**On the effect of charge and spin in $\text{He}^{(q)}@X_nZ_{12-n}H_{12}^{(n-2)}$ molecules,
with $X = \{C, Si\}$, $Z = \{B, Al\}$ and $q = \{0, +1, +2\}$, $n = \{0, 1\}$**

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Abstract: We study the effect of introducing $\text{He}^{(q)}$ $q = \{0, +1, +2\}$, into icosahedral molecules - $X_nZ_{12-n}H_{12}^{(n-2)}$, with $X = \{C, Si\}$, $Z = \{B, Al\}$ and $n = \{0, 1\}$ - to see the effect of charge and spin on the stability and potential existence for these endohedral complexes. For $q = 0$ and $q = +1$, all endohedral systems correspond to energy minima with the He atom/ion remaining inside the cage. However, when the charge of the He ion is $q = +2$, the He atom/ion is ejected from the $\text{He}^{(2+)}@B_{12}H_{12}^{(2-)}$ and $\text{He}^{(2+)}@CB_{11}H_{12}^{(-)}$ cages, but this is not the case for the $Al_{12}H_{12}^{(2-)}$ and $SiAl_{11}H_{12}^{(-)}$ cages, which retain the $\text{He}^{(2+)}$ ion inside. These results could be helpful for designing quantum bits with atoms encapsulated inside heteroatomic molecular icosahedral cages since the s , p and d atomic levels do not split under an icosahedral field.

1. Introduction

The control of electronic and magnetic properties of molecules is the tip of the iceberg within modern nanoscience and nanotechnology [1]. In the last two decades we have been involved in the study of the electronic structure of polyhedral (metalla)heteroborane molecules in their ground and excited states [2], and also exploring how the properties of these - isolated or connected - systems change as function of charge and spin [3-5]. In 2006, we proposed a photochemical window mechanism by which a $\text{Li}^{(+)}$ ion could be inserted inside and ejected from an icosahedral $\text{CB}_{11}\text{H}_{12}^{(-)}$ cage [6]. The work presented here regarding the ESPA2018 Conference is a preliminary study concerned with the stability and potential existence of endohedral compounds of $\text{He}^{(q)} - q = \{0, +1, +2\}$ – encapsulated inside icosahedral cages $\text{X}_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$, with $\text{X} = \{\text{C}, \text{Si}\}$, $\text{Z} = \{\text{B}, \text{Al}\}$ and $n = \{0, 1\}$. The encapsulation of atoms inside icosahedral heteroborane cages has also been previously studied [7-9]. However, we consider here for the first time the He atom/ion to be encapsulated inside the title cage compounds. He endohedral complexes are known, such as the $\text{He}@\text{C}_{60}$, which is produced by pressurizing C_{60} to ca. 3 bar in a noble-gas atmosphere [10]. Hydrogen can also be introduced in fullerenes [11].

2. Computational methods

In all geometry optimizations and electronic structure computations we use the hybrid Hartree-Fock / Density Functional Theory functionals B3LYP and B97D with the triple- ζ basis set 6-311+G(d,p), which includes polarization functions for all atoms, as implemented in the Gaussian program [12]. B97D is a Grimme's functional including dispersion [13], and the reason for using it in this work is the possibility that dispersion forces might have an influence into the final geometry of He endohedral complexes. All the geometries included in this work correspond to energy minima checked with frequency computations – zero imaginary frequencies as eigenvalues of the second derivative matrix of the energy versus nuclear displacements. The volumes of the optimized icosahedral cages – without and with the endohedral $\text{He}^{(q)}$ atom/ion - are obtained as the sum of the 20 tetrahedra – nuclei coordinates – formed by connecting the geometrical center of the icosahedron with three different vertices [9].

3. Results and discussion

3.1 Energy

We optimized the geometries of all icosahedral cages $X_nZ_{12-n}H_{12}^{(n-2)}$ - $X = \{C, Si\}$, $Z = \{B, Al\}$, $n = \{0, 1\}$ - without and with the $He^{(q)}$ atom/ion - $q = \{0, +1, +2\}$ - inside the cage using both functionals B3LYP and B97D. The optimized geometries (B3LYP) of all molecules are included in the Supplementary Information file. Figure 1 depicts the general structure of the systems included in this work. The electronic energies of all systems are reported in Table 1.

Figure 1. General structure of the endohedral complexes considered in this work, $He^{(q)}@X_nZ_{12-n}H_{12}^{(n-2)}$, with $X = \{C, Si\}$, $Z = \{B, Al\}$, $n = \{0, 1\}$, and $q = \{0, +1, +2\}$. There is a hydrogen atom connected to each vertex, not shown. Every vertex corresponds to a B or Al atom. For the hybrid cages, the large blue circle on top of the cage indicates C or Si in $CB_{11}H_{12}^{(-)}$ and $SiAl_{11}H_{12}^{(-)}$ respectively.

The energy difference between the endohedral complex and the forming parts

$$\Delta E = E\{He^{(q)}X_nZ_{12-n}H_{12}^{(n-2)}\} - E\{X_nZ_{12-n}H_{12}^{(n-2)}\} - E\{He^{(q)}\} \quad (1)$$

gives an idea of how much stability/instability the endohedral atom gives to the whole complex; thus, if the atom/ion inside the cage is too large (steric hindrance) or leads to a

repulsive interaction (due to charge, spin or else) then ΔE should be large and positive. On the other hand, a negative ΔE is an indication of a further stability of the endohedral complex as compared to the separated systems $\text{He}^{(q)}$ and $\text{X}_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$, or without the encapsulated atom/ion. Table 1 also gathers the ΔE energies for all the systems considered in this work.

Table 1. B3LYP and **B97D** energies with basis set 6-311+G(d,p) and optimized geometries for the title compounds. Energy in atomic units and ΔE (Eq. 1) in eV. All geometries correspond to energy minima (zero imaginary frequencies).

	Energy				Energy	
$\text{B}_{12}\text{H}_{12}^{(2-)}$	-305.762822 -305.559330		$\text{Al}_{12}\text{H}_{12}^{(2-)}$		-2916.933507 -2916.530706	
$\text{CB}_{11}\text{H}_{12}^{(-)}$	-319.057190 -318.842029		$\text{SiAl}_{11}\text{H}_{12}^{(-)}$		-2964.001487 -2963.605096	
	$E(q = 0)$	ΔE	$E(q = +1)$	ΔE	$E(q = +2)$	ΔE
$\text{He}^{(q)}$	-2.913028 -2.914361	---	-1.997021 -1.998125	---	0.000000 0.000000	---
$\text{He}^{(q)}@ \text{B}_{12}\text{H}_{12}^{(2-)}$	-308.414157 -308.209874	7.12 7.18	-308.385680 -308.187232	-17.03 -17.14	He ejected He ejected	---
$\text{He}^{(q)}@ \text{CB}_{11}\text{H}_{12}^{(-)}$	-321.691974 -321.478109	7.57 7.57	-321.500936 -321.294682	-12.16 -12.37	He ejected He ejected	---
$\text{He}^{(q)}@ \text{Al}_{12}\text{H}_{12}^{(2-)}$	-2919.803873 -2919.398388	1.16 1.27	-2919.776385 -2919.374907	-23.02 -23.02	-2919.622971 -2919.225192	-73.18 -73.32
$\text{He}^{(q)}@ \text{SiAl}_{11}\text{H}_{12}^{(-)}$	-2966.867607 -2966.467166	1.28 1.42	-2966.716379 -2966.321664	-19.53 -19.55	-2966.433364 -2966.044745	-66.17 -66.39

According to the computations gathered in Table 1, He and $\text{He}^{(+)}$ can be encapsulated inside all cages $\text{B}_{12}\text{H}_{12}^{(2-)}$, $\text{CB}_{11}\text{H}_{12}^{(-)}$, $\text{Al}_{12}\text{H}_{12}^{(2-)}$ and $\text{SiAl}_{11}\text{H}_{12}^{(-)}$. However, a charge of +2 for He implies its ejection outside the cages $\text{B}_{12}\text{H}_{12}^{(2-)}$ and $\text{CB}_{11}\text{H}_{12}^{(-)}$; but this is not the case for $\text{Al}_{12}\text{H}_{12}^{(2-)}$ and $\text{SiAl}_{11}\text{H}_{12}^{(-)}$, where complexes $\text{He}^{(2+)}@ \text{Al}_{12}\text{H}_{12}^{(2-)}$ and $\text{He}^{(2+)}\text{SiAl}_{11}\text{H}_{12}^{(-)}$ are formed respectively. The encapsulation energy ΔE (Eq. 1) – Table 1 – for these complexes shows an energy penalty of ~ 7 eV and ~ 7.5 eV for $\text{He}@ \text{B}_{12}\text{H}_{12}^{(2-)}$ and $\text{He}@ \text{CB}_{11}\text{H}_{12}^{(-)}$ respectively. Thus, even if He can be encapsulated inside these cages – stationary point of the energy versus nuclear displacement, an energy minimum, as shown in the computations - the process is not spontaneous, nor thermodynamically or kinetically stable. The computations only show that at $T = 0$ K one such molecule could exist. Only using high pressure, as in the case of $\text{He}@ \text{C}_{60}$ [10] the process could be viable, as we will discuss below regarding the shrinkage or swelling of cages. If we substitute B and C by Al and Si respectively, then the energy penalty ΔE lowers to ~ 1.3 eV for $\text{He}@ \text{Al}_{12}\text{H}_{12}^{(2-)}$ and

$\text{He@SiAl}_{11}\text{H}_{12}^{(-)}$ respectively, clearly indicating that the larger volume of the second row cages lowers the steric hindrance of having a closed shell He atom inside, pushing its electron density against the electron density of the respective cages. Of course, the -2 and -1 charges of the cages play an important role in the repulsive contribution to the encapsulated atom, adding up to the whole electron density.

Increase of the charge of the He atom from $q = 0$ to $q = +1$ for a given cage, gives a change of sign in ΔE and therefore we are talking about an additive stability or surplus energy with the fact of encapsulating an $\text{He}^{(+)}$ cation inside any of the $\text{X}_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$ icosahedral cages. Now we can say that one $\text{He}^{(+)}@X_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$ complex at $T = 0$ K is thermodynamically more stable versus separated $\text{He}^{(+)}$ and $\text{X}_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$ systems. The stability - ΔE - of the $\text{He}^{(+)}@X_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$ complexes increases in this order:

$$\text{He}^{(+)}@CB_{11}\text{H}_{12}^{(-)} < \text{He}^{(+)}@B_{12}\text{H}_{12}^{(-2)} < \text{He}^{(+)}@SiAl_{11}\text{H}_{12}^{(-)} < \text{He}^{(+)}@Al_{12}\text{H}_{12}^{(2-)} \quad (2)$$

We should note that this order of stability also applies for the $\text{He}^{(0)}@X_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$ complexes, but with a positive sign for ΔE . We can also define

$$\delta_1(\Delta E) = \Delta E(q = +1) - \Delta E(q = 0) \quad (3)$$

and

$$\delta_2(\Delta E) = \Delta E(q=+2) - \Delta E(q=+1) \quad (4)$$

then Table 1 shows clearly an enhancement of the stability due charge increase from $q = 0$ to $q = +1$ for a given complex. This enhancement is about $\delta_1 \sim 24$ eV and $\delta_1 \sim 20$ eV for $\text{He}^{(q)}@B_{12}\text{H}_{12}^{(2-)}$ and $\text{He}^{(q)}@CB_{11}\text{H}_{12}^{(-)}$ respectively when the He atom bears a $q = +1$ charge. Obviously, ΔE decreases considerably when the volume of the cage is larger – *vide infra* – as is the case of icosahedral cages built up with atoms below B and C in the Periodic Table,

Al and Si. In this latter case, δ_1 has similar values as compared to the B/C analogues, $\delta_1 \sim 24$ eV and $\delta_1 \sim 21$ eV for $\text{He}^{(q)}@ \text{Al}_{12}\text{H}_{12}^{(2-)}$ and $\text{He}^{(q)}@ \text{SiB}_{11}\text{H}_{12}^{(-)}$ respectively.

Finally, if we encapsulate $\text{He}^{(2+)}$ inside the title cages, only the endohedral $\text{Al}_{12}\text{H}_{12}^{(2-)}$ and $\text{SiB}_{11}\text{H}_{12}^{(-)}$ cages survive to the strong Coulomb and quantum-mechanical forces due to having such an ion/nucleus inside! For $\text{B}_{12}\text{H}_{12}^{(2-)}$ and $\text{CB}_{11}\text{H}_{12}^{(-)}$ the forces are too strong and the $\text{He}^{(2+)}$ ion is ejected outside the cages, the latter being closed again during the optimization process; hence, the stability of the $\text{B}_{12}\text{H}_{12}^{(2-)}$ and $\text{CB}_{11}\text{H}_{12}^{(-)}$ moieties, a universal fact of Polyhedral Boron Chemistry, always clustering the Boron atoms in order to enhance stability. The values of ΔE for $\text{He}^{(2+)}@ \text{Al}_{12}\text{H}_{12}^{(2-)}$ and $\text{He}^{(2+)}@ \text{SiAl}_{11}\text{H}_{12}^{(-)}$ are rather large and negative as compared to $\text{He}^{(+)}$ and $\text{He}^{(0)}$ complexes, -73 eV and -66 eV respectively. These are huge amounts of energy if we talk in terms of bonding energies or ionization energies. The values of δ_2 for $\text{He}^{(2+)}@ \text{Al}_{12}\text{H}_{12}^{(2-)}$ and $\text{He}^{(2+)}@ \text{SiAl}_{11}\text{H}_{12}^{(-)}$ are similar, -50 eV and -47 eV respectively, an indication that the relative stabilities (or energy stability difference) of complexes are quite close when increasing the charge on He from $q = +1$ to $q = +2$.

Given the fact that in all cases, including those in which He is ejected, the formal charge of $\text{He}^{(q)}$ in the final system is close to zero, we decided to check the stability of the cages after removing one and two electrons, by performing a geometry optimization at the B3LYP/6-311+G(d,p) level of theory, with energy minima for all Cages^(Q). Then, we considered the following stepwise process, as shown in Eq(5):

Table 2 shows the energy differences for the systems in Eq(5): when $\text{He}^{(q)}$, with $q = (+1, +2)$, is incorporated into the cage, the first step is basically an electron transfer from the cage to He (one and two electrons), as clearly shown in the first column of Table 2. In other words, the $\text{Cage}^{(Q+q)} + \text{He}^{(0)}$ system is always the lowest in energy, with much larger energy difference values when compared to $\text{Cage}^{(2-)} + \text{He}^{(2+)}$.

Table 2. Energy differences (bold, in eV) for the process: $[\text{Cage}^{(Q)} + \text{He}^{(q)} \rightarrow \text{Cage}^{(Q+q)} + \text{He}^{(0)} \rightarrow \text{endohedral system}]$, referred to the lowest energy system (0 eV). B3LYP/6-311+G(d,p) computations.

q	$\text{Cage}^{(Q)} + \text{He}^{(q)}$	$\text{Cage}^{(Q+q)} + \text{He}^{(0)}$	endohedral system
+1	$\text{B}_{12}\text{H}_{12}^{(2-)} + \text{He}^{(+)} = \mathbf{24.0}$	$\text{B}_{12}\text{H}_{12}^{(-)} + \text{He}^{(0)} = \mathbf{0.0}$	$[\text{He}@\text{B}_{12}\text{H}_{12}]^{(-)} = \mathbf{7.0}$
+1	$\text{CB}_{11}\text{H}_{12}^{(-)} + \text{He}^{(+)} = \mathbf{19.5}$	$\text{CB}_{11}\text{H}_{12}^{(0)} + \text{He}^{(0)} = \mathbf{0.0}$	$[\text{He}@\text{CB}_{11}\text{H}_{12}]^{(0)} = \mathbf{7.4}$
+1	$\text{Al}_{12}\text{H}_{12}^{(2-)} + \text{He}^{(+)} = \mathbf{24.2}$	$\text{Al}_{12}\text{H}_{12}^{(-)} + \text{He}^{(0)} = \mathbf{0.0}$	$[\text{He}@\text{Al}_{12}\text{H}_{12}]^{(-)} = \mathbf{1.2}$
+1	$\text{SiAl}_{11}\text{H}_{12}^{(-)} + \text{He}^{(+)} = \mathbf{20.8}$	$\text{SiAl}_{11}\text{H}_{12}^{(0)} + \text{He}^{(0)} = \mathbf{0.0}$	$[\text{He}@\text{SiAl}_{11}\text{H}_{12}]^{(0)} = \mathbf{1.2}$
q	$\text{Cage}^{(Q)} + \text{He}^{(q)}$	$\text{Cage}^{(Q+q)} + \text{He}^{(0)}$	encapsulated system
+2	$\text{B}_{12}\text{H}_{12}^{(2-)} + \text{He}^{(2+)} = \mathbf{73.8}$	$\text{B}_{12}\text{H}_{12}^{(0)} + \text{He}^{(0)} = \mathbf{0.0}$	$[\text{He}@\text{B}_{12}\text{H}_{12}]^{(0)} = \mathbf{\text{He ejected}}$
+2	$\text{CB}_{11}\text{H}_{12}^{(-)} + \text{He}^{(2+)} = \mathbf{73.9}$	$\text{CB}_{11}\text{H}_{12}^{(+)} + \text{He}^{(0)} = \mathbf{0.0}$	$[\text{He}@\text{CB}_{11}\text{H}_{12}]^{(+)} = \mathbf{\text{He ejected}}$
+2	$\text{Al}_{12}\text{H}_{12}^{(2-)} + \text{He}^{(2+)} = \mathbf{74.3}$	$\text{Al}_{12}\text{H}_{12}^{(0)} + \text{He}^{(0)} = \mathbf{0.0}$	$[\text{He}@\text{Al}_{12}\text{H}_{12}]^{(0)} = \mathbf{1.1}$
+2	$\text{SiAl}_{11}\text{H}_{12}^{(-)} + \text{He}^{(2+)} = \mathbf{67.3}$	$\text{SiAl}_{11}\text{H}_{12}^{(+)} + \text{He}^{(0)} = \mathbf{0.0}$	$[\text{He}@\text{SiAl}_{11}\text{H}_{12}]^{(+)} = \mathbf{1.2}$

Energy penalties for encapsulating $\text{He}^{(+)}$ into the cages are around ~ 7 eV and ~ 1 eV for $\{\text{B}_{12}\text{H}_{12}^{(2-)}, \text{CB}_{11}\text{H}_{12}^{(-)}\}$ and $\{\text{Al}_{12}\text{H}_{12}^{(2-)}, \text{SiAl}_{11}\text{H}_{12}^{(-)}\}$ cages respectively. When the charge is augmented to $\text{He}^{(2+)}$, as described above, He is ejected for $\{\text{B}_{12}\text{H}_{12}^{(2-)}, \text{CB}_{11}\text{H}_{12}^{(-)}\}$ due to the double cage $\rightarrow$ He electron transfer, and the encapsulation energy penalty remains basically the same for $\{\text{Al}_{12}\text{H}_{12}^{(2-)}, \text{SiAl}_{11}\text{H}_{12}^{(-)}\}$, namely, ~ 1 eV, with the He atom inside the cluster.

Finally, within this section, we discuss the role of the approximate dispersion correction term in the B97D functional for short interatomic distances, as function of the He charge. For the sake of clarity we also include the B3LYP functional used in this work (no dispersion corrections). In order to fulfill this issue, we take the optimized geometries for $\text{B}_{12}\text{H}_{12}^{(2-)}$ and $\text{He}^{(+)}@\text{B}_{12}\text{H}_{12}^{(2-)}$, and consider single-point energy computations with the geometries moving the He atom from the center of the icosahedron - (0,0,0) position – towards one B atom on any vertex. In the case of $\text{He}^{(2+)}@\text{B}_{12}\text{H}_{12}^{(2-)}$, since the He atom is ejected, we consider the optimised geometry of $\text{B}_{12}\text{H}_{12}^{(2-)}$. In Figure 2 we depict the dependence of energy versus displacement (d) of He towards B along the line joining these two atoms. For $d = 0$ Å, the He atom is at the very center of the perfect icosahedral cage. The initial distance between He and B is $d = 1.77$ Å. As the $\text{He}^{(q)}$ atom/ion, in the $\text{He}^{(q)}@\text{B}_{12}\text{H}_{12}^{(2-)}$ complex, moves along the He-B line towards the B atom of the vertex, the energy increases with different profiles. For $q = (0, +1)$ these profiles are similar and almost undistinguishable for both functionals.

However, for $q = +2$, there is remarkable difference in the energy profile for the different functionals, specially with d between 1.0 Å and 1.4 Å. Hence, the importance of dispersion corrections in the B97D functional. We should emphasize that these features do not change the fact that both functionals (B3LYP and B97D) predict the ejection of $\text{He}^{(2+)}$ when encapsulated inside $\text{B}_{12}\text{H}_{12}^{(2-)}$ and inside $\text{CB}_{11}\text{H}_{12}^{(-)}$.

Figure 2. Energy profile (au) ($E = E_0 - E_d$) for each complex $\text{He}^{(q)}@B_{12}H_{12}^{(2-)}$ as function of the distance d between He and any B atom from in $B_{12}H_{12}^{(2-)}$, and functionals B3LYP and B97D, the latter with dispersion corrections. The initial B-He distance is $d = 1.77$ Å. Basis set 6-311+G(d,p).

3.2 Volume

At this point we decided to calculate the volumes of the icosahedral cages, without and with the encapsulated atom/ions, in order to see the effect – shrinkage or swelling – of atom nature, charge and spin in the stuffing of the cages. Table 3 shows the calculated volume for all the cages and endohedral compounds included in this work.

Table 3. Volumes in $\text{\AA}^3$ for the $X_nZ_{12-n}H_{12}^{(n-2)}$ molecules and $He^{(q)}@X_nZ_{12-n}H_{12}^{(n-2)}$ endohedral compounds studied in this work, with $X = \{C, Si\}$, $Z = \{B, Al\}$, $q = \{0, +1, +2\}$ and $n = \{0, 1\}$. B3LYP and **B97D** computations with the 6-311+G(d,p) basis set. ΔV ($\text{\AA}^3$) corresponds to the difference between volume of the endohedral complex $He^{(q)}@X_nZ_{12-n}H_{12}^{(n-2)}$ and the volume of the cage $X_nZ_{12-n}H_{12}^{(n-2)}$.

	Volume							
	$B_{12}H_{12}^{(2-)}$	ΔV	$CB_{11}H_{12}^{(-)}$	ΔV	$Al_{12}H_{12}^{(2-)}$	ΔV	$SiAl_{11}H_{12}^{(-)}$	ΔV
---	12.44 12.67	---	12.04 12.31	---	43.10 43.29	---	41.91 42.04	---
$He^{(0)}@$	14.06 14.11	1.62 1.44	13.66 13.78	1.62 1.47	44.58 45.29	1.48 2.00	43.45 44.03	1.54 1.99
$He^{(+)}@$	14.41 14.41	1.97 1.74	14.16 14.18	2.12 1.87	45.20 46.01	2.10 2.81	44.36 45.07	2.45 3.03
$He^{(2+)}@$	He ejected He ejected	---	He ejected He ejected	---	46.54 47.62	3.44 4.33	46.19 47.59	4.28 5.55

The volumes are computed as follows [9]: Take the geometrical center of the icosahedron (R_G) and its vertices (P_i , $i = 1, 12$) and then calculate the volumes of the 20 tetrahedra T_j ($j = 1, 20$) formed by joining the four points $T_j = (R_G, P_i, P_{i'}, P_{i''})$; then the volume of the molecule is calculated as:

$$V = \sum_{j=1}^{20} T_j \quad (6)$$

As shown in Table 3, the volumes of the cages without the endohedral atom $He^{(q)}$ are $\sim 12 \text{ \AA}^3$ and $\sim 42 \text{ \AA}^3$ for the $\{B_{12}H_{12}^{(2-)}, CB_{11}H_{12}^{(-)}\}$ and $\{Al_{12}H_{12}^{(2-)}, SiAl_{11}H_{12}^{(-)}\}$ sets respectively. A difference of $\Delta V \sim 30 \text{ \AA}^3$ is considerable if we want to explain why certain atoms/ions could be retained or not inside the cage. The first remarkable feature from Table 3 is that there is always a swelling ($\Delta V > 0$) of the cage when a $He^{(q)}$ atom/ion is introduced

inside the cage, being $\Delta V \sim 1.5\text{-}2.0 \text{ \AA}^3$ for pure $\text{B}_{12}\text{H}_{12}^{(2-)}$ and hybrid $\text{CB}_{11}\text{H}_{12}^{(-)}$ cages when a $\text{He}^{(0)}$ atom is introduced inside the cage. Encapsulation of a charged $\text{He}^{(+)}$ cation does not change much this difference, up to $\Delta V \sim 2.0 \text{ \AA}^3$ also for pure $\text{B}_{12}\text{H}_{12}^{(2-)}$ and hybrid $\text{CB}_{11}\text{H}_{12}^{(-)}$. Surprisingly, the swelling effects are very similar for the cage analogues of the 2nd row of the Periodic Table, pure $\text{Al}_{12}\text{H}_{12}^{(2-)}$ and hybrid $\text{SiAl}_{11}\text{H}_{12}^{(-)}$! Hence, $\Delta V \sim 1.5\text{-}3.0 \text{ \AA}^3$ for $\text{He}^{(0)}$ and $\text{He}^{(+)}$ encapsulation, with the upper limit around $3 \text{ \AA}^3$ - $\text{He}^{(+)}\text{SiAl}_{11}\text{H}_{12}^{(-)}$ with the B97D functional. As we discussed above the $\text{He}^{(2+)}$ dication is ejected from the cages in $\text{B}_{12}\text{H}_{12}^{(2-)}$ and $\text{CB}_{11}\text{H}_{12}^{(-)}$ and the cages close again, due to the small volume of the cages – steric hindrance – and the Coulomb and quantum-mechanical forces exerted between a $\text{He}^{(2+)}$ nucleus and the electron density of a natural electron acceptor, just like (car)borane cages; hence, we withdraw further electron density from an electron acceptor and therefore the cage collapses, opening and ejecting the endohedral $\text{He}^{(2+)}$ system outwards. In other words, the $\text{He}^{(2+)}$ exerts a strong negative pressure from inside outwards the cage, as we will describe below. When the cage is larger by $30 \text{ \AA}^3$, as in $\text{Al}_{12}\text{H}_{12}^{(2-)}$ and $\text{SiAl}_{11}\text{H}_{12}^{(-)}$, the forces (pressure) towards the cage are lower and therefore the $\text{He}^{(2+)}$ can be encapsulated inside these cages. The swelling of the cage is from $\sim 4.3 \text{ \AA}^3$ to $\sim 5.5 \text{ \AA}^3$ for $\text{He}^{(2+)}\text{Al}_{12}\text{H}_{12}^{(2-)}$ and $\text{He}^{(2+)}\text{SiAl}_{11}\text{H}_{12}^{(-)}$. Therefore, in all endohedral systems, the inner atom/ion exerts a pressure towards the cage, to a much lesser extent for the larger clusters, as we will describe below.

These facts can be proven by calculating the negative derivative of the energy versus volume, which can be considered roughly the pressure exerted by the endohedral atom onto the cage [14]. Thus, we take the optimized geometries of the endohedral complexes $\text{He}^{(q)}@\text{X}_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$, then remove the endohedral atom and its charge $\text{He}_{(q)}$ and then perform a single-point energy computation on this geometry; this energy is labelled E_2 . Then we can define:

$$P = -\partial E/\partial V = -(E_2 - E_1)/\Delta V \quad (7)$$

where E_1 is the energy of the optimized icosahedral (empty)cages from Table 1 and $\Delta V = V_2 - V_1$, is the volume difference from Table 3. The results from Eq(7) are gathered in Table 4. The energy E_2 and V_2 is the result of the *cage swelling effect* due to the introduction of an endohedral atom/ion inside the cage.

Table 4. Electronic energies of the complexes $\text{He}^{(q)}@X_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$ with the endohedral atom and its charged removed from the complex at the optimized geometry of the corresponding endohedral complex. Pressure (in GPa) computed as $P = -(E_2 - E_1)/\Delta V$, where E_2 is the Energy in this Table and E_1 is the energy of the optimized empty cage $X_n\text{Z}_{12-n}\text{H}_{12}^{(n-2)}$ gathered in Table 1. ΔV are reported in Table 3. B3LYP/6-311+G(d,p) computations.

System	Energy	P(GPa)	System	Energy	P(GPa)
$[\text{He}^{(0)}]@B_{12}\text{H}_{12}^{(2-)}$	-305.738815	-65	$[\text{He}^{(0)}]@Al_{12}\text{H}_{12}^{(2-)}$	-2916.932021	-4
$[\text{He}^{(+)}]@B_{12}\text{H}_{12}^{(2-)}$	-305.718587	-98	$[\text{He}^{(+)}]@Al_{12}\text{H}_{12}^{(2-)}$	-2916.926564	-14
			$[\text{He}^{(2+)}]@Al_{12}\text{H}_{12}^{(2-)}$	-2916.909998	-30
System	Energy		System	Energy	
$[\text{He}^{(0)}]@CB_{11}\text{H}_{12}^{(-)}$	-319.030641	-72	$[\text{He}^{(0)}]@SiAl_{11}\text{H}_{12}^{(-)}$	-2963.999334	-6
$[\text{He}^{(+)}]@CB_{11}\text{H}_{12}^{(-)}$	-318.985245	-148	$[\text{He}^{(+)}]@SiAl_{11}\text{H}_{12}^{(-)}$	-2963.993414	-14
			$[\text{He}^{(2+)}]@SiAl_{11}\text{H}_{12}^{(-)}$	-2963.968053	-34

In an approximate view, we can define the endohedral atom as exerting a force towards the cage that increases its volume by a ΔV , namely, a negative pressure pushing outwards the nuclei of the cage. Let us remind that the cages always undergo a swelling by introducing a an $\text{He}^{(q)}$ atom inside, namely, $\Delta V > 0$. The notation in Table 4 with square brackets means that the endohedral atom and its charge have been removed from the system, leaving the geometry unchanged. An analysis of Table 4 sustains the idea that the larger the charge in the endohedral atom, the larger the “pressure” or force pushing towards the cage. When we introduce a $\text{He}^{(2+)}$ ion inside $B_{12}\text{H}_{12}^{(2-)}$ or $CB_{11}\text{H}_{12}^{(-)}$, the steric hindrance is so large that the cage breaks apart, the $\text{He}^{(2+)}$ ion is ejected and finally the cages closes back to its original structure; we predict that these should happen for $P \gg 100$ GPa. For the second row cages $Al_{12}\text{H}_{12}^{(2-)}$ and $SiAl_{11}\text{H}_{12}^{(-)}$, we can see that these “pressures” are lower, by an order of magnitude! , and therefore even $\text{He}^{(2+)}$ can be introduced into the cage and remain inside when optimizing the geometry of the system. Here we should emphasize that the concept of pressure is merely approximate and in order to give insight on the physical effects of introducing atoms inside cages, with different charges and spins.

3.3 Charge and spin density

Now we turn to the computed charges and spin densities (only for $S = 1/2$ systems) for the endohedral systems included in this work. Table 5 reports the Mulliken charges on He and the cages for the complexes included in this work. As expected, since He is very hard to polarize (IP = 26.6 eV!) and only a proton H^+ can be attached to it forming a bond [15], the Mulliken charge is very small on He, if not negligible in all complexes, and therefore most of the charge redistribution and concentration remains around the cages and close to them.

Table 5. Mulliken charges of the systems included in this work. B3LYP/6-311+G(d,p) computations.

	$He^{(0)}@B_{12}H_{12}^{(2-)}$	$He^{(0)}@CB_{11}H_{12}^{(-)}$	$He^{(0)}@Al_{12}H_{12}^{(2-)}$	$He^{(0)}@SiAl_{11}H_{12}^{(-)}$
q(He)	+0.20	+0.21	+0.06	+0.06
q(Cage)	-2.20	-1.21	-2.06	-1.06
	$He^{(+)}@B_{12}H_{12}^{(2-)}$	$He^{(+)}@CB_{11}H_{12}^{(-)}$	$He^{(+)}@Al_{12}H_{12}^{(2-)}$	$He^{(+)}@SiAl_{11}H_{12}^{(-)}$
q(He)	+0.20	+0.21	+0.06	+0.06
q(Cage)	-1.20	-0.21	-1.06	-0.06
	$He^{(2+)}@B_{12}H_{12}^{(2-)}$	$He^{(2+)}@CB_{11}H_{12}^{(-)}$	$He^{(2+)}@Al_{12}H_{12}^{(2-)}$	$He^{(2+)}@SiAl_{11}H_{12}^{(-)}$
q(He)	---	---	+0.06	+0.06
q(Cage)	---	---	-0.06	+0.94

As regard to spin densities for the $S = 1/2$ systems, namely, $He^{(+)}@X_nZ_{12-n}H_{12}^{(n-2)}$, these are shown in Figure 3. As we can see from Figure 3, the unpaired electron remains mostly around and nearby the cage atoms for $He^{(+)}@B_{12}H_{12}^{(2-)}$, $He^{(+)}@CB_{11}H_{12}^{(-)}$, $He^{(+)}@Al_{12}H_{12}^{(2-)}$, and $He^{(+)}@SiAl_{11}H_{12}^{(-)}$, and therefore the $He^{(+)}$ ion inside the cage hardly contributes to the spin density of the whole system. As we will describe in the conclusions, the $He^{(q)}$ endohedral atom/ion basically acts as a – hardly at all – polarized *iron sphere* inside the cage that pushes its closed-shell electron density towards the cage electron density, hence increasing its volume.

Figure 2. Spin densities (0.003 au/Å³) in (a) He⁽⁺⁾@B₁₂H₁₂⁽²⁻⁾, (b) He⁽⁺⁾@CB₁₁H₁₂⁽⁻⁾, (c) He⁽⁺⁾@Al₁₂H₁₂⁽²⁻⁾, (d) He⁽⁺⁾@SiAl₁₁H₁₂⁽⁻⁾. UB3LYP/6-311+G(d,p) computations.

4. Conclusions

From the results of this work we can conclude that:

- 1) The $\text{He}^{(q)}@X_nZ_{12-n}H_{12}^{(n-2)}$ endohedral compounds – $X = \{C, Si\}$, $Z = \{B, Al\}$, $n = (0,1)$ - correspond to energy minima in the potential energy hypersurface, with the $\text{He}^{(q)}$ atom/ion inside the cage, with charges $q = (0, +1, +2)$, *except for* $\text{He}^{(2+)}@B_{12}H_{12}^{(2-)}$ and $\text{He}^{(2+)}@CB_{11}H_{12}^{(-)}$, where the $\text{He}^{(2+)}$ ion is ejected from the cage, with the cage closing back [16] to its original geometry. This prediction can also be explained in terms of electron transfer from the cage to the $\text{He}^{(q)}$ ion, given the much larger ionization potentials of He and $\text{He}^{(+)}$, as compared to the ionization potentials of the cages included in this work.
- 2) The $\text{He}^{(q)}@X_nZ_{12-n}H_{12}^{(n-2)}$ endohedral compounds have lower energy than the separated systems $\text{He}^{(q)} + X_nZ_{12-n}H_{12}^{(n-2)}$ when $q = +1$ and $q = +2$ for those complexes that do not collapse.
- 3) Functionals B3LYP and B97D – the latter including dispersion corrections – give similar results with the 6-311+G(d,p) basis set, as regards to the stability of the complex or ejection of the He atom from inside the cage. However, the energy profiles of $\text{He}^{(q)}$ moving inside the $B_{12}H_{12}^{(2-)}$ cage are remarkably different for $q = +2$, when comparing B3LYP and B97D functionals, given the fact that the latter includes dispersion corrections.
- 4) The volume of the icosahedral cages *always increases* with the presence of the $\text{He}^{(q)}$ atom/ion inside, and to a larger extent when increasing the charge q .
- 5) An estimate of the force exerted from the endohedral atom/ion $\text{He}^{(q)}$ towards the cage can be defined approximately as the negative derivative of the energy versus volume, giving an estimate of the “pressure”, which is an order of magnitude lower for the cages from the second row elements, thus explaining why these cages can support an $\text{He}^{(2+)}$ inside without opening the cage and ejecting the $\text{He}^{(2+)}$ ion.

6) The possibility of synthesizing endohedral compounds with icosahedral cages of the type $A^{(q)}@X_nZ_{12-n}H_{12}^{(n-2)}$, where $X = \{C, Si\}$, $Z = \{B, Al\}$, $n = (0, 1)$ opens the door towards inserting not only $He^{(q)}$ ions, but also general $A^{(q)}$ atoms/ions, with open s , p and d shells. The advantage of inserting atoms/ions inside (pure) icosahedral cages is that the s , p and d atomic levels do not split under an icosahedral field and therefore the potential combinations of different electronic states is very rich. We hope that these results could be useful in the design of quantum bits [17], from electronic structure computations.

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14. Strictly speaking, the pressure thus defined is used in solid-state chemistry with periodic computations. Here we suggest the use of this derivative in order to estimate the force exerted by the endohedral atom towards the cage, since the cages always increase the volume by insertion of $He(q)$ no matter the charge $q = (0, +1, +2)$.
15. Protonation of He leading to the HeH^+ system was first produced in the laboratory in 1925, see Hogness TR and Lunn EG (1925) Phys Rev 26:44-55
16. Strictly speaking, the charge on the ejected He is not $q = +2$, but around $q = +0.01$. Therefore the main charge redistributions take place in and around the cage. The He atom is merely a sort of “iron sphere” passing through the opening cage in the ejection process.
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