Free radical scavenger properties of metal-fullerenes: C_{60} and C_{82} with Cu, Ag and Au (atoms and tetramers)

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ABSTRACT

In this report we present a theoretical study (Density Functional Approximation), focusing on the stability and the free radical scavenger capacity of metal-fullerenes. We also denominate free radical scavenger capacity as antioxidant or antiradical. Two different fullerenes have been considered for this investigation: C_{60} and C_{82}. Three transition metals were included to form the metal-fullerenes: copper, silver and gold (one atom and a cluster formed with four atoms). We analyzed the free radical scavenger capacity considering two mechanisms: electron transfer (ET) and radical adduct formation (RAF). From this report, it is evident that the presence of metals considerably improves the antiradical capacity of fullerenes. This may be useful for future applications of these systems.

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1. Introduction

Back in 1985, Kroto et al. [1] produced a remarkably stable cluster with 60 carbon atoms (C_{60}) which is classified as an allotrope of carbon. As the structure of this cluster resembles a geodesic dome, authors named C_{60} as buckminsterfullerene, in honor of Richard Buckminster Fuller who was an architect who popularized this structure. After the discovery of C_{60}, many others allotropes followed and the name was shortened to *fullerene*. Today this refers to molecules ranging from C_{20} to C_{270}, which constitute the fullerene family [2–6]. In these molecules, the suffix *ene* indicates that each carbon atom is covalently bonded to three others. These new carbon allotropes provoked great interest due to their special structural and electronic properties [7–23]. In particular, fullerenes can be considered very effective free radicals scavengers (in this report, we will use free radical scavenger, antioxidant and antiradical as synonymous) [15–23]. They neutralize reactive oxygen species (ROS) such as the superoxide radicals that produce the so-called oxidative stress that is correlated with chronic neurodegenerative diseases such as *Alzheimer* [24–27]. The capability to scavenge free radicals makes fullerenes very interesting due to potential applications in medicine and biochemistry. A large empty space within the structure of fullerenes offers the possibility of storing materials.

Apart from fullerenes, metal-fullerenes represent other interesting systems that include metals (atoms or clusters). Several investigations have reported on the methods of synthesis, stability and physicochemical properties of these systems [28–53]. During the past two decades, investigation of metal-fullerenes has attracted considerable interest, because of the possibility of using them to develop novel materials. They represent a challenge in terms of their synthesis and unique properties, with potential for a variety of applications [35–47]. It can be said that metal atoms and clusters functionalized fullerenes, increasing their reactivity.

Metal atoms and clusters of metal-fullerenes can either be localized inside the cage, *i.e.* encapsulated (endohedral) or outside (exohedral). In order to synthesize endohedral compounds, fullerenes are dissociated and the cage is opened to allow the insertion of several atoms, clusters and molecules. Apparently, endohedral fullerenes are *woven* around the atom or cluster in order to reside in the interior. This technique is named *molecular surgery* [29] and is a successful procedure used to encapsulate atoms, molecules and metal clusters within fullerenes. Techniques employed to produce these systems contemplate the dissociation of the fullerene surfaces, eliminating the possibility of calculating binding energies for the formation of these systems in a classical way *i.e.* considering that the reactants (fullerenes and metal atoms or clusters) are at infinite distance. It is therefore more real to calculate atomization energy for the purposes of experimental procedure, but even with this value, we do not represent *molecular surgery* as the metal-fullerene is not necessarily constructed using an atom by atom process. Methods to synthesize endo and exohedral metal-fullerenes are different and therefore their stability cannot be compared.

To obtain effective experimental yields, it is important to understand the chemical formation mechanism of metal-

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fullerenes and for this reason ongoing research is considering synthesis, using lasers and other methods. Previous reports specifically indicated the stability and reactivity of metal-fullerenes that included copper, silver and gold [50–55]. Studies of reactivity and the analysis of different electronic and magnetic properties indicate that the presence of these transition metals in endo and exohedral metal-fullerenes modifies physicochemical properties and increments chemical reactivity.

In spite of all these investigations, no previous reports have described the free radical scavenger properties of metal-fullerenes. As already pointed out in this introduction, fullerenes can be considered very effective antioxidants, as they behave as a *free radical sponge* [15–23]. Moreover, the presence of metal atoms and clusters improves the chemical reactivity of fullerenes, and it was previously reported that metals bonded to organic systems modify electron donor acceptor capacity and therefore antiradical capacity [56–60]. This information appears to suggest that fullerenes containing metals should improve capacity for trapping free radical species. Therefore, a good hypothesis would infer that the presence of metal atoms and clusters would improve the antiradical capacity of these fullerenes. Following these ideas, we report a theoretical study (Density Functional Approximation) concerning the stability and the free radical scavenger capacity of metal-fullerenes formed from two different fullerenes (C_{60} and C_{82}) and three transition metals: copper, silver and gold. We considered one metal atom in order to analyze the influence of the minimum amount of metal. We also investigated the effect of clusters formed from four atoms since it was reported before that this is the minimum size of the cluster that present interesting properties, for example, in photographic action [61]. Two free radicals were employed in this investigation: OH and OOH. The first one is the most reactive free radical and it reacts as soon as it is produced. The reactivity of the second is less than that of the first and for this reason allows us to discriminate and classify the systems using the reactivity as an indicator. Two mechanisms were used to analyze antiradical capacity: electron transfer (ET) and radical adduct formation (RAF). The presence of metals considerably improved the antiradical capacity of fullerenes.

2. Computational details

Gaussian 09 implementation [62] was used to calculate geometry optimization and electronic properties of C_{60} and C_{82}, interacting with metal atoms and clusters in gas phase. Initial geometries were fully optimized at M06/LANL2DZ level of theory [63–70]. In order to verify optimized minima, harmonic analysis was performed and local minima were identified (zero imaginary frequencies). To analyze the ET mechanism *i.e.* the capability to either donate or accept an electron, the vertical ionization energy (*I*) and the vertical electron affinity (*A*) were obtained from single point calculations of cationic and anionic molecules, using the optimized structure of the neutrals. FEDAM (Full Electron Donor-Acceptor Map) was previously reported as a visual tool [71–74]. In this map (see Fig. 1) *I* and *A* are plotted and allow us to classify substances as either donors or acceptors of electrons. Electrons will be transferred from molecules located down to the left of the map (good electron donors) to those molecules that are up to the right (good electron acceptors).

To study the RAF mechanism, several initial geometries were analyzed. Two free radicals were considered: OH and OOH. Free radicals were bonded to three different positions of endo and exohedral metal-fullerenes, as indicated in Fig. 2.

The RAF mechanism was studied according to the following reaction scheme.
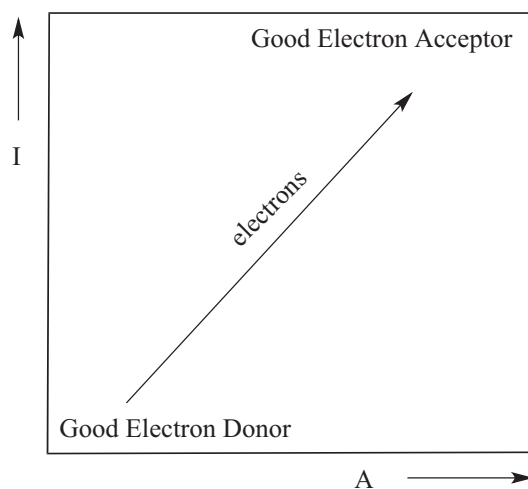
$$FUL\text{-}M_N + R \rightarrow [FULM_NR] \tag{1}$$

Fig. 1. Full Electron Donor-Acceptor Map (FEDAM).

$$\Delta G_{RAF} = G([FULM_NR]) - G(FUL\text{-}M_N) - G(R) \tag{2}$$

R is the free radical (OH or OOH); M represents Cu, Ag or Au in all cases; N is the number of metal atoms (1 or 4); FUL is C_{60} or C_{82}; FUL-M_N is the fullerene with the metal atom or cluster; FULM$_N$R is the adduct formed with the metal-fullerene and the free radical.

To analyze the suitability of the computational method we compare our results with available data for C_{60} and C_{82} [75] and we found a maximum error of seven percent in the ionization energy and less than three percent in the electron affinity.

3. Results and discussion

3.1. Endohedral and exohedral fullerenes

Fig. 3 reports the optimized geometries of endo and exohedral metal-fullerenes with one metal atom (Cu, Ag or Au; C_{60} and C_{82}, respectively). Endohedral metal-fullerenes present the metal atom in the middle of the cage. For the exohedral metal-fullerenes, the Ag—C bond distance (2.30 or 2.20 Å) is larger than the Au—C bond length (2.19 or 2.12 Å) due to the relativistic effects of the gold. Cu has the smallest atomic radius and for this reason Cu—C bond distances are the shortest (1.97 or 1.95 Å).

Optimized geometries of metal clusters (M_4) interacting with C_{60} and C_{82} are presented in Fig. 4. The metal cluster structure of endohedral metal-fullerenes is a tetrahedron, probably so as to avoid repulsive interactions with the carbon atoms. Exohedral metal-fullerenes present two different geometries for the cluster. The less stable structures are included in the Supplementary Material (Fig. 1SM). In the case of C_{60} metal-fullerenes, the rhombus structure of the metal tetramer is the most stable. In fact, Ag_4 and Au_4 do not present an optimized structure with a cluster as a tetrahedron. The results are different when the fullerene is C_{82}. In this case, the three metal clusters present both structures (rhombus and tetrahedron, see Figs. 4 and 1SM). For Cu_4 and Ag_4, exohedral metal-fullerene with the metal cluster as a tetrahedron is more stable than those with the rhombus. For Au_4, the planar rhombus structure is more stable than the tetrahedron. This is an expected result, as it is well known that gold clusters are planar for up to 13 atoms. Comparing data from Figs. 3 and 4, it is possible to see that the M-C bond distances are larger with clusters than with atoms.
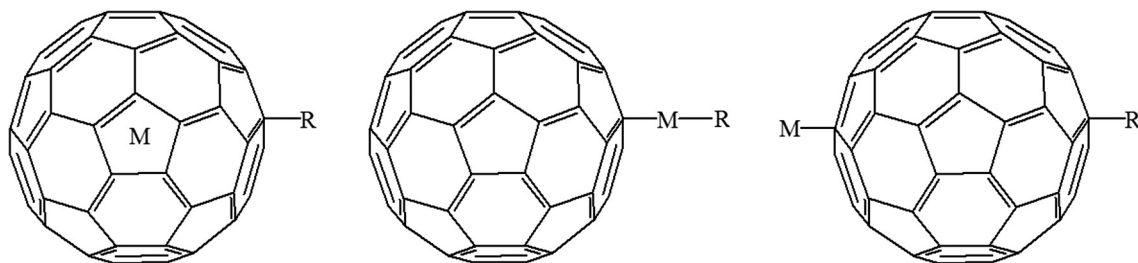
Fig. 2. Initial geometries for C_{60} and C_{82} endo and exohedral metal-fullerenes, used to analyze the RAF mechanism. M is either the metal atom (Cu, Ag or Au) or the tetramer (Cu_4, Ag_4 or Au_4). R is the free radical (OH or OOH).
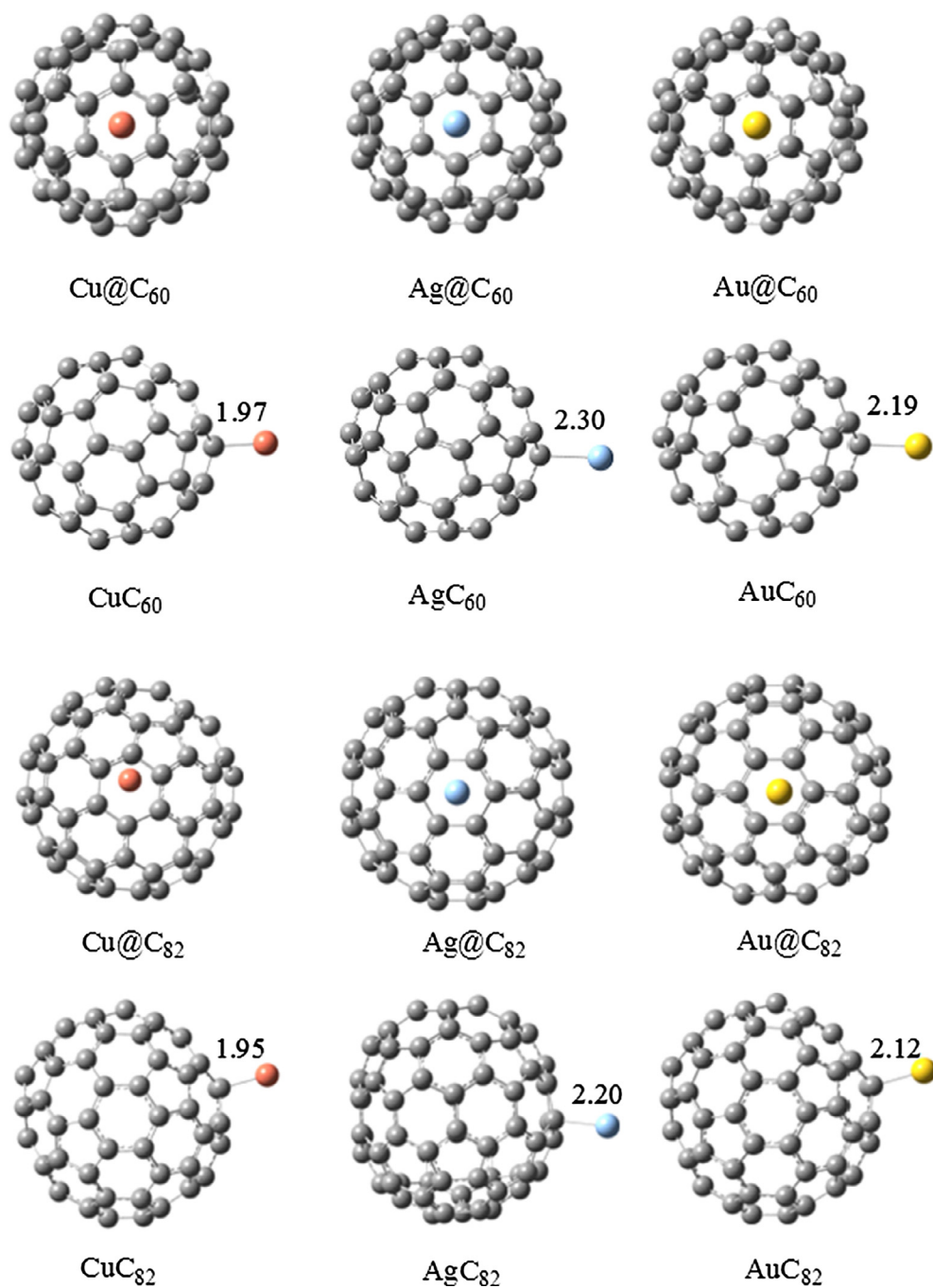

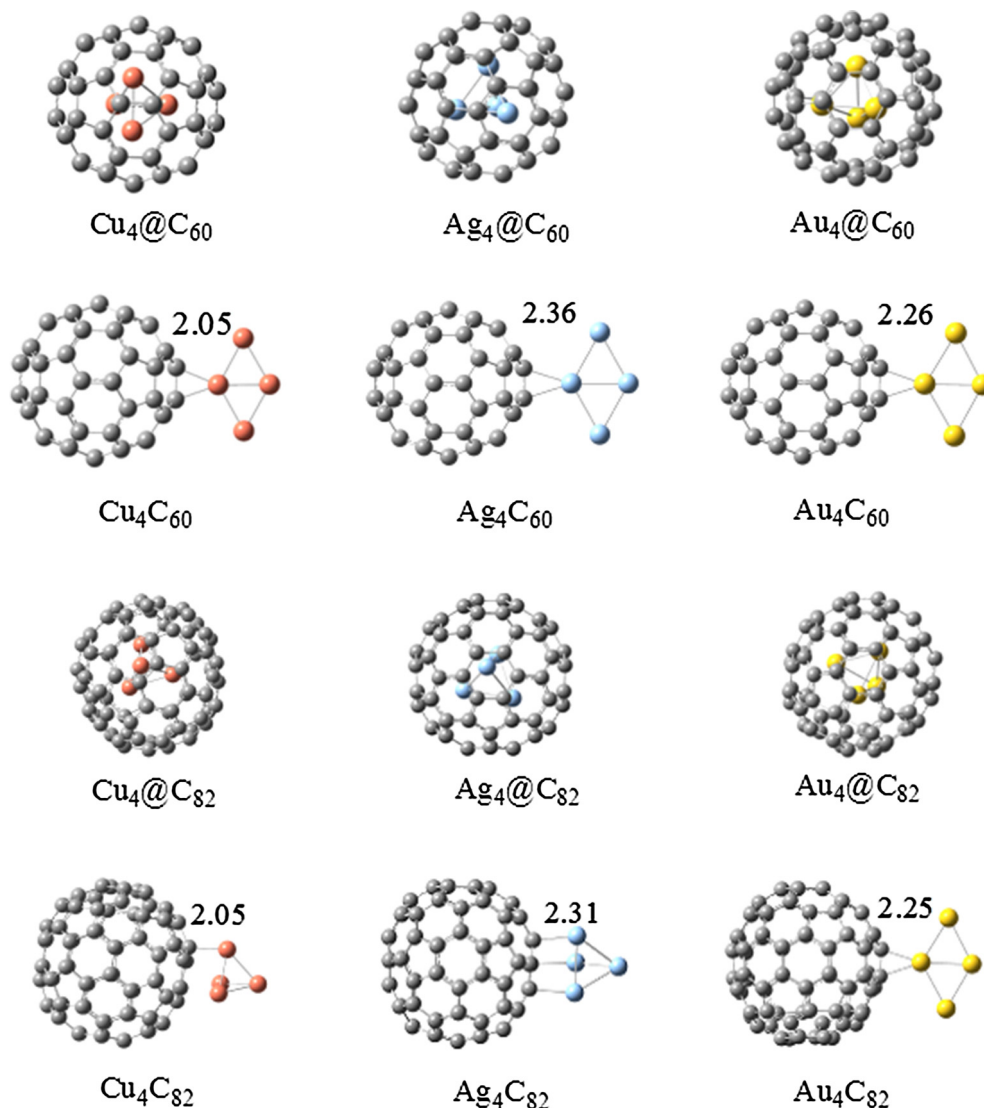**Fig. 3.** Optimized structures of endo and exohedral metal-fullerenes with one metal atom (Cu, Ag or Au; C_{60} and C_{82}).

Fig. 4. Optimized structures of the most stable structures of exo and endohedral metal-fullerenes with tetramers (Cu$_4$, Ag$_4$ or Au$_4$; C$_{60}$ and C$_{82}$).

3.2. Electron transfer mechanism

This investigation mainly intends to analyze the antioxidant properties of these systems and to compare fullerenes with the corresponding endo and exohedral metal-fullerenes. For this purpose, we analyzed the electron donor acceptor properties of these

systems. Table 1 reports the data from I and A of the structures previously discussed. These values are plotted in the FEDAM of Fig. 5. Values for C$_{60}$ and C$_{82}$ are included in red for purposes of comparison. The first notable result is that C$_{82}$ represents a better electron donor and better electron acceptor than C$_{60}$. Apparently, fullerene size influences antioxidant capacity, when considering this

Table 1
Vertical ionization energy (I) and vertical electron affinity (A) in eV of endo and exohedral metal-fullerenes.

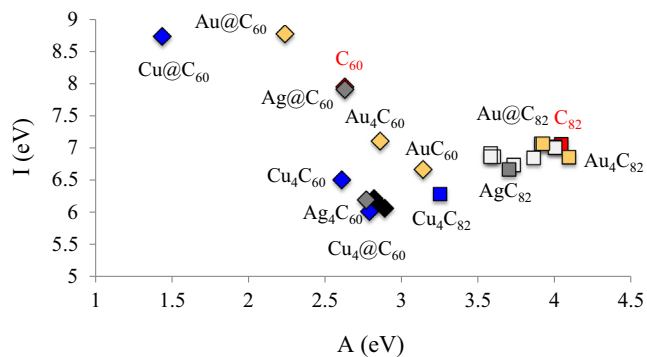| System	I	A	System	I	A
C$_{60}$	7.94	2.63	C$_{82}$	7.05	4.04
Cu@C$_{60}$	8.72	1.44	Cu@C$_{82}$	7.06	3.91
CuC$_{60}$	6.21	2.82	CuC$_{82}$	6.73	3.73
Ag@C$_{60}$	7.90	2.63	Ag@C$_{82}$	7.01	4.00
AgC$_{60}$	6.14	2.81	AgC$_{82}$	6.66	3.70
Au@C$_{60}$	8.76	2.24	Au@C$_{82}$	7.06	3.92
AuC$_{60}$	6.66	3.14	AuC$_{82}$	6.84	3.86
Cu$_4$@C$_{60}$	6.01	2.79	Cu$_4$@C$_{82}$	6.91	3.58
Cu$_4$C$_{60}$	6.50	2.61	Cu$_4$C$_{82}$	6.28	3.25
Ag$_4$@C$_{60}$	6.06	2.89	Ag$_4$@C$_{82}$	6.86	3.60
Ag$_4$C$_{60}$	6.19	2.77	Ag$_4$C$_{82}$	6.12	3.25
Au$_4$@C$_{60}$	6.14	2.84	Au$_4$@C$_{82}$	6.86	3.58
Au$_4$C$_{60}$	7.10	2.86	Au$_4$C$_{82}$	6.85	4.09

Fig. 5. FEDAM for systems being studied is reported. Rhombuses correspond to systems with C_{60}. Squares correspond to systems with C_{82}. Some indicators are colored to facilitate identification. Blue color corresponds to systems with Cu, grey to systems with Ag and yellow to systems with Au. Fullerenes without metals are presented in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mechanism. This comparison allows us to state that the presence of metal atoms and clusters modifies the electron donor acceptor properties of fullerenes. Generally, exohedral metal-fullerenes (MC_x) are better electron donors than the corresponding fullerenes. In the case of C_{60} systems, the presence of metal atoms and clusters at the surface of the fullerene (exohedral metal-fullerenes) also increase electron acceptor capacity (A is larger). In the case of C_{82}, metal clusters reduce the I values, making the systems better electron donors but A values are smaller than the C_{82} value, so they are worse electron acceptors. The best electron acceptor is Au_4C_{82} and the best electron donor is $Cu_4@C_{60}$. Notably, the presence of metals enhances the properties of C_{60} more than it does the characteristics of C_{82}. All systems with C_{82} are better electron acceptors than those with C_{60}, and some are also better electron donors.

In summary, there are two main results. Firstly, the size of the fullerene is related to the electron donor acceptor properties, *i.e.*,

the larger the system the better its electron-donor acceptor capacity. The second important result is that the presence of metal atoms and clusters of Cu, Ag and Au increases the electron donor acceptor properties of the systems and therefore, antioxidant capacity. Consequently, it is possible to conclude that the presence of metals is convenient.

3.3. Radical adduct formation

In order to analyze radical adduct formation, it is necessary to optimize the structure with the free radical bonded to the antioxidant molecule. As explained before (see Fig. 2), three different initial geometries were used in each case, and two free radicals (OH and OOH). Figs. 6 and 7 report the optimized structures of exo and endohedral metal-fullerenes (formed from the tetramer and C_{60} or C_{82}, respectively) interacting with OOH as an example. Other optimized structures of the adducts formed with OH and OOH are included as Supporting Material (Figs. 2SM–7SM). In all systems, bond length with a free radical is slightly longer when the bond is with any metal atom, than with a single carbon atom. This is related to the atomic radio of the metals.

To determine whether the presence of metal atoms improves the free radical scavenger capacity of C_{60} and C_{82}, it is necessary to compare the adduct formation Gibbs free energies (Eq. (2)) Table 2 reports the adduct formation Gibbs free energies of the most stable systems with OH. The reaction of C_{60} is less exergonic than with C_{82}. All adduct formation reactions are exergonic (with the sole exception of Ag@C_{82}-OH). Comparing endo and exohedral metal-fullerenes with C_{60}, it is apparent that the reaction is more exergonic, where exohedral fullerenes with free radicals are directly bonded to a single metal atom [C_{60}-M-OH]. With C_{82} metal-fullerenes, the reaction is more exergonic where free radicals are directly bonded to the metal cluster [C_{82}-M_4-OH]. Within the endohedral metal-fullerenes, the reaction is more exergonic for systems formed with metal clusters [$M_4@C_{60}$-OH and $M_4@C_{82}$-OH] than for those with metal atoms [$M@C_{60}$-OH and
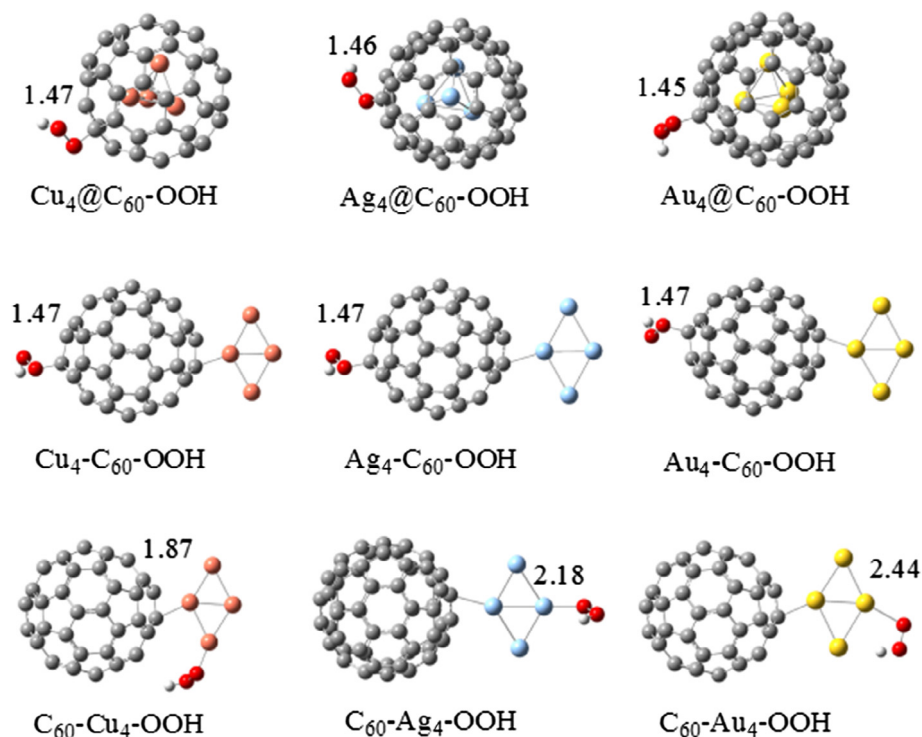

Fig. 6. Optimized structures of exo and endohedral metal-fullerenes (formed from the tetramer and C_{60}) interacting with OOH free radical. Some bond distances (in Å) are included.
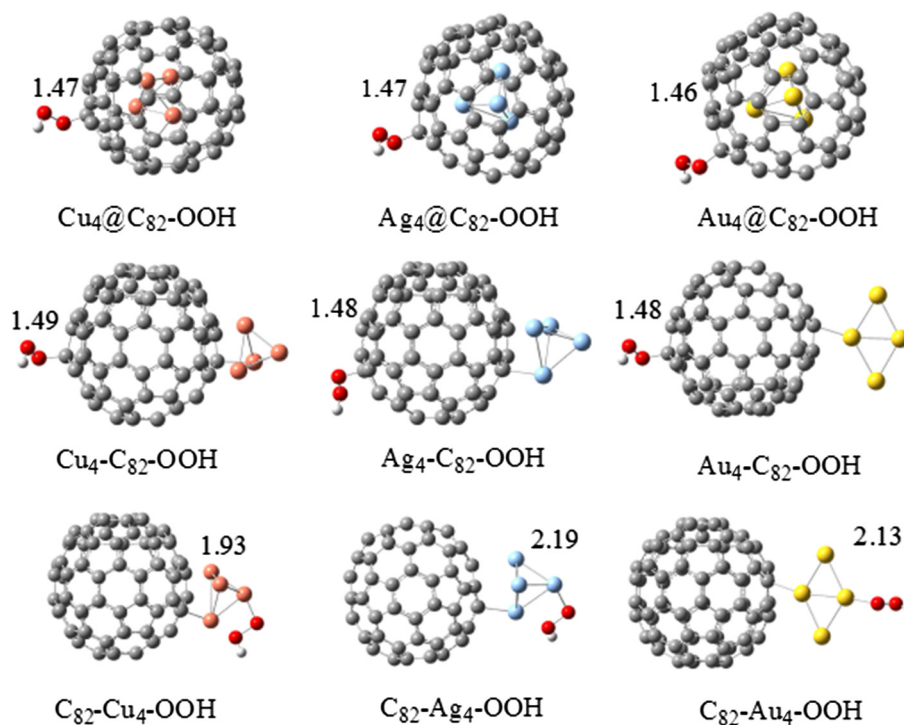
Fig. 7. Optimized structures of exo and endo metal-fullerenes (formed from tetramers and C_{82}) interacting with OOH free radical. Some bond distances (in Å) are included.

Table 2
Gibbs free energies (ΔG in kcal/mol) for the adduct formation reactions of endo and exohedral metal-fullerenes with OH free radical. Values for C_{60} and C_{82} are included for comparison purposes.

	C_{60} systems	ΔG	C_{82} systems	ΔG
	C_{60}-OH	−23.17	C_{82}-OH	−41.09
Cu endohedral	Cu@C_{60}-OH	−2.28	Cu@C_{82}-OH	−21.18
	Cu_4@C_{60}-OH	−44.25	Cu_4@C_{82}-OH	−32.79
Cu exohedral	Cu-C_{60}-OH	−24.89	Cu-C_{82}-OH	−14.01
	Cu_4-C_{60}-OH	−22.47	Cu_4-C_{82}-OH	−15.70
	C_{60}-Cu-OH	−71.99	C_{82}-Cu-OH	−48.11
	C_{60}-Cu_4-OH	−42.06	C_{82}-Cu_4-OH	−52.86
Ag endohedral	Ag@C_{60}-OH	−2.51	Ag@C_{82}-OH	1.82
	Ag_4@C_{60}-OH	−50.72	Ag_4@C_{82}-OH	−34.09
Ag exohedral	Ag-C_{60}-OH	−23.92	Ag-C_{82}-OH	−18.55
	Ag_4-C_{60}-OH	−23.06	Ag_4-C_{82}-OH	−35.31
	C_{60}-Ag-OH	−54.30	C_{82}-Ag-OH	−30.16
	C_{60}-Ag_4-OH	−30.09	C_{82}-Ag_4-OH	−42.73
Au endohedral	Au@C_{60}-OH	−5.96	Au@C_{82}-OH	−23.05
	Au_4@C_{60}-OH	−52.96	Au_4@C_{82}-OH	−36.56
Au exohedral	Au-C_{60}-OH	−20.62	Au-C_{82}-OH	−18.93
	Au_4-C_{60}-OH	−22.58	Au_4-C_{82}-OH	−19.33
	C_{60}-Au-OH	−57.39	C_{82}-Au-OH	−37.93
	C_{60}-Au_4-OH	−26.52	C_{82}-Au_4-OH	−69.06

M@C_{82}-OH]. In general, the capacity to scavenge OH free radical according to the RAF mechanism is increased with the presence of metal atoms and clusters. However, there are some metal-fullerenes with lower ΔG than the corresponding values for C_{60} and C_{82}. This is the case for endohedral metal-fullerenes with one metal atom [M@C_{60}-OH and M@C_{82}-OH]. In these systems, the presence of metal atoms does not improve the antioxidant capacity. Predictably, metal atoms and clusters will *attract* free radicals. The most exergonic reactions are those that produce C_{60}-Cu-OH and C_{82}-Au_4-OH.

The adduct formation Gibbs free energies for reactions with OOH are reported in Table 3. Notably, the reaction of C_{60} with this free radical is not exergonic, whereas it is with C_{82}. When metals are included, some of the metal-fullerenes of C_{60} present exergonic reactions with OOH. For this reason, it is possible to say that the presence of metals (atoms and clusters) improves the antioxidant capacity of C_{60}. Results are similar with C_{82}, as some systems present more negative values for Gibbs free energy than lone C_{82}, therefore improving antioxidant capacity.

However, in these systems not all adduct formation reactions are exergonic. There are seven and eight reactions (for C_{60} and C_{82} metal-fullerenes, respectively) that are endergonic. In order to improve the OOH scavenge capacity, it is important to select the systems according to the data of Table 3. With C_{60} metal-fullerenes the reaction is more exergonic for exohedral fullerenes with free radicals directly bonded to a single metal atom [C_{60}-M-OOH]. With C_{82} metal-fullerenes, the reaction is more exergonic for exohedral fullerenes where free radicals are directly

Table 3
Gibbs free energies (ΔG in kcal/mol) for the adduct formation reactions of endo and exohedral metal-fullerenes with OOH free radical. Values for C_{60} and C_{82} are included for comparison purposes.

	C_{60} systems	ΔG kcal/mol	C_{82} systems	ΔG kcal/mol
	C_{60}-OOH	−0.01	C_{82}-OOH	−17.38
Cu endohedral	Cu@C_{60}-OOH	20.88	Cu@C_{82}-OOH	2.72
	Cu_4@C_{60}-OOH	−21.35	Cu_4@C_{82}-OOH	−9.14
Cu exohedral	Cu-C_{60}-OOH	−1.81	Cu-C_{82}-OOH	9.01
	Cu_4-C_{60}-OOH	0.83	Cu_4-C_{82}-OOH	7.03
	C_{60}-Cu-OOH	−48.43	C_{82}-Cu-OOH	−25.88
	C_{60}-Cu_4-OOH	−19.69	C_{82}-Cu_4-OOH	−45.43
Ag endohedral	Ag@C_{60}-OOH	20.01	Ag@C_{82}-OOH	24.58
	Ag_4@C_{60}-OOH	−26.20	Ag_4@C_{82}-OOH	−11.50
Ag exohedral	Ag-C_{60}-OOH	0.05	Ag-C_{82}-OOH	4.78
	Ag_4-C_{60}-OOH	0.30	Ag_4-C_{82}-OOH	−11.89
	C_{60}-Ag-OOH	−30.05	C_{82}-Ag-OOH	−10.32
	C_{60}-Ag_4-OOH	−6.50	C_{82}-Ag_4-OOH	−33.58
Au endohedral	Au@C_{60}-OOH	17.30	Au@C_{82}-OOH	0.40
	Au_4@C_{60}-OOH	−29.51	Au_4@C_{82}-OOH	−13.35
Au exohedral	Au-C_{60}-OOH	2.54	Au-C_{82}-OOH	4.92
	Au_4-C_{60}-OOH	0.50	Au_4-C_{82}-OOH	3.53
	C_{60}-Au-OOH	−34.49	C_{82}-Au-OOH	−15.40
	C_{60}-Au_4-OOH	−3.55	C_{82}-Au_4-OOH	−7.45

bonded to the metal cluster [C_{82}-M_4-OOH]. The only exception is C_{82}-Au_4-OOH (Table 3). For gold, the reaction is more exergonic with one gold atom than with gold tetramer. Within the endohedral metal-fullerenes, the reaction is more exergonic for systems formed with metal clusters [M_4@C_{60}-OOH and M_4@C_{82}-OOH] than for those with metal atoms [M@C_{60}-OOH and M@C_{82}-OOH].

In summary, C_{82} is a better free radical scavenger than C_{60} and in many cases, the presence of metal atoms and clusters improves the antiradical capacity of fullerenes. All these results show that fullerenes can be functionalized with transition metal atoms and clusters in order to improve their antioxidant capacity. This could be very useful for future applications.

4. Concluding remarks

Optimized structures indicate that metal cluster structure of endohedral metal-fullerenes is a tetrahedron, probably in order to avoid repulsive interactions with carbon atoms. Clusters in exohedral metal-fullerenes present two different geometries: tetrahedron or rhombus. In the case of C_{60} metal-fullerenes, the rhombus structure of the metal tetramer is the most stable. In the case of C_{82}, exohedral metal-fullerenes with Cu_4 and Ag_4 are more stable with the cluster as the tetrahedron, than those which have the rhombus. For Au_4, the planar rhombus structure is more stable than the tetrahedron. This is a logical finding, as it is well known that gold clusters are planar up to 13 atoms.

The size of the fullerene relates to its electron donor acceptor properties, *i.e.*, the larger the system, the better its electron-donor acceptor capacity. Likewise, the presence of metal atoms and clusters of Cu, Ag and Au increases the electron donor capacity of the systems and therefore their antioxidant properties. Consequently, it is possible to conclude that the presence of metals is convenient.

All these results show that fullerenes can be functionalized with transition metal atoms and clusters, in order to improve antioxidant capacity. This could be very useful for future applications.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2017.06.015.

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