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Communication

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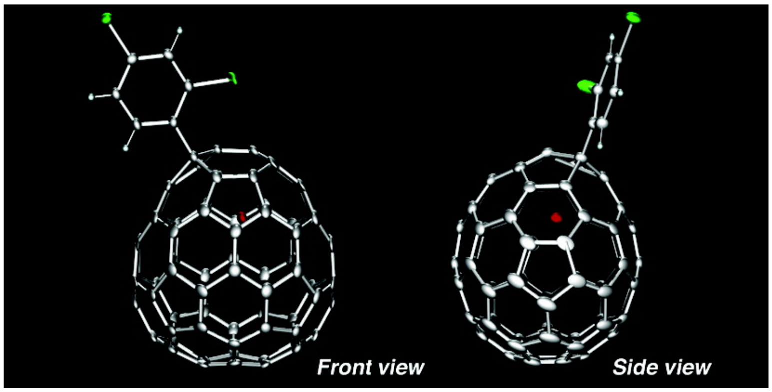

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COMMUNICATIONS

Missing Metallofullerene La@C_{74}

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Endohedral metallofullerenes have attracted special interest since they could lead to new spherical molecules with unique structure and properties that are unexpected for empty fullerenes.[1,2] In 1991, Smalley and co-workers reported that La@C_{60}, La@C_{74}, and La@C_{82} were produced especially abundantly in the soot, but only La@C_{82} was extracted with toluene.[3] Since then, the chemistry of soluble endohedral metallofullerenes has been started by centering on that of La@C_{82},[4−8] and up to now, many soluble endohedral metallofullerenes have been separated and characterized.[9] However, insoluble endohedral metallofullerenes, such as La@C_{60} and La@C_{74}, have not yet been isolated, although they are regularly observed in the raw soot by mass spectrometry. We herein report the first isolation of La@C_{74} as an endohedral metallofullerene derivative, La@C_{74}($C_6H_3Cl_2$). The structural determination has been performed by spectroscopic and, finally, X-ray crystallographic analysis, and the properties of La@C_{74} are discussed on the basis of the theoretical study.

Soot containing lanthanum metallofullerenes was produced by the DC arc discharge method,[10] and La@C_{74} was observed in the raw soot by LD-TOF mass spectrometry. Endohedral metallofullerenes and empty fullerenes were extracted with 1,2,4-trichlorobenzene (TCB) under reflux. The soluble fraction was separated by a multistage high performance liquid chromatograph (HPLC), and the three isomers were isolated, which have a molecular ion peak at m/z 1032−1027 attributed to La@C_{74} on the LD-TOF mass measurements. The EPR measurement of these isomers presented no signals, indicative of a closed-shell electronic structure (Figure S15 in the Supporting Information), although lanthanum monometallofullerenes are known as a open-shell electronic structure because of three-electron transfer from the encapsulated La atom to the carbon cage.[9,11,12] To shed light on the structure of these isomers, we performed MALDI-TOF mass spectroscopy. The spectra showed a new molecular ion peak at m/z 1179−1172 attributed to La@C_{74} (m/z 1027) adduct of the dichlorophenyl group ($C_6H_3Cl_2$, mass m/z 145). These results suggest that La@C_{74} reacts with TCB in the process of the extraction to produce the three isomers: La@C_{74}($C_6H_3Cl_2$)(A−C).

To determine the molecular structures of La@C_{74}($C_6H_3Cl_2$)(A−C), we performed ^{1}H NMR, ^{13}C NMR, and 2D NMR (HMQC and HMBC) of these isomers. The NMR spectra clearly exhibited the different structures of the dichlorophenyl group: isomer A = 2,4-dichlorophenyl group, isomer B = 2,5-dichlorophenyl group, and isomer C = 3,4-dichlorophenyl group. ^{13}C NMR signals due to the carbon cage and UV−vis−near-infrared absorption of isomers A−C were similar to each other. These results indicate that these three isomers have the same cage structure and addition position. ^{13}C NMR spectrum of isomer A (Figure 1) shows a total of 80 lines, indicating that it has C_1 symmetry. These signals can be accurately assigned to equivalent 74 lines from the C_{74} cage and 6 lines from the dichlorophenyl group. The signal at 58.5 ppm is assuredly assigned to the sp^3 carbon on C_{74} [C(1) in Figure 2] by ^{1}H−^{13}C long-range coupling NMR measurements. Finally, the X-ray crystallographic analysis[13] of isomer A unambiguously characterized the structure of the novel endohedral metallofullerene derivative with the C_{74}(D_{3h}) cage, as shown in Figure 2. The C_{74}(D_{3h}) cage is only one isomer of C_{74} satisfying the isolated pentagon rule (IPR).[14] La@C_{74}($C_6H_3Cl_2$) is found to be the first example of endohedral metallofullerene derivatives with only one bond between the fullerene cage and its substituent. The π-orbital axis vector

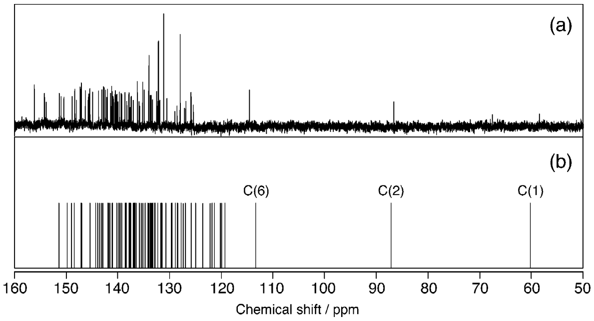

Figure 1. (a) ^{13}C NMR spectrum of La@C_{74}($C_6H_3Cl_2$) isomer A in CS_2 (acetone-d_6 in capillary as lock solvent) at 125 MHz. (b) ^{13}C NMR chemical shift of La@C_{74}($C_6H_3Cl_2$) isomer A calculated at the B3LYP-GIAO level.

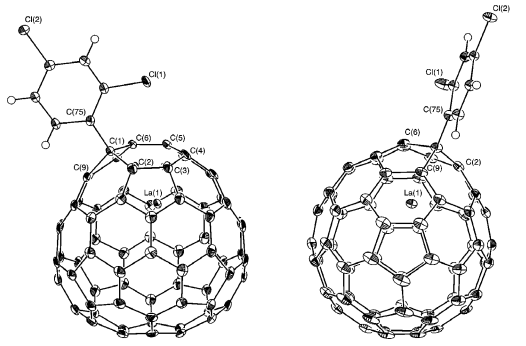

Figure 2. ORTEP drawing of one enantiomeric isomer of La@C_{74}($C_6H_3Cl_2$) showing thermal ellipsoids at the 50% probability level. The CS_2 molecules are omitted for clarity.

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Table 1. Electronic States, Ionization Potentials (eV), and Electron Affinities (eV) of $La@C_{74}$, $La@C_{82}$, and $Ca@C_{74}$[a]

compound	electronic state	Ip	Ea
$La@C_{74}(D_{3h})$	$La^{3+}@C_{74}{}^{3-}$	6.16	3.07
$La@C_{82}(C_{2v})$	$La^{3+}@C_{82}{}^{3-}$	6.19	3.38
$Ca@C_{74}(D_{3h})$	$Ca^{2+}@C_{74}{}^{2-}$	6.41	2.93

[a] From ref 16.

(POAV) pyramidalization angles θ_p[15] (0° for graphite and 11.6° for C_{60}) of C(2), C(6), and C(9) adjacent to the sp^3 carbon atom are 5.6, 10.6, and 6.8°, respectively. The encapsulated La atom is located at only one site near the dichlorophenyl group. The observed La(1)···C(1) distance of 3.070 Å agrees with the calculated value of 3.117 Å. Although the La atom in $La@C_{74}$ is located at the stable site along a C_2 axis on the σ_h plane, according to theoretical calculations, the La atom in $La@C_{74}(C_6H_3Cl_2)$ is situated at a slightly different position. This result indicates that introduction of the dichlorophenyl group has an effect on the position of the encapsulated La atom.

To assign two particular signals at 114.6 and 86.7 ppm on the ^{13}C NMR spectrum of isomer A, the ^{13}C NMR chemical shifts were calculated by the B3LYP-GIAO level.[16] It was found that the two signals at 114.6 and 86.7 ppm are attributed to the C(6) and C(2), respectively (Figure 1), which are adjacent to the sp^3 carbon on C_{74}.

In view of the production of $La@C_{74}(C_6H_3Cl_2)$ in process of the extraction, there is a great deal of interest in the reactivity of $La@C_{74}$. We carried out theoretical studies[16] on $La@C_{74}$. On the other hand, $M^{2+}@C_{74}{}^{2-}$ (M = Ca,[17] Ba,[18] Sm,[19] and Eu[20]) was recently isolated and characterized. In contrast to $La@C_{74}$, $M^{2+}@C_{74}{}^{2-}$ is soluble and very stable. So we also carried out theoretical studies[16] on $Ca@C_{74}$, in which Ca is encapsulated inside the D_{3h} cage of C_{74}. Theoretical studies[16] indicate that $La@C_{74}$ has an electronic structure described as $La^{3+}@C_{74}{}^{3-}$ and is paramagnetic. Interestingly, there are only small differences in the ionization potential (Ip) and electron affinity (Ea) between $La@C_{74}$, $Ca@C_{74}$, and $La@C_{82}(C_{2v})$ (Table 1). Therefore, the unconventionally high reactivity of $La@C_{74}$ cannot be explained on the basis of the Ip and Ea. So we next calculated the spin density distributions of $La@C_{74}$ and $La@C_{82}(C_{2v})$. For $La@C_{82}$, the spin densities are distributed onto all the carbons of C_{82}; as a result, each carbon has a small spin density. For $La@C_{74}$, however, it is noteworthy that about 50% of the total spin densities on C_{74} is localized on the three types of carbons, allowing these carbons to have high radical character. In fact, the dichlorophenyl radical, which may be produced by the reaction of TCB with reductant, such as lanthanum carbide in the raw soot, adds to one of the these carbons to give the stable adduct. From these results, unconventionally high reactivity of $La@C_{74}$ is ascribed to the high radical character of the C_{74} cage.

In conclusion, it is found that $La@C_{74}$ has a radical character on the $C_{74}(D_{3h})$ carbon cage, which can be trapped with a dichlorophenyl radical produced during the extraction. Addition of a dichlorophenyl group to $La@C_{74}$ leads to a stable and novel endohedral metallofullerene derivative, $La@C_{74}(C_6H_3Cl_2)$, with a closed-shell electronic structure.

We believe that there are still many insoluble and unknown endohedral metallofullerenes in raw soot. Successful isolation of insoluble $La@C_{74}$ as a stable derivative might constitute an important stepping-stone on the way to isolation of these unknown endohedral metallofullerenes and open the new metallofullerene chemistry.

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Supporting Information Available: Experimental details and spectroscopic and theoretical data for $La@C_{74}(C_6H_3Cl_2)$ and $La@C_{74}$. X-ray crystallographic details including a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data of a black needle of $La@C_{74}(C_6H_3Cl_2)\cdot 2(CS_2)$: MF = $C_{41}H_{1.5}Cl_1La_{0.5}S_2$, FW = 662.56, 0.19 mm × 0.07 mm × 0.07 mm, orthorhombic, *Pnma* (no. 62), $a = 20.5977(19)$ Å, $b = 13.7738(13)$ Å, $c = 15.3609(14)$ Å, $\beta = 90°$, $V = 4358.0(7)$ Å, $Z = 8$, $D_{calcd} = 2.020$ g cm^{-3}, μ(Mo Ka) = 1.361 mm^{-1}. An empirical absorption correction ($0.782 \leq T \leq 0.911$), π and ω scan, $\theta = 2.22-27.93°$, $T = 90$ K, 49 566 refractions collected (5402 independent $R_{int} = 0.0790$), $R1 = 0.0740$, $wR2 = 0.1431$ for all data, $R1 = 0.0539$, $wR2 = 0.1331$ for 5402 reflections ($I > 2.0\sigma(I)$) and 746 parameters. The maximum and minimum residual electron density is equal to 1.895 and −0.766 e Å^{-3}, respectively. These relatively high *R* values are due to general disorder of all $La@C_{74}(C_6H_3Cl_2)$ cage carbons.
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