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Accounts

Endohedral Metallofullerenes: New Spherical Cage Molecules with Interesting Properties

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Endohedral metallofullerenes (fullerenes containing metals inside the carbon cage) have long attracted special interest as new spherical molecules with novel properties. Recent important progress has been marked by successful isolation and purification in macroscopic quantities. With the availability of such purified samples, it has been possible to investigate the structures, electronic properties, and chemical reactivities. Very recent progress in the theoretical and experimental studies of endohedral metallofullerenes is summarized to show what are known or still unknown for the future material, catalytic, and biological applications.

Since the first proposal in 1985[1)] immediately after the discovery of the special stability of C_{60} (buckminsterfullerene),[2)] encapsulation of one or more metal atoms inside hollow fullerene cages (endohedral metallofullerenes) has long attracted special attention since it could give rise to new species or materials with novel properties which are unexpected for empty fullerenes. In 1991 Smalley and co-workers showed for the first time that several lanthanum-containing fullerenes can be produced by laser vaporization of graphite rods impregnated with the appropriate metal oxides, and extraction with toluene yields mostly $La@C_{82}$ as a stable complex (the symbol @ denotes that La is located inside C_{82}).[3)] Triggered by this success, great efforts have been made for the production and characterization of endohedral metallofullerenes. Up to now it has been demonstrated that group 3 metals (M = Sc, Y, La) and most lanthanide metals can be trapped inside the higher fullerenes such as C_{80}, C_{82}, and C_{84} (much less abundant than C_{60} and C_{70}) to form soluble and relatively stable endohedral metallofullerenes ($M_m@C_n$).[4)]

Because of the difficulty in producing pure samples in large quantities, the experimental characterization of endohedral metallofullerenes has been hindered. Important progress in the last two years is marked by the successful isolation and purification of metallofullerenes such as $Sc@C_{82}$,[5)] $Y@C_{82}$,[6)] $La@C_{82}$,[7)] $Gd@C_{82}$[8)] $La_2@C_{80}$,[9)] $Sc_2@C_{84}$,[10)] and $Sc_3@C_{82}$[11)] in macroscopic quantities. It is generally accepted that these extractable metallofullerenes take on endohedral structures. However, a definitive structure proof has to be performed for each of these metallofullerenes. In addition, the electronic structures and properties as well as the chemical reactivities have begun to be explored with the availability of purified samples.

In this Account, we summarize recent progress in the theoretical and experimental studies of endohedral monometallofullerenes and dimetallofullerenes in an attempt to clarify what are already known or still unknown. Although emphasis may be mainly put on our recent studies, the present purposes are to disclose (a) how metals are trapped inside fullerene cages, (b) what are cage structures, (c) what are the electronic states of metals and cages, and (d) how the electronic properties and chemical reactivities of empty fullerenes change upon endohedral metal-doping. It is hoped that these answers will be of great help in understanding the growth mechanism and developing new routes to bulk production of endohedral metallofullerenes as well as in their important applications in several fields as new molecules with novel properties.

Monometallofullerene ($M@C_{82}$)

Almost without exception, it is currently observed that $M@C_n$ is most abundantly extracted when $n = 82$ (a magic number) as a representative and stable monometallofullerene.

Metal Positions and Cage Structures. For the C_{82} fullerene, it is known that there are nine distinct isomers which satisfy the so-called isolated pentagon rule,[12)] as shown in Fig. 1. However, the measurement of the ^{13}C NMR spectrum showed that only three isomers with C_2, C_{2v}, and C_{3v} symmetries were produced in a ratio of 8 : 1 : 1.[13)] The high-

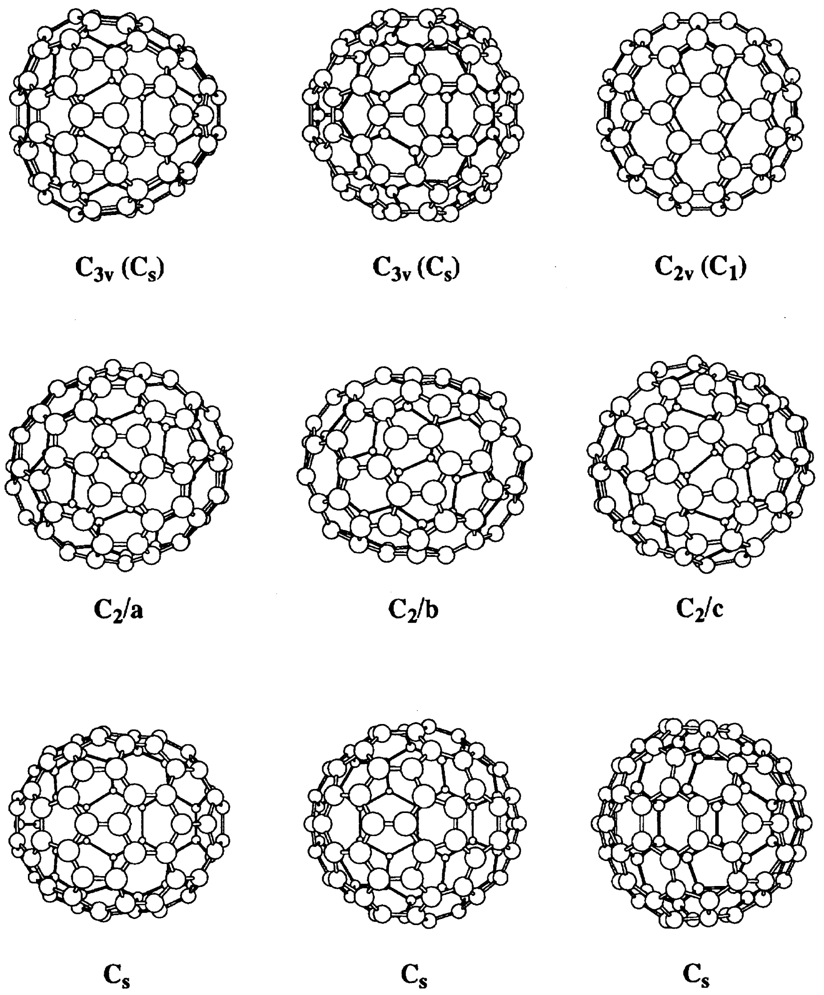


Fig. 1. Nine isomers of C_{82} which satisfy the isolated pentagon rule. Relaxed symmetries after geometry optimization are in parentheses.

est stability of the C_2 (a in Fig. 1) isomer was confirmed by calculations.[14)] However, it was found that the C_{2v} and C_{3v} isomers do not correspond to energy minima, but distort to have lower C_1 and C_s symmetries, respectively, because of energetic reasons and Jahn–Teller distortion.[14)] This contradicts the assignment of the observed NMR lines. However, a recent reinvestigation of the NMR lines with a newly purified C_{82} sample shows that one isomer with C_2 symmetry is produced while the two minor species are supposed to be other fullerenes.[15)] The most abundant production of the C_2 (a) isomer is also confirmed by the calculations with temperature effects.[16)]

It seems quite reasonable to assume that a metal (M) atom is trapped inside the C_2 (a) cage of C_{82} to form an endohedral complex (M@C_{82}). Thus, a metal atom was placed at the center of the C_{82} cage. However, it was found that the center is not energetically the most stable position.[14,17)] As Fig. 2a shows, M@C_{82} is most highly stabilized when the metal atom is moved along the C_2 axis toward the center of one hexagonal ring, regardless of the kind of M. This endohedral structure is consistent with the subsequent EXAFS studies of Y@C_{82}[18)] and La@C_{82}[19)] which show that the number of the nearest neighbor carbons is 6.

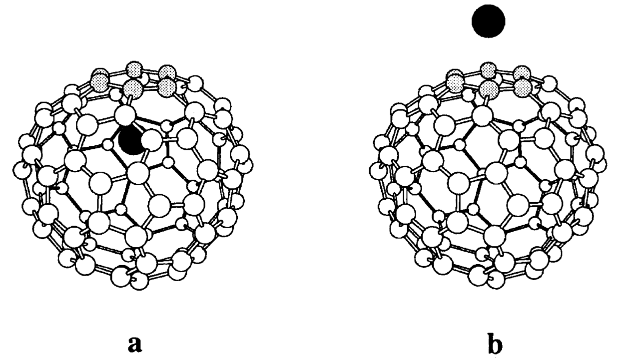


Fig. 2. The endohedral (a) and exohedral (b) structures of MC_{82}.

The structural feature can be more strongly supported from a recent synchrotron X-ray powder diffraction approach to Y@C_{82}.[20)] The electron density map obtained with a maximum-entropy method shows clearly that the Y atom is certainly encapsulated inside C_{82}. This provides the first direct experimental evidence of the endohedral nature of M@C_{82}. In addition, the density map reveals that Y is displaced from the center of C_{82}, as shown in Fig. 2a. Although the Y–C distance of 2.9 Å[20a)] estimated in the first report is significantly longer than our predicted values of 2.56—2.65 Å,[17)] the distance of 2.66 Å refined very recently[20b)] agrees almost perfectly with the predicted values. However, the cage symmetry and structure are not yet resolved from the X-ray study; these should be explored soon since they are important clues in disclosing the growth mechanism of endohedral metallofullerenes. A similar X-ray study of La@C_{82} is also in progress; however, no new information is yet obtained, except that La is located at the off-center positions inside C_{82}.[21)]

Electronic Structures. EPR spectroscopy provides useful information on electronic structures even with extracts containing a small amount of endohedral metallofullerenes. The first successful measurement of the EPR spectrum was achieved for La@C_{82}.[22)] An important observation is that the ^{139}La hyperfine coupling constant is very small and the g value is close to the free-spin value of 2.0023 (similar to those found for fullerene anion radicals). It has been suggested that the EPR feature is due to the fact that the La ($5d^1\ 6s^2$) atom donates its three valence electrons to the LUMO and LUMO+1 of C_{82} to form an endohedral complex with a $La^{3+}C_{82}{}^{3-}$ electronic structure. Subsequently, EPR studies were also successful for Sc@C_{82}[23)] and Y@C_{82}.[23c,24)] As observed for La@C_{82}, very small hyperfine coupling constants and near free-spin g values were observed. Therefore, it has been widely believed that the Sc and Y atoms have also a +3 charge inside C_{82}.

We have pointed out that the EPR data cannot always be direct evidence for $M^{3+}C_{82}{}^{3-}$.[17)] The electronic structures depend on the kind of entrapped metals. As is also apparent from the compact and low-lying d orbital of Sc shown in Fig. 3,[25)] the Sc ($3d^14s^2$) atom donates only its two 4s valence electrons to the LUMO of C_{82}, leaving behind its 3d electron on Sc: the resultant electronic structure is formally described as $Sc^{2+}C_{82}{}^{2-}$. However, transfer of all three valence electrons is increasingly favored upon going to Y@C_{82} and La@C_{82}, as originally interpreted from the EPR data. The electronic structure of $La^{3+}C_{82}{}^{3-}$ is also calculated with the La atom placed even inside the much more unstable C_{3v} cage of C_{82},[26)] while it is supported from the observations of the ultraviolet photoelectron spectrum,[27)] quadrupole coupling constant,[28)] and effective magnetic moment.[8b)] On the other hand, the difference in the electronic structures of Sc@C_{82} and La@C_{82} is well reflected in the differences in the anisotropic components of the hyperfine and g tensors[29)] and in the UV-visible absorption spectra.[4d,5)]

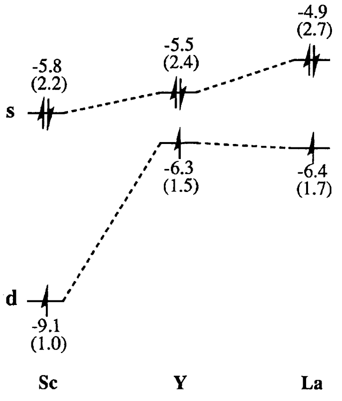


Fig. 3. The energy levels (eV) and sizes (Å) of atomic orbitals of Sc ($3d^14s^2$), Y ($4d^15s^2$), and La ($5d^16s^2$). The orbital sizes obtained by calculating $< r >$ are in parentheses.

The periodic trend from Sc to Y to La may suggest that lanthanides (4f block metals following La in the periodic table) donate three valence electrons to C_{82}. In fact, it has been proposed that lanthanide atoms such as Ce, Pr, Nd, Gd, Tb, Ho, Er, and Lu have a +3 charge inside C_{82}.[30)] However, a recent calculation of Ce@C_{82} shows that the Ce ($4f^15d^16s^2$) atom tends to donate only its two 6s valence electrons to C_{82}.[31a)] Encapsulations of the middle (Eu ($4f^76s^2$) and Gd ($4f^75d^16s^2$)) and last (Lu ($4f^{14}5d^16s^2$)) members in the lanthanide series inside C_{82} are also calculated.[4b,31b)] It is not surprising that the Eu atom donates only its two 6s valence electrons to C_{82} because of the absence of a low-lying d electron. However, the Gd and Lu atoms also tend to prefer a +2 charge inside C_{82} with $4f^75d^1$ (^{9}D) and $4f^{14}6s^1$ (^{2}S), respectively. This Gd^{2+} (^{9}D) state contrasts with the Gd^{3+} (^{8}S) state suggested from the magnetic data of Gd@C_{82};[8b,8c)] this discrepancy should be resolved in a future study. An interesting finding is that in Lu@C_{82} a large amount of the 6s electrons remains on Lu instead of the 5d electron, quite unlike the other cases, because of the large relativistic contraction and stabilization of the 6s orbital.[4b,31b)] This new finding may be confirmed in a future EPR study by observing a large hyperfine coupling constant.

It has been proposed that Sm@C_{82}, Eu@C_{82}, and Yb@C_{82} are very unstable under thermal desorption conditions, compared with other lanthanide fullerenes.[30a)] However, the binding energy of 114 kcal mol^{-1} calculated as an example for Eu@C_{82} is rather larger than those of 104 and 102 kcal mol^{-1} for Gd@C_{82} and Lu@C_{82}, respectively.[4b,31b)] In addition, the calculated ionization potential and electron affinity of Eu@C_{82} are comparable to those of Gd@C_{82} (see below). These suggest that Eu@C_{82} is not particularly unstable either thermodynamically or kinetically, unlike the proposal from the laser desorption and thermal desorption mass spectra.[30a)] It is likely that the EuC_{82} complex produced is exohedral, as shown in Fig. 2b, which is still 65 kcal mol^{-1} more stable than Eu + C_{82},[4b,31b)] although experimental confirmation is essential. In this context, it may be interesting to note that EuC_{82} shows significantly different retention times in HPLC.[32)] More interestingly, it has been shown that Sm, Eu, and Yb (volatile metals) are not trapped in the form of carbides inside carbon nanocapsules.[33)] It is also shown that these metals do not form stable neutral MC_n ($n = 2$—20) clusters which would lead to endohedral metallofullerenes.[34)] This may be ascribed to the larger promotion energies of Sm, Eu, and Yb for the $f^ns^2 \rightarrow f^{n-1}d^1s^2$ transitions upon the formation of bonds, associated with the stable f^6, f^7, and f^{14} electron configurations.[31b)]

Electronic Properties. Ionization potentials (I_p) and electron affinities (E_a) play an important role in characterizing electronic properties. It is instructive to compare these values of endohedral metallofullerenes with those of typical fullerenes such as C_{60} and C_{70} (whose properties have been widely investigated). However, no direct experimental data are yet available for endohedral metallofullerenes.[35] Therefore, the I_p and E_a values calculated recently are summarized in Table 1,[31,36] together with those of C_{60} and C_{70}. The calculated I_p and E_a values of 7.78 and 2.57 eV for C_{60} agree well with the available experimental values of 7.64[37] and 2.65[38] eV, respectively. It is hoped that the tabulation will be of great help in disclosing systematically the electronic properties as well as the reactivities of endohedral metallofullerenes.

It was suggested early that metallofullerenes have lower ionization potentials than empty fullerenes.[39] This can be now confirmed quantitatively in Table 1. The I_p values for $M@C_{82}$ are 1.2—1.6 eV smaller than those for C_{60} and C_{70}. In addition, Table 1 shows that the E_a values for $M@C_{82}$ are 0.4—0.7 eV larger than those for C_{60} and C_{70}. These indicate that endohedral metallofullerenes can act as a stronger electron donor as well as a stronger electron acceptor. This is consistent with the shifts of the first oxidation and reduction potential peaks measured in solution for $Y@C_{82}$[6] and $La@C_{82}$,[40] relative to those of C_{60} and C_{70}.

As Table 1 shows, endohedral metallofullerenes have rather similar ionization potentials. For example, the difference in I_p between $Sc@C_{82}$ and $La@C_{82}$ is only 0.3 eV, though the original LUMO level (occupied in $Sc@C_{82}$) of C_{82} is responsible for the ionization of $Sc@C_{82}$ while the original LUMO +1 level (singly occupied in $La@C_{82}$) of C_{82} for that of $La@C_{82}$. This is due to the fact that the energy gap between the original LUMO and LUMO +1 of C_{82} is only 0.6 eV.[17] Similar trends are also seen for E_a.

A remarkable finding is that the net charge on the M atom in $M@C_{82}$ is little changed even when $M@C_{82}$ loses or accepts an electron.[31,36] This allows the formal view that electron removal and gain take place on the C_{82} cage, with M acting as a positive core as in a sort of "superatom." In an attempt to confirm this view, the I_p and E_a of C_{82}^{2-} and C_{82}^{3-} were calculated by placing a point charge of 2+ or 3+ instead of the metal atom.[31,36] Such model calculations give the I_p and E_a values which agree well (in both magnitude and order) with those calculated for $M@C_{82}$; note that electron attachment to C_{82}^{2-} and C_{82}^{3-} is not significantly bound or unbound without the point charge. This supports again the view that endohedral metallofullerenes are composed of a positively charged core-metal and a negatively charged cage and are electrostatically bound.[17,31,36] Thus, it is expected that endohedral metallofullerenes such as $Y@C_{82}$ and $La@C_{82}$ behave like a Li atom, while $Sc@C_{82}$ and $Gd@C_{82}$ (in which the C_{82} cage has formally closed shell character) behave like a He atom. In this context, a recent STM study is interesting which shows that $Y@C_{82}$ forms dimers and trimers by a covalent interaction along the step edge of the Cu(111) clean surface in a way that the Li atom forms the Li_2 and Li_3 molecules.[41] In contrast, the monomer adsorption is dominant for $Gd@C_{82}$ and the intermolecular interaction is well understood with a weak van der Waals force.[42]

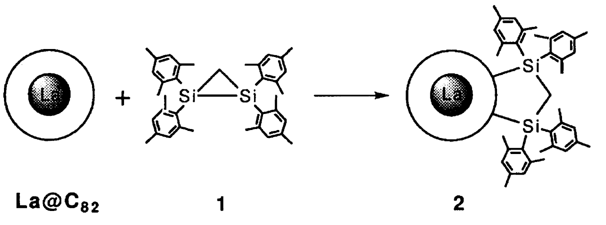
Table 1. The Ionization Potentials (I_p) and Electron Affinities (E_a) Calculated in eV for $M@C_{82}$ and Fullerenes

	I_p	E_a
$Sc@C_{82}$	6.45	3.08
$Y@C_{82}$	6.22	3.20
$La@C_{82}$	6.19	3.22
$Ce@C_{82}$	6.46	3.19
$Eu@C_{82}$	6.49	3.22
$Gd@C_{82}$	6.25	3.20
C_{60}	7.78	2.57
C_{70}	7.64	2.69

Reactivities. A huge number of experimental studies have been made to functionalize empty fullerenes such as C_{60} and C_{70} to understand the basic chemical properties and obtain new derivatives with interesting material, catalytic, or biological properties.[43] We have developed a new procedure to functionalize C_{60} and C_{70} by the addition of silicon and germanium compounds.[44—51] It is an interesting challenge to disclose how the reactivities of empty fullerenes are modified upon endohedral metal-doping.[52] Thus, we have undertaken the first exohedral functionalization of $La@C_{82}$ with 1,1,2,2-tetramesityl-1,2-disilirane (**1**) (Scheme 1).[53]

The photochemical reaction was first tested. It was verified from the LD-TOF and FAB mass spectra that the reaction leads to its 1 : 1 adduct (**2**); no molecular ion peaks ascribable to multiple-addition products were observed. It is noteworthy that $La@C_{82}$ can be also functionalized, as in the case of empty fullerenes. A more remarkable finding is that $La@C_{82}$ reacts thermally with **1**. This is in sharp contrast to the fact that empty fullerenes react with **1** only in a photochemical way.[46,47] Apparently, the facile thermal addition of **1** to $La@C_{82}$ is due to the stronger electron acceptor as well as the stronger electron donor properties (see Table 1). The EPR spectra measured during the reaction reveal the formation of at most two regioisomers with a different La isotropic splitting. This suggests that the regioselectivity as well as the reactivity of empty fullerenes could be highly controlled by endohedral metal-doping.

In order to see how the reactivity changes when a different metal is inside the cage, the reaction of $Gd@C_{82}$ with **1** was also investigated.[54] It is found that $Gd@C_{82}$ is functionalized both photochemically and thermally, as in the case of $La@C_{82}$. This is not surprising since the I_p and E_a of $Gd@C_{82}$ are comparable to those of $La@C_{82}$. Also successful have been the functionalizations of $La@C_{82}$ by digermirane[55] and diphenyldiazomethane.[56]



Scheme 1.

It is expected that these successful exohedral derivatizations of endohedral metallofullerenes trigger much more work and constitute an important stepping stone on the way to new practical applications since they can also serve as precursors of newer types of molecules. In this context, it should be emphasized that the present derivatizations differ significantly from those[57a)] of endohedral noble gas fullerenes such as He@C_{60} and He@C_{70}.[57)] In the chemical derivatizations of La@C_{82} and Gd@C_{82}, the degree of the electron transfer from the electropositive metal to the fullerene cage plays a crucial role and thereby tunes the electronic properties of the fullerene cage, unlike the noble gas case.

Isomers. It has been claimed from well-resolved EPR studies that an isomer with slightly different EPR signals exists for M@C_{82}.[23c,24c,58)] This isomer is much less stable in air and various solvents. The yield of the isomer is highly increased during arc synthesis in a low He buffer pressure region (< 60 Torr, 1 Torr = 133.322 *P*a).[59)] The origin of the isomer has long been a matter in dispute.[17)] It has been considered that the isomer originates from encapsulation of a metal atom inside a different fullerene cage, since the mass spectroscopic analyses confirm that it is not from MC_n with different *n*. With a purified sample of the isomer of La@C_{82},[60)] it has been successful to trace its reaction with disilirane (**1**) by using FAB mass and EPR spectroscopies.[61)] The disappearance of the isomer was observed but neither 1 : 1 adducts nor EPR active products were observed. On the other hand, the reaction with O_2 led to an EPR inactive product which fragments to $LaC_{82}O$. Apparently, these quite different reaction patterns are not explained in terms of a different cage structure. It seems rather reasonable to assume that the La atom is exohedrally attached on the C_{82} cage, as shown in Fig. 2b. According to the theoretical calculations of the exohedral complex,[4c,61)] the electronic structure is described as $La^{2+}C_{82}{}^{2-}$. However, the binding energy is still as large as 68 kcal mol^{-1}, contrary to usual expectation. The calculated small spin density on the s orbitals of La agrees with the observed small hyperfine coupling constant. The lower I_p of 5.57 eV is consistent with the fact that the isomer is more reactive toward O_2. As Fig. 4 shows, the C_{82}-derived vacant orbital level becomes higher in the exohedral complex; this is obviously unfavorable for the nucleophilic addition of **1** on the C_{82} cage. It is expected that the exohedral view of the isomer is further confirmed in a future study.

Dimetallofullerenes (Sc_2@C_{84} and La_2@C_{80})

Two metal atoms can even be encapsulated inside the higher fullerene cages to form extractable and air-stable endohedral complexes. Among these, Sc_2@C_{84} and La_2@C_{80} have attracted special attention as representative and abundant dimetallofullerenes.

Structures and Electronic States. For the C_{84} fullerene, there are 24 distinct isomers which obey the isolated pentagon rule.[12)] According to the ^{13}C NMR study,[13)] two isomers with D_2 and D_{2d} symmetries (numbered 22 and 23 in Ref. 12) are most abundantly produced as a 2 : 1 mixture. These two isomers are very close in energy and much more stable than the remaining 22 isomers. On the other hand, the endohedral nature of Sc_2@C_{84} has been strongly suggested from the observed STM[62)] and TEM[63)] images. According to the STM study, there are at least two different sizes in the image. Through the Hartree–Fock (HF) and nonlocal density functional (B3P) calculations (HF for geometry optimization and B3P for energies),[64)] we have predicted that Sc_2@C_{84} is most highly stabilized when two Sc atoms are placed inside the D_{2d} isomer along the C_2 axis bisecting the double bonds at the fusion of two hexagons.[65)] This endohedral structure has D_{2d} symmetry and its fully optimized structure is shown in Fig. 5a.[66)] In contrast to the empty case, encapsulation of two Sc atoms inside the D_2 isomer of C_{84} was calculated to be 11.6 kcal mol^{-1} less stable. A more stable endohedral structure was obtained by placing two Sc atoms inside the C_s isomer (numberd 10 in Ref. 12) of C_{84}. As shown in Fig. 5b, the optimized structure has C_s symmetry in which two Sc atoms are nonequivalently located in the C_s plane.[67)] This C_s structure is only 5.2 kcal mol^{-1} less stable than the D_{2d} structure.

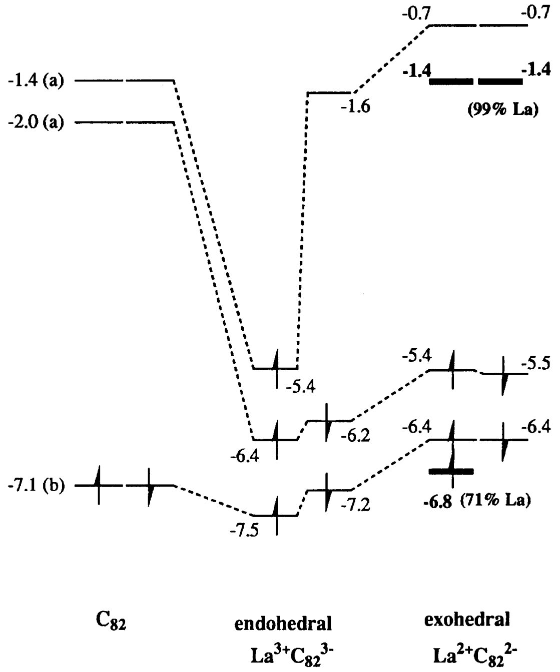


Fig. 4. The molecular orbital levels (eV) of C_{82} and LaC_{82}. Solid lines denote La-dominated orbitals.

With the availability of a purified sample, Shinohara and co-workers have recently succeeded in measuring the ^{13}C NMR spectrum of the most abundant isomer of Sc_2@C_{84}.[68)] The observed total 11 distinct ^{13}C NMR lines (10 strong lines of nearly equal intensity and one line of half intensity) agree perfectly with the D_{2d} structure (Fig. 5a) with 11 nonequivalent carbons (10(×8)+1(×4) carbons). This is the first determination of cage symmetry for endohedral metallofullerenes. This may suggest that energetically stable isomers are produced as major isomers even for endohedral metallofullerenes, as are so for empty fullerenes, although only the importance of the growth process and kinetics has often been emphasized. On the other hand, Miyake et al.

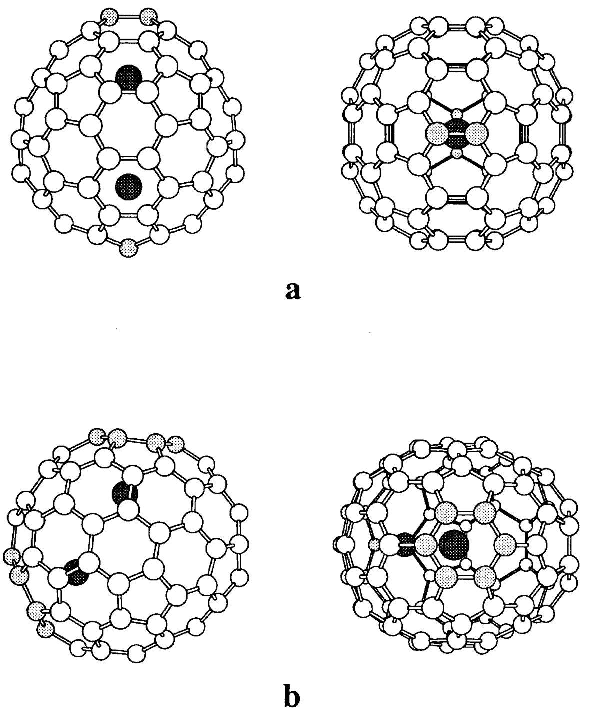


Fig. 5. Two views of the D_{2d} (a) and C_s (b) structures of $Sc_2@C_{84}$. (a) The Sc–Sc distance is 4.029 Å and each Sc is 2.358 Å far from the double bond carbons. (b) The Sc–Sc distance is 3.486 Å and each Sc is 2.403 and 2.404 Å far from the nearest hexagonal carbons.

have succeeded in observing the ^{45}Sc NMR spectrum which shows only one single ^{45}Sc signal.[69] This clearly confirms that two Sc atoms are equivalently located inside C_{84}, as shown in Fig. 5a.

It is recently possible to isolate two more isomers with a two-stage HPLC method.[68] A very recent ^{13}C NMR study shows total 46 lines (38+8 (half intensity)) for one of the isomers.[68b] This agrees with the C_s structure (Fig. 5b) with 46 nonequivalent carbons (38(×2)+8(×1) carbons). The ^{45}Sc NMR study at 298—363 K shows two distinct ^{45}Sc signals of equal intensity.[69] This confirms that two Sc atoms are nonequivalent in the temperature ranges, as shown in Fig. 5b. The HOMO (−6.4 eV) and LUMO (−1.9 eV) levels calculated at the HF level for the C_s structure are significantly higher and lower than the HOMO (−6.8 eV) and LUMO (−1.4 eV) levels of the D_{2d} structure, respectively.[67] This may suggest that the C_s isomer of $Sc_2@C_{84}$ is kinetically also less stable than the D_{2d} isomer.

We now turn to $La_2@C_{80}$. For C_{80}, there are seven isomers which satisfy the isolated pentagon rule,[12] as shown in Fig. 6. According to the HF and B3P calculations,[64] the D_2 and D_{5d} (D_5) isomers, close in energy, are the most stable isomers of C_{80} while the I_h (D_2) isomer is most unstable (in parentheses are relaxed symmetries after geometry optimization).[70] We have suggested that the D_2 isomer is most abundantly produced despite the closeness to $D_{5d}(D_5)$ in energy.[70] The characterization and isomer distribution of C_{80} (the first higher fullerene beyond C_{60} to allow I_h symmetry) have attracted considerable interest since C_{80} has been a "missing" fullerene between C_{60} and C_{96}[15] because of the difficulty in separation. However, the high abundance (> 90%) of the D_2 isomer has very recently been verified by the successful isolation and the analysis of the observed ^{13}C NMR lines.[71]

To determine the cage symmetry and structure of $La_2@C_{80}$, we have investigated several endohedral structures by placing La_2 inside the most stable D_2 and D_{5d} cages of C_{80} as well as the most unstable I_h cage.[70] In contrast to the empty case, it turned out that encapsulation of La_2 inside the I_h cage is 63—79 kcal mol^{-1} more stable at the B3P level. This is because the spherical I_h cage of C_{80} has only two electrons in the four-fold degenerate HOMOs and can accommodate six more electrons to form a stable closed shell electronic state. This endohedral structure with the I_h cage becomes most stable when two La atoms face the hexagonal rings of C_{80} in an equivalent way with D_{2h} symmetry, as shown in Fig. 7.

It could be argued that the energetic advantage does not necessarily mean its abundant production since it depends on the kinetic stability and formation mechanism. In this context, it should be noted that the cage-derived HOMO and LUMO levels become much lower and higher in the D_{2h} endohedral structure in Fig. 7.[70] Furthermore, it has been successful to measure and compare the oxidation and reduction potentials of $La_2@C_{80}$ and $Sc_2@C_{84}$ (D_{2d}), as mentioned later. The oxidation and reduction potentials of $La_2@C_{80}$ are higher and lower than those of $Sc_2@C_{84}$ (D_{2d}), respectively. This is satisfied only by the D_{2h} endohedral structure in Fig. 7.[70] Finally, we have very recently confirmed that two La atoms are equivalent and trapped inside the I_h cage, from the ^{139}La and ^{13}C NMR studies of $La_2@C_{80}$.[72]

In both $La_2@C_{80}$ and $Sc_2@C_{84}$, the distances between two metals are greatly increased, as shown in Figs. 5 and 7.[65—67,70] This indicates that two metal atoms are not encaged as a dimer. It is interesting that the long Sc–Sc distance of 4.029 Å predicted for $Sc_2@C_{84}$ (D_{2d}) is in good agreement with the recent experimental value of 3.95 Å from the X-ray study.[73] Such bond lengthening is not surprising since electron transfer from the bonding orbitals of La_2 and Sc_2 is highly favored in the cages. As a result of the transfer of almost three and two electrons from each La and Sc to C_{80} and C_{84}, respectively, the electronic structures are formally described as $(La^{3+})_2C_{80}{}^{6-}$ and $(Sc^{2+})_2C_{84}{}^{4-}$ in the ground singlet state.[65—67,70] The large red shifts of UV-visible absorption peaks observed for $Sc_2@C_{84}$ (D_{2d}) relative to C_{84}[10] are well explained as a result of the electron transfer. The electronic structure of $(Sc^{2+})_2C_{84}{}^{4-}$ is also consistent with the X-ray photoemission spectrum observed recently.[74] Two metals are highly stabilized in the endohedral structures: for example, $Sc_2@C_{84}$ (D_{2d}) is 217 and 234 kcal mol^{-1} more stable at the B3P level than Sc_2+C_{84} and 2Sc+C_{84}, respectively.[65,67] This stabilization is mostly electrostatic and due to polarization, as is also supported from the fact that neither significant positive overlap populations nor bond orders are found between metals and cage carbons.[65,70] The calculated singlet electronic states agree with the EPR studies which show no paramagnetic signal.[23a,23b]

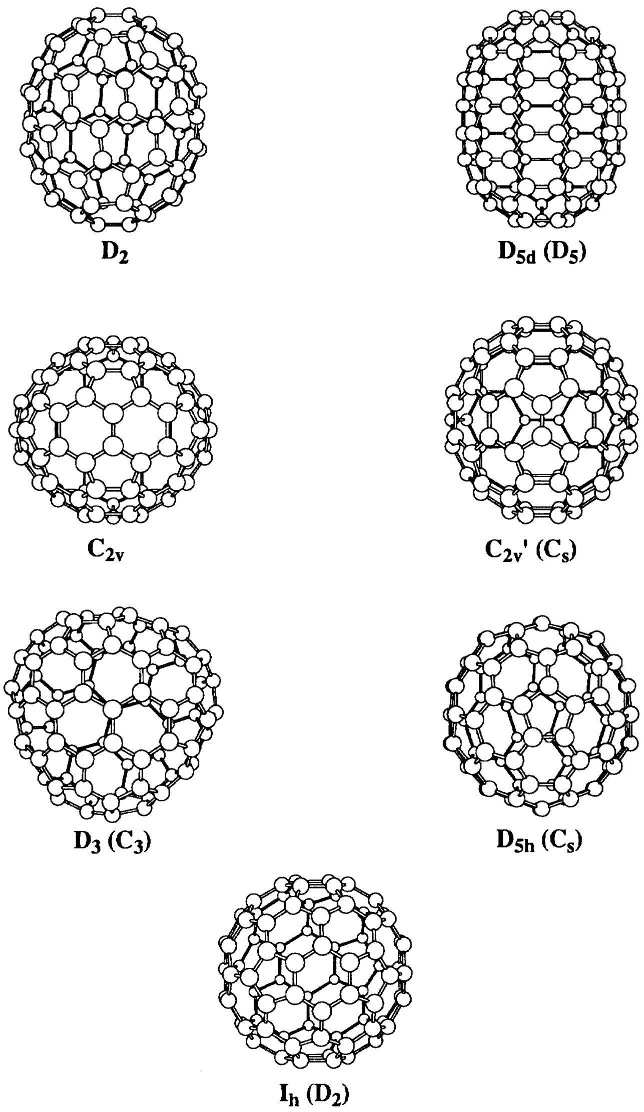

D_2 **D_{5d} (D_5)** **C_{2v}** **C_{2v}' (C_s)** **D_3 (C_3)** **D_{5h} (C_s)** **I_h (D_2)**

Fig. 6. Seven isomers of C_{80} which satisfy the isolated pentagon rule. Relaxed symmetries after geometry optimization are in parentheses.

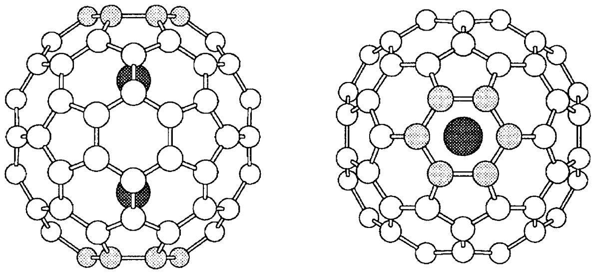


Fig. 7. Two views of the D_{2h} structure of $La_2@C_{80}$ optimized by placing two La atoms inside the I_h cage of C_{80}. The La–La distance is 3.655 Å and each La is 2.567—2.598 Å far from the hexagonal carbons of C_{80}.

Up to now, it has not been successful to extract $Sc_2@C_{80}$ and $La_2@C_{84}$ in macroscopic quantities, unlike the cases of $La_2@C_{80}$ and $Sc_2@C_{84}$. In this context, it is interesting that encapsulation of two Sc atoms inside the I_h cage of C_{80} leads to transfer of only two electrons from each Sc to C_{80}; a high reactivity is expected for $Sc_2@C_{80}$ since one of the four-fold degenerate HOMOs of C_{80} remains to be unfilled.[75] Two Sc atoms are rather more stabilized inside the D_{5h} cage of C_{80}. However, the HOMO and LUMO levels of $Sc_2@C_{80}$ calculated at the HF level are higher and much lower than those of $La_2@C_{80}$, respectively. On the other hand, it was calculated for the C_{84} (D_{2d}) case that $La_2@C_{84}$ has higher HOMO and lower LUMO levels than $Sc_2@C_{84}$.[75]

From gas phase ion mobility measurements, dimetallofullerenes with one exohedral and one endohedral metal atom, $M(M@C_n)$, have been identified.[76] When $n=74$, $Sc(Sc@C_n)$ and $La(La@C_n)$ were calculated to be 51 and 29 kcal mol^{-1} less stable at the B3P level than $Sc_2@C_n$ and $La_2@C_n$, respectively, while they become 70 and 75 kcal mol^{-1} less stable when $n=84$.[75] This agrees with the fact that encapsulation of two metal atoms is increasingly favored with an increase in n.

Reactivities. It is of great interest to disclose how the reactivities change when two metals are encapsulated inside

Table 2. Reactivities, Oxidation (E_{ox}), and Reduction (E_{red}) Potentials in V, and HOMO-LUMO Levels[a] in eV of Endohedral Metallofullerenes and Empty Fullerenes

	Reactivity		E_{ox}	E_{red}	HOMO	LUMO
	$h\nu$	Heat				
$La_2@C_{80}$	Yes	Yes	+0.56	−0.31	−7.18	−2.55
$Sc_2@C_{84}$	Yes	No	+0.53	−0.97	−6.77	−1.38
C_{60}	Yes	No	+1.21	−1.12	−8.33	−0.63
C_{70}	Yes	No	+1.19	−1.09	−7.97	−0.84
C_{76}	Yes	No	+0.81	−0.94	−7.42	−1.13
C_{78}	Yes	No	+0.85	−0.73	−7.44	−1.49
C_{82}	Yes	No	+0.72	−0.69	−7.36	−1.52
C_{84}	Yes	No	+1.04	−0.75	−7.79	−1.34
$La@C_{82}$	Yes	Yes	+0.07	−0.42		
$Gd@C_{82}$	Yes	Yes	+0.09	−0.39		

a) Calculated at the HF level for C_{60} (I_h), C_{70} (D_{5h}), C_{76} (D_2), C_{78} (C_{2v}), C_{82} (C_2), C_{84} (D_{2d}), $La_2@C_{80}$ (D_{2h}), and $Sc_2@C_{84}$ (D_{2d}).

fullerene cages. For this purpose, we have again investigated the reactions with disilirane (**1**).[66]

As is summarized in Table 2, we have found that both $La_2@C_{80}$ and $Sc_2@C_{84}$ (D_{2d}) can be functionalized by the photochemical addition of **1**. These are the first examples of the derivatization of endohedral dimetallofullerenes. We have also investigated the thermal reactions. As Table 2 shows, higher fullerenes C_{76}, C_{78}, C_{82}, and C_{84} as well as C_{60} and C_{70} do not react thermally with **1**. A remarkable finding is that $La_2@C_{80}$ reacts thermally with **1** to provide a 1 : 1 adduct(s). This is due to the low-lying La-derived LUMO level of $La_2@C_{80}$ which is 1—2 eV lower than those of the empty fullerenes, being consistent with the fact that $La_2@C_{80}$ has a lower reduction potential.[9] On the other hand, the thermal addition of **1** to $Sc_2@C_{84}$ (D_{2d}) is suppressed, as in empty fullerenes, because of the higher-lying LUMO level. This is consistent with the higher reduction potential of $Sc_2@C_{84}$. In this context, it is not surprising that both $La@C_{82}$ and $Gd@C_{82}$ react thermally with **1**, since they have low reduction potentials comparable to that of $La_2@C_{80}$. These results strongly suggest that the thermal additions are initiated by electron transfer from **1** to endohedral metallofullerenes with strong electron accepting power, regardless of the number of metals.

Are Metal Atoms Still inside Fullerene Cages ?

Up to here we have discussed nothing about the motion of encapsulated metals. However, it is an interesting question whether the metals are rigidly attached to cage carbons or move about. In an attempt to answer this question, it is of great help to provide insight into the nature of the inside of fullerene cages. For this purpose, we have investigated the aspect of the electrostatic potentials inside the $C_{80}(I_h)$, C_{82} (C_2), and C_{84} (D_{2d}) cages at the HF level.[77]

An interesting finding is that the values of the electrostatic potentials are all positive (i.e., destabilization for cationic species) at any positions inside the cages, reflecting that the probability of finding electrons inside is much smaller than that of finding them outside. Such positive values are not specific to the higher fullerenes but rather common to neutral carbon cages, as also found for C_{60} and C_{70}.[78] In other words, the inside of fullerene carbon cages is originally suitable for the accommodation of anionic or neutral species; in fact, anionic species are highly stabilized in fullerene carbon cages,[79] unlike fullerene silicon cages.[80]

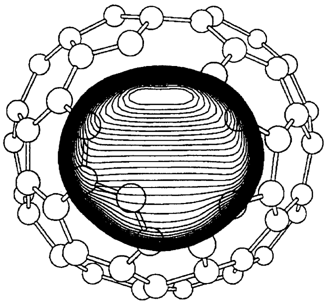


Fig. 8. The electrostatic potential map of $C_{82}{}^{2-}$.

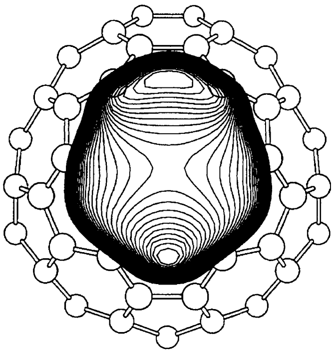


Fig. 9. The electrostatic potential map of $C_{84}{}^{4-}$.

However, the situation is drastically changed as electrons are transferred onto carbon cages.[77] To make this clearer, the electrostatic potentials calculated for $C_{82}{}^{2-}$ and $C_{84}{}^{4-}$ are shown in Figs. 8 and 9. These electrostatic potentials provide highly negative values (ca. −144 kcal mol^{-1} for $C_{82}{}^{2-}$ and ca. −281 kcal mol^{-1} for $C_{84}{}^{4-}$) and are very suitable for the accommodation of cationic species. This is a reason why encapsulated metals do not preserve a neutral state but prefer highly cationic states. Obviously, energy cost in electron transfer from metals to cages is smaller for metals with lower I_p and cages with higher E_a; in addition, it is overcome enough by resultant electrostatic attractions. It appears that the attractions are highly enhanced with an increase in the electron transfer. Thus, it may not be surprising that the atoms encapsulated up to now are mostly group 3 and lanthanide metals for which multiple ionizations are facile.

The positively charged metals should be most highly stabilized at the minima of the electrostatic potentials. Thus, the metal positions calculated for $M@C_{82}$ (Fig. 2a) and $Sc_2@C_{84}$ (Fig. 5a) correspond to the minima of the electrostatic potentials in Figs. 8 and 9, respectively. This again confirms that electrostatic interactions play a dominant role in stabilizing endohedral metallofullerenes.

In a strict sense, in $C_{82}{}^{2-}$ the minimum of the electrostatic potentials below a hexagon is displaced from the C_2 axis while two minima are exactly below and above the middle of the double bonds in $C_{84}{}^{4-}$. As Figs. 8 and 9 shows, however, the electrostatic potentials are flat around the minima. Accordingly, for example, the actual calculations of $Sc_2@C_{84}$ (D_{2d}) show that the energy changes are only ca. 1—2 kcal mol^{-1} at the B3P level even when each Sc atom moves off the minima by ca. 1 Å along the double bonds in C_{84}, although further large displacement leads to great destabilization.[77] These small energy changes suggest that metals are not still but are oscillating with a considerable amplitude at high speed even at room temperature.[81]

Much more interesting is the case of $C_{80}{}^{6-}$ (I_h). The electrostatic potential map shows almost concentric circles with no clear minima,[77] reflecting the round cage structure. According to the actual calculations of $La_2@C_{80}$, the overall barrier is ca. 5 kcal mol^{-1} at the B3P level even if two La atoms make the circuit of the inside of the cage.[77,82] This energy barrier is interesting since it can make the metals stop with a decrease in temperature and circulate at high speed with an increase in temperature. Such temperature control of metal motion inside fullerene cages may lead to an interesting "molecular device" with new electronic or magnetic properties.

The circuit of two La^{3+} atoms (with a large moment of inertia) inside C_{80} produces a magnetic field at the positions of La. In the ^{139}La NMR study, this should be reflected in the nuclear magnetic relaxation rate (hence, the line-width). Ordinarily, interaction between nuclear spins and the magnetic field (a spin-rotation interaction) does not contribute significantly to the relaxation time in solutions, since molecular rotation is dominantly quenched by neighbors. In $La_2@C_{80}$, however, the rotation of La_2 can be preserved due to the unique cage protection so that the spin-rotation interaction has a drastic effect on the relaxation process. Relaxation by the spin-rotation interaction leads to an increase in line-width with increasing temperature, unlike other types of relaxation.[83] We have recently succeeded in observing clearly the corresponding changes in the widths of the ^{139}La NMR line: 105 Hz at 305 K, 151 Hz at 323 K, 264 Hz at 343 K, and 920 Hz at 363 K.[72] This is the first experimental evidence for the circular motion of metal atoms in endohedral metallofullerenes.

In conclusion, the fundamental studies of endohedral metallofullerenes have greatly progressed in the last few years through a close interplay of theoretical calculations and experiments. It is noteworthy that these have been mostly achieved by several research groups in our country and constitute an important stepping stone on the way to the material, catalytic, and biological applications. To enrich these applications, new routes to bulk production of endohedral metallofullerenes are expected to be developed in the coming year, as once developed for fullerenes.[84]

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82) As Fig. 7 shows, $La_2@C_{80}$ is most stable when each La is directed to the center of the hexagonal ring of C_{80}. It is destabilized by 14.3 kcal mol^{-1} when each La is directed to the center of the pentagonal ring. Except this, La can freely move about with barriers of 4.9—5.5 kcal mol^{-1}. Therefore, there are many paths for the circuit of La. When each La circles about along the hexagonal rings, the barrier is the smallest (4.9 kcal mol^{-1}).

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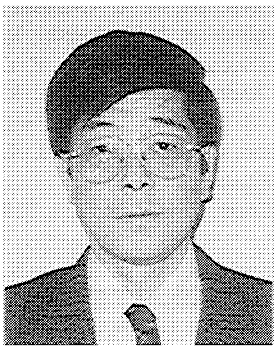

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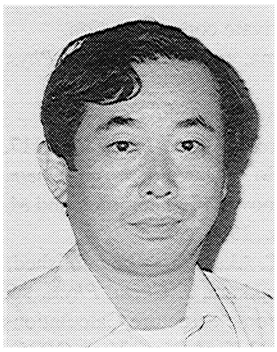

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