

Observation of Li cation encapsulated in C₆₀ fullerene cage by single-crystal charge density analysis

C₆₀ fullerene is the most promising nanocarbon material for a wide range of practical applications owing to its high productivity and flexible electrical and chemical properties. The encapsulation of atoms and molecule in C₆₀ fullerene is a promising method of developing application field. Various endohedral C₆₀ fullerenes have been synthesized since the discovery of the first metallofullerene La@C₆₀ in 1985. The macroscopic synthesis and molecular structures of the gas molecule endohedral C₆₀, H₂@C₆₀ and Ar@C₆₀, have been reported [1,2]. The physical and chemical properties of H₂@C₆₀ and Ar@C₆₀ are similar to those of empty C₆₀. The encapsulation of a metal atom is expected to change the properties of C₆₀ by metal ionization. However, the isolation and structure determination of M@C₆₀ (M: metal) have been precluded by the insolubility and high reactivity of M@C₆₀.

Recently, the bulk synthesis and complete isolation of Li@C₆₀ have been successfully carried out by researchers of idealstar Inc. and Tohoku University. A single crystal of [Li@C₆₀](SbCl₆) with typical dimensions of 60×40×10 μm³ was grown by the diffusion of CS₂ vapor into solution. However, it is generally difficult to determine the position of a Li cation from small crystals by X-ray diffraction analysis. We observed an encapsulation of a Li cation inside a C₆₀ cage by a single-crystal X-ray diffraction analysis of [Li@C₆₀](SbCl₆) crystals at BL02B1 beamline [3].

The single-crystal X-ray diffraction experiment was performed using a large cylindrical imaging plate camera [4]. The camera rapidly collects diffraction peaks over a wide diffraction angle range ($2\theta < 145^\circ$)

using an imaging plate with a wide dynamic range of 10⁶ and a three-axis goniometer ($-130 < \omega < 220^\circ$, $-5 < \chi < 60^\circ$, $-180 < \phi < 360^\circ$). The wavelength of X-rays used is 0.35 Å. The sample temperature was controlled using a He/N₂ gas flow system. The [Li@C₆₀](SbCl₆) crystal had a twinned monoclinic structure below room temperature. A phase transition from a twinned monoclinic structure to a single-domain orthorhombic structure was observed at ~320 K. The crystal structure of the orthorhombic [Li@C₆₀](SbCl₆) was determined at 370 K (space group *Amm*2, $a = 12.30$ Å, $b = 9.95$ Å, $c = 29.05$ Å, $V = 3555$ Å³). The orientations of C₆₀ cages and the position of a Li cation inside a cage were determined on the basis of charge density distributions by the maximum entropy method (MEM).

A charge density map for a [Li@C₆₀]⁺ is shown in Fig. 1(a). Two charge density peaks (red arrows) inside the C₆₀ cage were regarded as disordered Li cation occupying two off-centered sites that are crystallographically equivalent. This off-centered structure is quite different from the on-centered structure of the encapsulated gas molecule inside the C₆₀ cage [1,2]. The distance from the center of the C₆₀ cage to the Li cation is 1.34 Å, which is close to the theoretically predicted values. The inhomogeneous charge density distribution of the C₆₀ cage (shown as green in Fig. 1(a)) demonstrates the ratchet-type disorder of the cage with four orientations. In any orientation of C₆₀ fullerene, the Li cation lies in the vicinity of one of the six-membered rings (Fig. 1(b)) of the cage. This suggests the presence of an attractive force exerted between the six-membered ring and the Li cation.

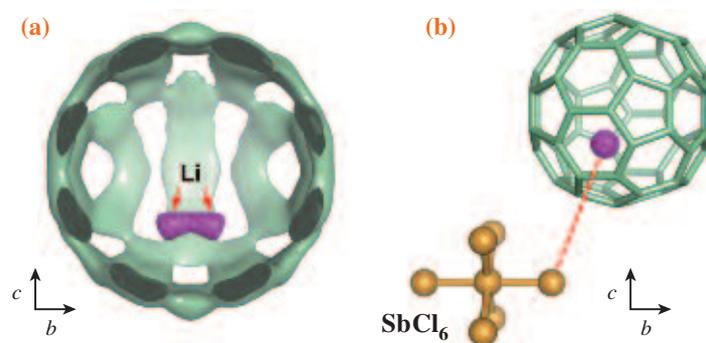


Fig. 1. (a) MEM charge density map of Li@C₆₀ cation in [Li@C₆₀](SbCl₆) crystal at 370 K. A 0.25 e/Å³ equi-charge density surface for a Li cation inside a C₆₀ cage is shown as magenta. A 2.0 e/Å³ equi-charge density surface is shown in green. The charge density at the two peaks for the Li cation (red arrows) is 0.38 e/Å³. (b) Geometrical relationships between Li@C₆₀ cation and adjacent SbCl₆ anion (orange). The structure of one molecular orientation for a Li@C₆₀ cation extracted from a disordered structure is shown. The nearest Li-Cl distance is 5.58 Å (red dashed line).

An electrostatic attractive interaction between a Li cation and SbCl_6^- anions should be crucial to determining the position of the Li cation in the C_{60} cage. Figure 1(b) shows the arrangement of an SbCl_6^- anion around a Li@C_{60} cation. The Li cation is close to a negatively charged Cl atom of the SbCl_6^- anion. The electrostatic attractive interaction between Li^+ and Cl^- through the cage should localize the Li cation at the two sites. The restriction of the free rotation of the C_{60} cage even at a high temperature of 370 K is regarded as a result of the attractive interaction between the localized Li cation and the six-membered rings.

The three-dimensional molecular arrangement of the $[\text{Li@C}_{60}]^+$ and SbCl_6^- units (Fig. 1(b)) constructs the layered crystal structure, as shown in Fig. 2. The slab structure formed by two-dimensional arrays of the $[\text{Li@C}_{60}](\text{SbCl}_6)$ units (Fig. 1(b)) perpendicular to the c -axis is clearly seen. In the slab, the first- and second-nearest intermolecular distances of the Li@C_{60} cations are 9.95 and 10.03 Å, respectively. The shorter distance (9.95 Å) between the adjacent Li@C_{60} cations is almost exactly the same as that of the close-packed pristine fcc C_{60} structure, whereas the interslab distance of the Li@C_{60} cations is

10.30 Å. The positively charged Li@C_{60} ions are periodically assembled on the two-dimensional negatively charged sheets of SbCl_6^- ions by the electrostatic attractive force between the Li cation and the Cl atom. This unique structural feature may exhibit interesting solid-state properties. The ^{13}C NMR spectrum of $[\text{Li@C}_{60}](\text{SbCl}_6)$ in solution shows that the Li cation is rapidly moving inside the C_{60} cage. These facts suggest that the position of the Li cation can be varied and controlled by adjusting the external field outside the C_{60} cage. Such position control by an external field can be widely used in electronics applications such as in single molecular switches and ferroelectric sheets.

The most striking feature of Li@C_{60} revealed in the present study, which has never been observed in conventional metallofullerenes, is the extremely high tendency of Li@C_{60} to form ion-pair states (species) such as $[\text{Li@C}_{60}](\text{SbCl}_6)$. Li@C_{60} can only be stabilized significantly under ambient condition when it coexists with an appropriate counteranion. The present methodology for the isolation and crystallization of $M@C_{60}$ can be widely applied to the existing Groups 2, 3, and 4 and all lanthanide metallofullerenes such as La@C_{60} and Gd@C_{60} [5].

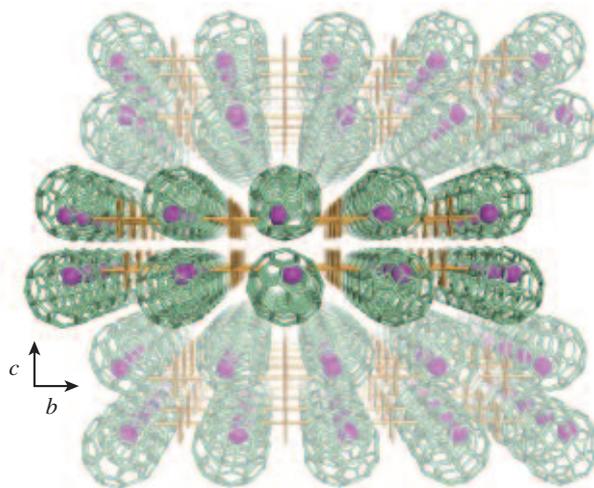


Fig. 2. Layered crystal structure of $[\text{Li@C}_{60}](\text{SbCl}_6)$. Slabs formed by two-dimensional arrays of $[\text{Li@C}_{60}](\text{SbCl}_6)$ units (Fig. 1(b)) are stacked along the c -axis. Three slabs (one layer in dense color and two outer layers in light colors) are shown in the figure.

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