

La₃N@C₉₂: An endohedral metallofullerene governed by kinetic factors?

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Supporting Information Placeholder

ABSTRACT: Different structures have been proposed so far for the C₉₂ isomer that encapsulates M₃N (M = La, Ce, Pr). We here show that the electrochemical properties of the predicted thermodynamic most abundant isomer for La₃N@C₉₂ do not agree with experiment and propose other alternatives before its X-ray structure could be solved.

INTRODUCTION

Fullerenes that contain metal atoms or metal clusters, the so-called endohedral metallofullerenes (EMFs),^{1,2} have attracted the interest of the scientific community in the last years due to their new properties that render them suitable candidates for applications in materials science and medicine.³⁻⁵ Since the discovery of Sc₃N@C₈₀ in 1999,⁶ a large number of nitride EMFs have been isolated and characterized, with essentially group 3 or lanthanide metals and cages that range from 68 to 96 atoms.⁷⁻¹² Their electronic structure can be easily understood considering that there is a formal transfer of six electrons from the cluster to the carbon cage (ionic model), i.e. (M₃N)⁶⁺@(C_{2n})⁶⁻.¹³ Based on this idea, in 2005 Poblet and co-workers formulated a simple orbital rule to identify the most appropriate hosting cages in nitride EMFs; these cages must have three low-lying unoccupied molecular orbitals and a sizeable energy gap between the LUMO+3 and the LUMO+2.^{14,15} Later, Popov and Dunsch reported an exhaustive computational study showing that the lowest-energy hexaanionic cages matched the characterized nitride EMFs, whenever the cluster fits appropriately in the cage.¹⁶ In 2010, we gave physical support to the orbital rule and showed that the structures with the largest separation between pentagons, the faces that mostly localize the negative charge, are the most suitable to encapsulate metal clusters, i.e. the so-called maximum pentagon separation rule.^{17,18} Recently, Solà and co-workers, following our work proposed that aromaticity also plays a role in the stability of EMFs.¹⁹

No crystallographic studies have been performed so far for nitride EMFs with cages larger than 88 carbon

atoms. Based on DFT computations and electrochemical experiments, isomers *T*(86)-C₉₂ and *D*₂(186)-C₉₆ were proposed to be the cages in M₃N@C₉₂ and M₃N@C₉₆ (M = Pr, Ce and La), respectively.^{15,16,20} Interestingly, isomer *D*₃(85)-C₉₂ is the lowest-energy hexaanion and Y₃N@C₉₂ EMF, but the computed HOMO-LUMO and electrochemical (EC) gaps do not match with the rather large EC value found in experiments (1.80 V).²⁰ A more recent computational work by Zhao and co-workers showed that IPR La₃N@C₂(36)-C₉₂ is the lowest-energy and the most abundant thermodynamic La₃N@C₉₂ isomer at high temperatures.²¹ The shape of the C₂(36)-C₉₂ cage allows a much better fitting of the large La₃N cluster with less strain and larger C··La distances than in other cages. However, as observed for some fullerenes, thermodynamic and kinetic stabilities are sometimes not correlated.²²⁻²⁴

We herein show that the computed electrochemical properties of the predicted thermodynamic most abundant La₃N@C₂(36)-C₉₂ isomer are not compatible with the experiments run so far and propose, after a thorough study within more than 17000 C₉₂ isomers, several cages that might encapsulate the large La₃N.

COMPUTATIONAL DETAILS

We have computed the hexaanions for all the IPR and non-IPR isomers with three or less adjacent pentagon pairs (APP) using semiempirical AM1 calculations with the Gaussian09 code.²⁵ Single-point energy calculations for all of these optimized geometries have been performed using density functional theory (DFT) methodology with the ADF 2012 program.^{26,27} The exchange-correlation functionals of Becke and Perdew (BP86) were used.^{28,29} Relativistic corrections were included by means of the zero-order regular approximation. Triple- ζ + polarization basis sets (TZP) were used to describe the valence electrons of the C, N and La. Frozen cores that consisted of (1) the 1s shell for C and N; (2) up to 4d shell for La, were described by means of single Slater functions.

The selected structures of hexaanionic isomers, as well as those of $\text{La}_3\text{N@C}_{92}$, were optimized at the same level of theory (BP86/TZP). In addition, the Grimme Dispersion D3 method was considered for the EMFs.³⁰

Selected structures of $\text{La}_3\text{N@C}_{92}$ were also calculated with (i) Gaussian09 using the B3LYP and M06 functionals, and the LANL2DZ for La atom and 6-31G(d) for C and N atoms as basis sets,^{31,32} (ii) Turbomole at B3LYP/def2-TZVP level.³³

IPR and non-IPR cages were identified by their symmetry and by the number assigned according to the spiral algorithm. The truncated numbering system that counts only IPR isomers is used for IPR cages.³⁴

RESULTS AND DISCUSSION

Given the formal six-electron transfer in nitride EMFs, the first step was to compute the hexaanions for all the IPR (86) and non-IPR isomers with up to three adjacent pentagon pairs (APP): 840 APP1, 5088 APP2 and 11006 APP3. Figure 1 shows that, even for the highly charged C_{92} cages, the pentagon adjacency penalty rule also applies; the lowest-energy IPR isomers are, on average, by around 20 $\text{kcal}\cdot\text{mol}^{-1}$, more stable than the lowest-energy APP1 cages, and so on and so forth. As already known, cage $D_3(85)$ is the one with the lowest energy, followed by $C_1(66)$ at 4.8 $\text{kcal}\cdot\text{mol}^{-1}$ and $C_2(65)$ and $T(86)$ at around 6.5 $\text{kcal}\cdot\text{mol}^{-1}$ (see Table 1). Cage $C_2(36)$ is 12 $\text{kcal}\cdot\text{mol}^{-1}$ higher in energy. When inserted the La_3N cluster, significant changes in the relative stabilities of the isomers take place. $\text{La}_3\text{N@C}_2(36)\text{-C}_{92}$, which shows now the lowest energy as pointed out by Zhao and co-workers,²¹ is stabilized by around 25 and 30 $\text{kcal}\cdot\text{mol}^{-1}$ with respect to $\text{La}_3\text{N@D}_3(85)\text{-C}_{92}$ and $\text{La}_3\text{N@T}(86)\text{-C}_{92}$, respectively. The large La_3N guest is much better accommodated inside the roomier interior of cage $C_2(36)$ than in other cages. The La-N and La...C distances confirm the much less strained situation in $\text{La}_3\text{N@C}_2(36)\text{-C}_{92}$ than in other isomers. For example, the average distances for cages 36, 85 and 86, are (La-N) 2.26, 2.20 and 2.18 Å, and (La...C) 2.68, 2.62 and 2.58, respectively. Therefore, the different stability trends observed for the EMFs compared to hexaanions are consequence of the large size of the La_3N cluster, i.e. *size matters*.

However, the predicted electrochemical properties of the lowest-energy $\text{La}_3\text{N@C}_2(36)\text{-C}_{92}$ isomer do not agree with the experimental cyclic voltammograms. The computed EC gap at BP86/TZP level is 0.900 V, in line with the small HOMO-LUMO gap (0.549 eV) and very far from the experiment (1.80 V). The present computational settings have been shown to predict rather well, with maximum errors within 150–200 mV, the EC gaps in the family of nitride EMFs as well as in other clusterfullerenes.^{35–37} Isomer $\text{La}_3\text{N@D}_3(85)\text{-C}_{92}$ had been also discarded previously by this same reason.²⁰

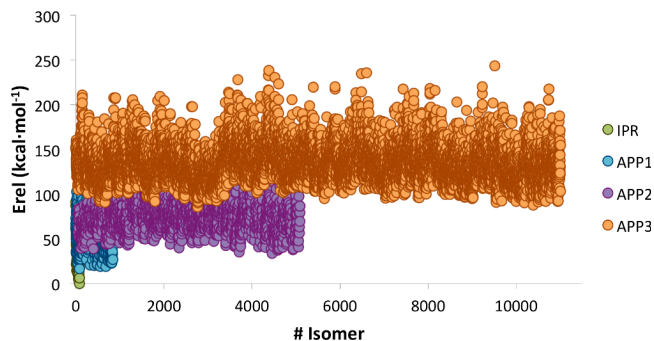


Figure 1. Relative energies (in $\text{kcal}\cdot\text{mol}^{-1}$) at BP86/TZP level of the 86 IPR, 840 APP1, 5088 APP2 and 11006 APP3 isomers of C_{92} .

We here looked among 17020 isomers (IPR and non-IPR cages up to APP3) to propose candidates that show reasonable energies and EC gaps compatible with experiments. We have used several filters to make a first selection of candidates that were then computed as nitride EMFs. Since there is a correlation between the HOMO-LUMO and EC gaps, we have chosen those hexaanions with HOMO-LUMO gaps larger than 1.1 eV (filter #1) and with not very large relative energies (up to 70 $\text{kcal}\cdot\text{mol}^{-1}$, filter #2). From a geometrical point of view, the non-IPR candidates (APP2 and APP3) must satisfy a proper distribution of the pentalene motifs (filter #3) so as the La_3N cluster can fit adequately without very large distortions. For APP2 cages, the angle between the centroid of one APP, the mass centre of the cage, and the centroid of the other APP, $\theta(\text{APP-MC-APP})$, should not show values very different from 120 degrees; moreover, the two distances between the mass center of the cage and the centroids of the APPs, $d(\text{MC-APP})$, should be similar (see Figure 2). For APP3 cages, the three APP-MC-APP angles should show values around 120 degrees and the MC-APP distances be rather similar (some of the cage candidates according to filter #3 are displayed in Figure 3). According to these three filters, we have finally computed more than 30 $\text{La}_3\text{N@C}_{92}$ isomers (see Table 1). Although in some cases the EMF is considerably stabilized in comparison with the hexaanion (as for example APP1: #126246; APP2: #124337, #103054; APP3: #103648, #125080), the relative energies are still too high compared to $\text{La}_3\text{N@C}_2(36)\text{-C}_{92}$.

We have also evaluated the thermodynamic stability up to high temperatures trying to mimic the conditions at which fullerenes are formed. We computed the molar fractions of the isomers in Table 1 up to 5000 K within the rigid rotor and harmonic approximation. Since the La_3N cluster is large and most of the cages that we consider are of non-IPR type, where the metal atoms interact with the pentalene moieties and the cluster is rather fixed, we consider that the conditions to apply the free-encapsulating model (FEM) by Slanina are not fulfilled.^{38,39} So, the FEM approximation is not used here.

Table 1. Relative energies (in kcal·mol⁻¹) at BP86/TZP level for the lowest-energy C₉₂⁶⁻ and La₃N@C₉₂ isomers.

Isomers ^a	APP	C ₉₂ ⁶⁻	La ₃ N@C ₉₂
126359 (36)	0	12.1	0.0
126388 (65)	0	6.7	8.4
126367 (44)	0	12.2	9.3
103625	1	16.8	12.6
125327	1	19.0	13.5
126389 (66)	0	4.8	13.6
126408 (85)	0	0.0	13.7
126246	1	23.9	15.6
116584	1	20.6	17.2
124451	1	22.4	18.1
124337	2	33.9	21.9
126409 (86)	0	6.4	25.3
99602	2	39.0	37.1
98617	2	39.6	38.8
110233	1	45.7	38.9
103054	2	53.5	40.7
103648	3	58.0	42.4
106637	2	50.1	42.7
101210	3	54.2	44.5
119390	2	56.7	44.5
103627	3	48.2	47.8
125080	3	64.9	48.4
103622	3	60.0	49.2
104356	3	61.5	49.8
101437	2	49.4	50.5
124567	2	55.5	52.2
98649	2	47.2	53.1
110493	3	70.1	54.0
98640	2	53.9	55.7
116937	3	68.7	57.4
98965	3	67.3	62.2
117031	3	74.3	62.2
100000	2	61.7	66.4

^a The number of APP and the number according the spiral algorithm by Fowler and Manolopoulos is also given (the truncated numbering for the IPR isomers is in parenthesis).³⁴

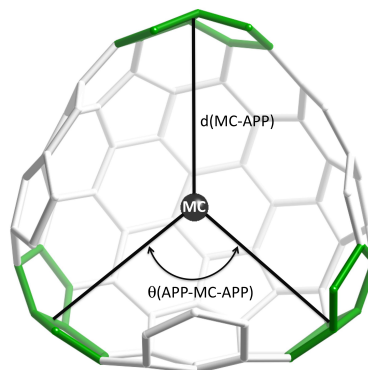


Figure 2. Representation of one non-IPR cage with three APPs (in green) where (i) the distance between the mass center (MC) of the cage and the centroid of one APP, $d(\text{MC-APP})$; and (ii) the angle between the centroid of one APP, the MC of the cage, and the centroid of another APP, $\theta(\text{APP-MC-APP})$, are highlighted (filter #3, see text).

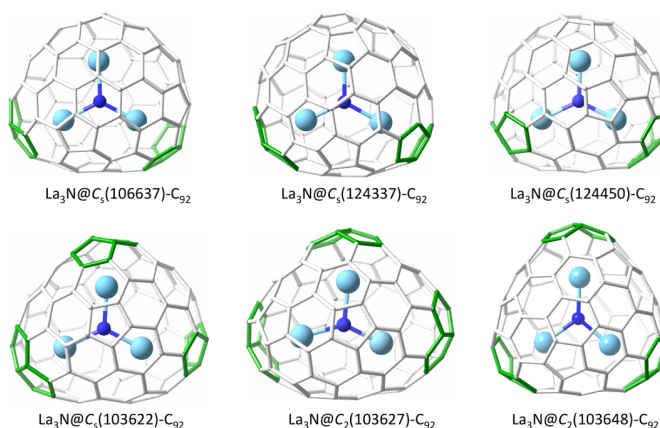


Figure 3. Cage candidates selected according to geometry considerations (filter #3, see text).

La₃N@C₂(36)-C₉₂ remains as the most abundant isomer for the whole range of temperatures (Figure 4), as found by Zhao, followed by isomer La₃N@C₂(44)-C₉₂, which also shows a rather low HOMO-LUMO gap. If we plot only those isomers with a HOMO-LUMO gap larger than 1.1 eV (at BP86/TZP level), Figure 5, we find as most abundant isomers, with molar fractions smaller than 5% at 2500 K, the IPR isomer La₃N@T(86)-C₉₂ and the non-IPR APP1 isomers La₃N@C₂(116584)-C₉₂, La₃N@C_s(124451)-C₉₂ and La₃N@C_s(103625)-C₉₂. La₃N@C_s(124337)-C₉₂ and La₃N@C₂(103648)-C₉₂, with molar fractions smaller than 2%, are the most abundant APP2 and APP3 isomers, respectively (see Figure 6). The predicted EC gaps for the latter three APP1 isomers, around 1.51 V (see Table 2), deviate somewhat more from the experiment (1.80 V) than usual values computed with the present settings (up to 200 mV). The computed EC gaps for the APP2 and APP3 isomers, 1.59 and 1.64, however, compare better with the experimental gap. Thus, besides the IPR cage T(86)-C₉₂, with the largest EC gap, the non-

IPR APP2 $C_5(124337)-C_{92}$ and APP3 $C_2(103648)-C_{92}$ would be likely candidates to encapsulate La_3N .

We have also considered some non-classical heptagon-containing isomers derived from $La_3N@C_2(36)-C_{92}$ and $La_3N@T(86)-C_{92}$, with structures which are similar to the recently characterized $LaSc_2N@C_5(hept)-C_{80}$.⁴⁰ We have found that they show rather high energies (> 45 kcal mol⁻¹) compared to $La_3N@C_2(36)-C_{92}$ and HOMO-LUMO gaps smaller than 0.8 eV, which make us discard them as candidates for $La_3N@C_{92}$ (see SI).

Finally, we confirmed that the main results of this work do not depend on the computational settings. Other density functionals (B3LYP and M06)^{31,32} provide analogous predictions for the relative stabilities of the lowest-energy as well as for the most abundant isomers at higher temperatures (see Table S4).

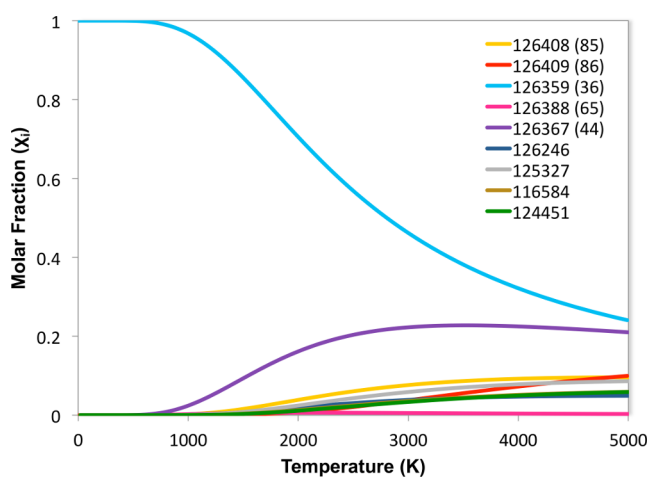


Figure 4. Representation of the molar fractions as a function of temperature for the predicted most abundant $La_3N@C_{92}$ isomers in Table 1.

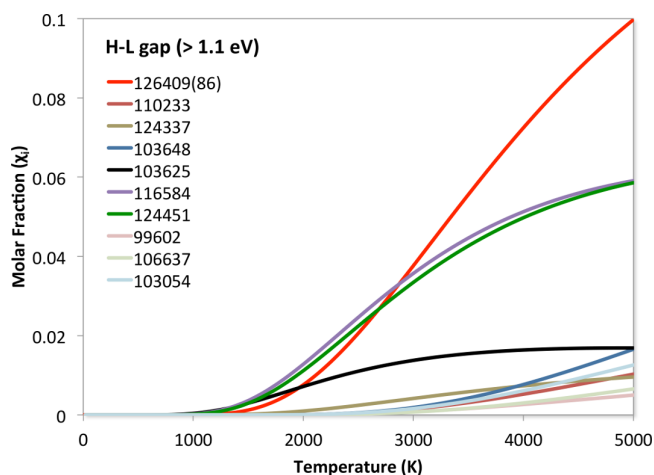


Figure 5. Representation of the molar fractions with respect to temperature for the most abundant $La_3N@C_{92}$ isomers with a HOMO-LUMO gap larger than 1.1 eV.

Table 2. Computed oxidation and reduction potentials, EC gaps and HOMO-LUMO gaps for some candidates of $La_3N@C_{92}$.^a

Isomer	APP	E_{ox}	E_{red}	EC	H-L gap
126359 (36)	0	-0.293	-1.194	0.901	0.547
126367 (44)	0	-0.221	-1.298	1.077	0.731
126388 (65)	0	-0.133	-1.466	1.333	1.001
126408 (85)	0	-0.259	-1.335	1.076	0.709
126409 (86)	0	0.143	-1.551	1.694	1.330
103625	1	-0.011	-1.529	1.518	1.147
116584	1	-0.060	-1.584	1.524	1.161
124451	1	0.009	-1.496	1.505	1.129
103054	2	-0.080	-1.585	1.505	1.171
124337	2	-0.003	-1.593	1.590	1.247
103648	3	-0.034	-1.673	1.638	1.285

^a Potentials and EC gaps in V and HOMO-LUMO gaps in eV.

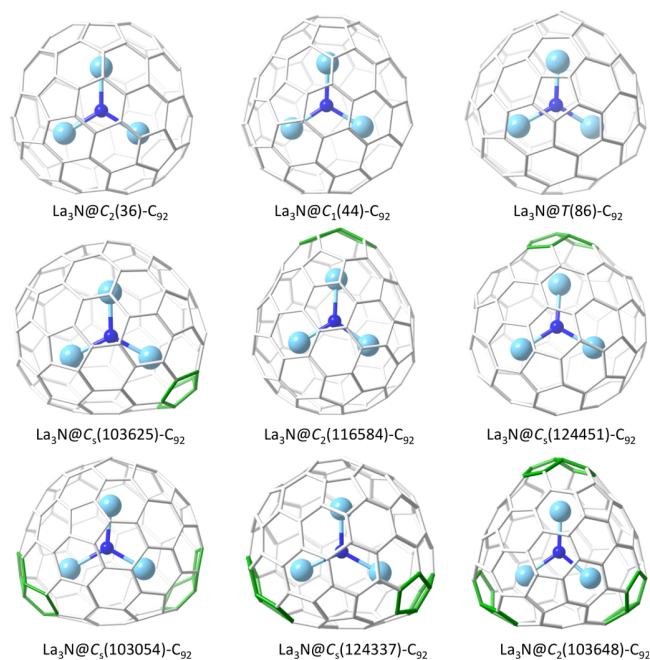


Figure 6. Optimized geometries for possible candidates of $La_3N@C_{92}$.

CONCLUSIONS

After an exhaustive exploration among a huge number of C_{92} isomers, the predicted most abundant cages under thermodynamic control do not show electrochemical (EC) gaps similar to the experimental values for $La_3N@C_{92}$. We here propose cages IPR $T(86)$ and non-IPR APP2 $C_5(124337)$ and APP3 $C_2(103648)$, as possible candidates to encapsulate large lanthanide nitrides

according to their computed large EC gaps, structures that should be ultimately confirmed by X-ray crystallography determination. Hence, formation of $\text{La}_3\text{N@C}_{92}$ might be governed by kinetic factors, as recently proposed for $\text{LaSc}_2\text{N@C}_s(\text{hept})\text{-C}_{80}$,⁴⁰ in contrast to the general behaviour of the other EMFs known so far. We do not discard, however, that the thermodynamic isomer could be detected in future experiments.

ASSOCIATED CONTENT

Supporting Information. Relative energies, free energies, and molar fractions for the full list of computed $\text{La}_3\text{N@C}_{92}$ isomers. The Supporting Information is available free of charge on the ACS Publications website.

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