Polyhedron 99 (2015) 177–185

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Endohedral dibenzenechromium

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ARTICLE INFO

Article history:
Received 3 March 2015
Accepted 26 June 2015
Available online 8 July 2015

Keywords:
Dibenzene chromium
Endohedral complexes
Theoretical simulations
Large fullerene complexes
Endo and exo isomers

ABSTRACT

The possibility of having a metallocene species, in which metal atoms as well as the corresponding aromatic rings appear within a fullerene sphere, is analyzed from a theoretical point of view. The complexes were simulated by joining a $Cr(C_6H_6)$ fragment to the inner wall of a C_{116} (T_h) fullerene. The large cage of this fullerene makes it possible to place two of these fragments within the sphere, so that several possibilities for isomers can be contemplated, and the mono-endo, di-endo, mono-endo-mono-exo and di-exo geometries can be modeled and compared.

1. Introduction

Since the discovery of fullerene [1,2], the study of this kind of substance has become one of the most popular themes in scientific research [3,4]. Endohedral complexes of fullerene are species, where an atom or a small cluster of atoms are confined within the shell of a fullerene [5]. This particular study topic constitutes one of the most investigated areas in Chemistry, Physics and Material Sciences [6].

The nature of the species confined within the shell can be very variable; they may only be metal atoms (mainly from the lanthanide family) [5] or small clusters containing metal atoms joined to nitrogen, oxygen or carbon atoms [7,8]; however there are very few reports describing endohedral fullerene cages containing transitional elements; to the best of our knowledge, the only exception is titanium [9,10]. The presence of a chromium atom within a fullerene would therefore be very notorious.

The objective in this work is to simulate an endohedral species where a chromium atom and a complete benzene ring are found within the cage of a large fullerene, aiming to produce an endohedral analog of a dibenzene-chromium. However this fragment would not be separated from the inner wall, as one of the two benzene rings belongs to the fullerene itself. The only similar investigation was proposed by Chistyakov and Stankevich [11], who simulated an analog of ferrocene, with the iron atom at the center of a little cage (for example $C_{40}H_{30}$), and both five-member rings at the polar extremities of the sphere, with direct bonds through the central iron atom.

There are several discussions concerning the possibility of metal atoms being joined to fullerene cages with different hapticities [12]. The case of η^5 exohedral complexes has been theoretically studied by several groups [13–18] and experimentally solved by Nakamura and his group [19–21]. It has been claimed that the formation of stable η^5-complexes between fullerenes and transition metals is highly improbable because the conjugated system is strongly delocalized, and the polarization of the atoms of the five-member face is weak [12]; however the formation of a “fence” of five organic groups around the five-member ring can help to localize the electrons and enable the simulation of the charge present in the cyclopentadienyl ion; indeed this was the strategy employed by Nakamura and his group, who managed to solve the problem [22].

All these problems arise mainly because the bond between iron and the cyclopentadienyl moiety has a strong electrostatic component. However a collateral study of similar structures would involve sandwich compounds from chromium, because the archetypical species of this metal, i.e., dibenzene-chromium has a bond based on covalent interactions due to zero oxidation for the central chromium atom. An experimental exo η^6 analog of this metal does not yet exist, but there are theoretical propositions [23] which demonstrate the possibility of its existence. Therefore the proposed molecules studied in the present work have chromium as the central species and the entire discussion is focused on the thermodynamic stability of these species, while also comparing them.

2. Methods

All calculations were carried out by applying a pure DFT method for energy evaluations. For the structures of all derivatives, Becke's

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http://dx.doi.org/10.1016/j.poly.2015.06.031

gradient corrections [24] for exchange and Perdew–Wang's for correlation [25] were applied. This is the scheme for the B3PW91 method, which forms part of the GAUSSIAN09 [26] Package. Calculations were performed using the 6-31G** basis set and full optimizations were carried out for all structures, as well as frequency calculations that were useful for achieving the absolute energy minima in each case.

3. Results and discussion

Since its discovery [27], dibenzene-chromium has been the object of several monographs [28,29] and studies [30,31]. It represents the model structure for the arene organometallic compounds and the reference molecule (together with ferrocene) for π organometallic chemistry. One of its most important characteristics is the Cr(0) condition at the metal center, as described previously. In the present work, it has been embedded within fullerene geometry.

The general description of the molecules being studied is as follows; a large fullerene structure can be part of a bis(benzene)chromium, sharing a six-member ring (or more) with a $Cr(C_6H_6)$ fragment. The chosen fullerene was C_{116} (6061) (**1**), a cage which was deliberately chosen for three main reasons: first it is large enough to comfortably receive one organometallic fragment or even two, second, it has an IPR structure that has been indicated as very possibly representing a stable molecule [32], and finally it has effective symmetry, belongs to the T_h point group and presents significant advantages for quickly producing stable optimized structures. The shape of this molecule can be seen in Fig. 1.

The C_{116} (T_h) has several sets which consists in a six membered face joint to six rings, four of them are other six membered cases and there are also two opposite five membered rings. The particular symmetry of this species allows to connect one of this sets with other similar by means a proper C_2 axis, the substitution of the fragment $Cr(C_6H_6)$ was made with a η^6 hapticity on one of this sets in the case of a mono-substitution or in two opposite connected by symmetry sets in the cases of di-substitution. Therefore there are several isomers that can be studied regarding their thermodynamic stability; however there is only one possibility studied here concerning the position of the metallocene into the sphere.

All the resultant molecules in which the host is the C_{116} (T_h) fullerene cage are the following:

- A mono-substituted endo complex.
- A mono substituted exo complex.
- A di-substituted endo complex.
- A di-substituted endo and exo (same time) complex.
- A di-substituted exo complex.

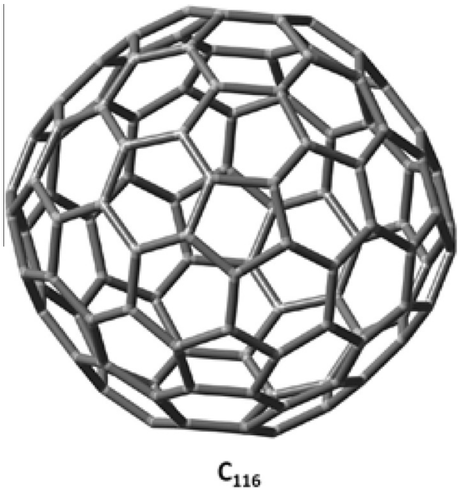
C_{116}

Fig. 1. Empty cage of C_{116} fullerene (**1**).

The description of these substances will be presented and analyzed in the following sections.

3.1. Mono substituted complexes

The first case corresponds to the mono-substituted endo complex (**2**), the shape of which can be seen in Fig. 2; the atoms corresponding to the embedded di-benzene-chromium are highlighted.

Free di-benzene-chromium (**3**) was calculated under the same conditions, for the purpose of comparison. The first important feature to consider is that the stable fullerene complex has a staggered di-benzene-chromium in strong contrast to (**3**), which is always found as an eclipsed species. This feature results from the influence of the electrons within the cage.

The distance between both aromatic rings also varies, as in the case of dibenzene-chromium, leading to a very symmetric (D_{6h}) and regular species. The bond length is almost the same in all cases and is about 3.184 Å. In contrast, in the case of the fullerene endo complex, the average for this value measured from edge to edge is 3.459 Å (the free aromatic ring is slightly sloping). This result is obviously the consequence of the distortion of the $Cr(C_6H_6)$ unit, but likewise it is important to consider that the top of the di-benzene-chromium that comes from the cage is distorted, due to the intrinsic curvature of the fullerene. Furthermore the free aromatic ring is immersed in an electron environment, which can also cause distortions.

The exo analog was also simulated; its shape can be seen in Fig. 2b, representing an analog similar to that studied previously with a C_{60} fullerene [23]. The energy comparison between both exo and endo structures reveals that the exo form is more stable than the endo, with a difference of 37.83 kcal/mol.

The molecular orbitals (MO) scheme, corresponding to di-benzene-chromium is shown in Fig. 3 and compared with both exo and endo species, as presented in Fig. 4.

The general shape of both interaction diagrams is more or less the same; indeed neither belong to a clear point group, although the geometry of the exo complex somewhat resembles the Cs point group. However, the position has few differences, possibly because of the position of the $(C_6H_6)Cr$ moiety, but mainly because the endo is a staggered species, whereas the exo is almost an eclipsed one. There is an interesting analysis that compares the nature of the bond in ferrocene and di-benzene-chromium [33]. This study concludes from the irreducible representations involved in the frontier molecular orbitals that the bond in ferrocene is mainly π in nature, whereas the equivalent in di-benzene-chromium is predominantly δ. In the present case, serious difficulties are encountered when carrying out a similar analysis, because of the lack of symmetry of these molecules and the concomitant absence of labels in the molecular orbitals. However, a qualitative analysis, based mainly on the HOMO's shape, suggests that in both cases the nature of the bond is π. The shapes of the frontier molecular orbitals for both species are shown in Fig. 5. This same phenomenon has been noted in the description of frontier molecular orbitals of other fullerene molecules that were simulated as having bonds with η^6 hapticity [23].

The form of the HOMO and HOMO − 1 orbitals coming from di-benzene-chromium is shown in Fig. 6 and the δ nature of the bond is demonstrated. This particular behavior is caused by the interaction of the dz^2 orbital from the chromium atom and the aromatic functions from the benzene rings. The double degenerated system corresponding to the HOMO − 1 set shows however the π interaction which appears to resemble those that appear as HOMO in the

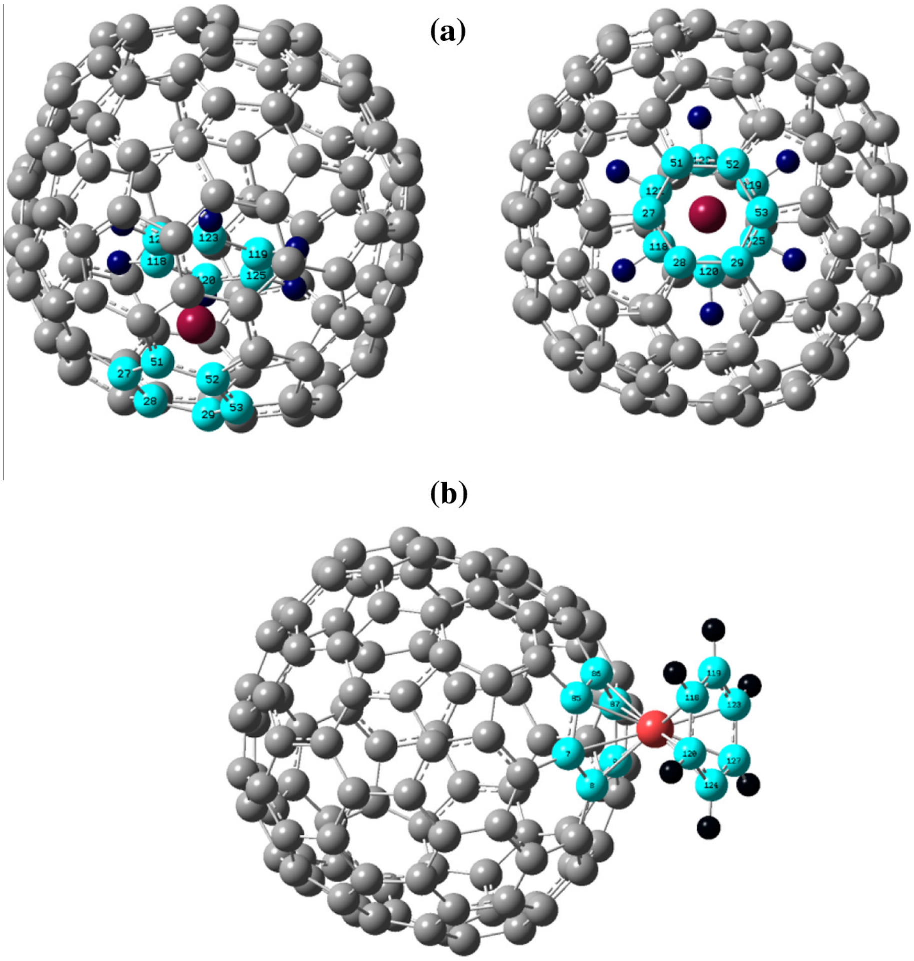

Fig. 2. (a) Two perspectives of the mono-endo-complex (**2**). (b) The mono-exo-complex (**4**).

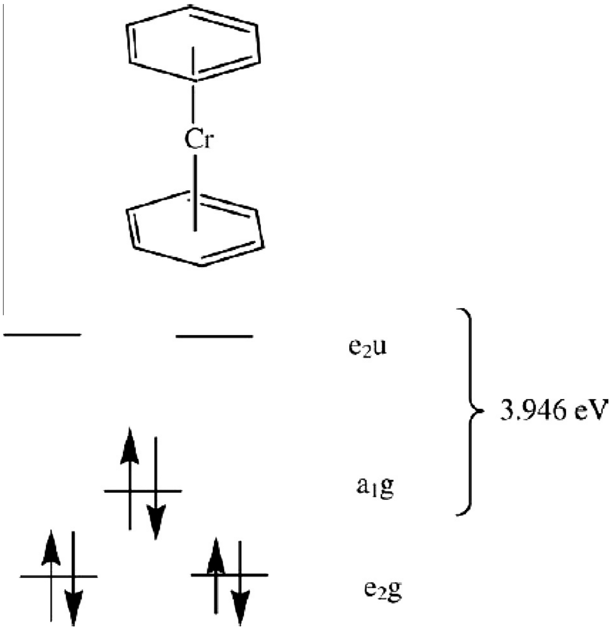

Fig. 3. Frontier molecular orbitals of compound (**3**).

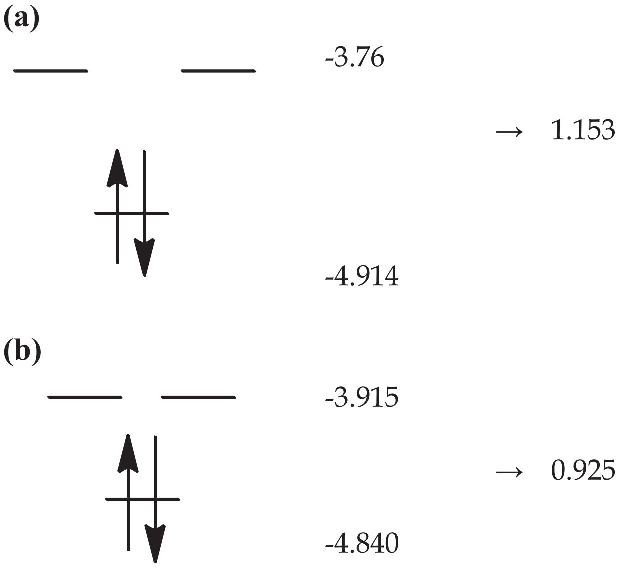

Fig. 4. Frontier molecular orbitals of the (a) exo mono-substituted complex and (b) the endo mono-substituted complex.

compounds being studied. This peculiar change in the position of the frontier molecular orbitals and their neighbors may be caused by the substitution of a fragment with six resonant electrons (i.e. an aromatic ring) with a fragment with at least 84 resonant electrons (i.e. fullerene C_{60}). In this case, however, the difference causes a significant change in the behavior of the new molecules. The energy difference suggests strong semiconductor behavior and moderate conductor behavior, even in the case of the endo.

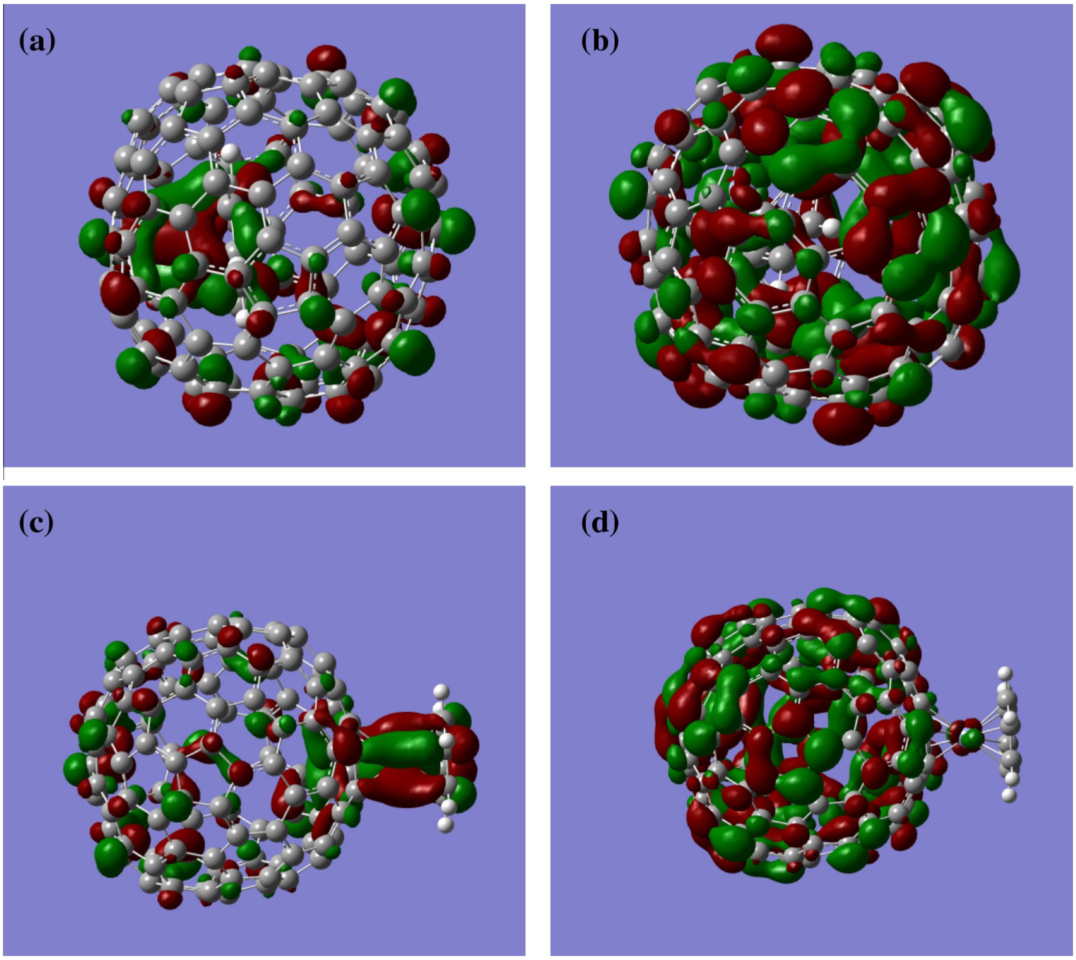

Fig. 5. Shapes of the frontier molecular orbitals of both mono-substituted derivatives.

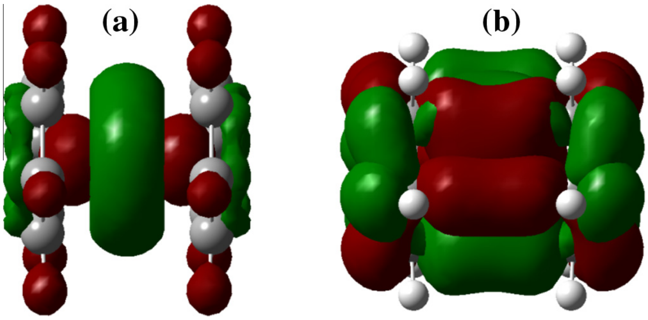

Fig. 6. First occupied molecular orbitals of di-benzene-chromium; (a) HOMO, (b) HOMO − 1.

The bond order values of both benzene rings joined to the chromium atom were determined; the Wiberg bond indices [34], revealed through NBO analysis, showed interesting differences. In the case of the endo complex, the average value of the bond between each carbon atom of the inner top and the central chromium atom is 0.22 and the total Cr–C_6 bond is 1.33. With respect to the top on the surface of the cage, the average individual value is 0.26, whereas the total is 1.59.

The same analysis applied to the exo complex yields a value of 0.27 for the average individual interaction and 1.61 for the total bond, in the case of the top on the surface, whereas the values for the external top are 0.36 and 2.14, respectively. It is easy to observe that the value with respect to the surface of the cage varies little. In both cases it is very similar; however the difference between the external and inner tops is dramatically different; clearly the bond is very efficient in the case of the external top. The di-benzene-chromium was also calculated under the same circumstances and their corresponding values are 0.38 and 2.28.

While the bond is stronger in the case of external tops, those on the surface, as well as the internal ones, have two factors that impede a better bond: first, the intrinsic distortion, and second, the electronic cloud that exists within the sphere in the second case.

The intrinsic stability of both complexes was analyzed considering the result of the free energy differences in the next homodesmotic reaction:

$$(C_6H_6)_2Cr + C_{116} \rightarrow (C_6H_6)C_{116} + C_6H_6$$

In both cases the result favors the formation of the complexes. In the case of the endo compound the difference is −38.05 kcal/mol whereas for the exo isomer the value is 88.7 kcal/mol.

3.2. Di-substituted complexes

Three cases are presented here: the completely endo complex, the completely exo-complex and the combination with one $Cr(C_6H_6)$ fragment within the cage and the other external. These shapes are presented in Figs. 7–9.

The complete endo isomer, once again shows the staggered conformation found in both di-benzene-chromium unities. The

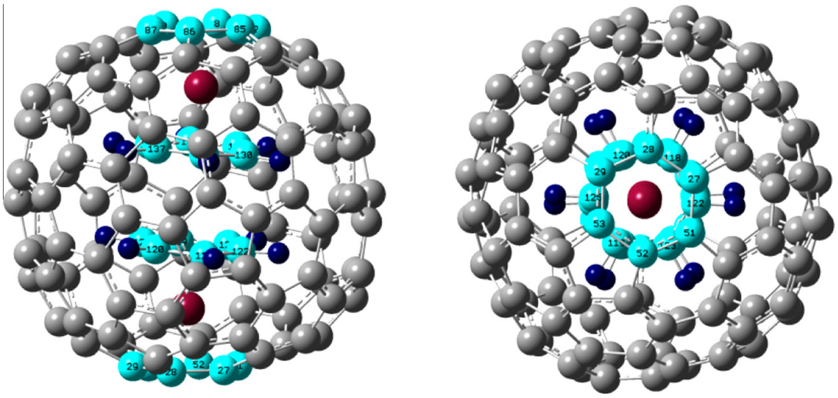

Fig. 7. Two views of the overall endo complex.

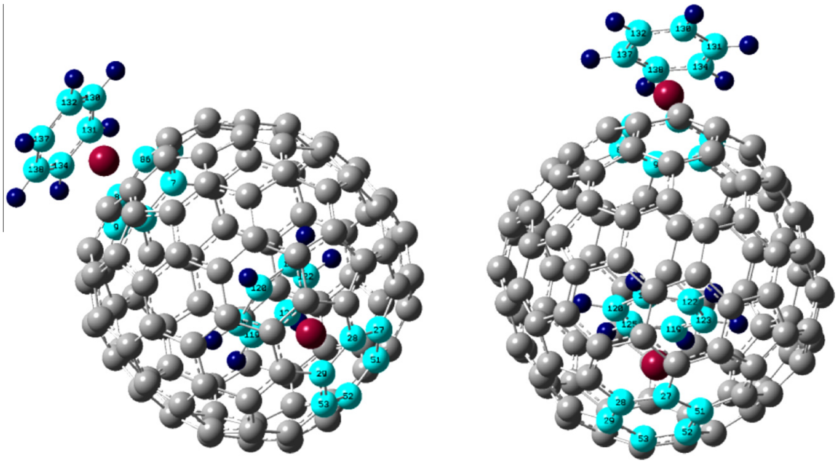

Fig. 8. Two views of the exo and endo complex.

average distances between both rings of this fragment are 3.325 Å in one case, and 3.318 Å in the other, with two very similar bond lengths. Note that these inner "metallocenes" are shorter than the one in the endo mono-substituted complex (3.459 Å). Similarly, the distance between the inner tops, i.e., the two benzene rings that remain within the cage is 2.75 Å, and it is important to note that these rings are eclipsed, because evidently there is certain repulsion between them, as described in the following.

Concerning the simultaneous exo and endo isomer, the data are marked differently for both organometallic fragments; the exo fragment is eclipsed and has an average distance between tops of 3.263 Å, whereas, the inner unit is staggered and the equivalent average length is 3.410 Å.

The complete exo isomer is not totally symmetric, because one fragment is eclipsed, whereas the other is a little deviated, however the distances are similar, 3.332 Å in the first case, and 3.419 Å in the other.

The Wiberg bond indices analysis manifests more or less a similar behavior with respect to the mono-substituted species, i.e., the external units show a slightly more effective bond than the internal ones and the numerical values are similar to those from the mono-substituted complexes. However, in the case of the totally endo complex, a curious feature emerges; the behavior on the external and internal rings contrasts with that of the mono-substituted case. This means that the internal rings manifests a more effective covalent bond between carbon and chromium atoms than

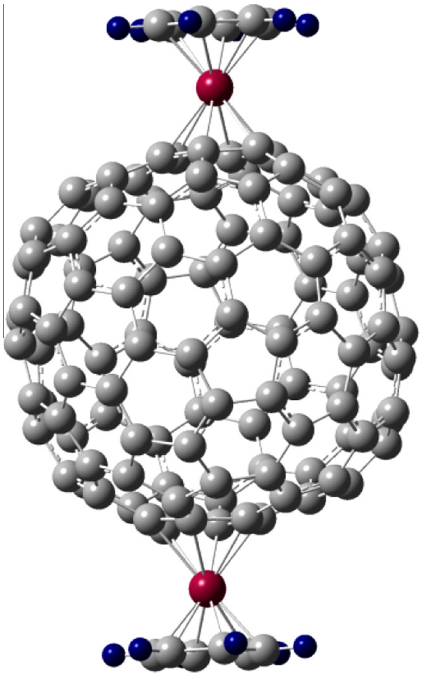

Fig. 9. The complete exo complex.

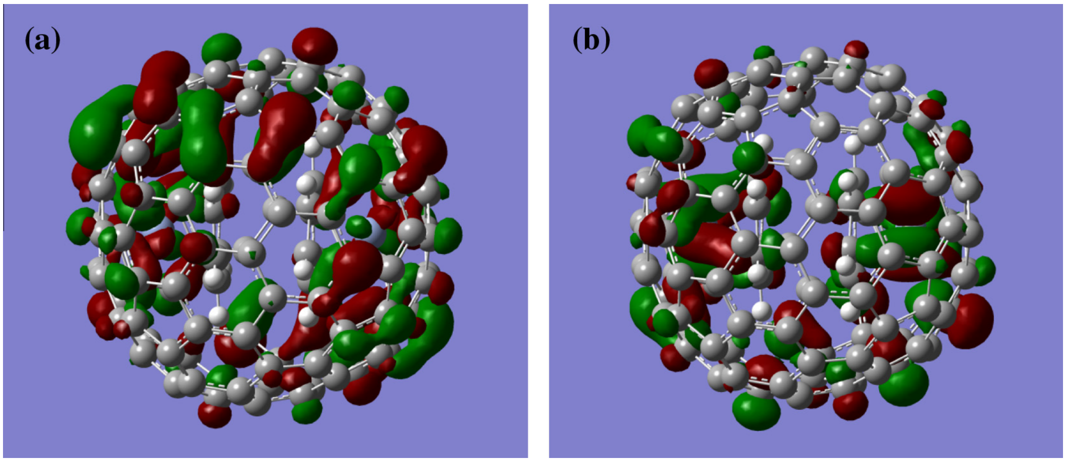

Fig. 10. Frontier molecular orbitals of the endo di-substituted complex, (a) HOMO, (b) LUMO.

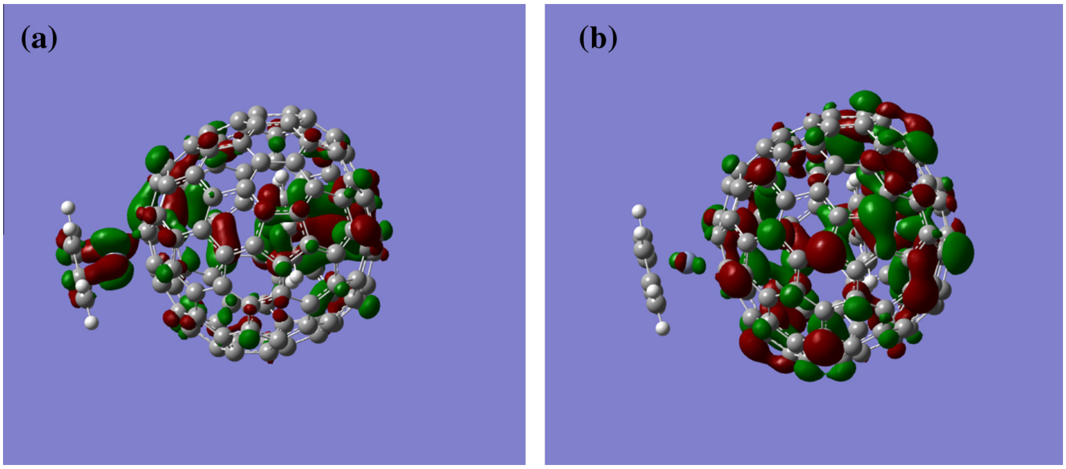

Fig. 11. Frontier molecular orbitals of the exo, endo di-substituted complex, (a) HOMO, (b) LUMO.

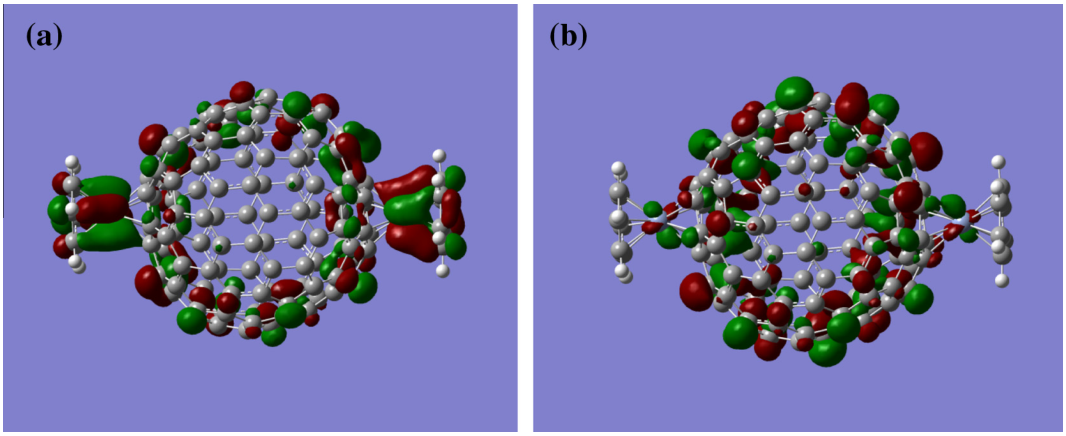

Fig. 12. Frontier molecular orbitals of the exo di-substituted complex, (a) HOMO, (b) LUMO.

the external one, and furthermore the bonds are slightly stronger than the mono-substituted case. The average value between chromium and a single carbon atom is 0.273 for the inner rings, with a cumulative 1.65 between chromium and the entire Cp substituent. On the other hand, the same bond between chromium and the individual carbon atoms on the surface ring has an average value of 0.255, with a cumulative of 1.53 for the interaction between the cyclopentadienyl fragment and the chromium center. The source of this phenomenon is the repulsion between both “upper” benzene rings within the cage, that forces both tops to a position closer to their respective chromium atom.

The corresponding shapes of molecular orbitals for the three species are shown in Figs. 10–12. The important factors to consider are: the first case is a fragment with a more complicated function,

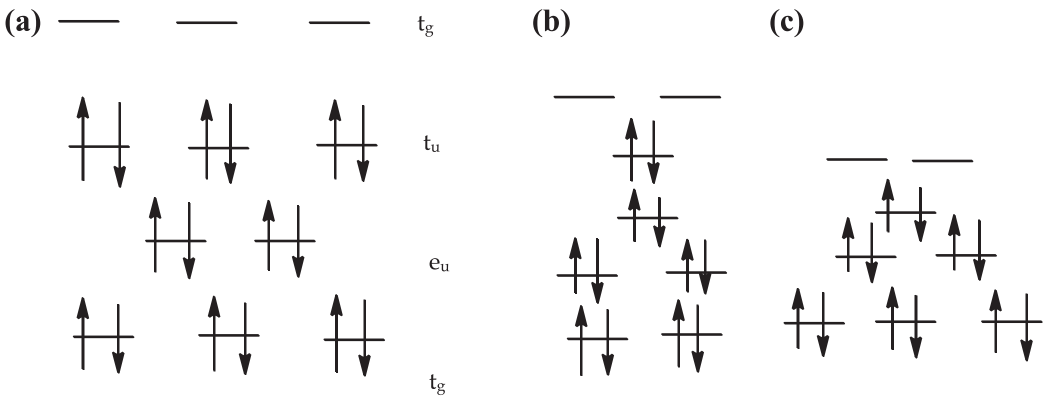

Fig. 13. Molecular orbital diagrams of (a) pristine C_{116}, (b) $Cr(C_6H_6)$ endo mono substituted complex, (c) $Cr(C_6H_6)$ endo di substituted complex.

but it is possible to appreciate the interactions between the chromium atom and all the surrounding carbons, and even more so in case of the LUMO.

Note that in the second and third cases the functions are in the opposite order; those functions which represent the π bond among carbon atoms and the central chromium are in the HOMO, whereas the LUMO in both cases is an orbital coming from the fullerene cage, with no participation on the part of the benzene rings.

Fig. 13 shows a comparison between the molecular orbital interaction diagram for free C_{116}, the endo mono-substituted complex and the endo di-substituted complex. The empty C_{116} fullerene is a symmetrical species; it belongs to the Th point group, as mentioned previously. The LUMO is a triple degenerate set which corresponds to the t_g irreducible representation, whereas the HOMO is also triple degenerated and belongs to the t_u irreducible representation. However, it is important to note that the HOMO − 1 and HOMO − 2 functions have energy values similar to that of the HOMO and perhaps they should be considered in bond schemes. HOMO − 1 is a double degenerated set with e_u irreducible representation and HOMO − 2 also has triple degeneration, and again it belongs to the t_g irreducible representation. The twelve electrons from the highest occupied molecular orbitals of the fullerene are expected to build bonds between the six member ring on the surface of the cage and the chromium atom. Likewise they are expected to be derived from the first highest molecular orbitals of the C_{116}. However, the double degenerated set is in the middle of the two triple degenerated groups. In the formation of both complexes, an important symmetry is therefore broken leading to energy stabilization, thereby leading to a new scheme with a new distribution of electrons. The resultant schemes show accidentally degenerated sets; two double in the case of the mono-substituted complex, and a double and a triple in the case of the di-substituted complex.

The semiconductor behavior of C_{116} made evident by its frontier molecular orbital gap of 1.578 eV is improved. In the case of the mono-substituted, which manifests 0.925 eV and even reaches the category of a weak conductor and in the case of the di-substituted complex showing an energy gap value of 0.760 eV. The intrinsic electrical currents inherent to fullerene and the accumulation of molecular orbitals in the frontier of HOMO and LUMO cause semiconductor behavior in this type of molecules. It seems however, that the presence of delocalized systems within the spheres can contribute to bringing the frontier molecular orbitals closer and improving its capacity as a conductor.

Again the intrinsic stability of these isomers is evaluated by means the free energy results of the next common homodesmotic reaction:

$$2(C_6H_6)_2Cr + C_{116} \rightarrow (C_6H_6)_2C_{116} + 2C_6H_6$$

The results show that the three species are thermodynamically stable but there are large differences among them. The free energy value for the totally endo complex is −138.05 kcal/mol, the same for the exo-endo isomer is −180.31 kcal/mol, whereas the result for the totally exo compound is −225.89 kcal/mol. The tendency is the same than in the case of monosubstituted complexes.

One interesting feature to consider is that fullerene molecules are electron scavengers [35]; it is known that in many cases the interaction of electron donor chemical species with fullerenes implies the transfer of electrons from the donor to the LUMO of the fullerene. Indeed, the endohedral complexes show this feature and it is expected to reach extra stability for this fact [6]. This possibility should therefore be explored in the present case. There are several studies in which the interaction between bis(benzene)chromium (or a similar organometallic complex) and fullerenes has been analyzed [36–38]; in all cases the formation of a fulleride is achieved. However, in all these cases the bis(benzene)chromium is found outside the cage, and keeps its shape in the net of the formed crystals and the interaction is performed with C_{60}. The situation is very different to the one presented here in which one of the aromatic rings of the organometallic complex belongs indeed to the fullerene. This same complex is into the cage and the fullerene is C_{116}, but anyway the power to trap electrons from the fullerene is present. The possibility was therefore studied.

Fig. 14 shows the NBO (natural bond order) charge analysis for the monosubstituted endo complex and the three isomers of the disubstituted complex. It is possible to see that the large accumulation of electrons is localized on the benzene rings belonging to the bis(benzene)chromium fragment in all cases. This is more evident for the external rings. In this same sense the shape of the molecular orbitals from Figs. 10–12 for all the cases show these rings have a large participation in the HOMO functions without exception. The MO interaction diagrams in Fig. 13 show indeed that HOMO is a single function with a strong participation of the bis(benzene)chromium fragment. The conclusion is that there is not electron transfer from the organometallic HOMO to the fullerene LUMO in the formation of the complexes, and thus they remain as a neutral species.

The possibility of an endo interaction between an independent bis(benzene)chromium as a cation and the C_{116} as a fulleride was also explored. However, it was not possible to reach a stable complex; indeed the cationic species of bis(benzene)chromium was modeled and it shows a strong free energy difference with the respect the neutral complex of 117.3 kcal/mol favoring the neutral configuration. It has more or less an eclipsed conformation (little deformed). The optimization of structure process of this ion into the cage do not reach a normal termination because the cage go to break in some moment of the iterative process and the cation

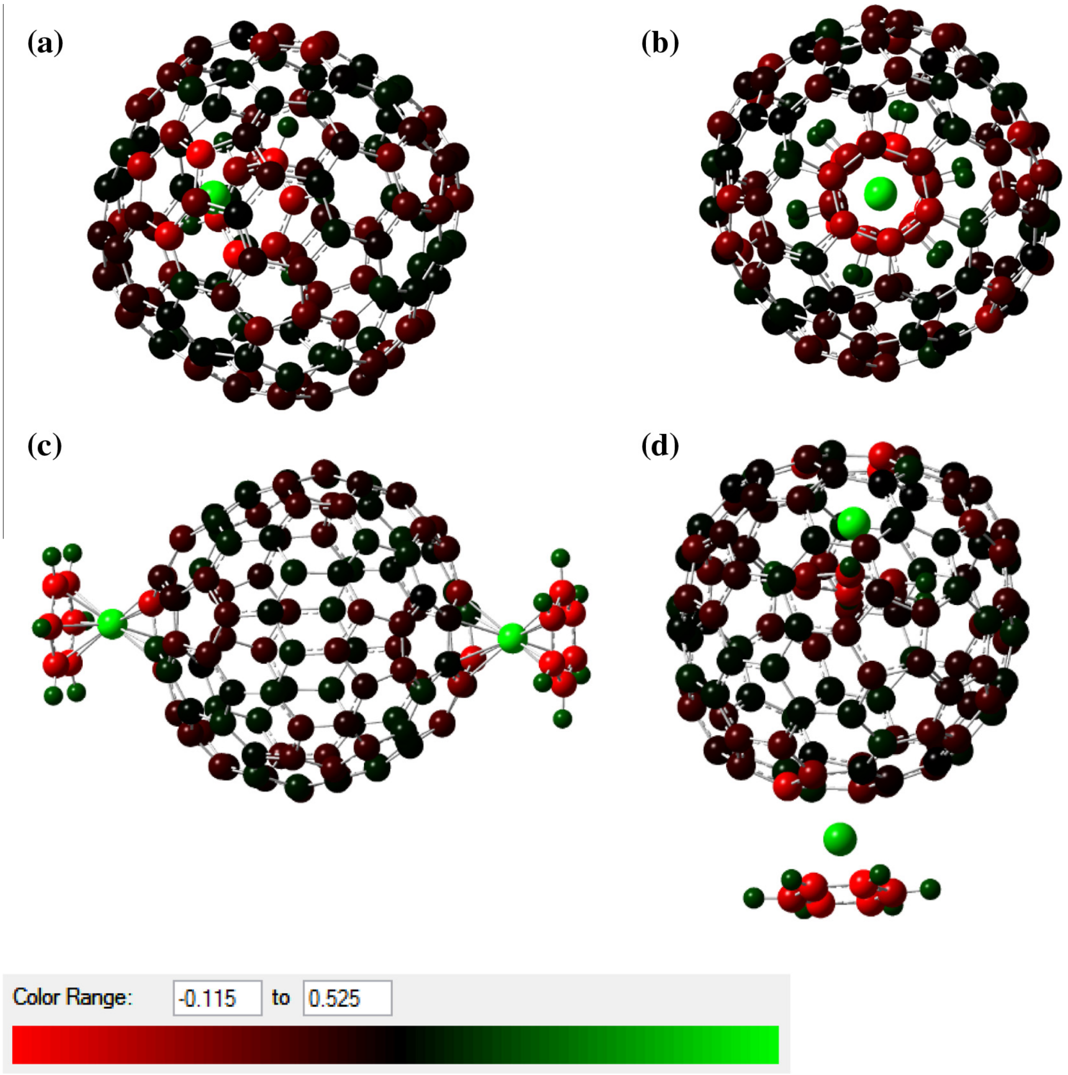

Fig. 14. NBO charge values of (a) mono-endo complex, (b) totally endo complex, (c) totally exo complex and (d) exo-endo complex.

shows the tendency to go away to the sphere; therefore, it is considered a failure process. The formation of complexes as those mentioned above implies the ionic interaction of fullerene and the organometallic fragment as exo complexes and they have the advantage of the formation of crystals. The systems however are different to that proposed here.

4. Conclusions

The possibility of existence of an endohedral metallocene has been explored. The endo-complexes of chromium with the central metal atom with oxidation number 0 were designed with a host in the form of a large and symmetrical fullerene (C_{116}) and compared with possible exo compounds. The energy results indicate that in all cases, the exo compounds should be more stable than the corresponding endo isomers, although the calculations also indicate intrinsic stability of all the isomers with respect to their parent molecules. The molecular orbital analysis indicates that the original C_{116} fullerene can easily receive the C_6H_6Cr fragment by donating six or twelve electrons in the mono and di substituted cases; likewise the original semiconductor behavior of the pristine fullerene is strengthened by the inclusion of one or two inner organometallic fragments.

Acknowledgment

The author is grateful with María Teresa Vázquez, Oralia Jiménez, Joaquín Morales, Alberto López and Cain González for technical help.

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