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$La_2@C_{72}$ and $Sc_2@C_{72}$: Computational Characterizations

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The $La_2@C_{72}$ and $Sc_2@C_{72}$ metallofullerenes have been characterized by systematic density functional computations. On the basis of the most stable geometry of 39 C_{72} hexaanions and the computed energies of the best endofullerene candidates, the experimentally isolated $La_2@C_{72}$ species was assigned the structure coded #10611. The good agreement between the computed and the experimental ^{13}C chemical shifts for $La_2@C_{72}$ further supports the literature assignment (Kato, H.; Taninaka, A.; Sugai, T.; Shinohara, H. *J. Am. Chem. Soc.* **2003**, *125*, 7782). The geometry, IR vibrational frequencies, and ^{13}C chemical shifts of $Sc_2@C_{72}$ were predicted to assist its future experimental characterization.

1. Introduction

Although the endohedral metallofullerene $La_2@C_{72}$ was prepared and isolated in 1998,[1] its structure was first proposed five years later by Kato et al.[2] on the basis of the observed 18-line ^{13}C NMR spectrum. Taking line broadening into account, all the lines had equal intensity. This pointed to D_2 symmetry, thus reducing the 11 189 possible C_{72} cage isomers to 24. Of these, two non-IPR D_2 C_{72} cages (coded #10611 and #10958), which satisfy the observed ^{13}C NMR pattern and have the least number of fused pentagons, were considered by Kato et al.[2] as the best candidates to encapsulate the two La atoms. Both these isomers have two pentagon−pentagon junctions, violating both the well-known isolated pentagon rule (IPR)[3] and the pentagon adjacency penalty rule (PAPR).[4] Since the energy of hexaanion #10611 was lower than that of #10958 (computed at RHF/3-21G) and the HOMO−LUMO gap of the #10611 hexaanion was greater, the latter (#10611) was chosen for the observed $La_2@C_{72}$ species. If confirmed, this structure would add another member to the family of metallofullerenes with non-IPR cages such as $Ca@C_{72}$,[5,6] $Sc_2@C_{66}$,[7] and $Sc_3N@C_{68}$.[8]

The empty C_{72} and C_{74} cages were once called "missing fullerenes".[9] With a rather small energy gap between the highest occupied and lowest unoccupied molecular orbitals,[10] the only available IPR isomer of C_{74} (with D_{3h} symmetry)[3c] has an open-shell electronic structure.[11] However, the C_{74} (D_{3h}) cage can be stabilized by direct reduction to the dianion,[9,12] by endohedral complexation (as in $Ca@C_{74}$,[13] $Ba@C_{74}$,[14] and $La@C_{74}$),[15] or by formation of exohedral adducts such as $C_{74}F_{38}$.[16] On the other hand, the only IPR isomer (with D_{6d} symmetry) of C_{72} has a HOMO−LUMO gap comparable to those of C_{60} and C_{70}. Nevertheless, a non-IPR C_{2v} species with a pentagon−pentagon fusion[5b,17] is predicted to be more stable than the IPR form; this is supported indirectly by the correlation between the computed and measured electron affinity and ionization energy of C_{72}.[18] Pristine C_{72} still has not been isolated,[2] perhaps due to its insolubility in fullerene HPLC solvents. However, endohedral complexes are known; two non-IPR cages could be present in comparable amounts in $Ca@C_{72}$.[6b,19]

We now report further computations at higher levels on C_{72} isomers, their hexaanions, and $La_2@C_{72}$ isomers. The results support Kato et al.'s assignment.[2] Moreover, we also characterize $Sc_2@C_{72}$ computationally; its isolation was reported in 1999,[20] but its structure has not been established.

2. Computational Methods

The initial full geometry optimizations followed by harmonic vibrational computations of $La_2@C_{72}$ and $Sc_2@C_{72}$ in D_2 symmetry employed the B3LYP density functional[21] with the 3-21G basis set for C and Sc and a double-ζ basis set (Lanl2DZ) with the effective core potential (ECP) for La[22] (denoted here by 3-21G∼dz). The geometries were then optimized at a higher level using the standard 6-31G* basis set for C and Sc, i.e., at the B3LYP/6-31G*∼dz level. The Gaussian 03 program[23] was employed.

NMR spectra were computed using the gauge-independent atomic orbital (GIAO) method.[24] In addition to the 6-31G*∼dz basis set, the CEP-4G, CEP-31G, and CEP-121G methods[25] also were employed for $La_2@C_{72}$. Perdew and Wang's[26] exchange and correlation functionals (PW91) were also employed to probe the effect of a different density functional. The limitations of the above ECP approaches were removed by employing the universal UGBS and UGBS1P Gaussian basis sets for La[27] with Douglas, Kroll, and Hess (DKH)[28] relativistic correction as an option. The computed ^{13}C chemical shifts of $La_2@C_{72}$ and $Sc_2@C_{72}$, relative to those of C_{60}, were converted to the TMS scale based on the experimental C_{60} value (δ = 143.15 ppm).[29] Note that the flexible character of the encapsulated

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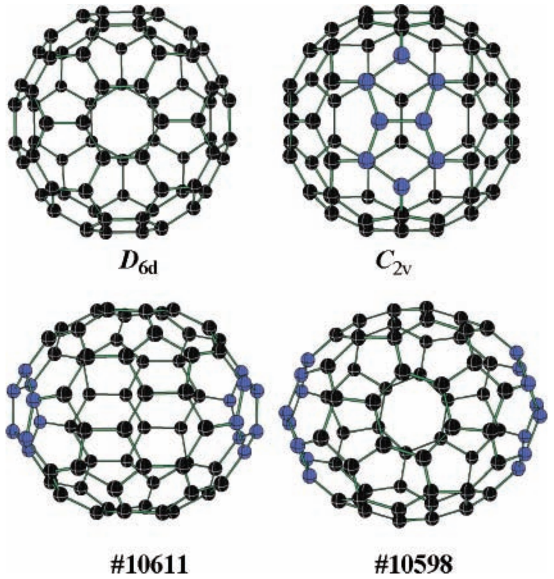


Figure 1. Isomers of C_{72}. The pentagon−pentagon fusions are highlighted in blue.

TABLE 1: Number of Pentagon−Pentagon Fusions (N_{PP}), the B3LYP/6-31G* Relative Energies (E_{rel}, kcal/mol), and HOMO−LUMO Gap Energies (Gap, eV) of C_{72} and C_{72}^{6-}

		C_{72}		C_{72}^{6-}	
isomers	N_{PP}	E_{rel}	Gap	E_{rel}	Gap
D_{6d}	0	11.5	2.50	73.4	1.03
C_{2v}	1	0.0	1.47	22.4	1.40
#10611	2	43.7	1.09	0.0	1.97
#10958	2	34.7	1.53	58.0	1.30

atoms inside the fullerene cage might influence the calculated properties, in particular the vibrational and NMR spectra,[30] but these effects have been neglected.

3. Results and Discussion

Relative Stability of C_{72} Hexaanions. The screening of a metallofullerene structure usually begins[5a,8a] by considering the charged empty cages; the magnitude of the negative charge is based on the expected electron donation from the encapsulated metal(s). Since the electronic structure of $La_2@C_{72}$ and $Sc_2@C_{72}$ can be described as $(M^{3+})_2C_{72}^{6-}$ (M = La, Sc),[1a] the C_{72}^{6-} hexaanions were computed first.

Topologically, 24 C_{72} cages have D_2 symmetry.[2,5b] In addition, the higher symmetry of 15 additional C_{72} cages (namely, five D_{2d}, five D_{2h}, three D_3, one D_6, and one D_{6d}) might be reduced to D_2 symmetry under experimental conditions. Hence, we computed all 39 of these cage hexaanions at the HF/3-21G//PM3 level; the #10611 isomer has, by far, the lowest energy, the next-best isomer, #10958, is 81.2 kcal/mol less stable. The energy separation between these two hexaanions changes to 58.0 kcal/mol at the B3LYP/6-31G* DFT level. Note that both the #10611 and #10958 isomers have the smallest number of pentagon−pentagon fusions among the D_2 C_{72} cages considered.

Although C_{72} has one IPR isomer, namely, with D_{6d} symmetry, its non-IPR C_{2v} isomer with one pentagon−pentagon fusion is the most stable neutral C_{72} cage.[5b] This C_{2v} structure violates both the IPR[3] and PAPR rules.[4] Our computed data for both the neutral and hexaanionic D_{6d} and C_{2v} isomers of C_{72} along with #10611 and #10958 are compared in Figure 1 and Table 1. The hexaanion and neutral isomer stability orders are quite different.

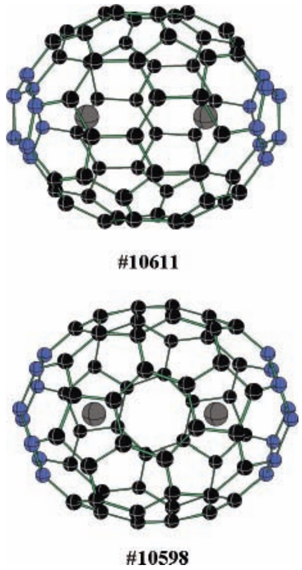
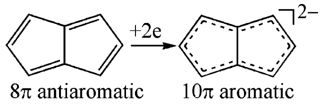


Figure 2. B3LYP/6-31G*∼dz-optimized structures of $La_2@C_{72}$ isomer. The $Sc_2@C_{72}$ has similar structures.

Consider the neutral order first: C_{2v} C_{72} with one pentagon−pentagon fusion has the lowest energy, followed by the D_{6d} IPR isomer (11.5 kcal/mol higher in energy) and the #10958 and #10611 isomers with two pentagon−pentagon fusions (34.7 and 43.7 kcal/mol, respectively, higher in energy) (Table 1). The stability of the more nearly spherical neutral non-IPR C_{2v} isomer may be explained by the large deviation of the ellipsoidal C_{72} (D_{6d}) geometry from a spherical shape. Using C_{50} as an example, Diaz-Tendero et al.[31] pointed out that sphericity influences the relative stability of fullerene isomers along with the IPR and PAPR rules, since nearly spherical shapes can be adopted even when they have a greater number of adjacent pentagons.

This stability order of the C_{72} hexaanions changes dramatically: the most stable isomer is the non-IPR isomer #10611, followed by the C_{2v}, the #10958, and the D_{6d} isomers (relative energies 22.4, 58.0, and 73.4 kcal/mol, respectively). Note that the IPR rule is violated by the C_{72} hexaanions to an even larger extent: isomer #10611 with two adjacent pentagon pairs wins out thermodynamically. Why? The net charges are mainly located in the polar region and formally convert the 8π antiaromatic pentalenes into 10π aromatic pentalene dianions.[32]



Relative Stability of $La_2@C_{72}$ and $Sc_2@C_{72}$ Isomers. We find that Kato et al.'s most likely $La_2@C_{72}$ #10611 structure does indeed have the most stable C_{72}^{6-} outer fullerene cage.[2] Direct computational comparisons of the #10611 and # 10958 $La_2@C_{72}$ isomers (Figure 2) confirm their assignment.

Both the #10611 and # 10958 isomers of $M_2@C_{72}$ (D_2, M = La, Sc) are local minima at B3LYP/3-21G∼dz. At all our levels of theory, the endohedral #10611 isomer is more than 50 kcal/mol lower in energy than its #10958 alternative (Table 2). This parallels the energy difference between the corresponding bare C_{72} hexaanions. This large energy advantage is decisive; it cannot be overcome by possible entropy differences even at very high temperatures.[13b,17a,19] For example, in the case of $Sc_2@C_{72}$, one has to increase the temperature to 3100 K in order to cross just the 0.1% population threshold for the minor species. The six vibrational frequencies related to the metal atom motions

TABLE 2: Relative Energies (ΔE_{rel}, kcal/mol) of $M_2@C_{72}$ (M = La, Sc) Isomers Computed with the B3LYP Functional

species	M−C (Å)[a]	ΔE_{rel} (kcal/mol) 3-21G∼dz	ΔE_{rel} (kcal/mol) 6-31G*∼dz
$La_2@C_{72}$ (#10958)	2.59	54.5	58.2
$La_2@C_{72}$ (#10611)	2.55	0.0	0.0
$Sc_2@C_{72}$ (#10958)	2.18	52.8	54.1
$Sc_2@C_{72}$ (#10611)	2.17	0.0	0.0

[a] The shortest M−C distance at the B3LYP/6-31G*∼dz level.

in the #10611 isomer are very low (22, 75, 95, 112, 207, and 214 cm^{-1} for $La_2@C_{72}$, as well as 54, 98, 149, 163, 227, and 293 cm^{-1} for $Sc_2@C_{72}$), indicating that the metal atom motions have relatively large amplitudes over the rather flat potential energy surfaces. The computed La−C distances (ca. 2.6 Å) (Table 2) are close to those in the previously computed La-encapsulated fullerenes,[5a] while the Sc atoms are closer to the cage (ca. 2.2 Å).

^{13}C and ^{139}La Chemical Shifts of $La_2@C_{72}$ and $Sc_2@C_{72}$. $La_2@C_{72}$. The 18 quartets of symmetry-equivalent atoms of the D_2 #10611 $La_2@C_{72}$ structure correspond to the 18 ^{13}C NMR lines of equal intensity deduced experimentally.[2] The observed 18-line $\delta^{13}C$ NMR spectrum ranges from 136 to 158.1 ppm.

The 18 ^{13}C NMR chemical shifts of the #10611 isomer are computed from 135.2 to 154.8 ppm at B3LYP/6-31G*∼dz and from 137.0 to 162.7 ppm at B3LYP/6-31G*∼UGBS1P & DKH (for the detailed ^{13}C NMR data see the Supporting Information). Both these computed $\delta^{13}C$ NMR intervals agree with the observed data quite well.[2] It is encouraging that the $\delta^{13}C$'s computed with the ECP basis set for La atoms also agrees with the experimental ^{13}C NMR data[2] although neither averaging over large-amplitude motions nor corrections for solvent effects are included. The somewhat larger computed ^{13}C NMR range of the #10958 isomer (129.6−158.8 ppm) is less satisfactory but does not in itself rule out this possibility.

Similarly, 18 ^{13}C NMR signals are expected for the most stable $Sc_2@C_{72}$ isomer (#10611). Computations show that these 18 signals range from 135.0 to 155.5 ppm, very close to the $La_2@C_{72}$ range. The metal atom influence is minor.

The experimental NMR of a mixture[2] found that ^{139}La in $La_2@C_{72}$ is 173 ppm more shielded than that in $La_2@C_{80}$. Hence, we computed $La_2@C_{80}$ at the same levels as $La_2@C_{72}$. Owing to a fast motion of the encapsulated La atoms in the I_h C_{80} cage, the $La_2@C_{80}$ system exhibits effective icosahedral symmetry in NMR determinations; its static symmetry in computations is method-dependent.[5a,33] At B3LYP/3-21G∼dz, the energy minimum has nearly D_{3d} symmetry. This geometry was employed for the chemical shift computations summarized in Table 3.

The computed ^{139}La chemical shift difference between $La_2@C_{72}$ and $La_2@C_{80}$ is underestimated considerably relative to the experimental value with all the La ECP basis sets. The $\delta^{139}La$ difference of the #10958 isomer always has the wrong sign. Although performing satisfactorily for ^{13}C (see above), ECP basis sets are too "truncated" to be suitable for computing heavy atom chemical shifts. The UGBS-computed ^{139}La chemical shift differences for the #10611 isomer are much larger, but the variations are considerable. A firm choice between #10611 and #10958 cannot be made on the basis of the data in Table 3. Computations at more sophisticated theoretical levels are needed. Improved models would consider not only a single static arrangement but also the motions of the encapsulated atom(s). The sampling might involve NMR calculations on various configurations that are accessible to the encapsulated atoms.

TABLE 3: $La_2@C_{80}$ − $La_2@C_{72}$ ^{139}La Chemical Shift Difference for #10611 and #10958 at Various Theoretical Levels Compared with Experiment

approach	$\Delta\delta$ $La_2@C_{80}$ − $La_2@C_{72}$ (ppm) #10611	#10958
B3LYP/3-21G∼dz	13	−32
B3LYP/6-31G*∼dz	14	−31
B3LYP/CEP-4G	12	−34
B3LYP/CEP-31G	15	−41
B3LYP/CEP-121G	17	−37
PW91/CEP-31G	16	−31
B3LYP/6-31G*∼UGBS	360	
B3LYP/6-31G*∼UGBS & DKH	280	
B3LYP/6-31G*∼UGBS1P & DKH	93	
observed	173	

TABLE 4: Computed IR-Active Vibrational Wavenumbers (v, cm^{-1}, Unscaled) and the Relative Intensities (I) for the #10611 $La_2@C_{72}$ Isomer at the B3LYP/3-21G∼dz Level of Theory[a]

symmetry	v	I	symmetry	v	I
B1	1047	0.21	B3	1360	0.49
B1	1285	0.63	B3	1368	0.36
B1	1298	0.23	B1	1376	1.00
B3	1301	0.37	B3	1387	0.70
B2	1327	0.39	B1	1441	0.32
B1	1350	0.35	B1	1498	0.23
B1	1355	0.24			

[a] Only those with relative IR intensities larger than 0.2 are presented.

TABLE 5: Computed IR-Active Vibrational Frequencies (v, cm^{-1}, Unscaled) and Relative Intensities of the #10611 $Sc_2@C_{72}$ Isomer at B3LYP/3-21G[a]

symmetry	v	I	symmetry	v	I
B1	913	0.21	B1	1359	0.44
B1	1292	0.32	B1	1376	1.00
B2	1308	0.20	B3	1385	0.56
B1	1320	0.55	B1	1386	0.27
B3	1324	0.46	B3	1397	0.50
B2	1341	0.33	B3	1435	0.32
B3	1341	0.33	B1	1479	0.22
B1	1345	0.34	B2	1516	0.24

[a] Only those with relative IR intensities larger than 0.2 are given.

Vibrational Frequencies. The infrared spectra of $La_2@C_{72}$ and $Sc_2@C_{72}$ have not been reported. While there are 216 total vibrational modes of D_2 $M_2@C_{72}$ (M = La, Sc), 55A + 53 B_1 + 54B_2 + 54 B_3, only the B_1, B_2, and B_3 symmetry modes are IR active. Thus, ideally $M_2@C_{72}$ should have up to 161 measurable IR frequencies, but the intensities of some of these will be weak. Tables 4 and 5 present the computed frequencies of the most stable isomers of $La_2@C_{72}$ and $Sc_2@C_{72}$, respectively (only the vibrational modes that have IR intensities larger than one-fifth of the strongest computed line are given). Due to the D_2 symmetry, the vibrational spectrum of $La_2@C_{72}$ is relatively simple with only a few intense signals, ranging between 1300 and 1500 cm^{-1}. This vibrational region also is important in the computed IR spectrum of $La_2@C_{80}$.[33]

4. Conclusions

Our systematic investigation helps characterize the $La_2@C_{72}$ and $Sc_2@C_{72}$ metallofullerenes. The "well-established" IPR and PAPR rules do not hold for the C_{72} hexaanions. Although having two pentagon−pentagon fusions, the #10611 C_{72}^{6-} isomer has the lowest energy among the 39 C_{72} hexaanions studied. This result corresponds with the high stability of the $La_2@C_{72}$ and

$Sc_2@C_{72}$ metallofullerenes having the same outer cage. The computed lower energy of the #10611 $La_2@C_{72}$ isomer supports its assignment[2] as the isolated endohedral species. The experimentally uncharacterized $Sc_2@C_{72}$ also is predicted to be the #10611 isomer; the computed ^{13}C NMR and IR spectra can be used to assist the future experimental characterization

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Supporting Information Available: Gaussian archive files of the B3LYP/6-31G*~dz-optimized structures and the detailed ^{13}C chemical shifts. This material is available free of charge via the Internet at http://pubs.acs.org.

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