

Calculated Production Yields in Metallofullerene Series

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ABSTRACT

The paper reports computations for all lanthanoids ($L@C_{74}$) based on encapsulation into the only C_{74} IPR (isolated pentagon rule) cage, for $Al@C_{82}$, $Sc@C_{82}$, $Y@C_{82}$ and $La@C_{82}$ based on encapsulation into the IPR C_{2v} , C_{82} cage, and also for the mixed (metal-sulfur) $Z_2S@C_{82}$ endohedrals. Their structural and energetic characteristics are used for evaluations of the relative production yields, employing the encapsulation Gibbs-energy terms and saturated metal pressures. It is moreover shown that the encapsulation potential-energy changes in such series can be well related to the mere ionization potentials of the free metal atoms.

Keywords: Endohedral fullerenes; carbon-based nanotechnology; molecular electronics; molecular modeling; molecular electronic structure; ionization potentials; metallofullerene stability islands.

1 INTRODUCTION

There are several well-established families of metallofullerenes based on one common carbon cage, for example $X@C_{74}$ or $Z@C_{82}$. Although the empty C_{74} fullerene [1] is not yet available in solid form, several related endohedral species $X@C_{74}$ have been known like $Ca@C_{74}$ [2,3], $Sr@C_{74}$ [4], $Ba@C_{74}$ [5] or $La@C_{74}$ [6-8], all based on the isolated pentagon rule (IPR) D_{3h} C_{74} cage. Another common metallofullerene family, $Z@C_{82}$, is based on the IPR C_{2v} , C_{82} cage - for example $Sc@C_{82}$ [9], $Y@C_{82}$ [10] and $La@C_{82}$ [6,11] (while $Al@C_{82}$ was never isolated). The present paper deals with computational evaluations of the structural, bonding and stability features in the homologous series $Z@C_{82}$ (Z: Al, Sc, Y, La) and in the lanthanoid series $L@C_{74}$ (L: La-Lu). Moreover, the treatment is also applied to the recently observed mixed (metal-sulfur) $Z_2S@C_{82}$ endohedrals [12,13]. Special interest is paid to the Gibbs-energy evaluations for estimations of the relative populations.

Fullerenes and metallofullerenes have represented objects of very vigorous research activities in connection with their expected promising nanoscience and nanotechnology applications, see e.g. [14-19]. In particular, various endohedral cage compounds have been suggested as possible candidate species for molecular memories and other future molecular-electronic devices. One approach is dealing with endohedral species with two possible location positions of the encapsulated atom [15]

while another concept of quantum computing aims at a usage of spin states of $N@C_{60}$ [16] or fullerene-based molecular transistors [17]. Although there can be (three-dimensional) rotational motions of encapsulates in the cages, the internal motions can be restricted by a cage derivatization [18] thus in principle allowing for a versatile control of the endohedral positions needed for the molecular-memory applications. However, a still deeper knowledge of various molecular aspects of the endohedral compounds is needed before their tailoring to nanotechnology applications is possible.

2 COMPUTATIONS

The full geometry optimizations were carried out using density-functional theory (DFT), namely employing Becke's three parameter functional with the non-local Lee-Yang-Parr correlation functional (B3LYP) in the combined basis set of the 3-21G basis for C atoms and the LanL2DZ basis set with the LANL2 effective core potential for the metal atoms (3-21G~la) as implemented in the Gaussian 03 program package [20]. In the optimized B3LYP/3-21G~la geometries, the harmonic vibrational analysis was then performed. Moreover, in the optimized geometries, higher-level single-point energy calculations were also carried out with the standard 6-31+G* (6-31+G*~la) basis set for C atoms, and finally also with the standard 6-311+G* basis for carbon atoms and the SDD basis with the SDD effective core potential for the metals (6-311+G*~sdd). The basis set superposition error (BSSE) was estimated by the Boys-Bernardi counterpoise method [21,22]. In addition to the traditional B3LYP functional, a newer MPWB1K functional suggested recently by Zhao and Truhlar [23] as the best combination for evaluations of long-range interactions has also been employed in this study.

The Gibbs energies were evaluated using the rotational-vibrational partition functions constructed from the calculated structural and vibrational data using the rigid rotator and harmonic oscillator (RRHO) approximation. Although the temperature region where fullerene or metallofullerene electric-arc synthesis takes place is not yet known, there are some arguments to expect it around or above 1500 K. Thus, the calculations here are presented for two illustrative temperatures of 1500 and 2000 K.

3 RESULTS AND DISCUSSION

Let us consider a series of metallofullerene formations with one common cage, $X@C_n$, and variable encapsulated metals, X. The equilibrium composition of

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the reaction mixture is controlled by the encapsulation equilibrium constants $K_{X@C_n,p} = \frac{p_{X@C_n}}{p_X p_{C_n}}$, expressed in the terms of partial pressures of the components. The scheme can be further simplified if we suppose that the metal pressure p_X is actually close to the respective saturated pressure $p_{X,sat}$ known from observations [24,25]. The relative yields in the metallofullerene series will be then proportional to the products: $p_{X@C_n} \sim p_{X,sat} K_{X@C_n,p}$.

More specifically, one can consider an overall stoichiometry of a metallofullerene formation:



The equilibrium composition of the reaction mixture is controlled by the encapsulation equilibrium constants $K_{X@C_n,p}$:

$$K_{X@C_n,p} = \frac{p_{X@C_n}}{p_X p_{C_n}}, \quad (2)$$

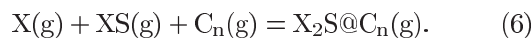
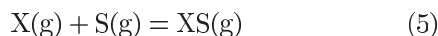
expressed in the terms of partial pressures of the components. Let us further suppose that the metal pressure p_X is actually close to the respective saturated pressure $p_{X,sat}$. The saturated pressures $p_{X,sat}$ for various metals are known from observations. The partial pressure of C_n can be eliminated in a rigorous way. If we consider the combined $p_{X,sat} K_{X@C_n,p}$ term

$$p_{X@C_n} \sim p_{X,sat} K_{X@C_n,p}, \quad (3)$$

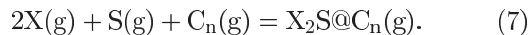
that directly controls the partial pressures of various $X@C_n$ encapsulates in an endohedral series (based on one common C_n fullerene), we get an applicable scheme, indeed. A more complex relation can be suggested for the sulfur containing [12,13] $Z_2S@C_{82}$ metallofullerene yields in the case of two different metals, X and Y ($K_{XS,p}$ denotes the equilibrium constant for model $XS(g)$ formation):

$$\frac{p_{X_2S@C_n}}{p_{Y_2S@C_n}} = \frac{p_{X,sat}^2 K_{XS,p} K_{X_2S@C_n,p}}{p_{Y,sat}^2 K_{YS,p} K_{Y_2S@C_n,p}}. \quad (4)$$

Here, two simultaneous equilibria are considered:



However, in a more straightforward way, just one process can be treated:



Even with this scheme, we still get in the master formula for the relative populations the second power of the saturated metal pressures.

Actually, the considered $p_{X,sat} K_{X@C_n,p}$ term can frequently (though not necessarily) be increasing with temperature. An optimal production temperature could be evaluated in a more complex model that also includes temperature development of the empty-fullerene partial pressure.

As an example, the computed relative populations for four members of the C_{82} -based metallofullerene family will be reported: $Al@C_{82}$, $Sc@C_{82}$, $Y@C_{82}$, and

$La@C_{82}$. For example, the B3LYP/6-31G*~dz encapsulation potential-energy change is for $Sc@C_{82}$, $Y@C_{82}$, and $La@C_{82}$ by 69.5, 80.7, and 89.9 kcal/mol, respectively, more negative than the term for $Al@C_{82}$. Interestingly enough, as shown in Fig. 1, there is a good correlation between the relative potential-energy changes upon encapsulation $\delta_{rel}\Delta E$ and the observed [26] metal relative ionization potentials $\delta_{rel}IP$, the finding being rationalized in the contribution, too.

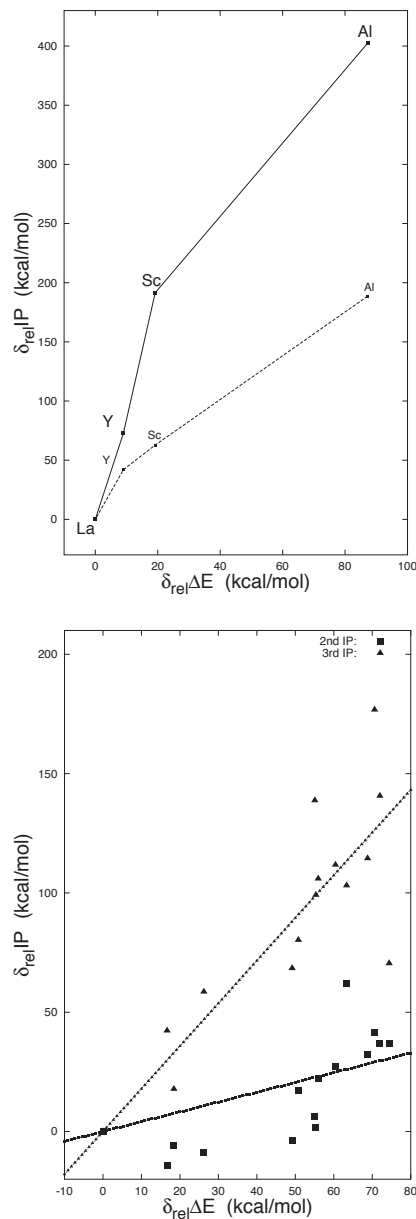


Fig. 1. The computed relative potential-energy changes upon encapsulation $\delta_{rel}\Delta E$ and the observed relative ionization potentials (IP) of the free atoms $\delta_{rel}IP$ for $Z@C_{82}$ (top: solid line - 3-rd IP, dashed line - 2-nd IP) and for lanthanoids (L: La-Lu) $L@C_{74}$ (bottom: black Δ - 3-rd IP, \blacksquare - 2-nd IP).

The $Z@C_{82}$ metallofullerenes have been known [14]

to be formed via metal encapsulations into the IPR C_{2v} C_{82} cage with a strong charge transfer from the metal to the cage leaving the metal between the Z^{2+} and Z^{3+} states. For example, the Mulliken atomic charge in $La@C_{82}$, $Y@C_{82}$, and $Sc@C_{82}$ is at the B3LYP/3-21G~la level calculated as 2.67, 2.38, and 2.44, respectively. However, the natural population analysis, for example at the B3LYP/6-311+G*~sdd level, produces for $La@C_{82}$, $Y@C_{82}$, and $Sc@C_{82}$ charges of 2.32, 2.05, and 1.77, respectively. The B3LYP/6-31+G*~dz potential-energy changes for the $Z@C_{82}$ series are presented in Fig. 1, showing a good correlation with the observed free-metal ionization potentials. To explain this correlation, three formal reaction steps can be considered for our illustrative series $Al@C_{82}$, $Sc@C_{82}$, $Y@C_{82}$ and $La@C_{82}$: (i) double- (or triple-) ionization of the free metal, (ii) double (or triple-) charging of the empty cage, and (iii) placing the metal di- (or tri-) cation into the di- (or tri-) anionic cage. The (ii) energy is identical for all members of the series, and the (iii) terms should be similar as they are controlled by electrostatics. The bonding situation in $Al@C_{82}$, $Sc@C_{82}$, $Y@C_{82}$ and $La@C_{82}$ can be surveyed by the highest C-Z Wiberg bond index. The very low values of the C-Z Wiberg index (at the B3LYP/6-311+G*~sdd level: 0.04 ~ 0.21) in $Z@C_{82}$ indicate that instead of a covalent bond, an ionic bond is formed between the metal and cage. Moreover, the feature that the stabilization of metallofullerenes is mostly electrostatic can also be documented [27] using the topological concept of 'atoms in molecules' (AIM) [28,29] which indeed shows that the metal-cage interactions form ionic (and not covalent) bonds. Hence, the free-metal ionization potentials should actually represent a critical yield-controlling factor - the computed relative potential-energy changes upon encapsulation $\delta_{rel}\Delta E$ and the relative observed ionization potentials of the free atoms $\delta_{rel}IP$ should according to the above three-step analysis be correlated:

$$\delta_{rel}\Delta E \sim \delta_{rel}IP. \quad (8)$$

The interesting correlation even somehow works for the whole lanthanoid series. Fig. 1 also presents the computed B3LYP/sdd potential-energy changes in the lanthanoid encapsulation $L@C_{74}$ (L: La-Lu) plotted against the observed free-atom relative ionization potentials. The correlation is not particularly good in this third series - the uniformity of the metal charges is not obeyed in the $L@C_{74}$ series. For example, the B3LYP/3-21G~cep Mulliken charge on L in $L@C_{74}$ equals to 3.03, 1.67, and 1.35 for $La@C_{74}$, $Yb@C_{74}$, and $Lu@C_{74}$, respectively. Nevertheless, the results basically support the suggested relationship: $\delta_{rel}\Delta E \sim \delta_{rel}IP$. In fact, such a correlation should operate for any homologous reaction series of metal encapsulations, i.e., into any type of a common carbon nanostructure. Moreover, this sort of reasoning should step by step explain the fullerene-encapsulation stability islands [30-35] known throughout the periodic system (though the underlying calculations are rather demanding).

The Gibbs-energy based treatment can also be applied to the recently observed mixed (metal-sulfur) $Z_2S@C_{82}$ endohedrals [12,13]. The computations here are dealing with the relative yields for Sc and Y. Fig. 2. shows the B3LYP/6-31G*~la optimized structures of $Sc_2S@C_{82}$ and $Y_2S@C_{82}$ for one selected 82 cage. As discussed above, there are several possible schemes for

the evaluation of the relative stabilities in this mixed case. Nevertheless, regardless the scheme applied, the computations predict that $Sc_2S@C_{82}$ should be produced in considerably larger amounts than $Y_2S@C_{82}$ which is in agreement with available observations [12,13]. Here, the population order originates in the fact that both energetics and saturated metal pressure favor Sc over Y.

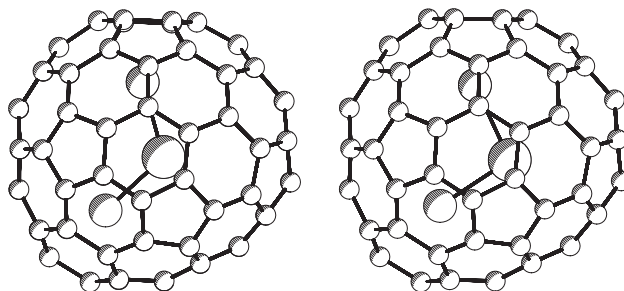


Fig. 2. The B3LYP/6-31G*~la optimized structures of two mixed metal-sulfur $Z_2S@C_{82}$ endohedrals: left - $Sc_2S@C_{82}$, right - $Y_2S@C_{82}$.

Although the energy terms are likely still not precise enough, their errors could be comparable in the series and thus, they should cancel out in the relative term $\frac{PZ,satKZ@C82,p}{PLa,satKLa@C82,p}$. This should be the case of, for example, the higher corrections to the RRHO partition functions, including motions of the encapsulate. The motion of the endohedral atom is highly anharmonic, however, its description is yet possible only with simple potential functions. As long as we are interested in the relative production yields, the anharmonic effects should at least to some extent be canceled out in the relative quotient $\frac{PZ,satKZ@C82,p}{PLa,satKLa@C82,p}$. In fact, we are dealing with a special case of clustering under saturation conditions [36-39]. The saturation regime is a useful simplification - it is well defined, however, it is not necessarily always achieved. Under some experimental arrangements, under-saturated or perhaps super-saturated metal vapors are also possible. This reservation is applicable not only to the electric-arc treatment but even more likely to newly introduced ion-bombardment production technique [40,41]. Still, eqs. (2)-(5) remain basically valid, however, the metal pressure has to be described by the values actually relevant. For some volatile metals their critical temperature could be overcome and the saturation region thus abandoned (though practically speaking, this could come into consideration with mercury and cesium). Anyhow, the saturation regime can give a kind of upper-limit estimates of the production yields.

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