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Quantum Chemical Study of Atomic Structure Evolution of Co_x/C_{60} ($x \leq 2.8$) Composites

**Pavel Avramov,*,[†,‡] Hiroshi Naramoto,[†] Seiji Sakai,[†] Kazumasa Narumi,[†]
Vasily Lavrentiev,[†] and Yoshihito Maeda[†,§]**

Takasaki-Branch, Advanced Science Research Center, Japan Atomic Energy Agency, Takasaki, 370-1292, Japan, and Department of Energy Science and Technology, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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The main features of the local atomic structure of novel Co_x/C_{60} ($x \leq 2.8$) complex mixtures were studied using the ab initio B3LYP/6-31G* method for a set of low- and high-energy $Co_n(C_{60})_m$ ($n = 1, 2, m = 2, 3$) clusters in low and intermediate spin states. For the $n = 1$ isomers the spin state $S = 1/2$ is energetically preferable, whereas the low-energy isomers of $n = 2$ have an intermediate spin state of $S = 1$. The η^2 (6−6 edge of C_{60}) type of cobalt ion coordination is preferable for both the $n = 1$ and $n = 2$ cases. The $\eta^{2'}$ (coordination with a 6−5 edge) and even the η^5 (C_5 fragment) types can serve as low- and high-energy intermediates for the cobalt ion's migration around the C_{60} cage. Formation of cobalt dimers can be the final stage of evolution of Co_x/C_{60} atomic structure approaching the equilibrium atomic geometry.

I. Introduction

Complex mixtures of C_{60} fullerenes and transition metals (TM) have attracted attention because of possible applications as promising functional materials (see, for example, refs 1−3). The TM_x/C_{60} composites can be considered as condensed complex compounds with incredibly controllable compositions and are the products of various types of vapor codeposition of transition metals and C_{60}.[3−5] Actually, the TM_x/C_{60} composites synthesized using atomic and molecular beams can be considered as complex mixtures of $TM_n(C_{60})_m$ compounds. To date, the atomic structure of the TM_x/C_{60} composites has not been well studied by either experimental or theoretical approaches. The further development of such compounds to obtain novel materials is impossible without detailed theoretical study of the species using sophisticated quantum chemical approaches.

Contrary to the TM_x/C_{60} composites, the $TM_n(C_{60})_m$ complexes with constant composition are well-known objects of coordination chemistry (see, for example, detailed reviews in refs 6 and 7) and can be synthesized and characterized using various chemical and spectroscopic methods. The detailed spectroscopic study of the atomic structure of the TM_x/C_{60} mixtures is limited for several reasons: the difficulty to precisely control the sample composition, the decomposition of C_{60} during synthesis, and the possible contamination from the atmosphere.[3−5]

The C_{60} cages can coordinate metallic ions in different fashions.[3,4] We denote here the coordination of a metal ion by a 6−6 edge of C_{60} as an η^2 type of coordination. Another possibility is coordination of an ion by a 6−5 edge. We denote this type of coordination as $\eta^{2'}$ as well. The η^5 and η^6 types of coordination mean a complex bond between the metal and the C_5 or C_6 fragments of the C_{60}, respectively. The η^3 type means coordination of a metallic ion bonded to a C_3 fragment of the carbon hexagon. And finally the η^1 type denotes coordination by one carbon atom of the C_{60} cage.

For the transition metals, the C_{60} fullerenes can serve as ligands of different hapticity and exhibit all possible types of coordination η^1 (ref 6) (Pt−fullerenyl radical), η^2 (refs 6−8), η^3 (refs 5 and 9), η^5 (refs 10 and 11), and η^6 (refs 7, 12, and 13). Some exotic structures like $C_{60}[Ir_2Cl_2(1,5\text{-COD})_2]_2$ may contain up to six metal ions as complex centers.[14−17]

In contrast with the cobaltocene $Co(C_5H_5)_2$, the Co_x/C_{60} species exhibit either η^2- or η^3-type coordination.[5,7,8] In the work of ref 5 the $Co_n(C_{60})_m$ clusters were produced by a combination of laser-independent vaporization—of the cobalt and C_{60} rods—and the molecular beam method. The vaporized cobalt and C_{60} molecules were cooled to room temperature by He carrier gas at 5−7 atm of pressure and then grown into the $Co_n(C_{60})_m$ clusters. For a qualitative study of the atomic structure of the species, a mass spectroscopy (MS) method was used in combination with chemical probe analysis. Detailed analysis of the data[5] shows the presence of large or sufficient amounts of the C_{60}, CoC_{60}, $Co(C_{60})_2$, $Co(C_{60})_3$, $Co_2(C_{60})_2$, $Co_2(C_{60})_4$, $Co_3(C_{60})_4$, and $Co_4(C_{60})_4$ species (it is necessary to note that the ratio of relative MS intensities of the $Co(C_{60})_2$ and $Co_2(C_{60})_2$ clusters is approximately 1:5 and only a trace amount of the $Co_3(C_{60})_2$ complex was detected.[5] Later, we will use this information for theoretical design of the structural models of local atomic structures of the Co_x/C_{60} composites). The reaction of the species with probe gases (CO, O_2, NH_3) in combination with the mass spectroscopy method allowed the authors[5] to make conclusions about the coordination type of the cobalt ions in the $Co_n(C_{60})_m$ complexes.

Although the structural data of work of ref 5 is indirect, qualitative, and measured for the positively charged clusters (this fact could lead to additional changes in structure and reactivity of the species), it is really important for understanding the structure and properties of the Co_x/C_{60} composites. Combining the mass spectroscopic data and chemical probe analysis the authors of ref 5 show that the cobalt ions in $Co_n(C_{60})_m$ clusters probably exhibit the η^3 type of coordination in some cases but definitely not η^5 or η^6 ones. The $Co(C_{60})_2$ cluster is

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* Corresponding author. E-mail: avramov.pavel@jaea.go.jp. Phone: +81 27 346 9670. Fax: +81 27 347 2501.

[†] Japan Atomic Energy Agency.

[‡] On leave from L.V. Kirensky Institute of Physics SB RAS, 660036 Krasnoyarsk, Russian Federation.

[§] Kyoto University.

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considered[5] to be a bent structure bridged with a Co ion between the fullerene cages, whereas the $Co(C_{60})_3$ cluster is a triangular planar structure. The $Co_4(C_{60})_4$ has an unusual "composite di-tetrahedral" structure with a Co_4 pyramid inserted into a $(C_{60})_4$ pyramid. Each side of the resulting structure is a $Co(C_{60})_3$ triangle with a cobalt ion between the fullerenes—each vertex of the $(C_{60})_4$ tetrahedron belongs simultaneously to three different $Co(C_{60})_3$ planes.[5] Actually, the $Co_4(C_{60})_4$ cluster is a tetramer of the $Co(C_{60})_3$ one.[5] In the same sense, the $Co_2(C_{60})_4$ is a dimer, and the $Co_3(C_{60})_4$ is a trimer of the $Co(C_{60})_3$ unit.[5] In the last cases, only two or three $(C_{60})_3$ planes of the $(C_{60})_4$ tetrahedron contain cobalt ions.[5] Finally, the structure of $Co_2(C_{60})_2$ cluster is considered[5] to be two bridged cobalt ions between two fullerene cages. No evidence of the existence of linear $Co-C_{60}-Co-C_{60}$ clusters has been recorded.[5]

In the work of ref 4 some features of the atomic structure of $Co_{2.8}/C_{60}$ composite (synthesized using combined atomic (cobalt) and molecular (C_{60}) evaporation and condensation) were determined using the Co K-edge XAFS analysis. It was shown that with the Co−C distance of 2.01 ± 0.01 Å the cobalt coordination number is equal to 6. The analysis of positron annihilation lifetime spectra[4] showed that for Co_x/C_{60} composites ($0 < x \leq 2.8$) a new low-dimension phase can be realized through the bridge formation between the C_{60} molecules by Co atoms with enlargement of the intermolecular distance as a result.

Several attempts were made to describe—theoretically—the structure and properties of the TMC_{60} complexes using empirical tight binding (TB) models and the TB-based molecular dynamics (MD) simulation technique (see, for examples, refs 18 and 19). Even on the TB level, the structural features of the $TM(C_{60})_2$ and $TM_2(C_{60})_2$ (TM = Ni, V) were correctly described in comparison with the existing experimental data.[12]

The atomic and electronic structure of the allyl, metallocene, and bis-η^6 benzene ($TM(C_2H_4)_n$, η^2 type of coordination, $TMCp_2$, η^5 type of coordination, Cp = C_5H_5 and $TMBz_2$, η^6 type of coordination, Bz = C_6H_6, respectively) sandwich complexes with d and f elements and was studied using a more advanced ab initio DFT approach.[20−27] It was shown that the DFT theory correctly describes the type of coordination, symmetry, and TM−C interatomic distances with high accuracy for all species.

On the basis of the Becke, Lee, Yang, and Parr (BLYP) version of the general gradient approximation (GGA), a Car−Parrinello MD simulation of the structure and the dynamics of the atomic base of the $C_{60}Ta_3$ system was performed.[27] It was shown that one Ta ion coordinates with C_{60} in an η^2 fashion, whereas the Ta_2 dimer reveals high mobility along the C_{60} cage. The ease of migration of the Ta_2 fragment around the C_{60} cage is the main structural peculiarity of the $C_{60}Ta_3$ complex.

The conditions of synthesis[4] for Co_x/C_{60} composites, using atomic and molecular beams with consequent condensation of the mixtures, imply that all possible types (both low- and high-energy species) of local atomic structures could be formed during the experiment. Because of this, the atomic structure of the species can evolve during—or shortly after—the synthesis to achieve relatively stable positions of the cobalt ions and the C_{60} cages. Migration of the Co ions around and between the fullerene cages is the most probable mechanism to achieve this. The first step to study the atomic structure evolution process is to find all possible local $Co_n(C_{60})_m$ isomers and intermediates. From a general point of view, hundreds of $Co_n(C_{60})_m$ structures in low and high energy and spin states can be realized. Unfortunately, due to the big number and complexity of the structures (hundreds of atoms including several TMs), it is hardly possible to find appropriate transition states on the isomerization reaction pathways. Because of this, we can only judge the atomic structure evolution of the Co_x/C_{60} composites based on the information about the atomic structure of all possible isomers and intermediates.

Presented here is a systematic theoretical ab initio DFT investigation of the atomic structure evolution of the Co_x/C_{60} composites in terms of the structure and energetic characteristics of a number of $Co_n(C_{60})_m$ clusters. This study is organized as follows: section II describes the computational methods and objects under investigation, followed by results and discussion in section III. Conclusions are presented in section IV.

II. Computational Details

The Gaussian 03[28] code was used to calculate the electronic structure of $Co_n(C_{60})_m$ clusters. Geometry optimization was performed by using the analytic energy gradients at a B3LYP/6-31G* level of theory.[29] All relative energies were calculated taking into account the basis set superposition error (BSSE). On the basis of the electronic structure calculations of the $Co_n(C_{60})_m$ clusters at the B3LYP/6-31G* level for the $Co_n(C_{60})_m$ systems, the BSSE was estimated in the range of 35−55 kcal/mol. Taking the BSSE corrections into account is really important to predict the correct energy values and relative stability of the species.

To study the atomic and electronic structure of the metallocene systems,[20] the HF approach as well as a wide variety of DFT potentials (BHLYP, B3LYP, BLYP, BP86, LSDA) were used. It was shown[20] that the B3LYP method[29] gives the best results among the approximations listed above. At present, the B3LYP method is probably the best tested approach among all ab initio DFT ones. It was designed[29] especially for correct description of the dissociation limit of a wide variety of molecules. The accuracy of the B3LYP method in describing the dissociation energies estimated for the G2 set is equal to 3.5 kcal/mol.[29−31]

The total B3LYP energy $E^{\mathrm{B3LYP}}_{\mathrm{Tot}}$ can be presented in the form $E^{\mathrm{B3LYP}}_{\mathrm{Tot}} = E^{\mathrm{True}}_{\mathrm{Tot}} + E^{\mathrm{m}}$, where $E^{\mathrm{True}}_{\mathrm{Tot}}$ is the exact total energy of the system and E^{m} is the B3LYP mistake. In such notations the dissociation energy of the AB → A + B process can be presented as

$$E^{\mathrm{B3LYP}}_{\mathrm{Diss}} = E^{\mathrm{B3LYP}}_{\mathrm{TotAB}} - E^{\mathrm{B3LYP}}_{\mathrm{TotA}} - E^{\mathrm{B3LYP}}_{\mathrm{TotB}} = E^{\mathrm{True}}_{\mathrm{TotAB}} - E^{\mathrm{True}}_{\mathrm{TotA}} - E^{\mathrm{True}}_{\mathrm{TotB}} + (E^{\mathrm{m}}_{\mathrm{AB}} - E^{\mathrm{m}}_{\mathrm{A}} - E^{\mathrm{m}}_{\mathrm{B}})$$

where the $E^{\mathrm{True}}_{\mathrm{TotAB}}$, $E^{\mathrm{True}}_{\mathrm{TotA}}$, and $E^{\mathrm{True}}_{\mathrm{TotB}}$ are true total energies of the AB, A, and B systems. The $E^{\mathrm{m}}_{\mathrm{AB}}$, $E^{\mathrm{m}}_{\mathrm{A}}$, and $E^{\mathrm{m}}_{\mathrm{B}}$ values denote the respective mistakes of the method. The true dissociation energy $E^{\mathrm{True}}_{\mathrm{TotAB}}$ is equal to $E^{\mathrm{True}}_{\mathrm{TotAB}} - E^{\mathrm{True}}_{\mathrm{TotA}} - E^{\mathrm{True}}_{\mathrm{TotB}}$. The accuracy of the method is determined by the $E^{\mathrm{m}}_{\mathrm{AB}} - E^{\mathrm{m}}_{\mathrm{A}} - E^{\mathrm{m}}_{\mathrm{B}}$ difference. In most cases the difference (see above) is equal to 3.5 kcal/mol.[31−33]

For a set of isomers with the same nature of chemical bonding and close atomic structures the mistakes $\{E^{\mathrm{m}}_{\mathrm{i}}\}$ are practically the same. Because of this, the difference in B3LYP total energies of isomers A and B ($E^{\mathrm{B3LYP}}_{\mathrm{TotA}} - E^{\mathrm{B3LYP}}_{\mathrm{TotB}}$) is close to the difference between the true energies of the species ($E^{\mathrm{True}}_{\mathrm{TotA}} - E^{\mathrm{True}}_{\mathrm{TotB}}$).

For example, the energy difference for a number of isomers of metallocenes[20] can be less than 1.0 kcal/mol. Such high accuracy of the B3LYP method in describing the relative stability of isomers of transition metal complexes allows us to avoid using more sophisticated but less tested DFT potentials like hybrid PBE0[32,33] or other GGA-based approaches.

The atomic structure of Co_x/C_{60} systems is characterized by its complexity.[3−5] Only general information, such as Co−C interatomic distances and possible coordination numbers, can be extracted from the structural spectroscopic experiments.[4,5] The unique atomic structure of C_{60} cage and the synthesis conditions are the reasons for the complex and irregular nature of the Co_x/C_{60} composites.[4] At the local atomic structure level, this should reveal[5] a large variety of possible coordination types of cobalt ions with close or equal coordination numbers. A large variety of interatomic distances and different spin states should also be found. The presence of the transition metal ions and partially negative charges of the fullerene cages (because of the oxidation of the cobalt ions by C_{60}[34]) should be followed by the electronic correlations.[35] As the result of all factors described above, no symmetry restrictions can be applied a priori to the $Co_n(C_{60})_m$ clusters. The complexity of the objects and a great number of possible isomers in different spin states make hardly possible—without taking into account the available experimental data and some basic features of the atomic structure of C_{60} cages—a theoretical design of the preliminary structural models of the $Co_n(C_{60})_m$ clusters.

To study the atomic structure of the Co/C_{60} species, we theoretically designed a number of $Co_n(C_{60})_m$ clusters with $n = 1$, 2 and $m = 2$, 3 with all possible coordinations of the cobalt ions and C_{60} sites. Such restrictions of the n and m numbers are based on the previous experimental study of the species presented in the work of ref 5. For the Co1 systems ($Co(C_{60})_2$ and $Co(C_{60})_3$ clusters) all possible types of coordination (η^6, η^5, η^3, η^2, $\eta^{2'}$, and η^1) in low ($S = {}^1/_2$) and middle ($S = {}^3/_2$) spin states were chosen as initial types of structures. Later, we will show that—for the neutral Co1 systems—the low $S = {}^1/_2$ state is energetically preferable.

To elaborate the structural models of $Co_2(C_{60})_2$ clusters (Co2 systems), we took into account the experimental data of ref 5. The experimental atomic structure of the $Co_2(C_{60})_2$ cluster is characterized by two bridged cobalt ions between the C_{60} cages. Theoretically, the two bridged cobalt ions can be involve in the chemical bonding of approximately 10−15% of the C_{60} surface (eight hexagons and six pentagons, for example, for the both cages), which is a smaller ratio than in the experiment.[5] As the initial structures of the double-bridged $Co_2(C_{60})_2$ clusters, the η^5, η^3, η^2, $\eta^{2'}$, and η^1 types of coordination of both cobalt ions were chosen, taking into account all possible combinations of the coordination types and positions of C_{60} cages. To check the importance of the single-bridged structures, we performed the electronic structure calculations of the $Co_2(C_{60})_2$ clusters with one bridged cobalt ion. All calculations of the $Co_2(C_{60})_2$ clusters were performed in low ($S = 0$) and intermediate ($S = 1$) spin states. Later we will show that for the neutral Co2 systems the intermediate $S = 1$ state is energetically preferable. Finally, to study the possible reaction pathways of the atomic structure evolution of the Co_x/C_{60} species, we performed calculations of various types on linear and bent $Co_2(C_{60})_3$ clusters.

To compare the theoretical results with the experimental mass spectroscopic and chemical probe method data,[5] we performed calculations on positively charged Co1 clusters in low ($S = 0$) and middle ($S = 1$) spin states. It was shown that the low ($S = 0$) spin state is preferable for such types of objects. Finally, the structure of 89 $Co_n(C_{60})_m$ ($n = 1$, 2, $m = 2$, 3) neutral and positively charged clusters in low and intermediate spin states were determined at the B3LYP/6-31G* level.

No high-energy η^6 isomers or intermediates have been determined in our B3LYP/6-31G* calculations. We have determined the atomic structure of only a couple of isomers of the η^3 type of coordination.

Each C_{60} site has its own coordination type with a cobalt ion. For the $n = 1$, we introduced special notations for the mixed structures like η^2/η^2 (coordination of a cobalt ion by two 6−6 edges of different C_{60} cages), $\eta^2/\eta^{2'}$ (one 6−6 and one 6−5 edge), η^2/η^5 (the 6−6 edge and C_5 fragment), and η^5/η^5 (two C_5 fragments). For the $n = 1$ no $\eta^5/\eta^{2'}$, η^2/η^3, $\eta^{2'}/\eta^{2'}$, $\eta^3/\eta^{2'}$, η^3/η^3, or η^3/η^5 structures were detected.

The case of $n = 2$ is more complex—it is necessary to consider the coordination types of both cobalt ions. For the $n = 2$, the η^5 fashion can be realized only in the case of one bridged cobalt ion between the C_{60} cages. Later we will show that such types of structures have really high relative energies. For the m and $n = 2$ all possible combinations of η^2 and $\eta^{2'}$ types of coordination ($\eta^2:\eta^2/\eta^2:\eta^2$, $\eta^2:\eta^{2'}/\eta^2:\eta^2$, $\eta^{2'}:\eta^{2'}/\eta^2:\eta^2$, $\eta^{2'}:\eta^2/\eta^2:\eta^{2'}$, $\eta^{2'}:\eta^{2'}/\eta^2:\eta^2$,′ and $\eta^{2'}:\eta^{2'}/\eta^{2'}:\eta^{2'}$, the colon separates coordination types of both cobalt ions within the same C_{60} cage, whereas the slash symbol separates different C_{60} sites) were determined as well as two high-energy mixed isomers with $\eta^3:\eta^2/\eta^2:\eta^2$ and $\eta^3:\eta^2/\eta^3:\eta^2$ types (the last structure has two additional sp^3 C−C bonds between the C_{60} cages). By keeping the initial nature of the cobalt ion's coordination fashion, the number of possible isomers of $Co_2(C_{60})_2$ in different spin states becomes really large (several dozens) because the relative positions of the C_{60} cages can be different.

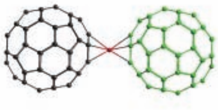
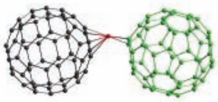
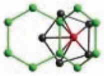
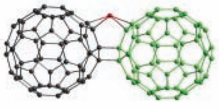
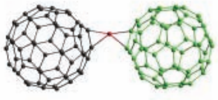
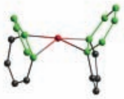
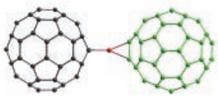
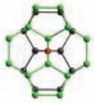
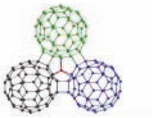
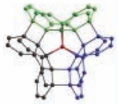
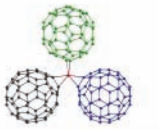
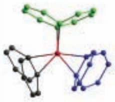
The linear or bent $Co_2(C_{60})_3$ structures mostly manifest the $n = 1$ types of coordination because of the absence of direct Co−Co interactions like in the $Co_2(C_{60})_2$ systems. In general, there are only a few unequivalent Co−Co positions, which differ from each other by the Co−Co distance and coordination fashion. Like in the case of $n = 1$, the η^2 type of coordination ($\eta^2/\eta^2:\eta^2/\eta^{2'}$) has the lowest energy. The $\eta^2/\eta^2:\eta^2/\eta^2$ (the η^2/η^2 type of coordination for both cobalt ions) fashion is the second in energy, and the $\eta^5/\eta^5:\eta^5/\eta^5$ one has the highest energy. Energetically, the mixed structures (such as $\eta^5/\eta^5:\eta^5/\eta^2$ or $\eta^2/\eta^5:\eta^5/\eta^2$, etc.) are between them.

III. Results and Discussion

III.a. $Co(C_{60})_2$ and $Co(C_{60})_3$ Clusters. Tables 1 and 2 present the relative energies, types of coordinations, and structural images (general and closest cobalt neighborhood) of all $Co(C_{60})_2$ and $Co(C_{60})_3$ (Table 1) as well as $Co(C_{60})_2^+$ and $Co(C_{60})_3^+$ (Table 2) clusters in low spin states ($S = {}^1/_2$ and 0, respectively). On the B3LYP/6-31G* level the doublet−quartet splitting for the neutral systems is from 2.5 (η^5/η^5 complex) to 36.4 (η^2/η^2 complex) kcal/mol. Because of this, we present the data of the low spin states only. All relative energies were calculated taking into account the basis set superposition error. The left/lower carbon atoms are in black, the right/upper carbon fragments are shown in green/blue, and the cobalt atom is in red.

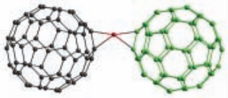
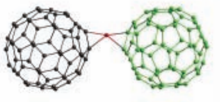
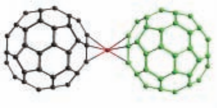
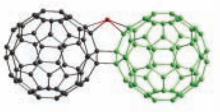
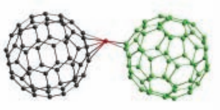
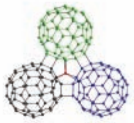
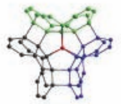
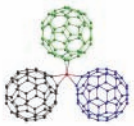
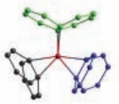
Even though the positively charged clusters cannot play any role in the formation of the local atomic structures of Co_x/C_{60} composites, they can be used as test systems to check the accuracy of the quantum chemical calculations. The theoretical B3LYP/6-31G* atomic structure of positively charged systems confirms the indirect experimental results[5] shown in Table 2: the $Co(C_{60})_2^+$ has a bent structure and the formation of additional Co−C bonds ($Co(C_{60})_3^+$ complex, with absolute minimum or zero relative energy), which sufficiently lowers the energy of the cluster (19.0 kcal/mol). Creation of an

TABLE 1: Types of Coordinations, Structures, and Relative Energies (kcal/mol) of $Co(C_{60})_2$ and $Co(C_{60})_3$ Clusters ($S = {}^1/_2$)^a

Type of coordination	General view	Closest cobalt neighborhood	Relative Energy (kcal/mol)
η^5/η^5			41.4
η^2/η^5			32.8
η^2/η^2 with one C-C bond			30.5
$\eta^2/\eta^{2'}$			28.9
η^2/η^2			15.2
$\eta^2/\eta^2/\eta^2$ with 3 C-C bonds			13.3
$\eta^2/\eta^2/\eta^2$			0.0

[a] All relative energies were calculated taking into account basis set superposition error. The left/lower carbon atoms are in black, the right/upper carbon fragments are shown in green/blue, and cobalt is in red.

TABLE 2: Types of Coordinations, Structures, and Relative Energies (kcal/mol) of $Co(C_{60})_2{}^+$ and $Co(C_{60})_3{}^+$ Clusters ($S = 0$)^a

Type of coordination	General view	Closest cobalt neighborhood	Relative Energy (kcal/mol)
η^2/η^2			19.0
$\eta^2/\eta^{2'}$			17.4
η^5/η^5			8.9
η^2/η^2 with one C-C bond			7.6
η^2/η^5			5.2
$\eta^2/\eta^2/\eta^2$ with 3 C-C bonds			0.3
$\eta^2/\eta^2/\eta^2$			0.0

[a] All relative energies were calculated taking into account basis set superposition error. The left/lower carbon atoms are in black, the right/upper carbon fragments are shown in green/blue, and cobalt is in red.

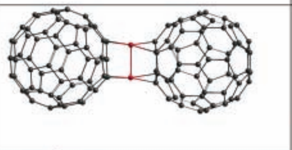
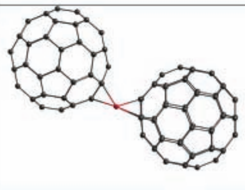
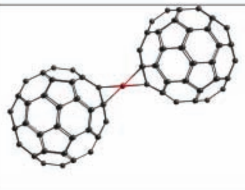
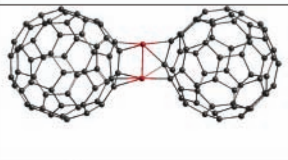
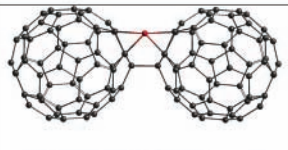
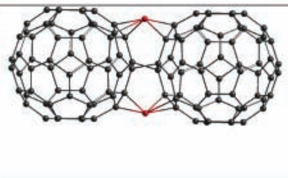
additional C−C sp^3 bond between the C_{60} cages ($Co(C_{60})_2{}^+$ with C−C bond) lowers the relative energy up to 7.6 kcal/mol above 0 and makes the bent angle bigger. Creation of additional C−C sp^3 bonds between the C_{60} cages ($Co(C_{60})_3{}^+$ with an additional six C−C bonds) does not change the energy of the system (0.3 kcal/mol on the 6-31G* level). The lowest in energy—$Co(C_{60})_3{}^+$ cluster—has a triangular planar structure like in ref 5 with the $\eta^2/\eta^2/\eta^2$ type of coordination (which is common for the cobalt−fullerene complexes).[7] We have determined some additional types of coordination such as $\eta^2/\eta^{2'}$ (see above, the Computation Details) as well as η^5/η^5 and η^2/η^5 ones. These isomers have high relative energies (up to 41−29 kcal/mol for the neutral systems). In spite of the η^5/η^5 isomer having the highest energy, this type of coordination was detected in the works of refs 10 and 11 and explained[25,26] by stabilization of the η^5 position by some saturation groups on the outer surface of the fullerenes.

A comparison of the positively charged systems (Table 2) and the neutral systems (Table 1) shows that ionization can cause some energetic and structural changes. For example, the staggered η^2/η^2 and $\eta^2/\eta^2/\eta^2$ (three 6−6 edges) types of coordination are preferable for the neutral $Co(C_{60})_n$ ($n = 2, 3$) clusters. Formation of additional C−C bonds between the fullerenes sufficiently increases the energy of the clusters (as low as 13.3 kcal/mol for $Co(C_{60})_3$ and as high as 30.5 kcal/mol for and $Co(C_{60})_2$ clusters). The eclipsed η^2/η^2 configuration of the $Co(C_{60})_2{}^+$ cluster has the highest energy (Table 2). Ionization results not only in the changing of the relative stability of the system, but in the symmetry state as well.

Comparison of the atomic structure of the zero-energy $Co(C_{60})_3$ cluster with the structural XAFS data[4] shows that B3LYP/6-31G* calculations (Table 1) can correctly describe both the coordination number for the Co_x/C_{60} composites (equal to 6 for the $Co(C_{60})_3$ cluster) and the Co−C interatomic distance with good accuracy (2.01 Å is the experimental value and 2.06 Å the theoretical one). Formation of the additional Co−C complex bonds (transition from a $Co(C_{60})_2$ system to a $Co(C_{60})_3$ system) decreases the energy up to 15.2 kcal/mol. The $Co(C_{60})_2$ clusters with different types of coordination ($\eta^2/\eta^{2'}$, η^2/η^5, and η^5/η^5) have sufficiently higher relative energies (from 28.9 up to 41.4 kcal/mol).

III.b. $Co_2(C_{60})_2$ Clusters. Only three structural types of $Co_2(C_{60})_2$ clusters can be realized due to the specific atomic

TABLE 3: Types of Coordinations, Structures, and Relative Energies (kcal/mol) of Some $Co_2(C_{60})_2$[a]

Number	General view	Detailed view	Coordination type	Energy (kcal/mol	$R_{Co\text{-}Co}$, Å
1 (S=1)			$\eta^2:\eta^{2'}/\eta^2:\eta^2$	0	2.73
2 (S=1)			$\eta^2:\eta^2/\eta^2:\eta^2$	9.4	2.98
3 (S=1)			$\eta^2:\eta^2/\eta^{2'}:\eta^{2'}$	19.1	2.973
4 (S=1)			$\eta^3:\eta^2/\eta^2:\eta^2$ (65:66:65/66:66)	30.4	2.41
5 (S=1)			$\eta^2:\eta^{2'}/\eta^2:\eta^{2'}$	49.0	3.21
6 (S=1)			$\eta^3:\eta^2/\eta^3:\eta^2$ (66:66:65/66:66:65)	80.3	5.61

[a] All relative energies were calculated taking into account basis set superposition error. The lower carbon atoms are in black, the right/upper carbon fragments are shown in green, and cobalt is in red.

structure of the C_{60} cage. The first one can be characterized by the existence of cobalt dimers bonding the C_{60} cages. The C_{60} cages of the second type can be bonded by both cobalt ions without formation of a metallic dimer, due to the possible formation of additional C−C bonds between the fullerene cages. The C_{60} cages of the third type can be bonded by one cobalt ion only, whereas the second ion coordinates with only one C_{60} cage. Later we will show that the second and the third types of clusters have high relative energies (∼50−100 kcal/mol).

The B3LYP/6-31G* calculations show that low-energy $Co_2(C_{60})_2$ isomers have the triplet spin state (Table 3). We determined 27 $Co_2(C_{60})_2$ isomers in the triplet state and 28 $Co_2(C_{60})_2$ ones in the singlet state within all three types. All isomers in the triplet state keep the main peculiarities of the atomic structure of the singlet analogs such as type of coordination, relative positions of the C_{60} cages, and Co−C distance (∼1.9 ÷ 2.1 Å). The typical singlet−triplet splitting for all isomers is equal to 40−70 kcal/mol. The transition from the singlet to triplet state leads only to enlarging the Co−Co distance of the cobalt dimers by approximately 0.2 ÷ 0.5 Å.

Some of the $Co_2(C_{60})_2$ isomers are presented in Table 3. The cobalt ions in metallic dimers present the η^2 and $\eta^{2'}$ or, in less extent cases, the η^3 types of coordination (see Table 3). The atomic structure of the three lowest energy isomers (isomers 1, 2, and 3, $S = 1$) clearly confirm the indirect structural data[5]—two cobalt ions between the C_{60} cages. Formation of the cobalt dimers is energetically preferable, even in the case of formation of additional C−C sp^3 bonds between the C_{60} cages (isomers 5 and 6). This fact is really important to understand the structures and properties of the Co_x/C_{60} composites. To some extent, during synthesis[4] such $Co_2(C_{60})_2$ complexes can be realized because of the radical character of C_{60} cages with attached metal ions.[34] Once formed, they can prevent the system from changing the positions of the cobalt ions because of the high energy required to destroy the additional sp^3 C−C bonds between the C_{60} cages.

The three lowest energy isomers are characterized by the η^2 and $\eta^{2'}$ coordination type. The C_{60} cages of the first isomer (relative energy 0 kcal/mol) are connected by a cobalt dimer through two C_6 fragments of both fullerenes (Table 3). The first C_{60} cage bonds with the Co_2 fragment through the middle of the C_6 fragments using 6−6 and 6−5 edges, whereas the second fullerene bonds with the Co_2 through two 6−6 edges ($\eta^2:\eta^{2'}/\eta^2:\eta^2$ coordination type). The second isomer has the relative energy equal to 9 kcal/mol and has an $\eta^2:\eta^2/\eta^2:\eta^2$ type of coordination of the Co_2 fragment through four 6−6 edges of the C_6 fragment. The third isomer has the relative energy equal to 19.1 kcal/mol and an η^2:η^2/$\eta^{2'}$:$\eta^{2'}$ type of coordination through two C_6 fragments. In this case the Co_2 dimer connects with two 6−6 edges of one C_6 fragment and with two 6−5 edges of the second one. All other η^2-type isomers have higher relative energies (from 23 up to 120 kcal/mol) and can be obtained by combining all possible coordinations of the two C_{60} cages and the Co_2 fragment.

Two isomers of $Co_2(C_{60})_2$ clusters (nos. 4 and 6, Table 3) reveal the η^3 type of coordination through a specific point on the C_6 fragment surface. Both isomers can only play some role during the atomic structure evolution because of the high relative energies (30 and 80 kcal/mol, correspondingly).

The initial presence of a wide set of $Co_2(C_{60})_2$ clusters in the Co_x/C_{60} mixtures[4] with similar energies can be followed by the process of isomerization (the Co ions hopping through the η^2, $\eta^{2'}$, and η^3 points on the surface of the C_{60} cages). The η^2:$\eta^{2'}$/η^2:η^2 and η^2:η^2/η^2:η^2 types of coordination are preferable, but other high-energy isomers can play some role as intermediate complexes in the process. Formation of additional C−C bonds between the C_{60} cages is not energetically preferable but may occur. If this happens, the new bonds should prevent the migration of the cobalt ions around the fullerene cages.

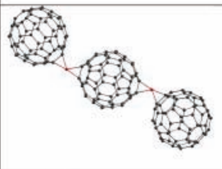
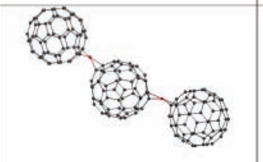
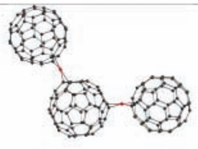
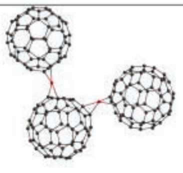
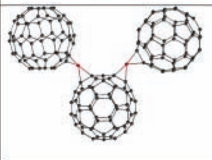
III.c. $Co_2(C_{60})_3$ Clusters. As mentioned in the Introduction and Computational Details, the linear or bent $Co_n(C_{60})_m$ clusters were not detected in the MS experiment.[5] Because of the presence of other types of high clusters like $Co_2(C_{60})_2$, $Co_2(C_{60})_4$, $Co_3(C_{60})_4$, and $Co_4(C_{60})_4$, one would imagine the probability of the random formation of the liner/bent $Co_2(C_{60})_3$ structures should be sufficiently higher than zero. The absence of the $Co_2(C_{60})_3$ clusters and high amount of the $Co_2(C_{60})_2$ ones can be partly explained by the fast transformation of $Co_2(C_{60})_3$ to $Co_2(C_{60})_2$. This occurs when the cobalt ions migrate around the central C_{60} cage, followed by the removal of one C_{60} when a double-bridged $Co_2(C_{60})_2$ cluster is formed.

To study the atomic structure evolution of Co_x/C_{60} composites, we calculated four sets of $Co_2(C_{60})_3$ clusters to model the process of cobalt ion migration around the C_{60} cages. Based on the calculations for the Co1 systems (Table 1), we propose the η^2/η^2:η^2/η^2 and η^2/η^2:η^2/$\eta^{2'}$ types of coordination of $Co_2(C_{60})_3$ clusters as energetically preferable and the pure η^5/η^5:η^5/η^5 and mixed η^5/η^5:η^5/$\eta^2\eta^5$ as the ones highest in energy. It is necessary to note that regardless of the high energy of the species, during the chemical synthesis,[4] even the η^5/η^5:η^5/η^5 and η^5/η^5:η^2/η^5 intermediates can play some role in the Co_x/C_{60} composite characterization.

The conformable η^5/η^5:η^5/η^5 and η^5/η^5:η^5/$\eta^2\eta^5$ complexes, with close Co−Co distances, are 10−15 kcal/mol higher in energy than the η^2/η^2:η^2/η^2 and η^2/η^2:η^2/$\eta^{2'}$ ones (Tables 4 and 5). The smaller the Co−Co distance the lower the energy of the η^5-type complexes. However, the η^5 structures are not suitable for the formation of the cobalt dimer structures because of features of the atomic structure of the species. The formation of the dimer structures, such as isomer 1 of $Co_2(C_{60})_2$ (Table 3), requires sufficient rearrangement of the cobalt ion's coordination type—from η^5 to η^2 ones and from η^5 to $\eta^{2'}$ ones. Because of this the η^5 complexes cannot play any role as direct precursors in the formation of cobalt dimers.

The η^2/η^2:η^2/η^2 and mixed η^2/η^2:η^2/$\eta^{2'}$ types of $Co_2(C_{60})_3$ structures have the lowest energy among the $Co_2(C_{60})_3$ clusters. The energy dependence of the η^2/η^2:η^2/η^2 clusters upon the Co−Co distance (Table 4, Figure 1) has a nonpattered character, whereas the energy dependence of the η^2/η^2:η^2/$\eta^{2'}$ ones has a maximum exactly at the middle of the Co pathway (Table 5 and Figure 1). The energies of the η^2/η^2:η^2/η^2 structures are 8−13 kcal/mol lower than the η^2/η^2:η^2/$\eta^{2'}$ ones.

TABLE 4: Structures and Relative Energies (kcal/mol) of η^2:η^2/η^2:η^2-type $Co_2(C_{60})_3$ Clusters[a]

Number	General View	Relative Energy (kcal/mol)	R_{Co-Co}, Å
1		35.3	10.728
2		34.3	10.179
3		36.2	8.579
4		38.0	6.054
5		34.4	5.231

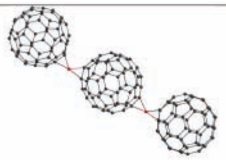
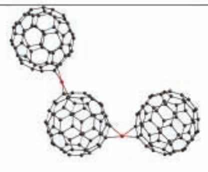
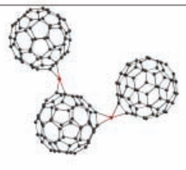
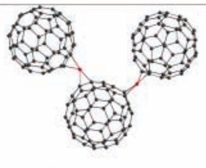
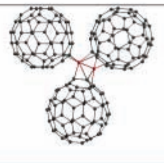
[a] All relative energies were calculated taking into account basis set superposition error.

The linear and bent $Co_2(C_{60})_3$ structures can be transformed to the $Co_2(C_{60})_2$ clusters through hopping of cobalt ions among the η^2 and $\eta^{2'}$ sites with, ultimately, the formation of cobalt dimers and subsequent removal of C_{60} fullerene. The possible reaction pathway of the cobalt ion migrating around the central C_{60} cage through η^2/η^2:η^2/η^2 and η^2/η^2:η^2/$\eta^{2'}$ sites is presented in Figure 1 by the color dots and red broken arrows. The colors of the dots reflect relative energies of the isomers and intermediates. The initial positions of both cobalt ions on the opposite sites of the central C_{60} cage are marked by a Co^1 and a Co^2 symbol (the first and second ions, respectively).

Without taking into account the relative orientation of the C_{60} cages in the $Co_2(C_{60})_2$ clusters, there are only three possible types of cobalt dimer coordinations around the C_6 fragments of the C_{60} cage. The first one is the global minimum isomer 1 of the η^2:$\eta^{2'}$ type (Table 3, the only one structure). This structure is schematically presented on the Figure 1 by a broken red line connecting the Co^1 position (red dot) and the brown dot reflecting the final position of the second cobalt ion (Co^2).

The second coordination of the η^2:η^2 type (the most representative example is isomer 2 (relative energy 9.4 kcal/mol) in Table 3) is presented by two red circles connected by a broken red line. This structure can be obtained through the same intermediate state (the dark blue circle) as isomer 1. Finally, the last high-energy isomer of the η^2:$\eta^{2'}$ type (the light blue circle connected to the red Co^1 position by the solid red line) can be obtained through alternative reaction pathways starting from the empty blue circles (in reality these positions were not

TABLE 5: Structures and Relative Energies (kcal/mol) of η^2:$\eta^{2'}$/η^2:η^2-type $Co_2(C_{60})_3$ Clusters[a]

Number	General View	Relative Energy (kcal/mol)	R_{Co-Co}, Å
1		43.0	10.495
2		48.6	9.529
3		49.2	7.593
4		43.5	6.420
5		42.4	2.530

[a] All relative energies were calculated taking into account basis set superposition error.

calculated, but the relative energies of the $\eta^{2'}$ intermediates should be close to the neighboring highest intermediate structure, violet circle, 49.2 kcal/mol).

The formation mechanism of the highest energy η^2:$\eta^{2'}$ structure is really special and proceeds without formation of an intermediate structure neighboring the C_6 fragment (like in the case of the two previous clusters). The absence of the corresponding intermediate structure is represented in Figure 1 by a "do not stop" traffic sign. The resulting $Co_2(C_{60})_3$ cluster, no. 5 from Table 5 (the analog of isomer 7 from Table 3) can be characterized by the existence of a direct Co−Co chemical bond with a length of 2.530 Å.

The migration of the second cobalt ion (Co^2) approaching the first one (Co^1) proceeds through a set of isomers and intermediates (see Figure 1). The energy difference between the initial $Co_2(C_{60})_3$ Co^2 position (pink circle, 35.3 kcal/mol) and the highest energy intermediate (violet circle, 49.2 kcal/mol), located exactly in the middle of the reaction pathway, is equal to 13.9 kcal/mol. From this point, an approach of the second cobalt ion to the first one leads to the consequent decrease of the energy of the system. After formation of the cobalt dimer, one C_{60} can be removed from the $Co_2(C_{60})_3$ system with formation of some kind of $Co_2(C_{60})_2$ isomer. The formation of the two lowest energy $Co_2(C_{60})_2$ isomers of η^2:$\eta^{2'}$ and η^2:η^2 types of coordination (0 kcal/mol and 9.4 kcal/mol) can proceed through the same intermediate state (43.5 kcal/mol, dark blue circle). The absence of $Co_2(C_{60})_3$ clusters in the mass spectra of the Co/C_{60} composites[5] confirms the instability of the species.

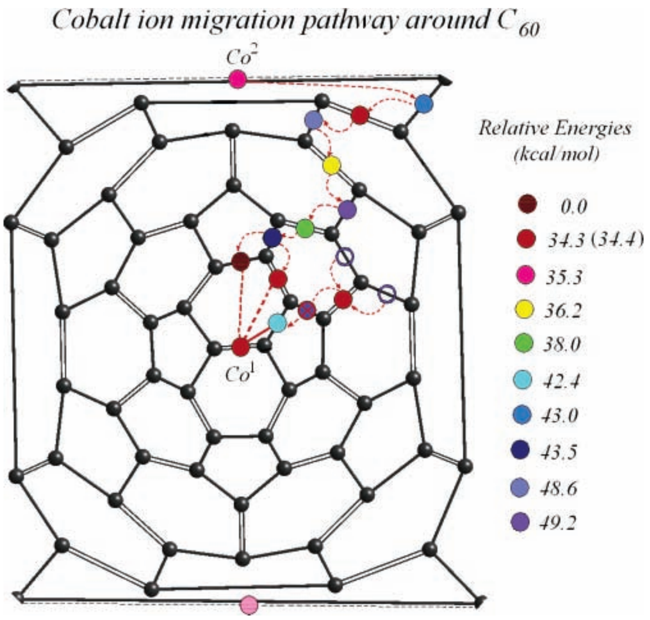


Figure 1. Schlegel diagram of cobalt ions migrating around the central C_{60} cage of the $Co_2(C_{60})_3$ type of cluster. The first cobalt ion (red dot Co^1) has a fixed position and is placed in the center of the 6−6 edge. The initial position of the second cobalt ion (pink dot Co^2) is in the center of the opposite 6−6 edge. Migration of the second cobalt ion around the C_{60} cage, through the 6−5 and 6−6 edges, is presented by red broken arrows and color dots reflecting the relative energies of isomers (η^2:η^2/η^2:η^2 type of coordination) and intermediates (η^2:$\eta^{2'}$/η^2:η^2 type of coordination). The carbon atoms are presented in black. The two lowest and highest carbon atoms are equivalent and are presented as half circles because of the specific Schlegel diagram projection. The Co_2 has a mirror image in the bottom of the figure (light pink dot) as well as the 6−6 edge bonded with it. Two violet empty circles denote the beginning of an alternative reaction pathway of the cobalt migration. The traffic sign "do not stop" denotes the absence of the intermediate state on the particular 6−5 edge.

IV. Conclusions

The atomic structure and relative energetic stability of a wide set of neutral and positively charged $Co_n(C_{60})_m$ ($n = 1, 2, m = 2, 3$) clusters with all possible coordinations of cobalt ions and C_{60} cages in different spin states ($S = 0, {}^1/_2, 1$, and ${}^3/_2$) were determined based on the B3LYP/6-31G* calculations. Theoretical results directly confirm the existing experimental structural data for the Co_x/C_{60} species. Results indicate that the η^2 type of coordination is energetically preferable for all combinations of m and n numbers. For the neutral systems with $n = 1$ the low spin state $S = {}^1/_2$ is energetically preferable. For the $n = 2$ cases, the intermediate $S = 1$ spin state is preferable. It was shown that, for the $n = 2$ case, the formation of the cobalt dimers is energetically preferable and can be realized through cobalt ion hopping between the η^2 (6−6 edge) and $\eta^{2'}$ (6−5 edge) sites of the C_{60} cages. The $\eta^{2'}$ types of structures as well as the η^5 type of structures—and mixed ones—can be realized in the complex Co_x/C_{60} mixtures during chemical synthesis as intermediate states and high-energy isomers.

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