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Metallofullerenes

Trimetallic Nitride Endohedral Fullerenes: Experimental and Theoretical Evidence for the $M_3N^{6+}@C_{2n}^{6-}$ model[**]

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The discovery of $Sc_3N@C_{80}$ by Dorn and co-workers in 1999 represented the beginning of a new field in the chemistry of endohedral fullerenes.[1] In less than a decade, the family of the metallic nitride endohedral fullerenes (MNEFs) was considerably expanded with the encapsulation of a new Group III metal (Y),[2] lanthanides (Er, Ho, Lu, Tm, Gd, Dy, Tb, Nd, Pr, and Ce)[2–10] and mixed-metal clusters.[11] Upon increasing the size of the encapsulated metal (from Sc to Gd), the yield of production of MNEFs usually decreases and a distribution of metallofullerenes is obtained, with cages ranging from C_{68} to C_{88}.[9] The C_{80} cage, however, remains the most abundant product. Recently, Echegoyen and co-workers reported the preparation of clusterfullerenes, such as $Nd_3N@C_{2n}$ ($40 \leq n \leq 49$), and observed the predominant formation of the larger cage C_{88}.[9]

It has been assumed that there is a formal transfer of six electrons from the encapulated guest to the fullerene cage. Poblet and co-workers associated the exceptional stability of $C_{80}(I_h)$ to the large HOMO–LUMO gap of the MNEF after encapsulation of the metallic nitride (MN) cluster by the carbon cage.[12] Based on the electron-transfer model, they not only rationalized the occurrence of the most abundant species that have been experimentally characterized, they were also able to predict the cage isomer for systems that have yet to be prepared.[13,14] Popov and Dunsch performed a systematic and detailed study for the most stable isomers of $M_3N@C_{2n}$ (M = Sc, Y; $34 \leq n \leq 49$). In most of the cases, the cage structures predicted by both groups coincide.[15]

Herein we report the synthesis, electrochemistry, and theoretical characterization of the large MNEFs $M_3N@C_{2n}$ family (M = La, Ce, and Pr; $n = 46$ and 48). The combined electrochemical and computational analyses of the series from $M_3N@C_{80}$ to $M_3N@C_{96}$ verify the ionic model $M_3N^{6+}@C_{2n}^{6-}$ for MNEFs.

$M_3N@C_{2n}$ (M = La, Ce, and Pr) metallofullerenes were synthesized in a conventional Krätschmer–Huffman arc reactor using a reactive gas atmosphere.[2] Graphite rods were packed with the corresponding metal oxide and graphite powder and then burned in a helium/ammonia atmosphere. The larger MNEFs were purified, isolated, and identified using HPLC, mass spectrometry, and energy dispersive spectroscopy (EDS) (see Supporting Information). Electrochemical studies were conducted in a 0.05 M solution of NBu_4PF_6 in *o*-dichlorobenzene (*o*-DCB). A 2 mm diameter glassy carbon disk was used as the working electrode. Ferrocene was added at the end of the experiments for internal reference of the potentials.

Figure 1 shows the cyclic voltammograms (CVs) and the Osteryoung square-wave voltametry (OSWV, anodic part) of $M_3N@C_{92}$ (M = La, Ce, and Pr) metallofullerenes. These compounds exhibit two irreversible reduction steps and a

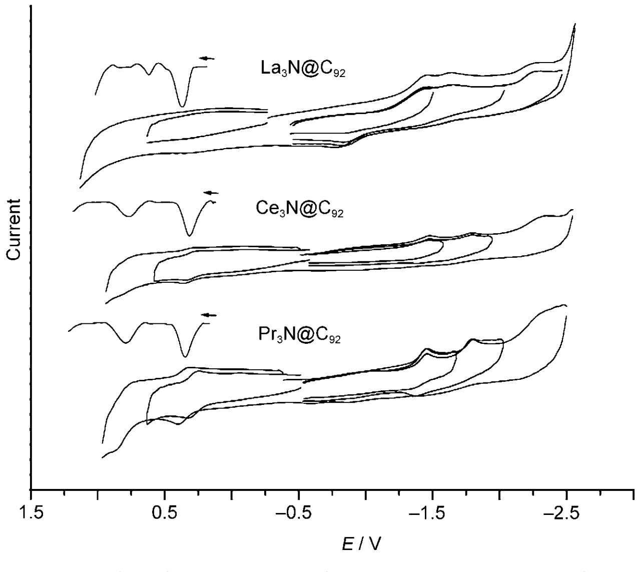

Figure 1. Cyclic voltammograms and Osteryoung square-wave voltammetry (OSWV) of $La_3N@C_{92}$, $Ce_3N@C_{92}$, and $Pr_3N@C_{92}$ in 0.05 M NBu_4PF_6/*o*-DCB with ferrocene as internal standard and a scan rate of 0.1 V s^{-1}.

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likely multielectronic third reduction. $M_3N@C_{92}$ metallofullerenes also show a monoelectronic reversible oxidation step and a second oxidation that is not well defined.

$M_3N@C_{96}$ (M = La, Ce, and Pr) metallofullerenes exhibit at least two irreversible reduction steps and two reversible oxidations (Figure 2). It is interesting that regardless of the encapsulated cluster, metallofullerenes exhibit similar redox behavior for a given carbon cage and similar electrochemical gaps (Table 2).

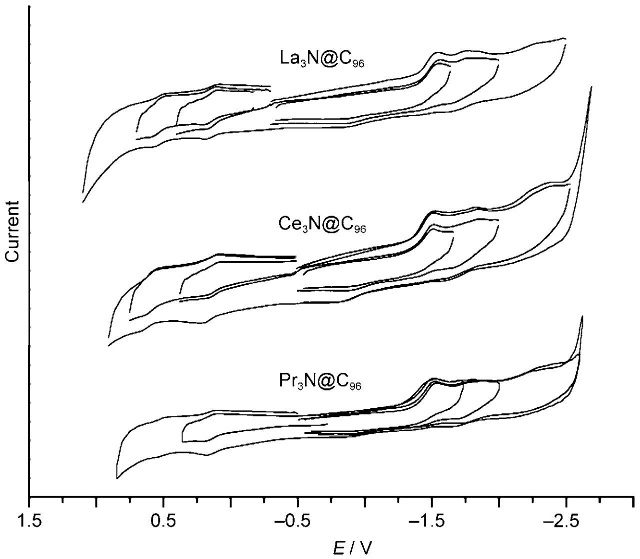

Figure 2. Cyclic voltammograms of $La_3N@C_{96}$, $Ce_3N@C_{96}$, and $Pr_3N@C_{96}$ in 0.05 M NBu_4PF_6/o-DCB with ferrocene as internal standard and a scan rate of 0.1 $V s^{-1}$.

DFT calculations[16] were carried out for $La_3N@C_{92}$ and $La_3N@C_{96}$ to understand the electronic and electrochemical properties of these MNEFs. The calculations for MNEFs were performed without symmetry restrictions. We have assumed that the fullerene cage corresponds to isomer **186** (see Figure 3) of symmetry D_2, which shows the highest gap between LUMO−4 and LUMO−3 for the free cage.[14] The same isomer was proposed by Popov and Dunsch for the Y_3N cluster in the C_{96} cage. The endohedral structure was optimized for several orientations of the MN unit inside the cage and it was found that the cluster may adopt some orientations with similar energies (within less than 2 kcal mol^{-1}). Figure 3 b shows the representation of one of the most stable orientations. As suggested by the low dependence of the electrochemical properties on the nature of the encapsulated metal, the participation of the metal nitride in the HOMO and LUMO is almost negligible. Based on the electronic structure of the free fullerene cage, Poblet et al.[14] proposed isomer **86** of C_{92} (see Figure 3) with symmetry *T* as the most suitable isomer to encapsulate a MN cluster. Nevertheless, Popov and Dunsch found isomer **85** ($Y_3N@C_{92}$) with D_3 symmetry more stable than isomer **86** by about 14 kcal mol^{-1} when the internal cluster is Y_3N[15]. If the metal is lanthanum, the difference in the stability between the two isomers is 7.7 kcal mol^{-1}, isomer **85** again being the most stable species.

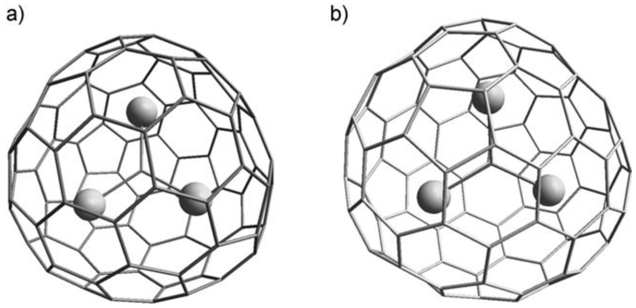

Figure 3. Structures for a) $La_3N@C_{92}$ (isomer **86**) and b) $La_3N@C_{96}$ (isomer **186**).

Table 1: Relative stability (ΔE), ionization potential (IP), electron affinity (EA), electrochemical (EG), and HOMO–LUMO (H–L) gap computed for $La_3N@C_{92}$ and $La_3N@C_{96}$.[a]

	Δ*E*	IP[b]	EA[b]	EG[b]	H–L
92:**85**	0.0	4.42	3.34	1.08	0.70
92:**86**	7.7	4.83	3.09	1.75	1.37
96:**186**	–	4.67	3.15	1.53	1.16

[a] Relative stabilities in kcal mol^{-1}, IP, EA, and H–L gap in eV, and EG in V. [b] Values computed in o-DCB media. For experimental values of EG see Table 2.

To verify the structures proposed for the C_{92} and C_{96} hosts we have computed the electrochemical gaps (EG) as the difference between the electron affinities and ionization potentials in solution (Table 1). This procedure has been used by our group in polyoxoanions with reasonable agreement between theory and experiments (see Ref. [17] for more details). Using *o*-DCB as solvent, the EG for C_{92}:**86** was computed to be 1.75 V, which is in very good agreement with the experimental value of 1.80 V. In contrast, the computed EG for C_{92}:**85** is only 1.08 V. This extremely low gap, which derives from the high electron affinity (EA) and low ionization potential (IP) of isomer **85**, excludes it as the host cage for C_{92}. The oxidation potentials (Figure 1, Figure 2, and Supporting Information) for $La_3N@C_{92}$ (+0.36 V) and $La_3N@C_{96}$ (+0.14 V) show that the compound with the C_{96} cage is easier to oxidize than that with the C_{92} cage. C_{92}:**85** would not be compatible with this behavior, because its IP is lower than the IP computed for C_{96}:**186** by 0.25 eV, which is derived from the high energy of the HOMO in $La_3N@C_{92}$ (isomer **85**). However, the IP computed for C_{92}:**86** perfectly matches the electrochemical data available. Its IP is higher than that of the compound with the C_{96} cage by 0.16 eV, a value that is very close to the experimental difference of 0.22 V. We can also compare this result with other cages. For example, the first oxidation peak for $La_3N@C_{92}$ appears at approximately the same potential as the one for $Sc_3N@C_{80}$ (D_{5h}), the difference is less than 20 mV.[22] Consistently the difference in the computed IPs is also very small (40 meV). Therefore, although C_{92}:**85** is computed to be somewhat more stable than C_{92}:**86** we assume that C_{92}:**86** is the host cage observed for $La_3N@C_{92}$. Popov and Dunsch have suggested that C_{92}:**85** could be kinetically unstable.[15] A 3D representation for $La_3N@C_{92}$ (isomer **86**) and $La_3N@C_{96}$ (isomer **186**) is given in Figure 3 (see the Supporting Information for more details).

The electrochemical characterization of the large fullerenes $M_3N@C_{2n}$ ($n = 46$ and 48) provides the basis for the comparison of cages between C_{80} and C_{96}. From the values compiled in Table 2 the following can be concluded: the difference between the first oxidation peak and the first reduction peak in a CV of a MNEF does not depend on the encapsulated metal nor does it correlate with the fullerene size. With the exception of $Sc_3N@C_{80}$, the HOMO and LUMO of MNEFs are cage orbitals, therefore the first oxidation and first reduction involve orbitals without (or very low) a contribution from the metal. The ionic model for MNEFs assumes that six electrons are transferred from the MN cluster to the fullerene thus filling the three lowest unoccupied orbitals of the cage.[12] In this model it would be expected that the EG of the endohedral fullerene should correlate with the electronic structure of the carbon cage. The energy difference between the LUMO−4 and LUMO−3 for a series of free cages is given in Table 3. Figure 4 shows the correlation between the average EG observed for MNEFs and the orbital gap in the free cage. The LUMO−4 changes by less than 0.3 eV, whereas for the LUMO−3 varies by more than twice that amount, explaining why the first oxidation potential in a CV of a MNEF is more sensitive to the cage than the first reduction potential is.[22] The excellent correlation between the electrochemical data and the orbital energies (Figure 4) corroborates the importance of the topology of the cage and not its size. The correlation in Figure 4 indicates that the oxidations and reductions occur on the cage. Since the reduction for $Sc_3N@C_{80}$ mainly occurs on the scandium orbitals[12] the correlation coefficient was calculated without taking into account the EG for this MNEF. This correlation also provides direct experimental evidence of the six-electron transfer in MNEFs. Other evidence suggesting the formal 3+ oxidation state for the metal in these species has already been reported.[25] Such a correlation was not found for the formal transfer of two and four electrons (see Supporting Information). A formal electron transfer of six electrons, however, does not mean that a real transfer of six electrons occurs between the two units. Covalent contributions to the bonding are also present for M = Sc, the most electronegative metal of the series.[15] In addition, the computation of the charge transfer depends significantly on the basis set and on the partition method (Table VIII Supporting Information). For example, the Mulliken population analysis for $M_3N@C_{2n}$ assigns an electron transfer that ranges between 1 and 2 e^- between the guest and the host, whereas the Multipole Derived Charge method enhances the ionic picture of the bond, predicting a transfer that may reach up to almost 4 e^- for some metal atoms and fullerene cages (see Supporting Information).

Table 2: Electrochemical gaps for several MNEFs.[a]

M	C_{80}	C_{84}	C_{86}	C_{88}	C_{92}	C_{96}
Sc	1.85					
Y	2.05					
Ce				1.38	1.80[b]	1.68[b]
Pr	2.05		1.78	1.40	1.81[b]	1.65[b]
Nd	2.05	1.75	1.82	1.40		
Gd	2.02	1.69		1.49		
Lu	2.04					
La					1.80[b]	1.68[b]
average	2.04[c]	1.72	1.80	1.42	1.80	1.67

[a] Values taken from references [9,10,23,24]. [b] This work. [c] Average for all MNEFs except for M = Sc.

Table 3: (LUMO−4)−(LUMO−3) orbital gaps in free carbon cages.

	C_{80}	C_{84}	C_{86}	C_{88}	C_{92}	C_{96}
IPR-isomer	**7** (I_h)	**51365** (C_s)[a]	**19** (D_3)	**35** (D_2)	**86** (T)	**186** (D_2)
LUMO-4	−3.59	−3.77	−3.57	−3.88	−3.63	−3.86
LUMO-3	−5.46	−5.09	−5.07	−4.73	−5.18	−5.04
Gap[b]	1.87	1.32	1.50	0.85	1.55	1.18

[a] Non-IPR (IPR: isolated pentagon rule) isomer. [b] Orbital gap (LUMO−4)−(LUMO−3) in eV.

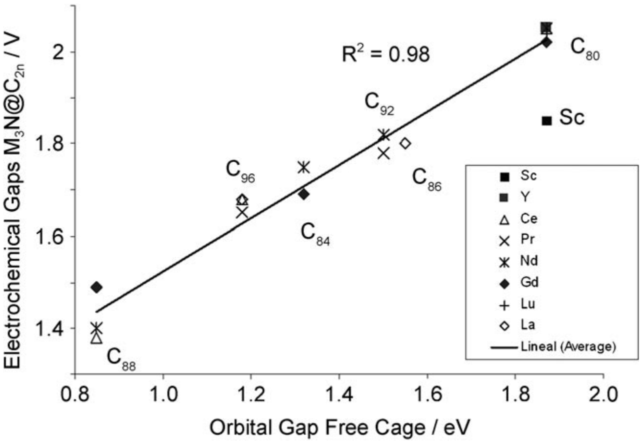

Figure 4. Correlation between electrochemical gaps and (LUMO−4)−(LUMO−3) orbital gaps in free carbon cages. Linear regression is done using average values for each metal except scandium (see text).

The UV/Vis-NIR spectra of the $M_3N@C_{2n}$ (M = La, Ce, and Pr; $2n = 92$ and 96) MNEFs are given in the Supporting Information. Although there is some correlation between the optical and calculated gaps for the MNEFs, the correlation is much poorer than for the EGs. The optical gaps depend strongly on the metal. It is not clear if this has an electronic origin or if it is due to the lack of sensitivity and precision owing to the tiny amounts of sample available for the UV/Vis spectral collection.

In conclusion, the new trimetallic nitride fullerenes based on lanthanum, cerium, and praseodymium represent the largest MNEFs isolated and studied to date. Their electrochemical properties together with DFT calculations provide supplementary evidence for the ionic model in MNEFs for cages ranging between C_{80} and C_{96}.

Experimental Section

Graphite rods (6 mm diameter) purchased from POCO were core-drilled (4 mm diameter) and packed with (3:1), (1:1), and (1:5) mixtures of graphite powder and CeO_2 (cerium oxide), Pr_6O_{11} (praseodymium oxide), and La_2O_3 (lanthanum oxide), respectively. The rods were annealed at 1000 °C for 12 h and then vaporized in a modified Krätschmer–Huffman reactor under a mixture of ammonia (20 mbar) and helium (200 mbar) using an arc current of 85 A. The soot collected from the arc reactor for each packed rod was extracted with CS_2 in a sonicator for about two hours. After removal of the solvent, the crude mixtures were washed with diethyl ether and acetone until the washings were no longer colored. The solids were dissolved in toluene and separated by HPLC using a semipreparative 10 mm × 250 mm Buckyprep-M column with a flow rate of 4 mL of toluene per minute. Isolated samples were then passed through a linear combination of Buckyprep and Buckyprep-M columns with a flow rate of 2.00 mL of toluene per minute without any further sign of isomeric separation. MALDI-TOF mass spectrometry was carried out using a Bruker Omni Flex. For the EDS analysis, the samples were deposited on TEM grids and the spectra were taken on a HD-2000 STEM, equipped with an Oxford EDS system. Cyclic voltammetry was carried out in a one-compartment cell connected to a BAS 100B workstation in a solution of *o*-DCB containing 0.05 M NBu_4PF_6. A 2 mm diameter glassy carbon disk was used as the working electrode. Ferrocene was added to the solution at the end of each experiment as internal standard and all the electrochemical potentials were referenced to its redox couple.

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