orca* 3.0.3 [7], and *Priroda* 10 [8].

To choose a calculation scheme that can properly describe structural and energetic properties of the structures studied in this work, a preliminary calculation was performed for the values of standard enthalpy of atomisation of particles of carbides of the MeC$_n$ (Me = Sc, Y, La; n = 2-6) scandium sub-group metals in the framework of the following calculation schemes (see Table 1). The results of the corresponding calculations are presented in the Table (Table 2).
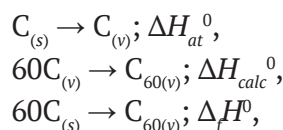
The data presented in the Table 2 shows that scheme 3 allows obtaining the values of standard enthalpy of atomisation of the MeC$_n$ particles that are the closest to the experimental data. Absolute error for the determination of this value does not exceed 94 kJ/mol.

Also, in the framework of each of the specified schemes, a calculation was performed for the following structural, spectral, and thermodynamic properties of fullerene C_{60}:

• r_{5-6} is the length of the C–C bond representing a common edge between five and six-membered cycles in the carbon cage of fullerene.

• r_{6-6} is the length of the C–C bond representing a common edge between two six-membered cycles.

• v_1–v_4 are the oscillation frequencies recorded in the IR spectrum of fullerene.

• $\Delta_f H^0$ is the standard enthalpy of formation of fullerene in the state of the ideal gas by graphite.

The data obtained while testing the calculation schemes is presented in the Table (Table 3).

The following scheme was used to calculate the value of $\Delta_f H^0$:

$$C_{(s)} \rightarrow C_{(v)};\ \Delta H_{at}^{\ 0},$$
$$60C_{(v)} \rightarrow C_{60(v)};\ \Delta H_{calc}^{\ 0},$$
$$60C_{(s)} \rightarrow C_{60(v)};\ \Delta_f H^0,$$

where $\Delta H_{at}^{\ 0}$ is the standard enthalpy of graphite atomisation (716.682 kJ/mol [14]), $\Delta H_{calc}^{\ 0}$ is the

Table 1. Tested Calculation Schemes

№	Functional	Basis Set for Carbon Atoms	Basis Set or Pseudopotential for Metal Atoms	Software Used for Calculation
1	B3LYP	D95(d, p)	SDD	Gaussian 09
2	mPW3PBE	D95(d, p)	SDD	Gaussian 09
3	mPW3PBE	DZP	DZP	Gaussian 09
4	PBE1PBE	D95(d, p)	SDD	Gaussian 09
5	PBE0	Def2-SVP	SDD	Orca 3.0.3
6	PBE	L1	L1	Priroda 10

Table 2. Standard Enthalpies of Atomisation of the MeCn Particles in the Gaseous Phase (Me = Sc, Y, La; n = 2–6)

Scheme	ΔH_{at}^0, kJ/mol						
	1	2	3	4	5	6	Experiment
ScC$_2$	1121	1170	1183	1160	1178	1284	1182 [9]
ScC$_3$	1645	1728	1748	1718	1773	1880	1777 [9]
ScC$_4$	2338	2432	2456	2425	2542	2621	2453 [9]
ScC$_5$	2896	3030	3057	3025	3173	3256	3131 [9]
ScC$_6$	3486	3642	3672	3638	3822	3907	3766 [9]
YC$_2$	1165	1210	1239	1206	1197	1310	1229 [10]
YC$_3$	1658	1740	1773	1736	1849	1881	1800 [9]
YC$_4$	2382	2475	2529	2472	2574	2658	2523 [9]
YC$_5$	2913	3044	3112	3044	3213	3270	3073 [9]
YC$_6$	3500	3644	3726	3644	3845	3919	3772 [9]
LaC$_2$	1217	1263	1286	1259	1287	1334	1259 [9]
LaC$_3$	1765	1851	1907	1850	1931	1946	1819 [11]
LaC$_4$	2453	2539	2597	2539	2655	2695	2515 [9]
LaC$_5$	3016	3151	3203	3153	3301	3315	3121 [11]
LaC$_6$	3601	3756	3802	3756	3940	3958	3757 [9]

Table 3. Calculated and Experimental Parameters of Fullerene C$_{60}$

Scheme	1	2	3	4	5	6	Experiment
r_{5-6}, pm	145.6	145.0	145.1	144.9	144.8	145.2	145.2 [12]
r_{6-6}, pm	140.0	139.6	139.7	139.4	139.4	139.7	139.7 [12]
v_1, sm^{-1}	521	522	523	527	536	522	527 [13]
v_2, sm^{-1}	586	593	595	598	600	577	576 [13]
v_3, sm^{-1}	1212	1230	1233	1241	1253	1183	1182 [13]
v_4, sm^{-1}	1466	1497	1497	1512	1515	1436	1429 [13]
$\Delta_f H^0$, kJ/mol	4082	2296	2405	2056	167	636	2530 [15]

enthalpy of formation of fullerene C$_{60}$ in the state of the ideal gas from gaseous (monoatomic ideal gas) carbon that was obtained during a computational experiment. Through a combination of corresponding thermochemical equations, the following expression was obtained for the calculation of $\Delta_f H^0$:

$$\Delta_f H^0 = 60\Delta H_{at}^0 + \Delta H_{calc}^0.$$

The presented data shows good reproducibility of geometric and spectral characteristics in the framework of the calculation scheme No.6 (values of the lengths of the C–C bonds correspond to the published data, deviations of oscillation frequencies do not exceed 7 cm^{-1}). However,
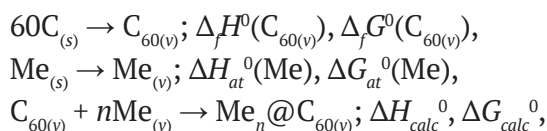
none of the schemes allow obtaining the data corresponding to the experiment on the value of enthalpy of formation of fullerene (in the case of scheme No.3, the deviation $\Delta_f H^0$ is 125 kJ/mol, which is about 5%). Since all thermodynamic characteristics are highly important for the assessment of the stability of compounds, it was decided to use scheme No.3 for further calculations as the one that describes the modelled structures most adequately, although the value of oscillation frequencies is reproduced worse in this scheme (deviation v_4 from the experimental value is 68 cm^{-1}).

To determine the possible isomers of endohedral derivatives of fullerene C$_{60}$, many

structures were generated that are different in the position of the metal atoms inside the carbon cage of fullerene and then optimised. The absence of imaginary frequencies in the IR spectra of these compounds showed that the obtained structures corresponded to the minimum on the surface of PE foam. To evaluate the thermodynamic stability, the values of enthalpy $\Delta_f H^0$ and the Gibbs energy of the formation $\Delta_f G^0$ of the endofullerene $Me_n@C_{60}$ from graphite and the crystal of the corresponding metal were determined as follows:

$$60C_{(s)} + nMe_{(s)} \rightarrow Me_n@C_{60(v)}.$$
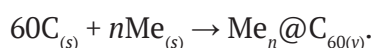
This characteristic was calculated using the reported data and the results of the computational experiment in the following way:

$$60C_{(s)} \rightarrow C_{60(v)};\ \Delta_f H^0(C_{60(v)}),\ \Delta_f G^0(C_{60(v)}),$$
$$Me_{(s)} \rightarrow Me_{(v)};\ \Delta H_{at}{}^0(Me),\ \Delta G_{at}{}^0(Me),$$
$$C_{60(v)} + nMe_{(v)} \rightarrow Me_n@C_{60(v)};\ \Delta H_{calc}{}^0,\ \Delta G_{calc}{}^0,$$

where $\Delta_f H^0(C_{60(v)})$ and $\Delta_f G^0(C_{60(v)})$ are standard enthalpy and Gibbs energy of formation of the gaseous fullerene C_{60} from graphite (2.530.0 and 2.474.5 kJ/mol [15]), $\Delta H_{at}{}^0(Me)$ and $\Delta G_{at}{}^0(Me)$ are atomisations of the corresponding metals (377.8 and 336.03 kJ/mol for scandium, 421.3 and 381.1 kJ/mol for yttrium, 431.0 and 393.56 for lanthanum [14]), $\Delta H_{calc}{}^0$ and $\Delta G_{calc}{}^0$ are corresponding calculation characteristics based on the results of quantum chemical modelling. Through a combination of these thermochemical equations, the following equations were obtained for the calculation of $\Delta_f H^0$ and $\Delta_f G^0$:

$$\Delta_f H^0 = \Delta_f H^0(C_{60(v)}) + n\Delta H_{at}{}^0(Me) + \Delta H_{calc}{}^0,$$
$$\Delta_f G^0 = \Delta_f G^0(C_{60(v)}) + n\Delta G_{at}{}^0(Me) + \Delta G_{calc}{}^0.$$

Enthalpy $\Delta H_b{}^0$ and Gibbs energy of encapsulation $\Delta G_b{}^0$ were used as another criterion of stability of endofullerenes. They quantitatively characterise energy costs for the process of the embedding of the originally formed cluster Me_n inside the carbon cage of fullerene, which occurs as follows:

$$Me_{n(v)} + C_{60(v)} \rightarrow Me_n@C_{60(v)}.$$
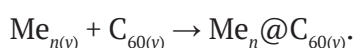
3. Results and discussion

3.1. Endofullerenes with one encapsulated atom

The results of the optimisation of the $Me@C_{60}$ structures indicate the absence of isomers for these compounds; the only possible structure

with the C_s symmetry is characterised by the location of the metal atom near one of the six-membered cycles in the fullerene structure (Fig. 1). The distance from the encapsulated metal atom to the nearest carbon atoms in the fullerene structure increases in the Sc < Y < La series (Table 4), which correlates with the ratio of covalent radii of these metals (144, 163, and 169 pm, respectively [14]). It should be noted that the sums of covalent radii of these metals and carbon are 221, 239, and 245 pm for scandium, yttrium, and lanthanum [14], which is 9–12 pm more than the greatest of the distances $r_i(Me-C_i)$, which is indicative of smaller covalent radii of these metals inside the carbon cage than in the corresponding crystal lattices. The basic doublet state is typical for these structures.
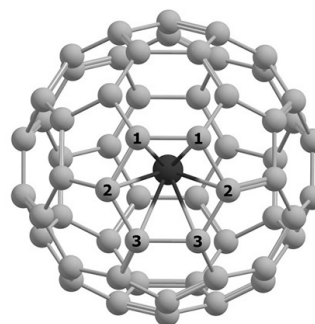

Fig. 1. Structure of the $Me@C_{60}$ (C_s) Endofullerenes

In the Sc > Y > La series (Table 4) a decrease of the values $\Delta_f H^0$ and $\Delta_f G^0$ was observed, which indicates the reduction of energy costs on the formation of corresponding endofullerenes in the series. It was also confirmed by negative values of enthalpy and encapsulation energies.

The process of formation of endofullerene is accompanied by redistribution of electron density between the penetrating metal atom and the carbon cage of fullerene. As the calculations show, the metal atom can obtain only a positive charge inside the fullerene cell in the $Me@C_{60}$ structures (Table 4), and there is no correlation between the value of this charge and the atomic number of the element: in the endofullerene $Y@C_{60}$ the metal atom has the highest charge (1.064 a.u.), $Sc@C_{60}$ has the lowest (0.577 a.u.), and an average value (0.865 a.u.) is typical for $La@C_{60}$.

The transfer of spin density from the encapsulated metal atom to the fullerene cage is also typical for the structures analysed in this section. In this case, a direct correlation is found

Table 4. Calculated Parameters for Endofullerenes of the Scandium Sub-Group with One Encapsulated Atom

|	Sc@C$_{60}$	Y@C$_{60}$	La@C$_{60}$
Symmetry	C$_s$	C$_s$	C$_s$
r(Me−C$_1$), pm	217	236	251
r(Me−C$_2$), pm	224	240	254
r(Me−C$_3$), pm	233	248	259
$\Delta_f H^0$, kJ/mol	2592	2540	2387
$\Delta_f G^0$, kJ/mol	2528	2478	2325
ΔH_b^0, kJ/mol	−315	−411	−575
ΔG_b^0, kJ/mol	−282	−378	−543
Q(Me), a.u.	0.577	1.064	0.865
S(C$_{60}$)	0.881	0.975	0.990

between the total spin density on the carbon cage and the atomic number of the element: the value S(C$_{60}$) is 0.881, 0.975, and 0.990 for Sc@C$_{60}$, Y@C$_{60}$, and La@C$_{60}$ respectively.

3.2. Endofullerenes with two encapsulated atoms

As opposed to endofullerenes with one encapsulated atom, there are isomers of Me$_2$@C$_{60}$ compounds and, particularly, of Sc$_2$@C$_{60}$. The calculation registered the presence of two types of structures in these compounds (Fig. 2):

A structure with the C_i symmetry, where the Me$_2$ cluster is located along the line connecting the centres of the opposite six-membered cycles in the structure of fullerene (Fig. 2.1), typical for Y$_2$@C$_{60}$ and the first isomer of Sc$_2$@C$_{60}$.

A structure with C_s symmetry, where the metal cluster is turned regarding the position described for the structure with C_i symmetry towards the edge that is common for two six-membered cycles (Fig. 2.2); this type of structure is typical for the second isomer of Sc$_2$@C$_{60}$ and La$_2$@C$_{60}$.
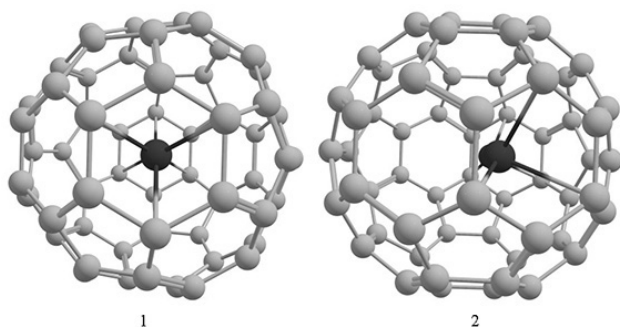
Fig. 2. Structure of the Me$_2$@C$_{60}$ Endofullerenes. C_i (1) and C_s (2) Symmetry

The basic singlet state is typical for the structures studied in this section.

As the calculation shows, during the encapsulation the length of the Me−Me bond increased by 20−65 pm depending on the nature of the metal (Table 5), and there was only a slight deformation of the carbon cage (the change in the lengths of the C−C bonds did not exceed 10 pm near the embedded atoms).

The values of $\Delta_f H^0$ and $\Delta_f G^0$ indicate a non-monotonic nature of the dependence of the enthalpy of formation of endofullerenes Me$_2$@C$_{60}$ on the nature of the metal: the formation of Y$_2$@C$_{60}$ is characterised by the greatest energy costs as compared to any isomers of Sc$_2$@C$_{60}$, while the formation of La$_2$@C$_{60}$ is more advantageous. On the contrary, the process of embedding a diatomic metal cluster inside a fullerene cell in the case of Sc$_2$@C$_{60}$ and La$_2$@C$_{60}$ is less preferable than for Y$_2$@C$_{60}$ (Table 5, ΔH_b^0, ΔG_b^0).

Just like for the structures described in the previous section, the transfer of electron density on the carbon cage from the encapsulated metal atoms is typical for Me$_2$@C$_{60}$. These atoms acquire a positive charge, which, in the case of Y$_2$@C$_{60}$, reaches 0.552 a.u. per atom. Since the basic singlet state is typical for the structures containing diatomic metal clusters inside a fullerene cell, the transfer of electron density on the carbon cage does not occur. Therefore, the values of total spin density on carbon atoms contained in fullerene for all the structures studied in this section are zero and are not presented in Table 5.

Table 5. Calculated Parameters for Endofullerenes of the Scandium Sub-Group with Two Encapsulated Atoms

	$Sc_2@C_{60}$ (1)	$Sc_2@C_{60}$ (2)	$Y_2@C_{60}$	$La_2@C_{60}$
Symmetry	C_i	C_s	C_i	C_s
r_0(Me–Me), pm	259	259	290	263
r(Me–Me), pm	324	310	310	290
$|r-r_0|$, pm	65	51	20	27
$\Delta_f H^0$, kJ/mol	2582	2594	2605	2393
$\Delta_f G^0$, kJ/mol	2517	2529	2547	2338
ΔH_b^0, kJ/mol	−640	−629	−689	−640
ΔG_b^0, kJ/mol	−593	−580	−635	−591
Q(Me), a.u.	0.254	0.234	0.552	0.512

3.3. Endofullerenes with three encapsulated atoms

The results of optimisation of geometry of the $Me_3@C_{60}$ compounds indicate the presence of isomers of $Sc_3@C_{60}$ и $La_3@C_{60}$, and the calculation shows the presence of two types of structures:

A structure with C_s symmetry, where a triatomic metal cluster is located along the line connecting the centres of two diametrical six-membered cycles (Fig. 3.1), typical for the first isomer of $Sc_3@C_{60}$ and the second isomer of $La_3@C_{60}$.

A structure with C_2 symmetry, where the Me_3 cluster is located along the line connecting the centres of two diametrical bicyclic fragments of C_{10} (Fig. 3.2); this structure was found in the second isomer of $Sc_3@C_{60}$, $Y_3@C_{60}$, and the first isomer of $La_3@C_{60}$.

The basic doublet state is typical for these structures.

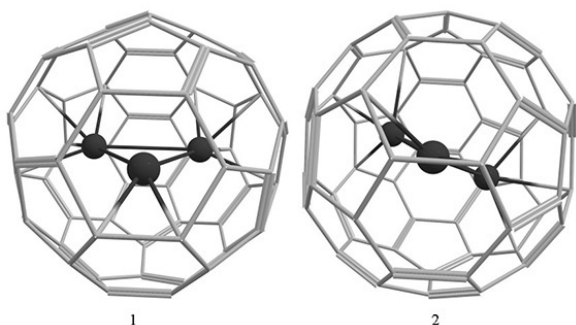As the calculation shows, triatomic clusters of the metals of the scandium sub-group are

shaped as an equiangular triangle both outside and inside the fullerene cell, so for the definitive description of their structures only one geometric parameter, the length of one of the Me–Me bonds, is sufficient. The presented data (Table 6) shows that the increase of the lengths of the Me–Me bonds (up to 17 pm) is typical for $Sc_3@C_{60}$ and $Y_3@C_{60}$, and a slight decrease (2 pm) is typical for $La_3@C_{60}$ during the encapsulation. In other words, the shape and the size of the cluster remain virtually unchanged when it is embedded in the fullerene cell. Particularly, the lengths of the C–C bonds near the encapsulated atoms increase more than in the case of the $Me_2@C_{60}$ structures (up to 20 pm), and a significant deformation of the carbon cage is observed as its shape becomes considerably different from the original spherical one.

During the transition from yttrium to lanthanum, the values of Δf_H^0 and Δf_G^0 decrease, which indicates the reduction of energy costs on the formation of endofullerenes corresponding to the metals from individual substances, while the increase of ΔH_b^0 in this series shows that La_3 is less inclined to be embedded in the fullerene structure when the process occurs in the gaseous phase (Table 6).

Different values of natural charges on metal atoms (particularly, for the first isomer of $Sc_3@C_{60}$) prove a thesis about the inequivalence of these atoms naturally arising from the analysis of the geometric structure of endofullerenes. For instance, the presence of two atoms with almost identical charges in the second isomer of

Fig. 3. Structure of the $Me_3@C_{60}$ Endofullerenes. C_s (1) and C_2 (2) Symmetry

Table 6. Calculated Parameters for Endofullerenes of the Scandium Sub-Group with Three Encapsulated Atoms

	$Sc_3@C_{60}$ (1)	$Sc_3@C_{60}$ (2)	$Y_3@C_{60}$	$La_3@C_{60}$ (1)	$La_3@C_{60}$ (2)
Symmetry	C_s	C_2	C_2	C_2	C_s
r_0(Me−Me), pm	281	281	281	284	284
r(Me−Me), pm	297	298	296	282	282
$\lvert r-r_0 \rvert$, pm	16	17	15	2	2
$\Delta_f H^0$, kJ/mol	2635	2637	2913	2834	2847
$\Delta_f G^0$, kJ/mol	2565	2581	2852	2790	2801
ΔH_b^0, kJ/mol	−782	−780	−573	−343	−329
ΔG_b^0, kJ/mol	−727	−710	−507	−270	−258
Q(Me), a.u.	0.044 0.067 0.068	0.024 0.025 0.025	0.349 0.349 0.349	0.319 0.320 0.320	0.327 0.328 0.330
$S(C_{60})$	0.942	0.721	0.204	0.223	0.356

$Sc_3@C_{60}$ correlates with the presence of the C_2 point group in this structure. However, the inverse proposition does not hold true: similar values of natural charges on the three atoms contained in the encapsulated cluster are typical for $Y_3@C_{60}$, although the analysis of the geometric structure does not reveal the presence of the lines of threefold symmetry in these compounds. The values of Q(Me) decrease during the transition from yttrium to lanthanum and, on the whole, have smaller values than the $Me@C_{60}$ and $Me_2@C_{60}$ compounds, although they remain positive, which also indicates that triatomic metal clusters of the scandium sub-group are less inclined to be embedded into a cell of fullerene C_{60}. This is also confirmed by smaller values of total spin density on the carbon cage of $Y_3@C_{60}$ и $La_3@C_{60}$, which makes the prospect of using the compounds of this type as contrasting agents for tomography highly questionable.

3.4. Endofullerenes with four encapsulated atoms

The calculation establishes the presence of two types of structures in the $Me_4@C_{60}$ endofullerenes:

A structure with C_s symmetry is characterised by the presence of a square Me_4 cluster inside a fullerene cell, and this cluster is located perpendicular to the line connecting the centres of two diametrically opposite five-membered cycles (Fig. 4.1); this type of structure is typical for the first isomer of $Sc_4@C_{60}$ and the first isomer of $Y_4@C_{60}$;

A structure with C_s symmetry, where the Me_4 cluster has a shape of a tetrahedron with the apexes located opposite four six-membered cycles in the structure of the carbon cage (Fig. 4.2); this type of structure is found in the second isomer of $Sc_4@C_{60}$, the second isomer of $Y_4@C_{60}$, and $La_4@C_{60}$.

Isolated tetratomic clusters of metals of the scandium sub-group have the shape of dihedral angles formed by two congruent isosceles triangles, and their geometry, in the general case, can be described by three parameters: the length of the bond r corresponding to the lateral side of one of the triangles, the length of the bond b forming the base of one of the triangles, and the angle α formed by the planes of the
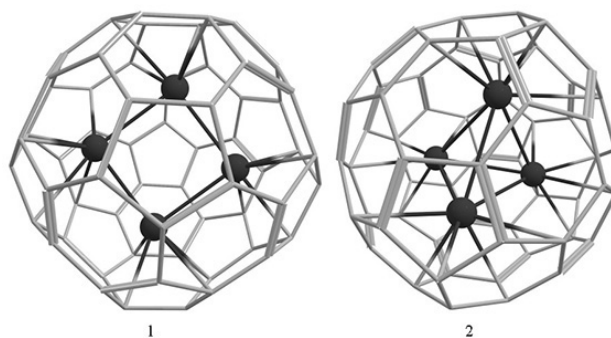

Fig. 4. Structure of the $Me_4@C_{60}$ Endofullerenes. Cs (First Isomer, 1) and C_2 (Second Isomer, 2) Symmetry

Table 7. Calculated Parameters for Endofullerenes of the Scandium Sub-Group with Four Encapsulated Atoms

	$Sc_4@C_{60}$ (1)	$Sc_4@C_{60}$ (2)	$Y_4@C_{60}$ (1)	$Y_4@C_{60}$ (2)	$La_4@C_{60}$
Symmetry	C_s	C_s	C_s	C_s	C_s
r_0, pm	288	288	288	288	275
r, pm	261	291	259	297	286
$|r-r_0|$, pm	27	3	29	9	11
b_0, pm	291	291	291	291	346
b, пм	366	294	370	293	285
$|b-b_0|$, pm	75	3	78	2	61
α_0, °	74.095	74.095	74.095	74.095	107.277
α, °	179.011	74.548	172.497	70.348	70.585
$|\alpha-\alpha_0|$, °	104.916	0.453	98.402	3.747	36.692
V_0, Å^3	2.882	2.882	2.882	2.882	2.530
V, Å^3	–	2.970	–	3.029	2.766
$\Delta_f H^0$, kJ/mol	2992	2778	3688	3398	3471
$\Delta_f G^0$, kJ/mol	2933	2718	3637	3353	3440
ΔH_b^0, kJ/mol	−574	−788	56	−234	297
ΔG_b^0, kJ/mol	−496	−710	138	−146	379
$Q(Me)$, a.u.	−0.020 −0.017 −0.085 −0.089	−0.042 −0.077 −0.088 −0.088	0.148 0.182 0.219 0.220	0.200 0.244 0.244 0.244	0.236 0.237 0.244 0.250

triangles (Fig. 5). The corresponding values of these parameters for isolated and encapsulated clusters are presented in Table 7. It is clear that a significant reduction in the lengths of the bonds r (by 27–29 pm) is typical for endofullerenes with square clusters; as for the compounds with tetrahedral clusters, only the dihedral angle noticeably changes assuming such values for $La_4@C_{60}$ and for the second isomer of $Y_4@C_{60}$
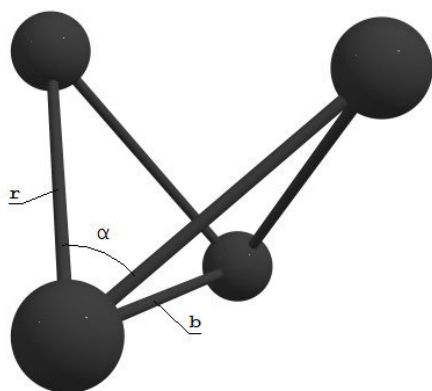
Fig. 5. Structural Parameters of the Me_4 Particles

that are almost identical to the value of the dihedral angle of the tetrahedron (~70.529°), and the lengths of the bonds slightly change (by 3–11 pm). At the same time, however, in all the cases an increase was observed in the volume V (Table 7) of the Me_4 particle in the encapsulated state by 3 – 5% as compared to the volume of the isolated particle.

The values of enthalpy and energy of formation of the $Me_4@C_{60}$ compounds are much higher than the values of the derivatives with triatomic encapsulated clusters; the values of enthalpy and energy of encapsulation become less negative. Positive values of ΔH_b^0 (for the isomer of $Y_4@C_{60}$ with a square cluster and $La_4@C_{60}$), which appear for the first time in the endofullerenes with this number of encapsulated atoms, are indicative of the thermodynamic impossibility of the formation of these compounds. Therefore, the maximum number of atoms that are capable of being embedded inside the carbon cage is three for lanthanum.

As for both isomers of $Sc_4@C_{60}$, the transfer of electron density from the carbon cage to the encapsulated cluster is typical for them, which leads to the appearance of a small negative charge (0.020–0.089 a.u. in the absolute value) on the atoms of the latter; as for $Y_4@C_{60}$ with a tetrahedral cluster, the transfer occurs in the opposite direction, and the metal atoms acquire the charge of 0.200–0.244 a.u.

3.5. Endofullerenes with five encapsulated atoms

As it was previously mentioned, the formation of endofullerenes with four or more encapsulated atoms is not typical for lanthanum, therefore only the results of modelling for the compounds $Sc_5@C_{60}$ and $Y_5@C_{60}$ are presented in this section. The calculation shows the presence of two types of structures in these compounds:

A structure with the C_s symmetry where the Me_5 cluster has a shape of a trigonal bipyramid and is placed inside the fullerene cell so that its line of threefold symmetry coincides with the line connecting the centres of two diametrically opposite bicyclic fragments of C_{10} (Fig. 6.1); this structure was found both in $Sc_5@C_{60}$ and $Y_5@C_{60}$.

A structure with the C_3 symmetry where the line of threefold symmetry of the Me_5 cluster (also having a shape of a trigonal bipyramid) coincides with the line of threefold symmetry of fullerene going through the centres of two diametrically opposite six-membered cycles (Fig. 6.2); this type of structure is also formed both in the case of $Sc_5@C_{60}$ and $Y_5@C_{60}$.

The basic doublet state is typical for these structures.

Both outside and inside the fullerene cell, the Me_5 clusters of metals of the scandium sub-group have the shape of a distorted trigonal bipyramid,
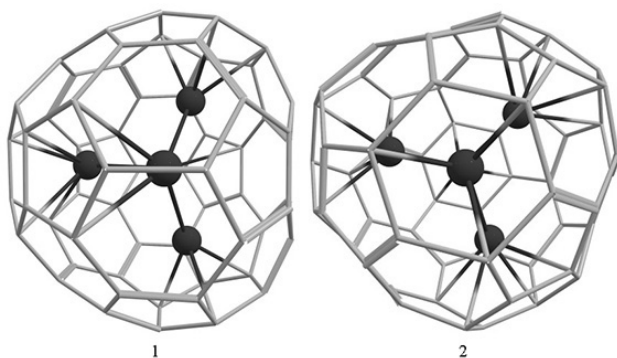
therefore only two parameters are sufficient for the description of their geometry: the lengths of the bonds r and d corresponding to the lateral edges and edges at the base of the pyramids forming a bipyramid (Fig. 7). The corresponding values are presented in Table 8. It is clear that the length of the bonds r decreases by 26–68 pm, while d can either decrease (by 15–48 pm in the case of $Sc_5@C_{60}$) or slightly increase (by 1–10 pm in the case of $Y_5@C_{60}$). It should be noted that the volume of the encapsulated cluster decreases as compared to the volume of the isolated one (V and V_0 respectively, see Table 8) regardless of the direction of the change of separate parameters. Moreover, while the volumes of isolated particles significantly differ (5.876 Å³ and 7.924 Å³ for Sc_5 and Y_5 respectively), they are rather similar for the encapsulated ones (5.521–5.693 Å³).

Negative values of enthalpy and the energy of encapsulation for endofullerenes of scandium indicate that they can be potentially formed by embedding the Sc_5 particle in the fullerene cell in the gaseous phase; in the case of $Y_5@C_{60}$, ΔH_b^0 is comparable with the energies of bond breaking in the fullerene (417 and 507 kJ/mol for $r6$–6 and $r5$–6 respectively [16]). Therefore, the formation of $Y_n@C_{60}$ compounds with $n > 4$ is not typical for endofullerenes of yttrium.

Atoms of scandium inside the carbon cage acquire a small negative charge (Table 8), and while for the first of isomers of $Sc_5@C_{60}$ the most negative charges (−0.218 a.u.) are found in the atoms located along the line of threefold symmetry of the encapsulated cluster, for the second isomer the most negative charges are located on the atoms of the equatorial section
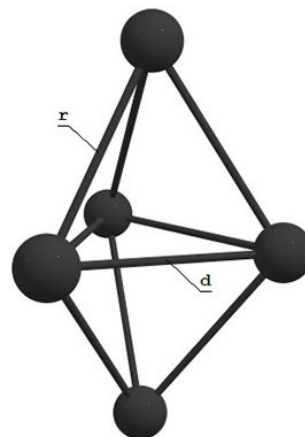

Fig. 6. Structure of the $Me_5@C_{60}$ Endofullerenes C_s (1) and C_3 (2) Symmetry

Fig. 7. Structural Parameters of the Me_5 Particles

Table 8. Calculated Parameters for Endofullerenes of the Scandium Sub-Group with Five Encapsulated Atoms

	$Sc_5@C_{60}$ (1)	$Sc_5@C_{60}$ (2)	$Y_5@C_{60}$ (1)	$Y_5@C_{60}$ (2)
Symmetry	C_s	C_3	C_s	C_3
r_0, pm	290–296	290–296	321–327	321–327
r, pm	262–270	265–271	254–273	253–274
$|r-r_0|$, pm	26–28	25	54–67	53–68
d_0, pm	287–298	287–298	317–330	317–330
d, pm	302–346	314–326	307–336	310–331
$|d-d_0|$, pm	15–48	27–28	6–10	1–7
V_0, Å³	5.876	5.876	7.924	7.924
V, Å³	5.531	5.693	5.521	5.572
$\Delta_f H^0$, kJ/mol	3164	3175	4292	4298
$\Delta_f G^0$, kJ/mol	3109	3119	4251	4256
ΔH_b^0, kJ/mol	−560	−549	504	510
ΔG_b^0, kJ/mol	−471	−461	599	604
$Q(Me)$, a.u.	−0.033 −0.033 −0.100 −0.218 −0.218	−0.079 −0.090 −0.107 −0.141 −0.147	−0.012 0.059 0.084 0.212 0.212	0.025 0.051 0.074 0.224 0.235
$S(C_{60})$	0.127	0.363	0.412	0.391

of the Me_5 particle. Despite the direction of the transfer of electron density from the carbon cage towards the metal cluster, the value of total spin density on the carbon cage for these compounds is within the range of 0.127–0.363.

3.6. Endofullerenes with six and seven encapsulated atoms

As it was previously shown, the maximum number of encapsulated atoms is 4 and 5 for the endohedral derivatives of yttrium and lanthanum respectively, and the formation of such endohedral derivatives $Me_6@C_{60}$ and $Me_7@C_{60}$ is typical only for scandium. The calculation states the presence of three types of structures in $Sc_6@C_{60}$:

A structure with C_s symmetry (isomer 1), where the Me_6 cluster has the shape of a tetragonal bipyramid with the apexes located opposite the centres of bicyclic fragments of C_{10} in the fullerene structure (Fig. 8.1);

A structure with C_s symmetry (isomer 2), where the metal cluster has the shape of a tetragonal bipyramid with one metal atom in
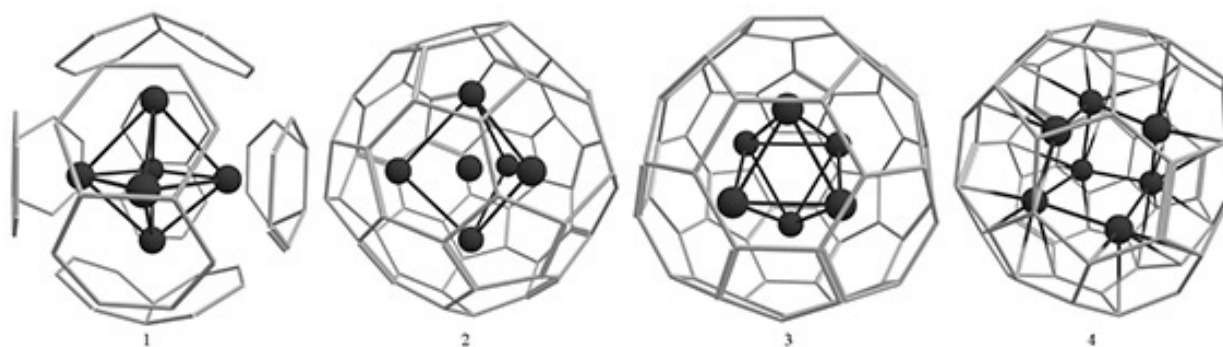

Fig. 8. Structure of the $Me_6@C_{60}$ and $Me_7@C_{60}$ Endofullerenes. C_s (1), C_s (2), and C_{3v} (3) Symmetry for the $Me_6@C_{60}$ Isomers. Index (4) Indicates the Structure of $Me_7@C_{60}$ Endofullerene with Undefined Symmetry

the centre and a line of threefold symmetry directed along the line connecting the centres of two diametrically opposite fragments of C_{12}, formed by two six-membered cycles and one five-membered cycle (Fig. 8.2);

A structure with C_{3v} symmetry (isomer 3), where the metal cluster has the shape of an octahedron with one of the lines of threefold symmetry coinciding with the line of threefold symmetry of fullerene going through the centres of diametrically opposite six-membered cycles (Fig. 8.3).

The Sc_6 cluster in the gaseous phase has the shape of a pentagonal bipyramid devoid of one of the atoms located in the equatorial plane. Due to the great differences in the geometry of isolated and encapsulated clusters, the comparison of their geometric parameters is meaningless, therefore in this section we will compare only the volumes of the corresponding particles. The data presented in Table 9 shows that the deformation of the metal cluster during the encapsulation is typical for all the $Sc_6@C_{60}$ compounds and is accompanied by a decrease in its volume. As for the first and the third isomers of $Sc_6@C_{60}$, the volume of the Sc_6 particle inside the fullerene cell is 5 – 6% smaller than the original. As for the second isomer, this effect is more pronounced and the volume of the encapsulated cluster is 31% smaller than the volume of the isolated one. However, it should be noted that in the structure that is typical for this isomer, the central atom of scandium becomes close to the atoms forming a trigonal bipyramid at a distance of 195–202 pm, which is 86–93 less than a double covalent radius of scandium (288 pm), and the distance between the atoms themselves reaches 371 pm, thus exceeding the double covalent radius of scandium by 83 pm. Due to considerable strains in the structure, the formation of such a compound is thermodynamically disadvantageous, as was evidenced by strongly positive values of enthalpy and energy of encapsulation (693 kJ/mol, see Table 9). For the first and the third isomers of $Sc_6@C_{60}$ this value becomes negative, which shows that corresponding structures can be potentially formed as a result of embedding of the Sc_6 particles in the fullerene cell in the gaseous phase. Metal atoms inside the carbon cage acquire small negative charges within the range of −0.261 – −0.053 a.u.

The addition of one atom of scandium to the Sc_6 particle in the gaseous phase results in the formation of the Sc_7 cluster with a shape of a regular pentagonal bipyramid. However, in the encapsulated state the symmetry of this cluster is broken, and it acquires the shape of a deformed cube devoid of one of the apexes (Fig. 8.4). In

Table 9. Calculated Parameters for Endofullerenes of the Scandium Sub-Group with Six and Seven Encapsulated Atoms

	$Sc_6@C_{60}$ (1)	$Sc_6@C_{60}$ (2)	$Sc_6@C_{60}$ (3)	$Sc_7@C_{60}$
Symmetry	C_s	C_s	C_{3v}	-
V_0, Å³	9.311	9.311	9.311	15.254
V, Å³	8.818	6.410	8.725	9.184
$\Delta_f H^0$, kJ/mol	3723	4591	3752	4578
$\Delta_f G^0$, kJ/mol	3673	4541	3702	4530
ΔH_b^0, kJ/mol	−176	693	−146	599
ΔG_b^0, kJ/mol	−76	792	−47	705
Q(Me), a.u.	−0.261 −0.156 −0.130 −0.114 −0.114 −0.084	−0.738 −0.579 −0.563 −0.491 −0.474 3.328	−0.203 −0.190 −0.124 −0.100 −0.054 −0.053	−0.328 −0.206 −0.152 −0.056 −0.019 0.002 0.014
S(C$_{60}$)	–	–	–	0.197

this case, the distortions of the carbon cage are so significant that it is impossible to assign any group of symmetry to the $Sc_7@C_{60}$ structure; analysis of the elements of symmetry points to the C_2 group, where the line of two-fold symmetry is in one plane with the diagonal of the "cube" and goes through its edge, as the one that describes the structure of endofullerene most adequately, although the error in this case is 16.7%.

The Sc_7 cluster appears to be highly compressed inside the carbon cage, and its volume in the encapsulated state is 40% smaller than in the isolated state (see Table 9); the bonds between the metal atoms have the length of 230–267 pm, which is 21–58 pm less than in the case of the double covalent radius of scandium. As for this structure, the values of enthalpy and energies of encapsulation are positive (599 kJ/mol), which indicates that it is impossible to form the $Sc_7@C_{60}$ endofullerene by embedding a metal cluster inside the carbon cage in the gaseous phase. Therefore, the formation of the endohedral derivatives of $Me_n@C_{60}$ with $n > 6$ is not typical for scandium.

4. Conclusions

Analysis of structural and thermodynamic characteristics of endofullerenes of the scandium sub-group metals allows revealing a number of patterns that become apparent with the growing number of encapsulated atoms. For instance, the theoretical limit at which the formation of the endohedral structure of $Me_n@C_{60}$ through embedding of the Me_n particle in the fullerene cell remains possible from the thermodynamic point of view is $n = 6$ for scandium, 4 for yttrium, and 3 for lanthanum. In addition, the most stable derivatives are those with a diatomic (or triatomic, in the case of scandium) metal cluster inside the carbon cage, as considerable deformations of both the fullerene cage and the Me_n particle were observed in the models of endofullerenes with larger encapsulated clusters.

A redistribution of electron density between two parts of the structure being formed is typical for endofullerenes of the scandium sub-group metals, however, the direction of the transition and the degree of manifestation of this effect depend on the number of encapsulated atoms. As the number of metal atoms grows, the total charge on the encapsulated cluster decreases in the structure of endofullerene: in the $Me@C_{60}$ – $Me_3@C_{60}$ endofullerenes the metal atoms have a positive charge, in $Me_4@C_{60}$ separate atoms acquire small in the absolute value negative charges, while the presence of only negative charge on the metal atoms is typical for the $Me_5@C_{60}$ – $Me_6@C_{60}$ structures.

A considerable decrease in the value of the total spin density in the carbon cage for structures in a basic doublet state is also observed with the growing number of encapsulated atoms in the structure of the endofullerene, which limits the possibility of the use of endofullerenes with more than one encapsulated atom as contrasting agents for NMR tomography.

Acknowledgements

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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All authors have read and approved the final manuscript.

Translated by Marina Strepetova

Edited and proofread by Simon Cox