

Calculated relative yields for $\text{Sc}_2\text{S}@C_{82}$ and $\text{Y}_2\text{S}@C_{82}$

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Received: 15 July 2011 / Accepted: 16 September 2011 / Published online: 4 October 2011
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Abstract The paper reports computations for a newly observed class of the mixed, sulfur-containing $\text{X}_2\text{S}@C_{82}$ metallofullerenes, namely for $\text{X} = \text{Sc}$ and Y , based on encapsulation into the C_s and C_{3v} C_{82} isolated pentagon rule cages. Their structural, vibrational, and energetic characteristics from the density-functional-theory calculations with the standard 6-31G* and LanL2DZ basis sets are used for the evaluations of the relative production yields. The encapsulation Gibbs energy terms from the partition functions combined with the observed saturated metal pressures are employed. A model scheme is used dealing with the XS template gas-phase presence. The computations predict that $\text{Sc}_2\text{S}@C_{82}$ should be produced in considerably larger amounts than $\text{Y}_2\text{S}@C_{82}$ which is in agreement with available observations. The yield order

originates in the fact that both energetics and saturated metal pressure favor Sc over Y.

Keywords Hetero-metallofullerenes · Quantum-chemical Gibbs energy evaluations · Computed cluster stabilities · Optimized syntheses · Carbon nanostructures

1 Introduction

The fullerene discovery [1] followed by their electric-arc synthesis [2] has opened the way toward a new, vast family of carbon nanostructures, especially metallofullerenes and nanotubes [3]. However, the fullerene/metallofullerene/nanotube stabilities still cannot be easily predicted—large-scale calculations are essentially needed. Moreover, the theoretical/computational prediction tools need to be based on numerous simplifications and approximations. As an instructive successful example, let us mention that the computations could confirm [4–6] particular stability of all the isolated isomers of empty fullerenes. More recently, research interest has been shifted to metallofullerenes and nanotubes.

There are several well-established families of metallofullerenes based on one common carbon cage, for example $\text{X}@C_{74}$ or $\text{Z}@C_{82}$. Although the empty C_{74} fullerene [7] is not yet available in solid form, several related endohedral species $\text{X}@C_{74}$ have been known like $\text{Ca}@C_{74}$ [8, 9], $\text{Sr}@C_{74}$ [10], $\text{Ba}@C_{74}$ [11] (while $\text{Mg}@C_{74}$ was never isolated), and also for some lanthanoids, especially $\text{La}@C_{74}$ [12–14], all based on the isolated pentagon rule (IPR) D_{3h} C_{74} cage. Another common metallofullerene family, $\text{Z}@C_{82}$, is based on the IPR C_{2v} C_{82} cage—for example $\text{Sc}@C_{82}$ [15], $\text{Y}@C_{82}$ [16], and $\text{La}@C_{82}$ [12, 17] (while $\text{Al}@C_{82}$ was never isolated). Moreover, more than one atom can be encapsulated, and some of the

Dedicated to Professor Shigeru Nagase on the occasion of his 65th birthday and published as part of the Nagase Festschrift Issue.

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encapsulated atoms can be different [18, 19]. Very recently, Dunsch et al. [20] and Echegoyen et al. [21, 22] have introduced a new type of sulfur-containing metallofullerenes, especially $\text{Sc}_2\text{S}@C_{82}$ and also $\text{Y}_2\text{S}@C_{82}$. The present paper deals with computational predictions of their relative production yields, thus supplying a topical example in our efforts [23] in stability evaluations in series of metallofullerene formations $\text{X}@C_n$ with one common cage C_n and variable (though somehow similar or linked) encapsulates X.

Fullerenes and metallofullerenes have represented targets of very vigorous research activities owing to their expected promising nanoscience and nanotechnology applications, see e.g., [24–28]. In particular, various endohedral cage compounds have been suggested as plausible candidate species for molecular memories and other future molecular electronic devices. One molecular memory approach is built on endohedral species with two possible location sites of the encapsulated atom [24] while another concept for molecular computers aims at a usage of spin states of $\text{N}@C_{60}$ [25] or fullerene-based molecular transistors [26]. Although there can be three-dimensional rotational motions of encapsulates in the cages [27], the internal motions can be restricted by a cage derivatization [28], 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 and other carbon nanostructures is needed before their tailoring to nanotechnology applications is possible. The quantum-chemical computations of virtually any type of nanocarbon [4–6, 29–50] have indeed constantly aided [29, 51] all branches of fullerene science.

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 standard 6-31G* basis for C atoms and the LanL2DZ basis set with the LANL2 effective core potential for the sulfur and metal atoms (6-31G*~1a~1a) as implemented in the Gaussian 03 program package [52]. In the optimized B3LYP/6-31G*~1a~1a geometries, the harmonic vibrational analysis was then performed. Moreover, in the optimized geometries, single-point energy calculations were also carried out with the standard 6-31G* basis on S atoms (6-31G*~1a). In fact, the B3LYP/6-31G*~1a~1a treatment has a better convergence compared with the B3LYP/6-31G*~1a approach (in addition to the traditional B3LYP functional, a newer MPWB1K

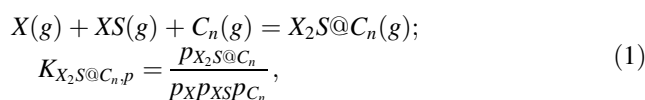
functional [53] has also been partly tested in this study, though it does not exhibit a better convergence). The basis set superposition error (BSSE) was estimated by the Boys-Bernardi counterpoise method [54, 55]. The original Boys-Bernardi counterpoise method was suggested [54] for dimers with a fixed geometry. Although a BSSE-respecting geometry optimization would be possible [55], it is rather practical only for simpler systems. Still, in order to reflect the cage distortion, a straightforward steric-corrected BSSE treatment has recently been suggested [23].

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, also applied in our previous studies [4–6, 56]. The present study is mostly based on calculations, only a small portion of observed data [57–59] is needed in some steps. 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 1,500 K. Thus, the calculations here are presented for two illustrative temperatures of 1,500 and 2,000 K.

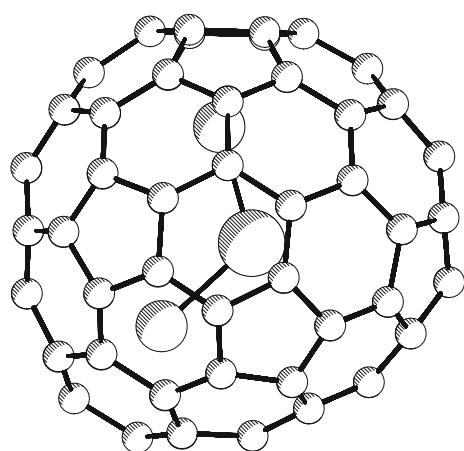
3 Results and discussion

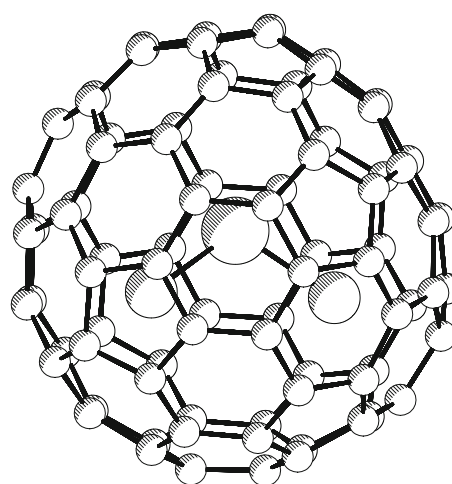
The study is focused on the two C_{82} IPR cages observed [20–22] with the $\text{X}_2\text{S}@C_{82}$ species, namely the cages conventionally labeled as $C_{s\text{-}\#6}$ and $C_{3v\text{-}\#8}$, and the computations here deal with the encapsulation of Sc or Y atoms (see Figs. 1 and 2). Table 1 shows that the computed relative encapsulation energies for $\text{Sc}_2\text{S}@C_{82}$ and $\text{Y}_2\text{S}@C_{82}$ are not very sensitive to the basis set selection and inclusion of the BSSE term.

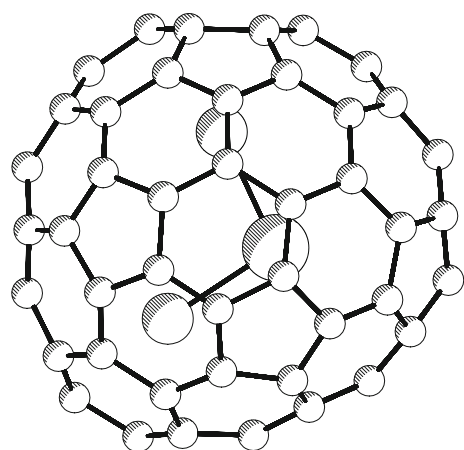
However, as metallofullerene syntheses deal with high temperatures, the mere potential energy changes are not enough to understand the metallofullerene-formation thermodynamics and other terms are to be taken into consideration. Still, we would like to design a relatively simple, practical computational scheme, where a part of the terms actually cancels out. Let us start with a presumption that the diatomic species XS exist as significant templates in the hot gas phase so that we can deal with an encapsulation process:

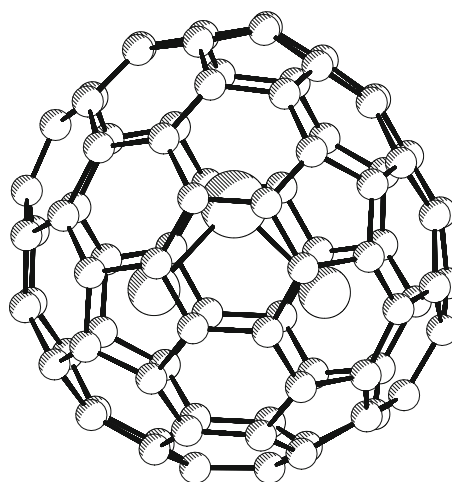


characterized by its encapsulation equilibrium constant $K_{X_2S@C_n,p}$ expressed in the terms of partial pressures of the components. The encapsulation equilibrium constant is interrelated with the standard encapsulation Gibbs energy change $\Delta G_{X_2S@C_n}^o$:



$$\text{Sc}_2\text{S}@C_{82} // C_s - \#6$$


$$\text{Sc}_2\text{S}@C_{82} // C_{3v} - \#8$$


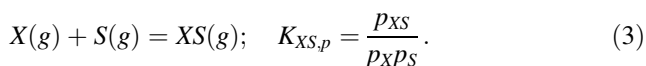
$$\text{Y}_2\text{S}@C_{82} // C_s - \#6$$


$$\text{Y}_2\text{S}@C_{82} // C_{3v} - \#8$$

Fig. 1 The B3LYP/6-31G*~la~la optimized structures of $\text{Sc}_2\text{S}@C_{82}$ and $\text{Y}_2\text{S}@C_{82}$ —encapsulation into the C_s -#6 C_{82} IPR cage

$$\Delta G_{X_2S@C_n}^o = -RT \ln K_{X_2S@C_n,p}. \quad (2)$$

The XS template formation is then described by another equilibrium constant, $K_{XS,p}$:



In the terms from Eqs. 1 and 3, the $X_2S@C_n$ metallofullerene yield reads:

$$p_{X_2S@C_n} = p_X p_{XS} p_{C_n} K_{X_2S@C_n,p} = p_X^2 p_S p_{C_n} K_{XS,p} K_{X_2S@C_n,p}. \quad (4)$$

Let us further suppose that the metal pressure p_X is actually close to the respective saturated pressure $p_{X,sat}$:

$$p_X \approx p_{X,sat}. \quad (5)$$

Then, the yield ratio r for two different metals, X and Z , is simply given:

Fig. 2 The B3LYP/6-31G*~la~la optimized structures of $\text{Sc}_2\text{S}@C_{82}$ and $\text{Y}_2\text{S}@C_{82}$ —encapsulation into the C_{3v} -#8 C_{82} IPR cage

$$r = \frac{p_{X_2S@C_n}}{p_{Z_2S@C_n}} = \frac{p_{X,sat}^2 K_{XS,p} K_{X_2S@C_n,p}}{p_{Z,sat}^2 K_{ZS,p} K_{Z_2S@C_n,p}}. \quad (6)$$

While the saturated pressures $p_{X,sat}$ for various metals are known from observations [57, 58], the partial pressure of C_n is a less clear quantity. The same is true for p_S as sulfur is likely above its critical temperature [58] at the metallofullerene-synthesis conditions. Their convenient canceling-out can actually be derived in a rigorous form. In order to observe the relative populations in a metallofullerene series, one can think on an experiment where all the considered metals are simultaneously placed in the electric-arc chamber. This experiment would obviously ensure the same conditions for every member of the series. Moreover, the terms p_{C_n} and p_S in Eq. 4 will be in this arrangement

Table 1 The calculated relative encapsulation energetics (kcal/mol) of $Y_2S@C_{82}$ versus $Sc_2S@C_{82}$

Product ^a	C_s -#6	C_{3v} -#8
B3LYP/6-31G* ~ la ~ la		
$Y_2S@C_{82}$	14.97	14.66
$Sc_2S@C_{82}$	0.0	0.0
B3LYP/6-31G* ~ la ~ la & BSSE		
$Y_2S@C_{82}$	16.50	15.85
$Sc_2S@C_{82}$	0.0	0.0
B3LYP/6-31G* ~ la & BSSE		
$Y_2S@C_{82}$	16.86	14.77
$Sc_2S@C_{82}$	0.0	0.0
$\Delta\Delta G_{X_2S@C_{82}}^o$ B3LYP/6-31G* ~ la ~ la		
$Y_2S@C_{82}$	18.60	12.06
$Sc_2S@C_{82}$	0.0	0.0

The relative encapsulation potential energy changes, or the relative standard encapsulation Gibbs energy changes $\Delta\Delta G_{X_2S@C_{82}}^o$ at $T = 2,000$ K, computed in the B3LYP/6-31G* ~ la ~ la optimized geometries for Eq. 1

^a Encapsulation in C_s -#6 or C_{3v} -#8 C_{82} IPR cage, see text

just common for all the members of the series, and thus, it can indeed be canceled out. Hence, we can consider just the combined $p_{X,sat}^2 K_{XS,p} K_{X_2S@C_n,p}$ terms as the useful comparison expressions.

Table 2 presents the computed formation equilibrium constants $K_{XS,p}$, which show that the ScS and YS model templates should indeed be present in the gas-phase reaction mixture even at high temperatures. For the sake of consistency, the same level of theory is applied for the evaluation of $K_{XS,p}$ and $K_{X_2S@C_n,p}$. Although $K_{XS,p}$ could be computed at higher levels, it is not critical for an evaluation of the XS presence in the reaction mixture. Moreover, what is needed for the endohedral predictions is just the ratio of the products $K_{XS,p} K_{X_2S@C_n,p}$ where a cancelation operates. Incidentally, other models could be considered—for example with the X_2S templates or with just free atoms. Interestingly enough, even with such models, we would get the second power of the saturated metal pressure, $p_{X,sat}^2$, in the resulting comparison expressions (some of the alternative models can actually lead to the same relative populations). As long as we consider the XS templates according to Eq. 1, the decomposition scheme for the

Table 2 The B3LYP/6-31G* ~ la ~ la & BSSE formation equilibrium constants $K_{XS,p}$ (atm^{-1}) for ScS and YS as model templates

T (K)	ScS	YS
1,500	1.45×10^{10}	3.05×10^{11}
2,000	2.37×10^6	2.44×10^7

The standard state—ideal gas phase at 101,325 Pa pressure

BSSE evaluation should deal with three sub-units (X; XS; C_n). Then, there are two choices for the X and XS sub-units though the energy difference is not large. Table 1 therefore actually reports their arithmetic mean.

Table 3 presents the cumulative output of the calculations—the relative yields r of $Sc_2S@C_{82}$ with respect to $Y_2S@C_{82}$ evaluated within the ScS/YS template model at the B3LYP/6-31G* ~ la ~ la level. The used saturated metal pressures were previously extrapolated [23, 60, 61] from available observed data [57, 58]— $p_{Sc,sat}$ is by about one order of magnitude higher than $p_{Y,sat}$ in the considered temperature region (as the normal boiling temperature [58] of Sc is by some 500 K lower compared to Y). Table 3 lists both, the partial relative yields for the individual C_{82} cages and the total yield, which considers the contributions from the two production channels accordingly. It turns out that the production of $Sc_2S@C_{82}$ is always considerably higher than of $Y_2S@C_{82}$ which is in agreement with the available observations [20–22]. The $Sc_2S@C_{82}$ production has an advantage of lower encapsulation potential energy change (Table 1— $Y_2S@C_{82}$ is higher in energy as the larger Y_2S unit is less suitable for the C_{82} cages) and of higher saturated metal pressure (though it is not enhanced by the template-formation equilibrium constant $K_{XS,p}$ —Table 2). The present study deals with just the two C_{82} IPR cages observed [20–22] for $Sc_2S@C_{82}$ species—in principle, another C_{82} cage could be more convenient for the Y_2S case. Let us mention that our temperature choice is supported by recent fullerene pyrolysis [62], where decomposition of C_{78} started around 1,320 K while decomposition of C_{76} around 1,380 K (though the experiment dealt with empty fullerenes only). Thus, temperatures much higher than the observed thresholds are not very likely for metallofullerene synthesis. The computations suggest that for the C_{3v} -#8 cage, $Y_2S@C_{82}$ is by three orders of magnitude less populated than $Sc_2S@C_{82}$. This population order compares with computations [60] for $X@C_{74}$ where the production yield of $Sr@C_{74}$ is by two to three orders of magnitude smaller than that for $Ba@C_{74}$ and for $Ca@C_{74}$ by three to five orders lower than for

Table 3 The relative yield r of $Sc_2S@C_{82}$ versus $Y_2S@C_{82}$ calculated within the ScS/YS template model

C_s -#6	C_{3v} -#8	Total
$T = 1,500$ K		
33,134	6,274	12,720
$T = 2,000$ K		
5,184	1,001	1,939

See Eq. 6; $Sc_2S@C_{82} \gg Y_2S@C_{82}$

The energy and entropy terms evaluated at the B3LYP/6-31G* ~ la ~ la level; saturated metal pressures extrapolated from available observed data [57, 58]

Ba@C₇₄. However, all the evaluations suppose the saturated metal vapor which is not necessarily achieved in the experiment.

The suggested stability evaluation scheme is about the most sophisticated treatment that is computationally feasible at present. In some reaction series, the stability evaluations can be reduced to considerably simple terms as documented [23, 60, 61, 63] by the (mono-metal) series X@C₇₄ or Z@C₈₂ where a stability correlation with the observed [59] free-metal ionization potentials works well. The correlation can be explained [23, 62] using the finding by Kobayashi and Nagase [64] (using the AIM concept [65, 66]) that the stabilization of metallofullerenes has mostly electrostatic origin. It is yet to be tested if such a simple reduction could be possible also for hetero-metallofullerenes treated here. The relative-stability evaluation scheme used in this work is intentionally built with just one intermediate in order to get simple formulas that allow for ample cancelation—a complex reaction mixture would not be treatable this way. Other schemes could still be designed and some of them can become equivalent [67] owing to the cancelation.

Even if the energy terms are still not precise enough, their errors could be comparable in a reaction series, and thus, they should cancel out approximately in the relative terms like Eq. 6. This should also 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(s) is highly anharmonic; however, such its description is yet possible only for simpler systems. 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 terms. As encapsulate motions can be relatively free inside, a modification of the RRHO treatment has been suggested [6] called floating encapsulate model (FEM), which gives better agreement for encapsulations in several isomeric cages. However, the present relative-stability issue should not be particularly sensitive to the FEM treatment. Anyhow, anharmonicity corrections are one of the aspects for more comprehensive studies in future. Such a partial cancelation also takes place [68, 69] with contributions of the electronic partition functions to the relative populations. More generally, we are dealing with a special case of clustering under saturation conditions [70–73]. 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 [74, 75]. Still, the governing thermodynamic equations remain valid; however, the metal

pressures have to be described by the values actually relevant. A generalized treatment of this type can also be designed for step-wise multi-atom encapsulations [76, 77]. Anyhow, the saturation regime can give a kind of upper-limit estimates of the production yields.

Acknowledgments The reported research has been supported by a Grant-in-aid for Scientific Research on Innovative Areas (No. 20108001, “ π -Space”), Scientific Research (A) (No. 20245006), Nanotechnology Support Project, the Next Generation Super Computing Project (Nanoscience Project), Nanotechnology Support Project, and Scientific Research on Priority Area (Nos. 20036008, 20038007) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan; by the National Science Council, Taiwan-ROC; and by the Ministry of Education of the Czech Republic (MSM0021620857), including the access to the MetaCentrum computing facilities (LM2010005), and the Czech Science Foundation/GACR (P208/10/0179). Last but not least, referee’s valuable comments are highly appreciated, too.

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