Structure Elucidation

An Anomalous Endohedral Structure of Eu@C_{82} Metallofullerenes[**]

*Bao-Yun Sun, Toshiki Sugai, Eiji Nishibori,
Kenichi Iwata, Makoto Sakata, Masaki Takata, and
Hisanori Shinohara**

Trivalent metallofullerenes such as La@C_{82} and Ce@C_{82}, in which the metal ions prefer to take a trivalent charge state, have been extensively investigated.[1] However, studies on metallofullerenes encapsulating divalent Sm, Eu, Tm, and Yb metal ions have been limited because of the known low yields in the production of these metallofullerenes despite the development of some improved production and extraction methods during the past several years.[2] This situation has resulted in the structures of such metallofullerenes not having been studied in detail. The variety of encaged metal ions and charge transfer as well as the movement of entrapped metal ions are expected to provide different physical properties. Therefore, it is necessary to study the structure and electronic properties of metallofullerenes in this divalent group.

The Eu ion in Eu@C_{82} was shown by experiment to transfer two electrons to the fullerene cage.[2c] There are no unpaired electrons on the Eu@C_{82} cage and charge transfer results in the $4f^7 5d^0 6s^0$ electronic configuration, which gives rise to the fullerene having paramagnetic character. It is thus difficult to determine the structure of the cage and the symmetry of the complex by NMR spectroscopy. XRD measurements have become the only way to access the detailed structure of Eu@C_{82} fullerenes.

X-ray analysis performed using a combination of the maximum entropy method (MEM) and Rietveld refinement (the MEM/Rietveld method[3]) has proven to be a powerful method for the accurate determination of the structures of metallofullerenes. The endohedral nature of a series of metallofullerenes, such as La, Y, Sc, and Gd@C_{82},[4] Sc_3@C_{82}, La_2@C_{80}, Sc_2@C_{84}, Sc_2@C_{66}, and Sc_2C_2@C_{84}[5] has been determined successfully by this method.

In the present study the structures of the two isomers of Eu@C_{82}(I, III) were successfully determined by the MEM/Rietveld method using synchrotron X-ray powder diffraction data. The endohedral structure of Eu@C_{82}(III) is exceptional in view of the fact that the Eu ion is adjacent to the C=C double bond on the C_2 axis of the C_{2v} carbon cage, whereas the metal ions (such as La, Y, Sc, Er, Lu) in the normal mono-metallofullerenes are adjacent to a hexagon of the C_{82} cage, except for Gd@C_{82}.[4d,6]

Similar to previous studies of La-, Y-, Sc-, and Gd@C_{82},[4] Sc_3@C_{82},[5a] La_2@C_{80},[5b] as well as Sc_2@C_{84},[5c] the Eu@C_{82}(I, III) crystals are assigned to monoclinic $P2_1$ (no. 4) space groups from the peak positions of the Bragg reflections. The lattice parameters for both isomers are slightly different from each other, namely, $a = 18.2870(4)$, $b = 11.2381(2)$, $c = 11.2371(2)$ Å, $\beta = 107.769(3)°$ for isomer I of Eu@C_{82} and $a = 18.3143(5)$, $b = 11.2478(2)$, $c = 11.2308(3)$ Å, and $\beta = 107.706(3)°$ for isomer III.

The experimental data were analyzed by the MEM/Rietveld method.[3] The reliability factors of the final Rietveld refinement for Eu@C_{82}(I and III) are $R_I = 4.58\%$ and $R_{wp} = 2.64\%$ and $R_I = 4.57\%$ and $R_{wp} = 1.79\%$, respectively. The fitting results of the final Rietveld refinement for the two isomers are shown in Figure 1 a, b. The number of observed structure factors derived in this analysis was 623 and 602 for isomers I and III, respectively. The MEM analysis was carried out by dividing the unit cell into $90 \times 60 \times 60$ pixels using a MEM program called ENIGMA.[7]

The obtained MEM charge-density distribution (from 0.0 to 2.0 e Å^{-3} with 0.2 e Å^{-3} intervals) and the equicontour density map of the MEM charge density of the half section of Eu@C_{82}(I) (drawn at 1.67 e Å^{-3}) are shown in Figure 2. Both the mirror plane and the double bond at the mirror plane are parallel to the Figure plane and vertical to the Figure plane in Figure 2 a and b, respectively.

The MEM charge-density distribution in Figure 2 a and b shows clearly that there is a charge-density maximum inside the C_{82} cage which can be assigned to the entrapped metal ion. The density maximum is not at the center but close to the carbon cage, as in other metallofullerenes such as La-, Y-, Sc-, and Gd@C_{82}.[4] The charge densities at the middle points between the Eu ion and the neighboring carbon atoms in positions A, B, and C of Eu@C_{82}(I) are 0.218, 0.207, and 0.224 e Å^{-3}, respectively, which are much less than the corresponding density for Gd@C_{82}.[4d]

The equicontour density map of the MEM charge density of the half section in Figure 2 c visualizes the three-dimen-

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[*] Dr. B.-Y. Sun, Dr. T. Sugai, Prof. Dr. H. Shinohara
Department of Chemistry
Nagoya University
Nagoya 464-8602 (Japan)
and
CREST, Japan Science Technology Corporation
c/o Department of Chemistry
Nagoya University
Nagoya 464-8602 (Japan)
Fax: (+81) 52-789-1169
E-mail: noris@cc.nagoya-u.ac.jp

Dr. E. Nishibori, K. Iwata, Prof. Dr. M. Sakata
Department of Applied Physics
Nagoya University
Nagoya 464-8603 (Japan)

Prof. Dr. M. Takata
Japan Synchrotron Radiation Research Institute
1-1-1 Kato, Mikazuki-cho, Sayo-gun, Hyogo 679-5198 (Japan)
and
CREST, Japan Science Technology Corporation

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Supporting information for this article (the relative yields of the three isomers and experimental section) is available on the WWW under http://www.angewandte.org or from the author.

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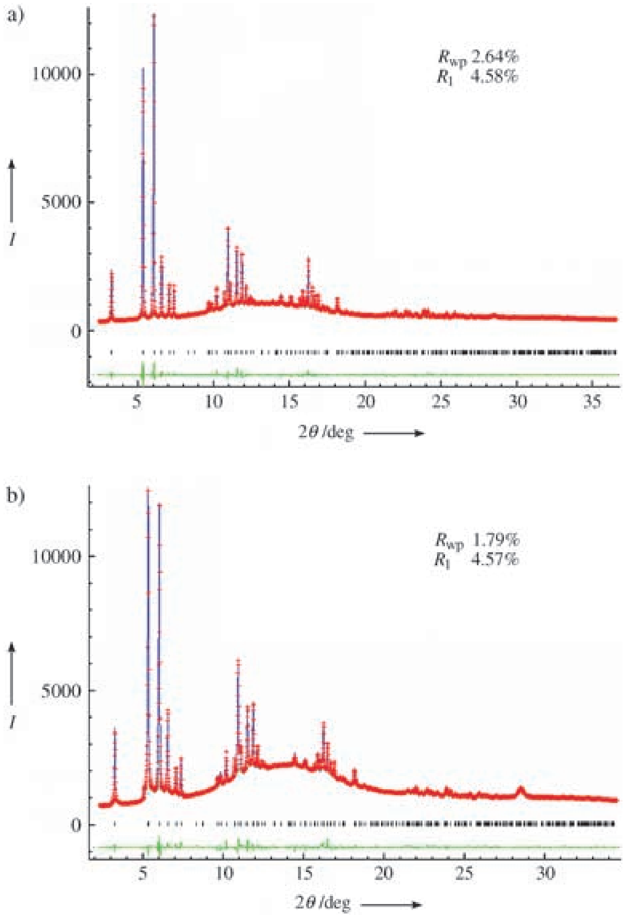

Figure 1. The Rietveld fitting results of $Eu@C_{82}$: a) isomer I with C_s (no. 6) symmetry and b) isomer III with C_{2v} symmetry.

sional structure of the cage and the entrapped metal ion. The obtained endohedral cage structure has a network of six- and five-membered rings corresponding to C_s (no. 6) symmetry.[8] The charge density of the Eu ion can clearly be seen inside the cage. The total number of electrons inside the region described by the red circle was estimated to be 61.0(8) e, which is very close to that of the divalent Eu ion (61 e). This result indicates that the Eu ion is encaged within C_{82} and the formal electronic structure should be expressed as $Eu^{2+}@C_{82}^{2-}$, which is consistent with the previous result based on EELS analysis.[2c] This finding confirms that the Eu ion prefers to take a +2 charge state in the C_{82} fullerene cage and to form the $4f^7 5d^0 6s^0$ half-filled configuration.

Figure 3 shows the side and top views of the corresponding schematic molecular structure of $Eu@C_{82}$(I) based on the X-ray analysis. The obtained structural model indicates that the metallofullerene has C_s (no. 6) symmetry.[8] The mirror plane is on the Figure plane in the side view (Figure 3 a) and is vertical to the Figure plane in the top view (Figure 3 b). The Eu ion (colored turquoise) is located near the top of the carbon cage in Figure 3 a, adjacent to the C–C double bond on the mirror plane but not to the six-membered ring at the other end of the cage. A similar endohedral structure was reported from a theoretical calculation for $Ca@C_{82}$ with C_s(c), namely, C_s (no. 6) symmetry.[9] The distance between the Eu ion and the cage center is 1.59(4) Å and that between the Eu ion and the nearest (two) carbon atoms is 2.51(3) Å, which is much less than the calculated Ca···C distance in C_s-$Ca@C_{82}$ (2.639(2) Å).[9]

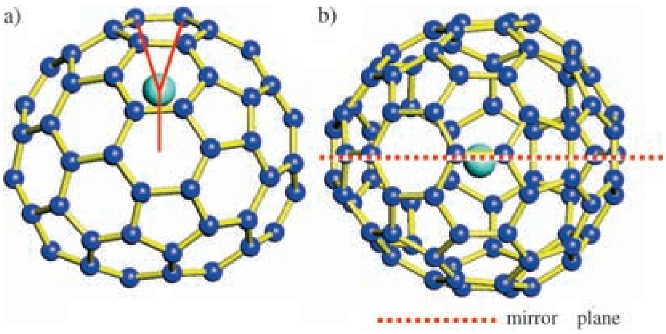

Figure 3. The side view (a) and the top view (b) of $Eu@C_{82}$(I) with C_s (no. 6) symmetry.

There are nine distinct isomers for the C_{82} cage which satisfy the so-called isolated pentagon rule (IPR).[8] Three of them have C_s symmetry, which are designated as C_s (no. 2), C_s (no. 4), and C_s (no. 6) according to Fowler and Manolopoulos.[8] It is known that the minor isomer of $La@C_{82}$ and one isomer of $Tm@C_{82}$, normally designated as $La@C_{82}$(I) and $Tm@C_{82}$(I), respectively, have been determined to have C_s symmetry by ^{13}NMR spectroscopic studies.[2a,10] However, one-dimensional ^{13}NMR measurements can not determine

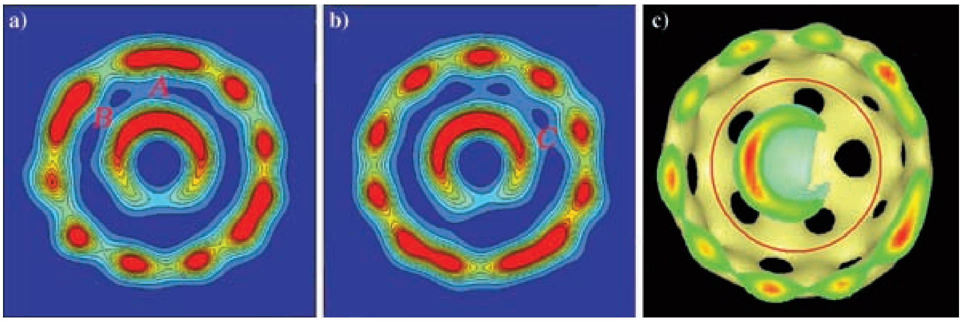

Figure 2. The MEM charge-density distribution (a, b; contour lines are drawn from 0.0 to 2.0 e Å^{-3} with 0.2 e Å^{-3} intervals) and the equicontour density map of the MEM charge density of the half section (c; drawn at 1.67 e Å^{-3}) of $Eu@C_{82}$(I) with C_s (no. 6) symmetry. Positions *A*–*C* are discussed in the text.

definitively the final C_s symmetry, that is, whether it is no. 2, 4, or 6. The present XRD experiment enables us, for the first time, to identify that Eu@C$_{82}$(I) possesses C_s (no. 6) symmetry.

Only one of the nine IPR isomers of C$_{82}$ has C_{2v} symmetry.[8] Most of the C$_{82}$-caged metallofullerenes, such as La-, Y-, Sc-, and Gd@C$_{82}$, have been determined to have C_{2v} symmetry by synchrotron X-ray diffraction studies.[4] The present X-ray measurement shows that Eu@C$_{82}$(III) also possesses C_{2v} symmetry.

The MEM charge-density distribution (from 0.0 to 2.0 e Å^{-3} with 0.2 e Å^{-3} steps, as for isomer I) and the contour line surface of Eu@C$_{82}$(III) (drawn at 1.67 e Å^{-3}, as for isomer I) are shown in Figure 4. The direction of the C_2 axis is vertical to the double bond at the C_2 axis and parallel to the Figure plane in both Figure 4a and b, but the direction of the double bond at the C_2 axis is parallel to the Figure plane in Figure 4a and vertical to the Figure plane in Figure 4b. The MEM charge density clearly shows that the cage structure of Eu@C$_{82}$(III) has C_{2v} symmetry (Figure 4a and b). Similar to isomer I, a charge-density maximum is located at an off-center position, which should be the encaged Eu ion. The overlapped charge densities between the Eu ion and the neighboring carbon atoms in Eu@C$_{82}$(III) are 0.186, 0.215, and 0.189 e Å^{-3} for positions A, B, and C, respectively, which are similar to those in isomer I. The number of electrons contained within the red circle is 61.2(7) e (see Figure 4c). This value is also close to that of an Eu^{2+} ion with 61 e, thus indicating that the Eu center also takes a divalent charge state in this isomer. The six- and five-membered rings can clearly be seen, and the structure has C_{2v} symmetry.

The corresponding schematic molecular structure based on the analysis of Eu@C$_{82}$(III) is shown in Figure 5. The side and the top views show that the Eu ion (colored turquoise) is located in the C_{2v}-symmetric cage and is adjacent to the C–C double bond along the C_2 axis in Eu@C$_{82}$(III). These endohedral structures of Eu@C$_{82}$(I and III) can be contrasted to those of the conventional C$_{82}$-based mono-metallofullerenes such as La-, Y-, and Sc@C$_{82}$.[4a–c] Only the mono-metallofullerene Gd@C$_{82}$[4d] is similar to the present Eu@C$_{82}$ case, in which the Gd ion located close to the C–C double bond on the C_2 axis of C_{2v}-C$_{82}$. The distance between the Eu ion and the cage center is 1.70(5) Å, which is less than that between the La ion and the cage center in C_{2v}-La@C$_{82}$ (1.96(9) Å).[4a]

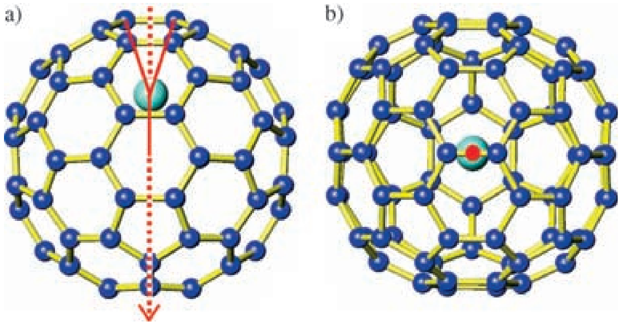

Figure 5. The side view (a) and the top view (b) of Eu@C$_{82}$(III) with C_{2v} symmetry.

The nearest Eu···C distance (between the Eu ion and two C atoms of the double bond) is 2.50(1) Å in the C$_{2v}$ cage, which is close to those in La-, Y-, and Sc@C$_{82}$ (ca. 2.5 Å).[4a–c]

A recent theoretical calculation[6] on Gd@C$_{82}$ showed that the position of the metal near the C–C double bond is preferred to the position adjacent to a hexagon if relaxation of the cage is considered. The strong overlap in the charge density between the Gd ion and the cage and the back donation of electrons from the C–C double bond stabilize the Gd ion at the position adjacent to the double bond.[6] The calculated total energy is 2.83 eV lower than that at the position adjacent to the six-membered ring. It should be noted that both Gd^{3+} and Eu^{2+} ions have a half-filled configuration [Xe]^{54}4f^7.

The overlap in the charge density between the Eu ion and the cage is different from that in Gd@C$_{82}$. The charge density at the middle point between the Eu ion and the nearest carbon atoms in C_{2v}-Eu@C$_{82}$(III) (position A in Figure 4) is 0.186 e Å^{-3}, which is only about one-fifth of that found in C_{2v}-Gd@C$_{82}$ (0.996 e Å^{-3}).[4d] Similarly, the charge density at the middle point between the Eu ion and the nearest carbon atoms in the C_s-Eu@C$_{82}$(I) case (position A in Figure 2) is only 0.218 e Å^{-3}, which is similar to that found in C_{2v}-Eu@C$_{82}$(III). The results strongly suggest that the interaction between the entrapped Eu ion and the carbon cage is much weaker than that exerted in Gd@C$_{82}$. This weaker interaction has also been suggested by a downfield shift of the Raman vibration frequency of the metal cage[2e,11] in Tm@C$_{82}$ and Eu@C$_{74}$. Such low-energy modes in Tm@C$_{82}$ and Eu@C$_{74}$ are

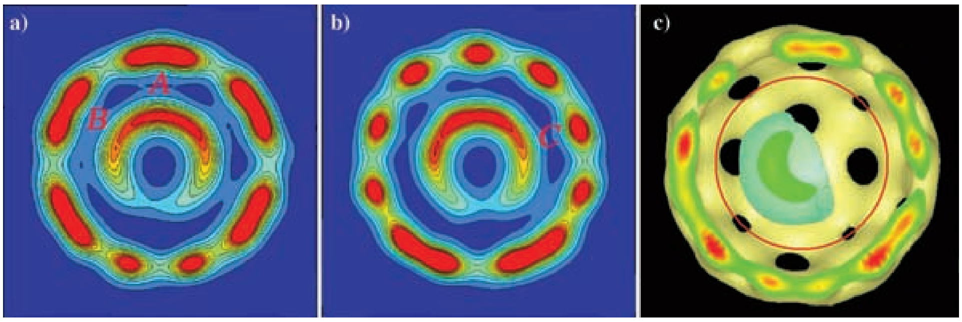

Figure 4. The MEM charge density distribution (a, b; contour lines are drawn from 0.0 to 2.0 e Å^{-3} with 0.2 e Å^{-3} intervals) and the equicontour density map of the MEM charge density of the half section (c; drawn at 1.67 e Å^{-3}) of Eu@C$_{82}$(III) with C_{2v} symmetry. Positions *A–C* are discussed in the text.

lower in frequency than those in trivalent metallofullerenes. The present MEM charge density reveals that the nature of the chemical bonding between the Eu ion and the cage should be highly ionic.

The overlapped charge densities in positions B and C in Eu@C_{82}(III) in Figure 4 are 0.215 and 0.189 e Å^{-3}, respectively, which is similar to that between the Eu ion and the nearest carbon atoms (0.186 e Å^{-3}). The charge densities in Eu@C_{82}(I) in Figure 2 are 0.207 and 0.224 e Å^{-3} for positions B and C, respectively, which are similar to 0.218 e Å^{-3} at position A as in Eu@C_{82}(III). Figures 2 and 4 show that the Eu ion moves over a spatially confined domain both in the C_s (no. 6) and C_{2v} cages. The obtained charge density of the Eu ion exhibits a hemispherical shape at room temperature, which is much wider than those observed in Sc@C_{82} and Gd@C_{82}.[4c,d]

As previously mentioned, the endohedral structure of C_{2v}-Eu@C_{82} is significantly different from that of C_{2v}-Sc@C_{82}[4c] although both of them are divalent metallofullerenes. Firstly, the Eu metal ion is located at the opposite position of that of the Sc ion along the C_2 symmetry axis. Secondly, the Sc ion does not move inside the C_{82} cage even at room temperature and shows a spherical charge-density distribution, whereas the Eu ion floats inside the cage as is clearly seen in Figure 4. The different interaction in Eu@C_{82} and Sc@C_{82} evidently induces the different endohedral structure of the metal ions in the C_{82} cage.

In the present study, a weak intramolecular interaction between the Eu ion and the carbon cage should be one of the important reasons why the yield of Eu–metallofullerenes has been the lowest of the metallofullerenes so far studied. Undoubtedly, if the interaction between the cage and the metal is weak, such as in Eu–metallofullerenes, the probability of losing the metal ion before the closure (that is, completion) of the fullerene cage should increase. The fact that the relative yield of Eu@C_{82} is only about 3 % of that of Er@C_{82} or La@C_{82} is consistent with this growth process.

The cage structures of Eu@C_{82} (isomers I and III) have been determined to have C_s (no. 6) and C_{2v} symmetry, respectively, by XRD measurements combined with the MEM/Rietveld analysis. Unlike other M@C_{82} (M = Sc, Y, La, and other lanthanide elements) mono-metallofullerenes (except Gd@C_{82}), the Eu ion is adjacent to the C–C double bond on the mirror plane of the C_s (no. 6) symmetric structure in Eu@C_{82}(I) and adjacent to the C–C double bond (not to a hexagon) on the C_2 axis of a C_{2v} structure of Eu@C_{82}(III). The obtained charge-density mappings for Eu@C_{82}(I, III) show that the charge densities of the Eu ions form a nearly hemispherical shape at room temperature, thus indicating that the Eu ion is floating in the C_{82} cage.[12]

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[12] CCDC-265613(Eu@C_{82}(I)) and CCDC-265614(Eu@C_{82}(III)) 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.