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Iron complexes of nanodiamond: Theoretical approach

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ABSTRACT

Simulated compounds have been proposed for organometallic clusters of nanodiamond with iron; the complexes take advantage of carboxylic ending in order to form a comprehensive bond with the metal ion. The performance is notorious; it seems that the control of electronic behavior is localized on both, the metallic atom and the carboxylic fragments, but not on the intrinsic nanodiamond unities, however, the presence of these nanodiamond ligands is fundamental to establish a sort of electronic confinement, which is responsible of the peculiar electronic behavior. The nature of the frontier molecular orbitals is also studied.

1. Introduction

Nanodiamond is a material that has been the object of several studies over the last few years [1]. This material has varying properties depending on purity, size, phase, etc. [2]. Diamond nanoparticles have drawn significant attention from a wide range of researchers for use in a variety of applications including plating; lubricating oils; polishing and biomedical devices [3]. The production of large quantities of sub 10 nm nanodiamonds involves a top-down approach, which includes milling luminescent high pressure, high temperature (HPHT) microdiamonds into 7 nm particles and then forming water dispersible colloidal quasi-spherical nanodiamonds [4].

There are several features to consider concerning the morphology of a nanodiamond. The size of the clusters is important for stability reasons. Galli and Barnard [5] have suggested that a large nanodiamond cluster consists of three parts, first a diamond core made up of sp^3 hybridized carbon atoms, a superior fullerene-like shell of sp^2 carbon atoms and a surface where all the dangling bonds are completed with either hydrogen or functional groups. Therefore, it is predictable that a nanodiamond particle would be different from others at the surface with different properties, although the core may be similar in all cases. The main method for synthesis of this material involves detonation [6]; this feature implies that the parent substance used as explosive will be responsible for the dopants that may form part of the clusters and therefore it is possible to have several different kinds of material depending on their origin.

The size of nanodiamond nanoparticles can vary from 1.7 to 5.2 nm [7]. Thus the smallest particle is the size of three fullerene (C_{60}) spheres, and it is predictable that any of these could manifest point group symmetry. Due to this feature, it is difficult to design a model for general study. Likewise, it has been observed that many nanoparticles have a metal [8], boron, silicon or nitrogen dopant [9]; and any of these will change dramatically their properties. Again, it is possible to discover different materials proffering a variety of applications. All these ideas suggest that it is possible to design smaller molecules, which manifest nanodiamond properties.

The main goal of this work is to propose an iron organometallic complex, which manifest nanodiamond properties. The design of the molecules in this study is in agreement with the restrictions and characteristics of large nanodiamond particles and take advantage of these, as well as it corresponds to the intrinsic chemistry of metallic clusters. They represent a semiconductor species.

2. Methods

Calculations were carried out using a pure DFT method for energy evaluations, applying Becke's gradient corrections [10] for exchange and Perdew–Wang's for correlation [11]. This is the scheme for the BPW91 method that forms part of the Gaussian 09 Package [12]. All calculations were performed using the 6-31G** basis set. Frequency calculations were carried out at the same level of theory in order to confirm that the optimized structures were at a minimum of the potential surfaces. To estimate the magnetic moment NMR calculations were performed with the GIAO method [13].

3. Results and discussion

In order to evaluate the effect on the electronic properties due to the size and the shape of the cluster, different fragments of

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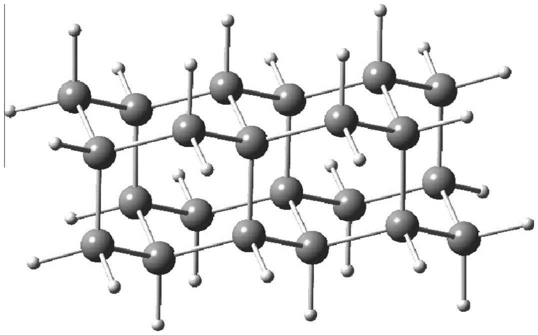
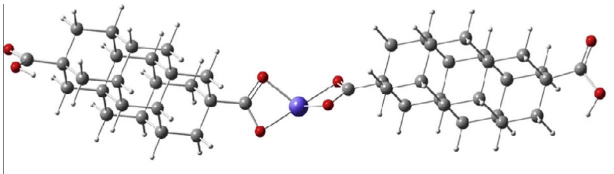
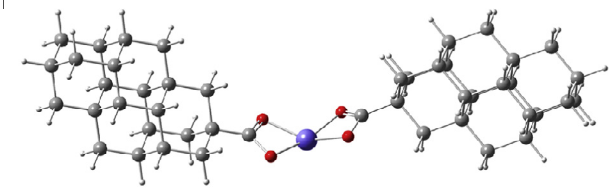


Fig. 1. Structure of a nanodiamond cluster ($C_{22}H_{28}$).



(a) with terminal carboxyl radicals $C_{26}O_8Fe$



(b) without terminal carboxyl radicals $C_{24}H_{27}O_4Fe$

Fig. 3. Iron coordination complexes of nanodiamond $C_{22}H_{28}$.

nanodiamonds were optimized as the first task. An sp^3 set of 12, 22, 29 and 35 carbon atoms saturated by hydrogen atoms was chosen (C_xH_y, $x = 12, 22, 29, 35$; $y = 22, 28, 36, 36$). The analysis is centered in the cluster of 22 carbon atoms. Therefore, the results for the $x = 12, 29, 35$ systems are mentioned when they are necessary.

The shape of the nanodiamond ligand with $x = 22$ can be seen in Fig. 1.

The fragment was chosen as to represent a pristine sp^3 center that belongs to the C_{2h} point group and is therefore expected to manifest all the characteristics of a pure nanodiamond (i.e. electrical insulator, low reactivity, high net energy, etc.), likewise this sample has no secondary structures. Other authors [14] have suggested units of this kind, but in this case, the sample was constructed searching for the preservation of symmetry in the new clusters.

The strategy consists in comparing the molecular orbital schemes of all the analyzed structures. Several features have been taken into account. In first place, the intrinsic size of the nanodiamond ligands, in second instance, the presence or absence of external ligands on the clusters, and in the final item the adopted arrangement of the carboxylic ligands around the iron atom.

The molecules under study were designed following a same model, i.e. a central iron atom joint to two nanodiamond ligands bearing carboxylic ligands as chelating agents. The result should be a square planar coordination complex, however there are important distortions in all cases. They will be described in each particular case. It is obvious that the iron complexes with six coordination are more stable, besides the tetrahedral four coordination are also common for a first row metal, however in the present case the geometry was adopted because the optimization of the geometry in the four coordination case yield these results. A forthcoming work is prepared in which the six coordination case will be shown.

Firstly, the reason to choose nanodiamond clusters as ligands was the insulator nature of these species. The insulator behavior is shown in the corresponding diagram portraying molecular orbital interaction in Fig. 2. It is possible to see that the energy difference between HOMO and LUMO is 6.88 eV and indeed the LUMO shows a positive value making it difficult for this species to react.

The second step was to build the complexes. For this task, two carboxyl radicals substituted at the edges of the molecule were chosen. There are two potential designs for this sample; the first one has the inner carboxyl radicals interacting with the metal atom, in addition to two more at the extreme edges that can work as trappers of other metals or reactive points. The second one is the same shape for the inner radical and the iron atom, but without terminal trappers. These structures are presented in Fig. 3.

The effect of the size of the nanodiamond units was studied changing the ligands on the two models showed above.

The first notorious feature appears at this point, the structures shown in Fig. 3 present a center with a puckered square. Most iron complexes have a tendency to belong to the *T* or *Td* point group. There are only a few complexes that belong to the D_{4h} point group; all of them may present certain distortions, which arise from steric effects, dangling bonds, etc. In the present case, the center shows a puckered D_{2d} structure, depicting geometry not commonly found in this kind of molecule. It seems that there is not enough strong steric impediment around the aforementioned center. Therefore, it is probable that this distortion arises only from electronic reasons. The electronic behavior of both derivatives is very interesting, but in fact very different in each case, thus they deserve to be analyzed individually.

The first case is the molecule with terminal carboxyl radicals ($C_{26}O_8Fe$). The behavior is practically that of a strong semiconductor species. The molecular orbitals diagram is presented in Fig. 4.

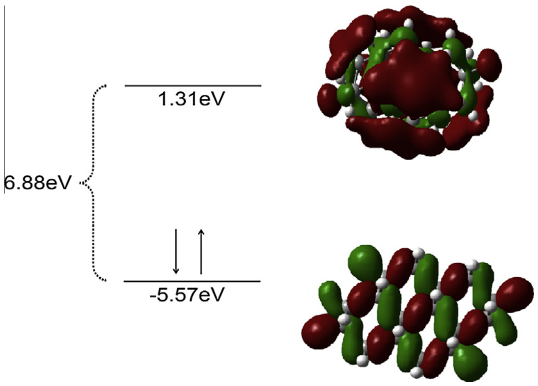


Fig. 2. Frontier molecular orbitals diagram of a nanodiamond ($C_{22}H_{28}$).

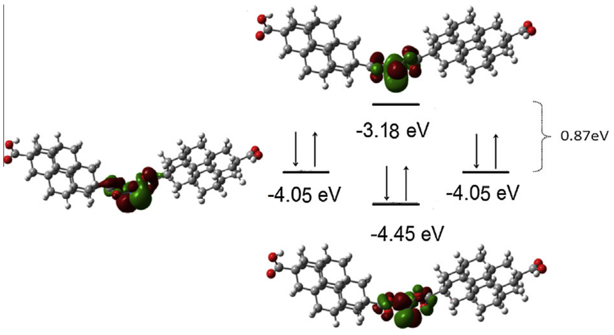


Fig. 4. Frontier molecular orbital diagram of compound ($C_{26}O_8Fe$).