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Endohedral Fullerenes

Dichlorophenyl Derivatives of La@C_{3v}(7)-C_{82}: Endohedral Metal Induced Localization of Pyramidalization and Spin on a Triple-Hexagon Junction**

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Endohedral metallofullerenes (EMFs), that is, fullerenes with metal atom(s) inside, continue to attract broad interest from the scientific community because of their unique structures, fascinating properties, and potential applications in biomedicine, electronics, photovoltaics, and materials science.[1]

Although C_{60} and C_{70} are the most abundant empty fullerenes, when Smalley and co-workers performed the first toluene extraction of La EMFs in 1991, they surprisingly found that La@C_{82} is the most accessible EMF in solution.[2] Thus, 82 has been viewed as a magic number for EMFs, and La@C_{82} is a prototypical EMF. Electron paramagnetic resonance spectroscopy and HPLC studies revealed that two isomers of La@C_{82} exist in solution.[3] Theoretical calculations predicted that La@C_{2v}(9)-C_{82} and La@C_s(6)-C_{82} are the two most likely candidates,[4] and this was soon confirmed by ^{13}C NMR data of the anions of La@C_{82},[5] as well as X-ray structures of several derivatives of La@C_{2v}(9)-C_{82}.[6]

It is expected that other C_{82} isomers can also be found, because as many as nine possible isomers of C_{82} satisfy the isolated-pentagon rule (IPR).[7] However, two cages [C_{2v}(9) and C_s(6)] are exclusively found for M@C_{82} with trivalent M (M = Y, Ce, Pr, Gd, etc.).[8,9] Only when the type of encapsulated metal species is changed can other C_{82} cages be formed, because the number of electrons transferred from metal to cage differs. A divalent metal (e.g., Yb) tends to template the C_2(5)-C_{82} cage along with the C_{2v}(9)-C_{82} and C_s(6)-C_{82} isomers because they are the most stable for C_{82}^{2-}.[4,10] When encapsulating two metal atoms or a bimetallic cluster, the C_{3v}(8)-C_{82} cage is generated; sometimes the C_{2v}(9)-C_{82} and C_s(6)-C_{82} cages are also formed. Representative examples are M_2C_2@C_{82} (M = Sc, Y, or Er)[11] and M_2S@C_{82} (M = Sc, Y, Dy, or Lu).[12] The most impressive example is Gd_3N@C_{82} which has the non-IPR C_s(39663)-C_{82} cage.[13] In summary, four IPR isomers and one non-IPR cage have been isolated for EMFs having a C_{82} cage together with the only empty isomer C_2(3)-C_{82}.[14] Because the cage structures substantially alter the physical and chemical properties of EMFs, it is still desirable to discover other new structures having the same metal core, which may have different properties. However, no La@C_{82} isomer with a cage other than C_{2v}(9)-C_{82} and C_s(6)-C_{82} has been reported to date.

Recently, we developed a method to extract EMFs from soot using 1,2,4-trichlorobenzene (TCB).[15] Because of the presence of highly reactive dichlorophenyl radicals generated by refluxing TCB, which react readily with some insoluble EMF species, several missing-cage EMFs La@C_{2n} ($2n$ = 72, 74, 80) were isolated in the form of their dichlorophenyl derivatives.[15] This method is so powerful that not only missing-cage species could be isolated, but new cages of other higher EMFs can also be obtained. Here we report the first isolation and unambiguous structural identification of a new C_{82} cage, namely, C_{3v}(7)-C_{82}, captured as La@C_{82}($C_6H_3Cl_2$). More interestingly, NMR and X-ray results reveal that the dichlorophenyl group is singly bonded to a triple-hexagon junction (THJ) carbon atom on the C_3 axis, so that the high C_{3v} symmetry is preserved in the adducts. This is the only example of fullerene derivatives in which a single addend is linked to one of the THJ carbon atoms, which are believed to be the least reactive on a fullerene cage. Theoretical studies unveil that this special THJ carbon atom has pronounced radical character due to strong metal–cage interactions.

Charts of the HPLC separation of La@C_{82}($C_6H_3Cl_2$) are shown in Figure S1 of the Supporting Information. Two isomers, **1a** and **1b**, were isolated and their purities were estimated as higher than 99% by HPLC (Figure S2, Supporting Information) and MALDI-TOF mass spectrometry (Figure S3, Supporting Information). Both **1a** and **1b** are EPR-silent (Figure S4, Supporting Information), and this suggests connection of the dichlorophenyl group by a single bond to the carbon cage, which quenches the paramagnetism of La@C_{82}.[6b,15]

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The cage structure of the newly isolated La@C_{82} isomer inspires considerable curiosity: it might be one of the two known La@C_{82} isomers [$C_{2v}(9)$ or $C_s(6)$][5,6] or an undiscovered one. ^{13}C NMR measurements were first performed to obtain structural information. In sharp contrast to the previous ^{13}C NMR data of La@$C_{2n}(C_6H_3Cl_2)$ ($2n=72$, 74, 80),[15] which always display the same number of signals as the number of cage carbon atoms because of C_1 symmetry, the ^{13}C NMR spectra of both **1a** and **1b** include only 18 signals in the aromatic region, three of which can be assigned to the dichlorophenyl group (Figures S5 and S6, Supporting Information). Consequently, only 15 signals are from the fullerene cage, among which 12 have full intensity and three half intensity. This [3 × 3 C, 12 × 6 C] pattern does not correspond to either of the two known La@C_{82} isomers but more likely to one of the two C_{3v}-C_{82} isomers.[7] If we assume that the weakest line has not been detected, then it would lead to the $C_{3v}(7)$-C_{82} cage. If the weakest line is undetected and one line of full intensity contains two half-intensity lines because of coincidental overlap, then the $C_{3v}(8)$-C_{82} cage is also possible (see Figure S7 and Table S1 of the Supporting Information for further details). In either case, addition of the dichlorophenyl group must have taken place on the only carbon atom along the C_3 axis for which the high C_{3v} symmetry is maintained. Therefore, this new La@C_{82} isomer may have either the $C_{3v}(7)$-C_{82} or the $C_{3v}(8)$-C_{82} cage.

The ^{1}H NMR data reveal that **1a** and **1b** are structural isomers with different dichlorophenyl substituents (Figure S8, Supporting Information). Compound **1a** has a 2,5-dichlorophenyl group, as found previously for La@$C_{2n}(C_6H_3Cl_2)$(**B**) ($2n=72$, 74, 80), and **1b** a 3,4-dichlorophenyl group, corresponding to La@$C_{2n}(C_6H_3Cl_2)$(**C**) ($2n=72$, 74, 80).[15] No 2,4-isomer corresponding to La@$C_{2n}(C_6H_3Cl_2)$(**A**) ($2n=72$, 74, 80) was isolated in this work, that is, formation of the regioisomers is a random process.

^{139}La NMR spectrometry was used to characterize the behavior of the internal La atom. A broad peak is observed at $\delta=-456$ ppm for **1a** and $\delta=-468$ ppm for **1b** (Figure S9, Supporting Information). As summarized in Table 1, the above values are very close to that determined for the anion of La@$C_{2v}(9)$-C_{82} ($\delta=-470$ ppm),[6a] which has the same cage size. However, these values are all more positive than those of La@$C_{72}(C_6H_3Cl_2)$(**B**) ($\delta=-603$ ppm), La@$C_{74}(C_6H_3Cl_2)$(**B**) ($\delta=-513$ ppm), and La@$C_{80}C_6H_3Cl_2$(**B**) ($\delta=-500$ ppm) with smaller cages.[15] These results show that the cage size strongly affects the chemical shift of the internal ^{139}La nucleus. Furthermore, the line widths of the ^{139}La NMR signals of **1a** and **1b** at 300 K are 502 and 568 Hz (Table 1), respectively, and thus they are much sharper than those of La@C_{72}-$(C_6H_3Cl_2)$(**B**) (2100 Hz), La@$C_{74}(C_6H_3Cl_2)$(**B**) (2000 Hz), and La@$C_{80}C_6H_3Cl_2$(**B**) (5500 Hz),[15] that is, the high symmetry (C_{3v}) of **1a** and **1b** endows the ^{139}La nucleus with a much longer transverse relaxation time (T_2) in NMR measurements than in La@$C_{2n}(C_6H_3Cl_2)$ ($2n=72$, 74, 80) with a lower (C_1) molecular symmetry. These findings shed new light on the structures and properties of EMFs, especially the strong interactions between the single metal atom and the fullerene cage in mono-EMFs; they will be useful for the application of EMFs as molecular devices.

Table 1: ^{139}La NMR data of **1a**, **1b**, La@$C_{2n}(C_6H_3Cl_2)$(**B**) ($2n=72$, 74, 80),[15] and [La@$C_{2v}(9)$-C_{82}]$^-$$nBu_4N^+$.

Compound	Molecular symmetry	Chemical shift [ppm]	Line width [Hz]
1a	C_{3v}	−456	502
1b	C_{3v}	−468	568
La@$C_{72}(C_6H_3Cl_2)$(**B**)	C_1	−603	2100
La@$C_{74}(C_6H_3Cl_2)$(**B**)	C_1	−513	2000
La@$C_{80}(C_6H_3Cl_2)$(**B**)	C_1	−500	5500
[La@C_{82}]$^-$$nBu_4N^+$	C_1	−470	2600

Since the NMR data are not conclusive for a definite assignment of the cage structure, crystallization of **1a** and **1b** was performed. Single crystals of **1a** suitable for X-ray analysis were obtained. From the ORTEP of **1a** presented in Figure 1,[16] it is unambiguous that the cage is $C_{3v}(7)$-C_{82}, not $C_{3v}(8)$-C_{82}. The 2,5-dichlorophenyl group is singly bonded to THJ carbon atom C(1). The distances between C(1) and the three adjacent cage carbon atoms are similar (1.56, 1.57, 1.58 Å), consistent with the C_{3v} symmetry. Although orientational disorder of the cage exists, only one position of La is observed. The La atom is located closely under C(1) where the addend is bonded, and the C_3 axis passes through both C(1) and La. The La−C(1) distance of 2.72 Å indicates a strong metal–cage interaction.

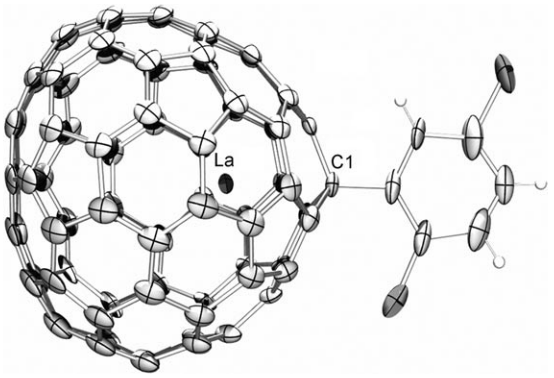

Figure 1. ORTEP drawing of **1a** with thermal ellipsoids at 50% probability. Only one orientation of the cage is shown and the toluene molecule is omitted for clarity.[16]

The THJ carbon atoms are well known to be the least pyramidal C atoms on a fullerene cage and are accordingly less reactive than other types, for example, triple-pentagon junctions (TPJs) and pentagon–pentagon–hexagon junctions (PPHJs), both of which only exist in non-IPR fullerenes, as well as pentagon–hexagon–hexagon junctions (PHHJs).[17] As a result, no fullerene derivative having fewer than 38 substituents has substituents singly bonded to THJs.[18] Only upon severe derivatization are some THJs substituted to stabilize the resulting molecule by, for example, formation of local aromaticity. Such cases are only found for $C_{2n}F_{38}$ ($2n=70$, 74).[19] The structures of EMFs are more complicated because of the presence of metal atoms. Nevertheless, both experimental and theoretical results reflect that the internal metal atoms tend to coordinate with PPHJs and PHHJs instead of THJs (no TPJs have been found for EMFs).[20] For EMF derivatives containing singly bonded substituents reported to date, no addend was found to connect to THJs, with the sole exception of $Sc_3N@C_{80}(CF_3)_x$ ($x = 14$, 16), in which four THJs are substituted for $x = 14$ and eight for $x = 16$.[21] Because a large number of addends exists for $Sc_3N@C_{80}(CF_3)_x$, it does not appear surprising that formation of negatively charged aromatic pentagons and their coordination with the internal Sc atoms are the main driving forces for such addition patterns. However, in the case of **1a** and **1b**, the only substituent prefers to append to one of the THJ carbon atoms, instead of any PHHJ.

The abnormal addition pattern of **1a** and **1b** stimulated us to resort to theoretical calculations for a reasonable explanation. The p-orbital axis vector (POAV) values[22] and SOMO spin densities of La@C_{3v}(7)-C_{82} were calculated. Detailed data are presented in Figure S10 of the Supporting Information. Figure 2 shows a plot of POAV values against SOMO spin densities of the 16 types of nonequivalent carbon atoms of La@C_{3v}(7)-C_{82}. Both values of C(1) are evidently higher than those of the others. Accordingly, such an exceptionally high radical character of C(1) makes it very reactive toward dichlorophenyl radicals during the extraction process. In the optimized structure of La@C_{3v}(7)-C_{82} (Figure 2, right), the La atom is located closely to C(1) along the C_3 axis. The La–C(1) distance of 2.714 Å is identical to that determined by X-ray analysis. Accordingly, the close contact between C(1) and La atom must be the origin of the localization of high pyramidalization and high spin on C(1).

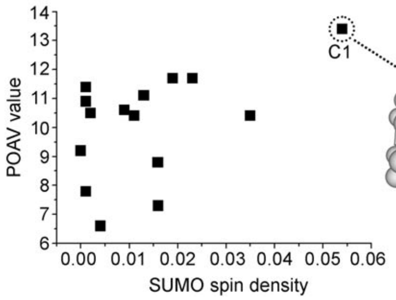

Figure 2. Left: Plot of SOMO spin densities against POAV values of La@C_{3v}(7)-C_{82}. Right: Optimized structure of La@C_{3v}(7)-C_{82}.

One more interesting finding is that the X-ray results presented above do not support the theoretical prediction that La@C_{3v}(8)-C_{82} should be obtained because it is 16.1 kcal mol^{-1} more stable than La@C_{3v}(7)-C_{82}. In fact, a similar phenomenon was found previously for La@C_{80}: La@C_{2v}(3)-C_{80} is 12.4 kcalmol^{-1} less stable than La@C_{2v}(5)-C_{80}, but only the former was isolated as its dichlorophenyl derivatives.[15c] The reason is now clear: derivatization changes the energy order so that La@C_{2v}(3)-C_{80} binds strongly with substituents and its derivatives prevail in solution. This explanation is also applicable to the current findings. The pronounced radical character makes La@C_{3v}(7)-C_{82} fairly reactive toward dichlorophenyl radicals during the extraction process, so that it was extracted as derivatives. In contrast, the POAV values and SOMO spin densities of the cage carbon atoms of La@C_{3v}(8)-C_{82} (Figure S11 and S12) are more uniform, so they have decreased radical character and the overall reactivity of the molecule toward radicals is lower. Consequently, La@C_{3v}(8)-C_{82} is not extracted and may still exist in the soot.

Electronic properties of **1a** and **1b** were characterized by UV/Vis/NIR spectrometry (Figure S13, Supporting Information). The spectra of **1a** and **1b** are fundamentally identical, with distinct absorptions at 490, 590, 710, and 800 nm. The onset observed at 900 nm corresponds to a large band gap (1.38 eV). These results indicate that 1) dichlorophenyl substitution has made pristine La@C_{3v}(7)-C_{82} fairly stable and 2) the substitution pattern of the dichlorophenyl group has a negligible effect on the electronic structures of the adducts.

Electrochemical properties of **1a** and **1b** were also examined. Both exhibit three reversible reduction processes and one oxidation wave that is less reversible (Figure S14, Supporting Information), consistent with our previous findings that the cations of mono-EMFs are less stable than the anions.[5,8] Table 2 summarizes the redox potentials of **1a** and **1b**, as well as those of La@$C_{2n}(C_6H_3Cl_2)$(**B**) ($2n = 72$, 74, 80)[15] and La@C_{2v}(9)-C_{82} for comparison. The identical redox potentials of **1a** and **1b** confirm the same cage structure and the same position of the substituent. Moreover, the reduction potentials of these dichlorophenyl derivatives with different cage sizes are all similar to each other, but the oxidation potentials vary with the cage size. If the value of La@$C_{72}(C_6H_4Cl_2)$, which has a pair of unconventional fused pentagons, is excluded, the oxidation potentials of La@$C_{2n}(C_6H_3Cl_2)$ ($2n = 74$, 80, 82) increase concomitantly with increasing cage size. Although the reason remains somewhat unclear, the results are informative for the synthesis of EMF-based materials applicable in electronics and photovoltaics.

Table 2: Redox potentials[a] [V vs. Fc/Fc$^+$] of **1a**, **1b**, La@$C_{2n}(C_6H_3Cl_2)$(**B**) ($2n = 72$, 74, 80),[15] and La@C_{2v}(9)-C_{82}.

Compound	$^{Ox}E_1$	$^{Red}E_1$	$^{Red}E_2$	$^{Red}E_3$
1a	0.65	−1.12	−1.42	−1.94
1b	0.66	−1.11	−1.42	−1.92
La@$C_{72}(C_6H_3Cl_2)$(**B**)	0.42	−1.00	−1.36	−1.64
La@ $C_{74}(C_6H_3Cl_2)$(**B**)	0.24	−1.08	−1.38	−1.93
La@$C_{80}(C_6H_3Cl_2)$(**B**)	0.36	−1.07	−1.43	−1.89
La@C_{2v}(9)-C_{82}	0.07	−0.42	−1.34	−1.53

[a] Determined by differential pulse voltammetry in 1,2-dichlorobenzene with 0.1 M nBu$_4$NPF$_6$ at a Pt working electrode.

In conclusion, an unprecedented isomer of La@C_{82} with the C_{3v}(7)-C_{82} cage has been isolated as dichlorophenyl derivatives. The NMR and X-ray crystallographic results show that the dichlorophenyl group is singly bonded to a THJ carbon atom on the C_3 axis, whereby high C_{3v} symmetry is maintained. Density functional calculations reveal that this special THJ carbon atom is considerably more reactive toward radicals than others as a result of strong metal–cage interactions. This is the only example of a fullerene derivative in which a single substituent is linked to one of the THJ carbon atoms, which are believed to be the least reactive.

Furthermore, comparison of La@C_{2n}($C_6H_3Cl_2$) ($2n = 72$, 74, 80, 82) revealed that the chemical shift of the internal ^{139}La nucleus and the oxidation potential of these dichlorophenyl derivatives depend on cage size. These results have provided new insights into the interplay between the structures and properties of EMFs. They are expected be useful in future design and creation of EMF-based materials for molecular electronic devices and photovoltaics. The isolation of La@C_{3v}-C_{82} derivatives suggests that other unknown EMF species remain in raw soot, and more powerful extraction methods should be devised to access them.[23]

Experimental Section

Experimental details are similar to those reported in reference [15] and are given in the Supporting Information.

Black single crystals of **1a** were obtained by layering a toluene solution with hexane. X-ray data were collected with an AXS SMART APEX machine (Bruker Analytik, Germany) at 90 K. CCDC 783962 (**1a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical calculations were conducted with the Gaussian 03 program package.[24] The molecular structures were optimized at the B3LYP level[25] with the relativistic effective core potential (ECP)[26] and the LANL2DZ basis set for La and 6-31G(d) basis set[27] for C, H, and Cl.

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[16] Crystal data of a black needle of 2 **1a**·C_7H_8: $C_{183}H_{14}Cl_4La_2$, FW = 2631.56, $0.27 \times 0.18 \times 0.03$ mm, orthorhombic, $P2_12_12_1$, $a = 11.260(5)$, $b = 28.242(5)$, $c = 28.523(5)$ Å, $V = 9070.5(5)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.927\ \text{g cm}^{-3}$, $\mu(\text{Mo}_{K\alpha}) = 1.130\ \text{mm}^{-1}$, $\theta = 3.04$–$27.48°$; $T = 90$ K; $R_1 = 0.1225$, $wR_2 = 0.2810$ for all data; $R_1 = 0.1098$, $wR_2 = 0.2734$ for 18444 reflections ($I > 2.0\sigma(I)$) with 1177 parameters. Maximum residual electron density 12.317 e Å^{-3}.

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