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Missing Metallofullerene with C_{80} Cage

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Abstract: Many insoluble metallofullerenes are called *missing metallofullerenes*. These metallofullerenes have not yet been isolated despite their detection in raw soot using mass spectrometry. They have been anticipated to show unique structures and properties that differ considerably from those of soluble metallofullerenes. Herein, a missing metallofullerene, La@C_{80}, was extracted and isolated as a derivative, La@$C_{80}(C_6H_3Cl_2)$. The structure of La@$C_{80}(C_6H_3Cl_2)$ was determined unambiguously using single-crystal X-ray crystallographic analysis. In fact, La@C_{80} has a novel C_{80} cage, C_{2v}-C_{80} (80:3), which has not been reported. The calculation of La@C_{80} with C_{2v}-C_{80} (80:3) cage shows that La@C_{2v}-C_{80} (80:3) has a radical character as well as small ionization potential (Ip) and electron affinity (Ea), which are indicative of high reactivity. On the basis of those results, La@C_{2v}-C_{80} (80:3) is expected to interact strongly and bond with amorphous carbon or other fullerenes in soot that is made insoluble in common organic solvents.

Introduction

Endohedral metallofullerenes have attracted much attention not only for their unique structures and properties, but also for their ability to stabilize novel fullerene isomers that have never been found experimentally in the empty form.[1] Recently, many endohedral metallofullerenes have been reported with various cage sizes, structures, and properties, and encapsulated species. Among these, many studies have been conducted for endohedral metallofullerenes with the C_{80} cage, such as M_2@C_{80} (M = La[2] and Ce[3]), M_3N@C_{80} (M = Sc, Y, Gd, Tb, Dy, Ho, Er, and Tm),[4] and Sc_3C_2@C_{80},[5] and Sc_4O_2@C_{80}.[6] The C_{80} cage has been recognized as the most frequent fullerene cage in metallofullerene. There are seven IPR-satisfying isomers for C_{80} (see Supporting Information Figure S1).[7] Three isomers, D_{5d}-C_{80} (80:1)[8] and D_2-C_{80} (80:2)[9] as a pristine and C_{2v}-C_{80} (80:5) as a trifluoromethyl derivative,[10] have been isolated and characterized. On the other hand, previous reports show that metals are encapsulated inside D_{5d}-C_{80} (80:1),[11] D_{5h}-C_{80} (80:6),[4,12] and I_h-C_{80} (80:7)[2−6,13] isomers. This family has two uninvestigated members: C_{2v}-C_{80} (80:3) and D_3-C_{80} (80:4).

Meanwhile, divalent and trivalent monometallofullerenes, M^{II}@C_{80} (M^{II} = Ca, Sr, Ba)[14] and La@C_{80},[15] have been detected using UV−visible-near-infrared absorption and EPR spectroscopy, although their structures have not been established. The cage structures of metallofullerenes are controlled by the amount of electron transfer to carbon cages. The electron transfer in M@C_{80} differs from that in M@C_{80}, M_3N@C_{80}, Sc_3C_2@C_{80}, and Sc_4O_2@C_{80}, suggesting that M_2@C_{80} has a cage isomer that differs from those previously reported. Recently, we extracted, isolated, and characterized missing metallofullerenes such as La@C_{72} and La@C_{74} as derivatives: La@$C_{72}(C_6H_3Cl_2)$ and

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$La@C_{74}(C_6H_3Cl_2)$.[16,17] Those studies showed that raw soot has many elusive *missing metallofullerenes*, which have interesting structures and properties. This derivatization method has emerged as a powerful tool for the extraction, isolation, and identification of missing metallofullerenes. We herein report the first structural determination of a monometallofullerene derivative, $La@C_{80}(C_6H_3Cl_2)$, using spectroscopic and X-ray crystallographic analysis. In fact, $La@C_{80}(C_6H_3Cl_2)$ has no cage structure such as C_{2v}-C_{80} (80:5), D_{5h}-C_{80}(80:6), and I_h-C_{80} (80:7) suggested by theoretical calculations for $La@C_{80}$, but a less stable cage, C_{2v}-C_{80} (80:3). In addition, the unique electronic properties and high reactivity of $La@C_{80}$ are discussed based on the calculations.

Experimental Section

General. Soot containing lanthanum metallofullerenes was produced using the previously reported arc discharge method.[18] Both empty fullerenes and metallofullerenes were extracted from the raw soot with 1,2,4-trichlorobenzene (TCB) at its boiling temperature for 15 h. The soluble fraction was separated using a four-stage high performance liquid chromatography (HPLC) with toluene as the eluent. Six isomers of metallofullerene derivatives, $La@C_{80}(C_6H_3Cl_2)$, were isolated. In the first stage, a 5PYE column (ϕ 20 mm × 250 mm; Cosmosil, Nacalai Tesque, Inc.) was used for rough separation of $La@C_{80}(C_6H_3Cl_2)$ from the other fullerenes. In the second stage, $La@C_{80}(C_6H_3Cl_2)$ was separated from $La_2@C_{78}$ using a 5PBB column (ϕ 20 mm × 250 mm; Cosmosil, Nacalai Tesque, Inc.). In the third stage, $La@C_{80}(C_6H_3Cl_2)$ was separated from $La_2@C_{72}$ using a Buckyprep-M column (ϕ 20 mm × 250 mm; Cosmosil, Nacalai Tesque, Inc.). During the fourth stage, the six isomers of $La@C_{80}(C_6H_3Cl_2)$ were isolated completely using a Buckyprep column (ϕ 20 mm × 250 mm; Cosmosil, Nacalai Tesque, Inc.). The purity of the isolated species was confirmed using HPLC and LD-TOF mass spectrometry. The MALDI-TOF mass was measured using a spectrometer (BIFLEX III; Bruker AXS GmbH, Germany) with 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix. The ^{13}C NMR spectra were measured at 125 MHz using a spectrometer (AVANCE 500; Bruker AXS GmbH) with a CryoProbe system in carbon disulfide with a capillary tube of acetone-d_6 as an external lock. The vis-NIR spectra were measured using a spectrometer (UV 3150; Shimadzu Corp., Japan). Cyclic voltammography was done using a potentiostat/galvanostat (CW-50; BAS). The ^{139}La NMR spectrum was measured in carbon disulfide at 84.7 MHz on a spectrometer (AVANCE 600; Bruker AXS GmbH). The ^{139}La chemical shift was calibrated with 0.6 M $LaCl_3/D_2O$ as an external reference. The X-ray crystallographic analysis was done at 90 K (SMART APEXII ULTRA; Bruker AXS GmbH).

Computations. All calculations were done using the Gaussian 03 program.[19] Geometries were optimized with the hybrid density functional theory at the B3LYP level[20] with the relativistic effective core potential[21] and the LANL2DZ basis set for La and 6-31G(d) basis set[22] for C, H, and Cl. For calculations of Ip and Ea, the larger 6-31+G(d) basis set was used for C. For GIAO calculations of ^{13}C NMR chemical shifts,[23] the larger 6-311G(d) basis set was used for C.

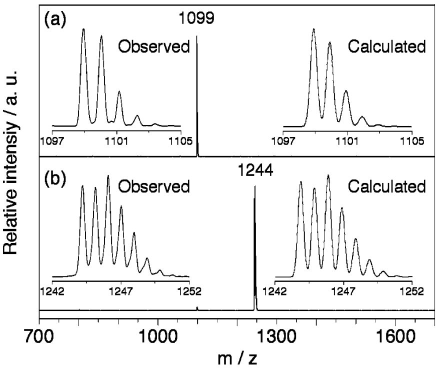

Figure 1. (a) LD-TOF mass and (b) MALDI-TOF mass spectra of $La@C_{80}(C_6H_3Cl_2)$ (A).

Results and Discussion

Soot containing lanthanum metallofullerenes was produced using the arc discharge method.[18] Three adducts (A, B, and C) were extracted in 1,2,4-trichlorobenzene and isolated from the raw soot using a method reported previously.[16,17] The purities of these three isomers were confirmed using HPLC with various columns. The three isomers have different retention times in HPLC with a Buckyprep column. The LD-TOF mass spectra of the adducts show a peak at *m/z* 1104−1099, which is attributed to $La@C_{80}$ (*m/z* 1099) because of the loss of the dichlorophenyl ($C_6H_3Cl_2$) group (*m/z* 145) (Figure 1a). The MALDI-TOF mass spectra of the adducts show a molecular ion peak at *m/z* 1251−1244 which is attributed to the adduct of $La@C_{80}$ (*m/z* 1099) with the $C_6H_3Cl_2$ group (*m/z* 145) (Figure 1b). This suggests that the adducts are formed during extraction by the reaction of $La@C_{80}$ and 1,2,4-trichlorobenzene, as found for the $La@C_{72}$ and $La@C_{74}$ cases. The EPR measurement shows that the adducts are EPR inactive, indicative of a closed-shell electronic structure. To shed light on the structures of $La@C_{80}(C_6H_3Cl_2)$ (A, B, and C), we performed ^1H NMR, ^{13}C NMR, and 2D NMR (HMQC and HMBC) measurements. The NMR spectra show that the isomers A, B, and C have 2,4-dichlorophenyl, 2,5-dichlorophenyl, and 3,4-dichlorophenyl groups, respectively. Similar UV−visible-near-infrared absorption (see Supporting Information Figure S6) and ^{13}C NMR signals for the carbon cage (see Supporting Information Figure S7) were observed for A, B, and C, indicating that these three isomers have the same cage structure and addition site. The ^{13}C NMR spectra of A, B, and C show 86 lines (80 lines from the C_{80} cage and 6 lines from the dichlorophenyl group), indicating that these isomers have C_1 symmetry. The signal at 60−57 ppm is certainly assigned to the sp^3 carbons on C_{80} by ^1H−^{13}C long-range coupling NMR measurements. The ^{139}La NMR spectra of A, B, and C exhibit a single broad signal with a line width of 5500 Hz at 300 K. The ^{139}La NMR chemical shifts at −493 (A), −500 (B), and −488 (C) ppm are close to those observed for $[La@C_{2v}\text{-}C_{82}Ad\text{-}I]\text{-}n\text{-}Bu_4N^+$ (−420 ppm)[24] and $[La@C_{2v}\text{-}C_{82}]\text{-}n\text{-}Bu_4N^+$ (−470 ppm)[25] with cage size similar

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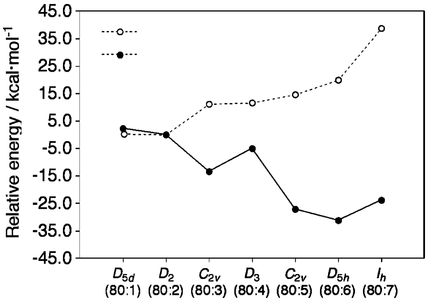

Figure 2. Relative energies of the C_{80} (dashed line) and C_{80}^{3-} isomers relative to the D_2 (80:2) isomer.

to that of C_{80}, and are significantly higher than those observed for La@C_{72}($C_6H_3Cl_2$) (A) (−605 ppm)[17] and La@C_{74}($C_6H_3Cl_2$) (A) (−511 ppm)[16] with the same substituent and smaller cage. These suggest a relation between the ^{139}La NMR chemical shift and the carbon cage size in lanthanum metallofullerenes.

The electron transfer from encapsulated species to a fullerene cage plays an important role in the structure and properties of metallofullerenes. Theoretical calculations have shown that D_{5d}-C_{80} (80:1) and D_2-C_{80} (80:2) isomers are more stable than other isomers.[26,27] Consequently, D_{5d}-C_{80} (80:1) and D_2-C_{80} (80:2) isomers have been isolated.[8,9] In contrast, the most unstable D_{5h}-C_{80} (80:6) and I_h-C_{80} (80:7) isomers are highly stabilized when metals or metal clusters are encapsulated because electrons are transferred from the encapsulated metals or metal clusters to C_{80}. Therefore, metallofullerenes with D_{5h}-C_{80} (80:6) and I_h-C_{80} (80:7) cages have been isolated.[2−13] In an attempt to determine the cage structure of La@C_{80}($C_6H_3Cl_2$), we conducted theoretical calculations for seven isomers of C_{80} and C_{80}^{3-} that satisfy the isolated pentagon rule because lanthanum monometallofullerenes are known to have the electronic state described as M^{3+}@C_n^{3-} because of three-electron transfer from M to C_n (Figure 2).[26,27] Theoretical calculations show that the most stable D_{5d}-C_{80} (80:1) and D_2-C_{80} (80:2) cages are highly destabilized upon accepting three electrons and become the most unstable for C_{80}^{3-}. Instead, C_{2v}-C_{80} (80:5), D_{5h}-C_{80} (80:6), and I_h-C_{80} (80:7) cages, which are highly unstable in the neutral state, are highly stabilized upon accepting three electrons. Therefore, the cage structure of La@C_{80}($C_6H_3Cl_2$) is likely to originate from C_{2v}-C_{80} (80:5), D_{5h}-C_{80} (80:6), or I_h-C_{80} (80:7).

We performed X-ray crystallographic analysis of La@C_{80}($C_6H_3Cl_2$) (A) (Figure 3). It is particularly interesting that the cage structure of La@C_{80}($C_6H_3Cl_2$) is C_{2v}-C_{80} (80:3), although C_{2v}-C_{80} (80:5), D_{5h}-C_{80} (80:6), and I_h-C_{80} (80:7) are found to be the most stable for C_{80}^{3-} according to theoretical calculations. In the calculations for La@C_{80}, La@C_{2v}-C_{80} (80:5) is 12.4 kcal/mol more stable than La@C_{2v}-C_{80} (80:3). A two-step description is useful to clarify why the C_{2v}-C_{80} (80:3) cage is observed. The first step deals with the high-temperature gas-phase formation of the pristine La@C_{2v}-C_{80} (80:3) and La@C_{2v}-C_{80} (80:5) with the same cage symmetry. The second step models the reaction with the solvent that produces the La@C_{80}($C_6H_3Cl_2$) derivatives with C_{2v}-C_{80} (80:3) and C_{2v}-C_{80} (80:5) cages. To have a more reliable description of the thermodynamic terms, the Gibbs free energies were evaluated instead of mere potential-energy values and representative temperatures of 1500 and 298 K were considered with the first and second reaction, respectively (a more advanced SDD basis set was used for La[28]). Although La@C_{2v}-C_{80} (80:5) is lower in energy, the derivatization changes the energy order so that after the derivatization, La@C_{2v}-C_{80} (80:3) is expected to prevail in the solution. When the computed Gibbs free energy terms are converted into the equilibrium constants and concentrations, the model evaluation suggests that the La@C_{2v}-C_{80} (80:3)/La@C_{2v}-C_{80} (80:5) concentration ratio in solution should be equal to about 67. This result suggests that La@C_{2v}-C_{80} (80:3) in the pristine form is less stable, but La@C_{2v}-C_{80} (80:3) in the raw soot or solution preferentially binds covalently and the derivative therefore becomes more abundant in the extract. On the other hand, La@C_{2v}-C_{80} (80:5) does not react during the extraction because of the stability and is not extracted if La@C_{2v}-C_{80} (80:5) is produced by arc discharge and exists in the raw soot.

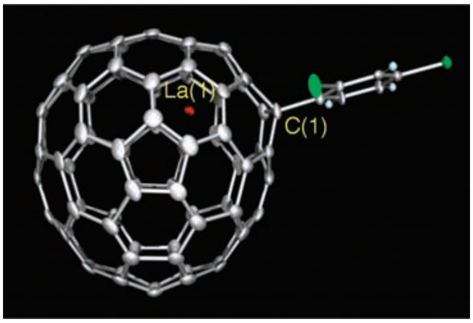

Figure 3. Crystal structure of one enantiomeric isomer of La@C_{80}($C_6H_3Cl_2$) (A) at 90 K showing thermal ellipsoids at the 30% probability level. Minor La atoms and toluene molecules are omitted for clarity.

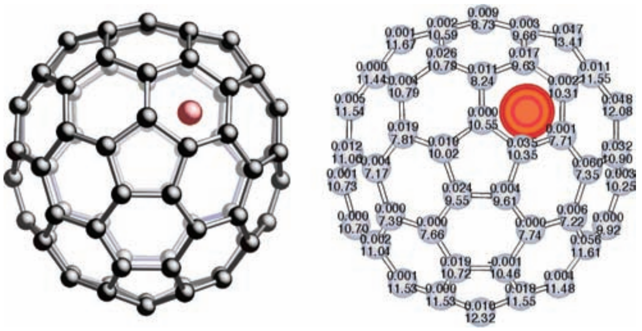

Figure 4. (a) Optimized structure and (b) SOMO spin density (upper) and π-orbital axis vector (POAV) value (lower) of La@C_{2v}-C_{80} (80:3).

Actually, La@C_{80}($C_6H_3Cl_2$) (A) is chiral; the ratio of its enantiomers is 1:1. It is racemic in the crystalline state. The asymmetric unit, which is the smallest portion of a crystal structure to which crystallographic symmetry is applicable to generate one unit cell, in these compounds consists of one La@C_{80}($C_6H_3Cl_2$) (A) molecule, which is disordered with the two enantiomers with 0.6:0.4 ratios, and 1.5 molecules of toluene. The encapsulated La atom located near the addition position and disordered at three positions—La(1), La(2), and La(3)—in each enantiomer (see Supporting Information Figure S16). The occupancy ratios of La(1), La(2), and La(3) in the major enantiomer with 60% ratio in the asymmetric unit are, respectively, 51.6%, 7.5%, and 1.6%. (The occupancy ratios of La(1)′, La(2)′, and La(3)′ in the minor enantiomer with 40%

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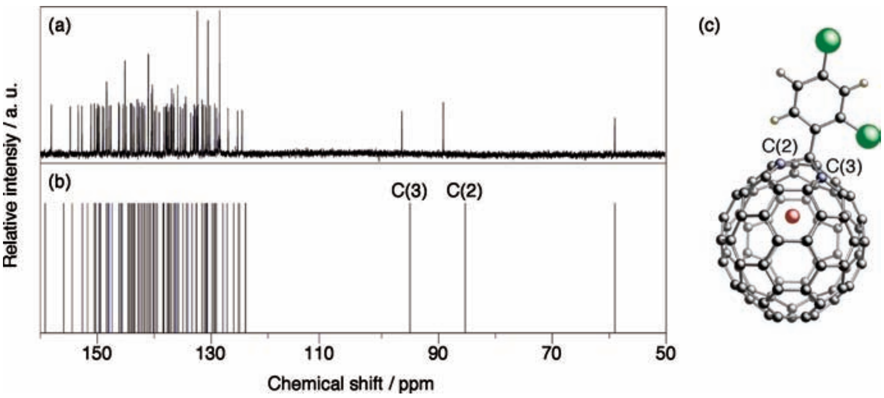

Figure 5. (a) ^{13}C NMR spectrum of La@$C_{80}(C_6H_3Cl_2)$ (A) in CS_2 (acetone-d_6 in capillary as lock solvent) at 125 MHz; (b) ^{13}C NMR chemical shift of La@$C_{80}(C_6H_3Cl_2)$ (A) calculated at the GIAO level; and (c) the optimized structure of La@$C_{80}(C_6H_3Cl_2)$ (A).

Table 1. Redox Potentials (V),[a] Ionization Potentials (eV),[b] and Electron Affinities (eV)[b] of La@C_{2v}-C_{80}(80:3), La@$C_{80}(C_6H_3Cl_2)$ (A), La@D_2-C_{72}, La@$C_{72}(C_6H_3Cl_2)$ (A), La@D_{3h}-C_{74}, La@$C_{74}(C_6H_3Cl_2)$ (A), La@C_{2v}-C_{82}, and La@C_s-C_{82}

compound	$^{ox}E_1$	$^{red}E_1$	Ip/Ea
La@C_{2v}-C_{80} (80:3)			5.95/3.01
La@$C_{80}(C_6H_3Cl_2)$ (A)	0.31	−1.09	6.42/2.73
La@D_2-C_{72}[c]			5.91/2.94
La@$C_{72}(C_6H_3Cl_2)$ (A)[c]	0.44	−1.00	6.57/2.66
La@D_{3h}-C_{74}[d]			6.16/3.07
La@$C_{74}(C_6H_3Cl_2)$ (A)[d]	0.30	−1.05	6.34/2.56
La@C_{2v}-C_{82}[e]	0.07	−0.42	6.19/3.38
La@C_s-C_{82}[f]	−0.07	−0.54	6.05/3.21

[a] Versus Fc/Fc$^+$. In 1,2-dichlorobezene with 0.1 M (n-Bu)$_4$NPF$_6$ at a Pt working electrode. CV: scan rate, 20 m·s^{-1}. [b] All Ip and Ea were calculated using the Gaussian 03 program; ref. 28. [c] Ref 17. [d] Ref 16. [e] Ref 30. [f] Ref 31.

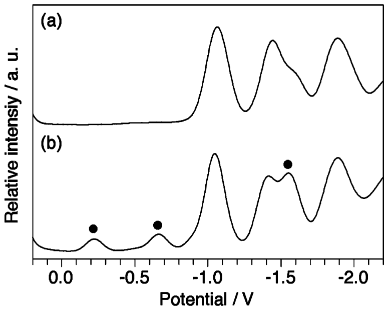

Figure 6. Differential pulse voltammograms of La@$C_{80}(C_6H_3Cl_2)$ (A) at first scan and (b) after several scans. New waves are marked as black circles.

ratio in the asymmetric unit are 35.8%, 1.6%, and 1.9%, respectively. The total of the abundance ratios of La atoms is 100%.) We performed DFT calculation of the relative energies for three observed geometries, which have the same cage structure, but in which La atoms are localized at different positions. The geometry of La(1) with the highest occupancy ratio is the most stable in the three observed geometries and agrees well with the optimized structure (see Supporting Information Figure S16). The position of the La(1) atom in La@$C_{80}(C_6H_3Cl_2)$ (A) is almost identical to that in La@C_{2v}-C_{80} (80:3) (Figure 4). The DFT calculations suggest that three electrons on the La atom are transferred to $C_{80}(C_6H_3Cl_2)$, the resultant electronic structure being formally described as La^{3+}[$C_{80}(C_6H_3Cl_2)$]$^{3-}$. Therefore, the La^{3+} cation is located near the minimum of the electrostatic potentials inside [$C_{80}(C_6H_3Cl_2)$]$^{3-}$. The observed La···C(1) distance of 3.170 Å is almost identical to the calculated value of 3.148 Å. The addition position (C(1)) of the dichlorophenyl group has both high SOMO spin-density and the high π-orbital axis vector (POAV) pyramidalization angle[29] in La@C_{2v}-C_{80} (80:3) (Figure 4). These results suggest that the high reactivity of La@C_{2v}-C_{80} (80:3) toward radical species can be ascribed to the radical character and local strain of the C(1) atom.

To assign two particular signals at 96.45 and 89.16 ppm on the ^{13}C NMR spectrum of isomer A, the ^{13}C NMR chemical shifts were calculated (Figure 5). Results show that the two signals at 94.98 and 85.20 ppm are attributed to the C(3) and C(2), respectively, which are adjacent to the sp^3 carbon atom on C_{80}. For La@$C_{72}(C_6H_3Cl_2)$[17] and La@$C_{74}(C_6H_3Cl_2)$,[16] the chemical shifts of the some adjacent carbons atoms to the sp^3 carbon atom were observed similarly at a lower field than other carbon atoms on the cage.

In view of the fact that La@C_{80} is not extracted in common organic solvents and La@$C_{80}(C_6H_3Cl_2)$ is produced instead during the extraction process, there is considerable interest in the electronic properties and reactivity of La@C_{2v}-C_{80} (80:3). We calculated the ionization potential (Ip) and electronic affinity (Ea) of La@C_{2v}-C_{80} (80:3). As Table 1 shows, La@C_{2v}-C_{80} (80:3) has a smaller Ip than La@C_{2v}-C_{82}. The calculated Ip and Ea values of La@C_{2v}-C_{80} (80:3) are similar to those of the reported missing metallofullerenes, La@C_{72} and La@C_{74}, and smaller than those of La@C_{2v}-C_{82} which is known as a conventional lanthanum metallofullerene. Because of its radical character and small Ip, La@C_{2v}-C_{80} (80:3) might interact strongly and bind with amorphous carbon or other fullerenes in soot, and thereby become insoluble in common organic solvents. The adduct, La@$C_{80}(C_6H_3Cl_2)$ (A), has a higher Ip than La@C_{2v}-C_{80} (80:3), this being also supported by their redox potentials (Table 1). These results suggest that the addition of a dichlorophenyl group to La@C_{2v}-C_{80} (80:3) engenders stable endohedral metallofullerene derivatives, which can be extracted in common organic solvents. The redox potentials, ionization potentials, and electron affinities of La@C_{2v}-C_{80} (80:3), La@$C_{80}(C_6H_3Cl_2)$ (A), La@C_{72},[17] La@D_2-$C_{72}(C_{6v}H_3Cl_2)$ (A),[17] La@D_{3h}-C_{74},[16] La@$C_{74}(C_6H_3Cl_2)$ (A),[16] and La@C_{2v}-C_{82}[30] and La@C_s-C_{82}[31] are presented in Table 1.

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In cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements (see Supporting Information Figure S18), new waves appeared at −0.22, −0.66, and −1.57 V versus Fc/Fc$^+$ in 1,2-dichlorobezene with 0.1 M (n-Bu)$_4$NPF$_6$ (Figure 6). The color of solution of La@C$_{80}$(C$_6$H$_3$Cl$_2$) (A−C) in o-dichlorobenzene with (n-Bu)$_4$NPF$_6$ was altered slightly. It is particularly interesting that, in EPR measurements, the solutions after CV and DPV measurement of La@C$_{80}$(C$_6$H$_3$Cl$_2$) (A, B, and C) have octet signals, whose g-values are 1.9987 (A), 1.9987 (B), and 1.9985 (C), and hyperfine coupling constants (hfcs) are 10.557 (A), 10.767 (B), and 10.662 (C) G (see Supporting Information Figure S20). These results suggest that La@C$_{80}$(C$_6$H$_3$Cl$_2$) was decomposed and changed to a radical species during CV and DPV measurements. These octet signals resemble the characteristic EPR signals of lanthanum monometallofullerene. In addition, the redox potentials of new waves agree with the first reduction potential ($^{\mathrm{red}}E_1 = -0.73 \pm 0.1$ V) and oxidization potential ($^{\mathrm{ox}}E_1 = -0.16 \pm 0.1$ V) predicted from Ip and Ea (see Supporting Information Figure S19). Consequently, these new waves in CV and DPV measurement and octet signal in EPR measurement are attributed to pristine La@C_{2v}-C$_{80}$ (80:3). In the CV and DPV measurements of La@C$_{80}$(C$_6$H$_3$Cl$_2$), the dichlorophenyl group is retained to provide La@C_{2v}-C$_{80}$ (80:3) with an open-shell electronic structure. This EPR signal differs from those of two La@C$_{80}$ isomers reported previously,[15] whose g-values are 2.0010 and 2.0011, and hfcs are 2.405 and 2.037 G, respectively, indicating that these structures differ from La@C_{2v}-C$_{80}$ (80:3). The isolation and characterization of the radical species with the octet signal is now in progress.

Conclusions

It is determined that La@C$_{80}$(C$_6$H$_3$Cl$_2$) has the C_{2v}-C$_{80}$ (80:3) cage. This carbon cage differs from the C_{2v}-C$_{80}$ (80:5), D_{5h}-C$_{80}$ (80:6), and I_h-C$_{80}$ (80:7) cages proposed by DFT calculations. The La@C_{2v}-C$_{80}$ (80:3) without the C$_6$H$_3$Cl$_2$ group is less stable. However, the addition of a dichlorophenyl radical on the less stable La@C_{2v}-C$_{80}$ (80:3) with high radical character engenders the stable La@C$_{80}$(C$_6$H$_3$Cl$_2$) with a closed shell structure. It is proposed that La@C_{2v}-C$_{80}$ (80:3) in soot binds with amorphous carbons or other missing metallofullerenes. The insolubility reported for missing metallofullerenes such as La@C$_{72}$ and La@C$_{74}$[16,17] can be attributed to their covalently linked polymeric nature because of the high reactivity resulting from the radical character, as well as small band gap fullerenes.[32,33] Isolation of the La@C$_{80}$(C$_6$H$_3$Cl$_2$) derivative suggests that many other insoluble and unknown endohedral metallofullerenes remain in the raw soot, which will present new opportunities for extension of the new material science of metallofullerenes.

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Supporting Information Available: Experimental details and spectroscopic and theoretical data for La@C$_{80}$(C$_6$H$_3$Cl$_2$) and La@C$_{80}$; X-ray crystallographic details including CIF file; complete refs 19 and 24. This material is available free of charge via the Internet at http://pubs.acs.org.

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