A Density Functional Study of Ce@C$_{82}$: Explanation of the Ce Preferential Bonding Site

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Ce has been found experimentally to be preferentially incorporated into the C$_{82}$ isomer of C_{2v} symmetry as have other lanthanoids in M@C$_{82}$ (M = La, Pr, Nd, etc.). We have investigated the underlying reason for this preference by calculating structural and electronic properties of Ce@C$_{82}$ using density functional theory. The ground-state structure of Ce@C$_{82}$ is found to have the cerium atom attached to the six-membered ring on the C_2 axis of the C$_{82}$–C_{2v} cage, and the encapsulated atom is found to perturb the carbon cage due to chemical bonding. We have found Ce to favor this C_{2v} chemisorption site in C$_{82}$ by 0.62 eV compared to other positions on the inside wall of the cage. The specific preference of the metal atom to this six-membered ring is explained through electronic structure analysis, which reveals strong hybridization between the *d* orbitals of cerium and the π orbitals of the cage that is particularly favorable for this chemisorption site. We propose that this symmetry dictated interaction between the cage and the lanthanide *d* orbital plays a crucial role when C$_{82}$ forms in the presence of Ce to produce Ce@C$_{82}$ and is also more generally applicable for the formation of other lanthanoid M@C$_{82}$ molecules. Our theoretical computations are the first to explain this well-established fact. Last, the vibrational spectrum of Ce@C$_{82}$ has been simulated and analyzed to gain insight into the metal-cage vibrations.

Introduction

Many of the rare earth elements have been encapsulated in fullerene (C$_{82}$) cages, and much attention is paid to the electronic and structural properties of endohedral metallofullerenes with f electrons such as Ce@C$_{82}$,[1–15] Pr@C$_{82}$,[16–17] Gd@C$_{82}$,[18–22] Tm@C$_{82}$,[23] etc. The advantage of isolating the metal atom from the surrounding environment has made endohedral fullerenes interesting for many fields.[24] One such application is in quantum information processing (QIP), where the isolated electron spin on the metal atom could be used as a nanosized qubit in quantum computers.[25] The optical transition occurring due to the crystal field effect of the cage on the unfilled f orbitals of the lanthanoids leads to the possibility of producing lasers out of metallofullerenes.[26] The conductivity of the solid metallofullerenes depends upon the electron donor capacity of the encapsulated lanthanoid, and hence they are a prospect for use as superconductors.[27] In addition, there are possible medical applications for doped fullerenes. They have, e.g., been suggested for use as encapsulated contrasting agents for magnetic resonance imaging (MRI), which means that effective but toxic agents such as lanthanoids can be used because they can be made nontoxic by incorporation into fullerenes.[28–29]

Cerium is one of the most reactive elements of the rare earth group, and the complex physics accompanying its single-occupied 4f band that is close to the Fermi level has baffled scientists for many decades. The properties of Ce@C$_{82}$ as a molecule and as a material depend largely on the endohedral atom and its 4f, 5d, and 6s electrons. It has been shown that cerium acts as an *n*-dopant and has an oxidation state of +3 in Ce@C$_{82}$.[3,4,7] When C$_{82}$ is formed around a Ce atom, two cage isomers are found, the C$_{82}$–C_{2v} isomer and a C$_{82}$–C_s isomers,

with the C_{2v} isomer being four times more abundant.[7] None of these isomers is the most stable for empty C$_{82}$.[30–32]

Rietveld refinement for the X-ray diffraction pattern suggests that cerium in the major isomer (Ce@C$_{82}$–C_{2v}) is situated off-center by around 2 Å, possibly on the C_2 axis retaining the symmetry of the cage.[7] Extended X-ray absorption fine structure[7] (EXAFS), X-ray diffraction pattern,[8] and nuclear magnetic resonance[9] (NMR) studies for Ce@C$_{82}$ have also suggested that the cerium ion resides on or around the C_2 axis of the C$_{82}$–C_{2v} cage. Computational reports are available for a wide variety of metallofullerenes,[33–48] while only a few theoretical studies have been performed for Ce@C$_{82}$.[1,43] Nagase et al. have considered Ce at positions on the symmetry axis of C$_{82}$–C_2 and found that it prefers to bind to the six-membered ring on the symmetry axis over bonding in C_2 symmetry to a C=C double bond, but no off-axis positions were considered.[1] It should be noted that one of the C$_{82}$–C_2 isomers was used in this study, not the C$_{82}$–C_{2v} isomer.[7] Further density functional calculations have been reported for the Ce@C$_{82}$ anion, but an in-depth study of other possible positions inside the cage have not been carried out, which is crucial to confirm the ground state structure.[11] In this paper, we have made a comprehensive theoretical investigation of Ce@C$_{82}$ to study its structural and electronic properties using density functional theory (DFT). Particular emphasis has been paid to explore the experimental claim that cerium bonds inside the C$_{82}$–C_{2v} cage in such a way that the C_{2v} symmetry is preserved,[6–10] i.e., possible bonding at off-center locations within the cage has been scrutinized exhaustively. We have verified that Ce@C$_{82}$ is most stable in C_{2v} symmetry and that Ce forms rather strong chemical bonds to the cage. The reason for such localized chemisorption has also been explored, and its implications on the formation of the less stable C$_{82}$–C_{2v} cage around Ce rather than the most stable C$_{82}$–C_2 isomer is discussed.[30–32] Further, we have also simulated the vibrational spectrum of the molecule.

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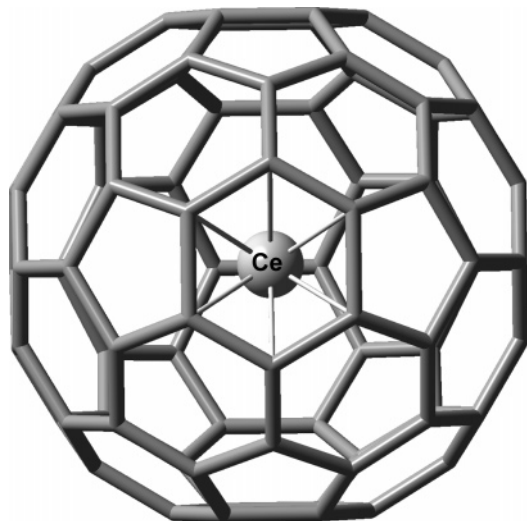
Figure 1. DFT-optimized structure of Ce@C$_{82}$. The C_2 axis is perpendicular to the plane of the paper and has a hexagon at one end and a double bond at the other end.

Computational Methods

We have used unrestricted DFT with the generalized gradient approximation (GGA) exchange-correlation functional PBE[50] employing the RI approximation[51] and a dense grid (m5) as implemented in Turbomole 5.9.[52,53] A polarized valence triple-ζ basis set (TZVP) was used for carbon.[54] For cerium, the ECP-28-MWB effective core potential and the accompanying 30 valence electron basis set has been used.[55] Calculations at the same level have been applied to the C$_{82}$ and C$_{60}$ cages and also for La@C$_{82}$ and Ce@C$_{60}$. Calculations employing the polarized valence double-ζ (DZVP) basis set for carbon[56] and the ECP-46-MWB effective core potential and 12 valence electron basis set for Ce[57] have also been carried out.

Results and Discussions

We have computed Ce incarcerated in the major C$_{82}$–C$_{2v}$ isomer, and we have found that Ce@C$_{82}$ is most stable as a triplet. The singlet is 90 meV higher in energy at the ground-state binding site. In this study, geometry optimization starting from several initial geometries, obtained by placing Ce at each symmetry inequivalent six-membered ring of the C$_{82}$–C$_{2v}$ cage, has been carried out. Irrespective of the initial position, the metal atom preferred one specific chemisorption site on the C_2-axis, where it binds to the six-membered ring on the symmetric axis (see Figure 1), except for a few cases where two other local minima were found for which Ce binds to four carbon atoms rather than to six as observed in the global minimum, and they are both considerably higher in energy (0.62 and 1.10 eV). Such a C_{2v} symmetric minimum has also been reported for La@C$_{82}$ using DFT.[37–41] Rather surprisingly we could not find even local-minima binding at the center of other six-membered rings of the cage. Instead the cerium atom, when placed elsewhere on the cage wall, migrates during the geometry optimization toward the six-membered ring on the C_2 axis. In the equilibrium structure, the distances between cerium and the carbons of the six-membered ring are 2.534 Å (4 bonds) and 2.537 Å (2 bonds), which compares well with the EXAFS value of 2.473 Å for the nearest carbon neighbor.[7] The carbon–carbon conjugated bonds in the empty C$_{82}$–C$_{2v}$ cage range from 1.429 to 1.430 Å, which also compares well with MEM/Rietveld analysis reported values of 1.36–1.47 Å for the stable C$_{82}$–C$_2$ cage.[31] On binding, cerium locally distort the cage which can be seen

from the elongation of the C–C bonds involving the carbons bound to Ce by 0.022–0.042 Å compared to the undoped cage. To elucidate the bonding nature of cerium inside fullerenes, calculations were also carried out for Ce@C$_{60}$, which reveal that cerium prefers 6-fold coordination also in C$_{60}$. The bond lengths of cerium to the nearest carbons are in the range 2.466–2.477 Å. The binding energy calculated for Ce@C$_{60}$ is 5.10 eV, while for Ce@C$_{82}$ it is 6.69 eV indicating that Ce binds more strongly within the C$_{82}$–C$_{2v}$ cage than inside C$_{60}$.

The position of the metal atom inside the cage decides the stability, electronic properties, and also the entire symmetry of the molecule. We have considered factors such as electrostatic interaction, symmetry, and energies of the orbitals available for interaction to find the reason for this strong chemisorption of the cerium atom to one particular ring of the cage. Two explanations have been put forward previously, concerning the electrostatic potential of the inside of the cage,[37,44] and the localization of the lowest-unoccupied molecular orbital (LUMO) to the binding site.[49] We have found no evidence of the confinement of the unoccupied orbitals of C$_{82}$–C$_{2v}$ to the six-membered ring on the symmetry axis as suggested by Andreoni et al.,[49] and the difference of 0.62–1.10 eV cannot be explained entirely by electrostatic interactions. We put forward an alternative explanation for the preferential binding site, which is complementary to the electrostatic potential. Looking at the Mulliken charges of the empty cage shows that the six-membered ring on the C_2 axis has a very distinct charge pattern with strong positive and negative charges and inspection of the C$_{82}$ MOs (see Figure 2c) reveal that there are a multitude of cage orbitals that have the correct symmetry making it ideal for interacting with the cerium d orbitals. We have compared this six-membered ring to the other 30 six-membered rings of the C$_{82}$–C$_{2v}$ cage, of which there are 10 symmetry-inequivalent ones. There are three different types of six-membered rings (see Figure 2a), and the one preferred by Ce is of type 1. It has the two most positively charged carbon atoms (top and bottom carbon in Figure 2b) and four distinctly negative carbon atoms (shared with the surrounding five-membered rings). No other six-membered ring has such a pronounced charge pattern with such gerade symmetry—not even one of the other five type 1 six-membered rings—which is so perfectly suited for hybridization with the Ce d orbital. This symmetry argument of overlap with Ce d is supported by the observation of Ce d character in energy levels 2–7 eV below the highest-occupied molecular orbital (HOMO) for Ce@C$_{82}$, which has been investigated through Mulliken population analysis of the eigenvalue spectrum.[58] The energy levels with cerium contribution show considerable shift and splitting of Ce f, d, and s compared to the free atom but show the strongest hybridization for the d orbital of the metal atom and the π orbitals of the cage. Such hybridization has been observed for other M@C$_{82}$ (M = Sc, Y, La, Ce, Gd) as well, which all have the C$_{82}$–C$_{2v}$ cage as the most abundant C$_{82}$ isomer.[1,21,34] Since no other ring in the C$_{82}$–C$_{2v}$ cage has this charge pattern, the metal atom moves to this site in our geometry optimizations to bond through its d orbital. We conclude that the local symmetry, for maximization of the Ce d interaction with the cage, and the partial charges on the carbon atoms, which facilitate charge transfer and strengthens the electrostatic interaction, is the reason for preferential chemisorption. It is reasonable to assume that a six-membered ring with the surrounding type 1 structure (see Figure 2) is initially formed when fullerenes are grown in the presence of Ce[2] and that this local symmetry dictates what C$_{82}$ isomer is grown, which is also seen for other lanthanoids. This effect also

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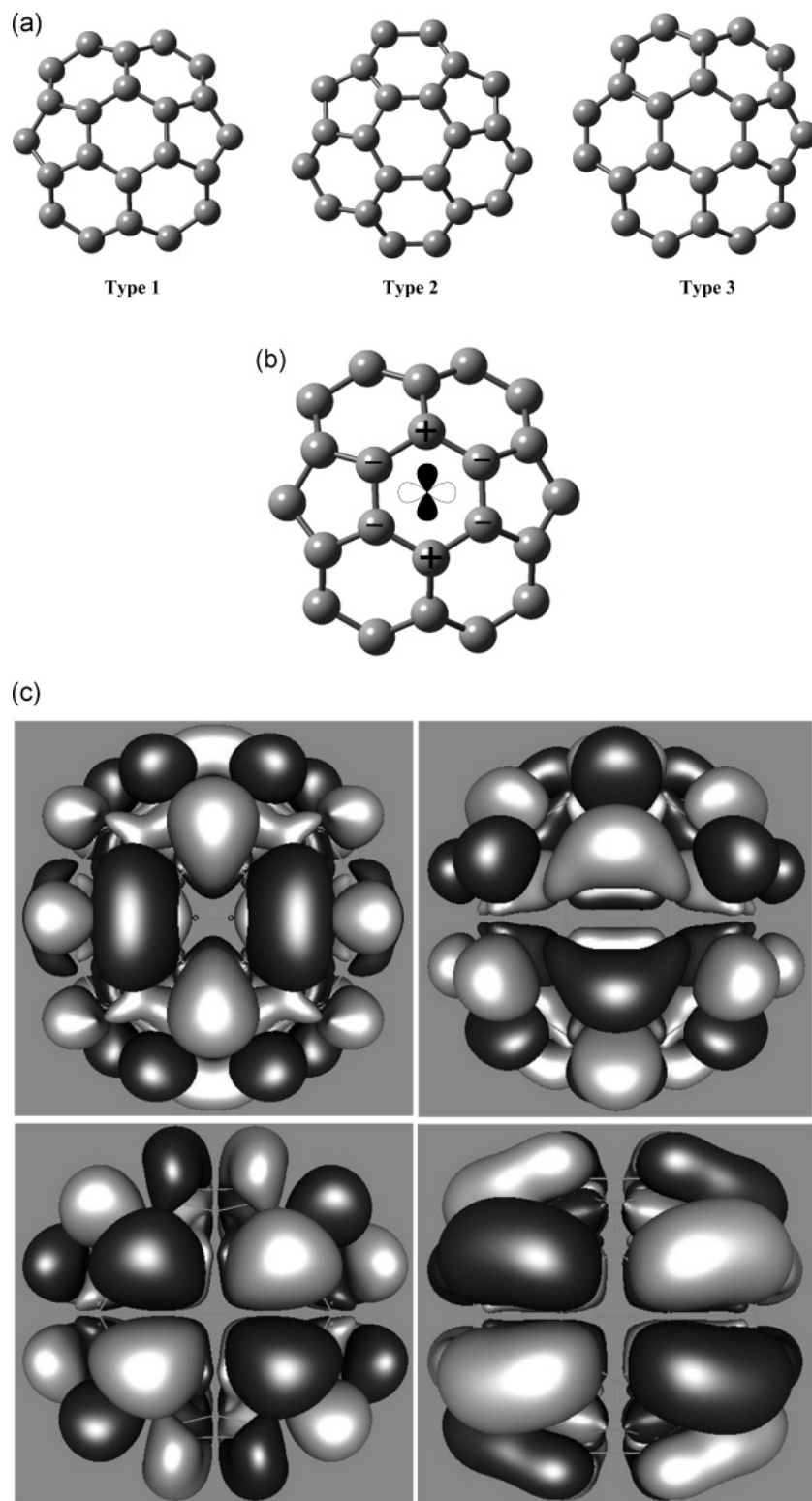
Figure 2. (a) The three types of six-membered rings of the C$_{82}$−C$_{2v}$ cage: there are six of type 1, four of type 2, and one of type 3. (b) Observed charge pattern on the type 1 six-membered ring that is preferred by the Ce atom. (c) Representative molecular orbitals of C$_{82}$−C$_{2v}$ with the symmetric features that make them suitable for bonding with Ce d orbitals.

explains the stronger Ce bonding in C$_{82}$ compared to C$_{60}$ as mentioned above, since the six-membered rings of C$_{60}$ has local C$_{3v}$ symmetry and hence does not comply as well with d hybridization with the metal atom. Further, the HOMO of Ce@C$_{82}$ is dominated by Ce f, showing that cerium inside the cage retains its f character, which in turn affects the local magnetic field of its neighboring carbons explaining the

temperature-dependent shifts in NMR for Ce@C$_{82}$, which is not observed for La@C$_{82}$.[9]

The definition of Mulliken charges has its limitations but, when used correctly, can still give useful information about partial atomic charges. The computed Mulliken charges show that Ce in Ce@C$_{82}$ has donated 0.42 electrons to the cage, which corresponds to the oxidation state of +3. Mulliken charges are

Vibrational frequency [cm⁻¹]
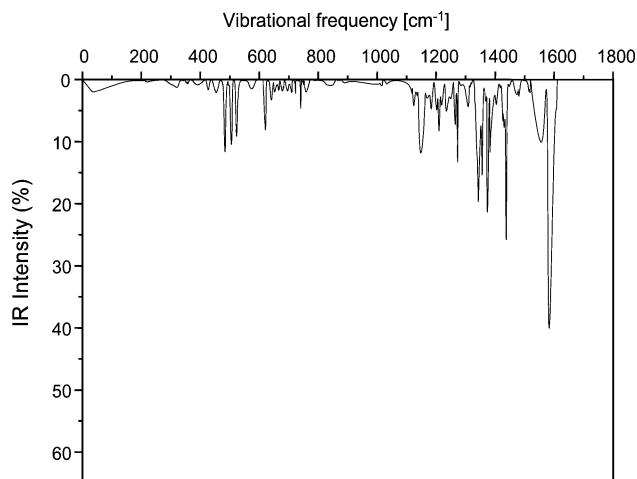
Figure 3. Calculated vibrational spectrum of Ce@C$_{82}$. IR signal intensity plotted as a function of vibrational frequency.

(a) **(b)**
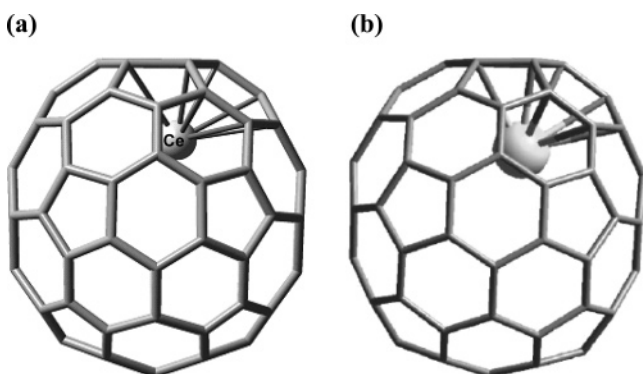
Figure 4. Comparison of spurious minima for (a) Ce@C$_{82}$ and (b) La@C$_{82}$ (copied with permission from ref 49). This C_s symmetric structure results when minimum number of active electrons is used for La and Ce.

not as pronounced as oxidation numbers, since the electrons are not simply donated to the cage (and subsequently delocalized over its entire surface) but shared in chemical bonds with the cage (and hence localized), i.e., they are therefore a better measure of charge transfer. These shared electrons will then follow any dynamical motion of the metal atom within the cage. It is a common, but faulty, hypothesis that endohedral metal atoms donate a number of electrons equal to their oxidation number to the fullerene LUMO and that the resulting zwitterion can be described by adding this number of electrons to the empty cage, without specific inclusion of the metal atom.[37,44,59] Such an approximation not only overestimates the charge transfer but ignores the important (localized) hybridization between the metal atom and the cage. A more accurate picture of the charge transfer can be made by looking at the atomic orbital contributions to the Mulliken charges. This shows that cerium donates 0.81 each of its 6s α and β electrons to the cage but only a negligible amount of its 4f electron (0.13). This is compensated by considerable back donation into 5d (−0.88) and also into 6p (−0.45). This p back donation is too large to be an artifact arising from the use of p polarization functions in atom-centered basis sets and thus constitutes a real effect that should be investigated experimentally.

The vibrational spectrum has been calculated for the ground state of Ce@C$_{82}$ and has confirmed that it is a true minimum (see Figure 3). We find absorption bands between 32 and 1609 cm⁻¹ for Ce@C$_{82}$–C_{2v}, which compare well with the DFT study of La@C$_{82}$ of K. Kobayashi et al. (27−1661 cm⁻¹).[60] We have

found three vibrations[5,43] below 200 cm⁻¹, and they involve the movement of the cerium atom. Indeed the empty cage has vibrations between 205 and 1617 cm⁻¹. This also agrees well with what has been reported for La@C$_{82}$.[5,60]

We have in addition made calculations of Ce@C$_{82}$ using the DZVP basis set for carbon and the ECP-46-MWB ECP with accompanying DZVP basis set for cerium (see the Computational Methods section). These computations also resulted in preferential cerium bonding to the six-membered ring on the C_2 axis of C_{82} but not in the center of the ring, resulting in a C_s symmetric structure. At this level of theory the C_s symmetric ground state is 29 meV lower in energy than the C_{2v} structure and the C_s symmetric structure resembles the structure reported for La@C$_{82}$ (see Figure 4).[49] La@C$_{82}$ has since been found to be most stable in C_{2v} symmetry.[37−41] These spurious C_s minima result from the use of inaccurate ECPs and the inclusion of too few valence electrons for lanthanum and cerium.

Conclusion

A complete DFT study of Ce@C$_{82}$ inside the C_{82}−C_{2v} isomer has been carried out, and our results show a C_{2v} symmetric Ce@C$_{82}$ ground state. Ce is found to bond to the six-membered ring on the symmetry axis. The preferential bonding is explained by the symmetry compatibility of this six-membered ring with the Ce d orbital. Such symmetry preference is argued to play an important role during the growth of Ce@C$_{82}$ and other endohedral lanthanides and might be the reason the C_{82}−C_{2v} cage is so abundant for many metallofullerenes. Electronic structure analysis reveals that the charge transferred to the cage by Ce is not delocalized but remains local in the chemical bonds between Ce and the carbon cage and on neighboring carbon atoms. Cerium in Ce@C$_{82}$ retains its f character and the simulated vibrational spectrum of Ce@C$_{82}$ describes low-energy modes, which are due to the metal atom vibrations.

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