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Where Does the Metal Cation Stay in Gd@C_{2v}(9)-C_{82}? A Single-Crystal X-ray Diffraction Study

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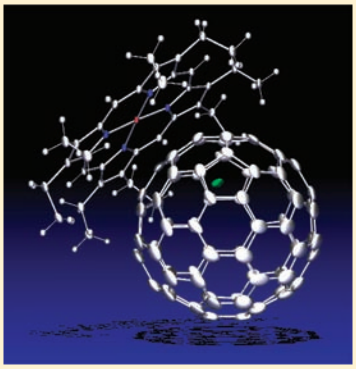
Supporting Information

ABSTRACT: Metal positions in endohedral metallofullerenes (EMFs) are of special importance because their molecular symmetry and intrinsic properties are strongly influenced by the location and motion of the encapsulated metals. X-ray analyses of the cocrystals of Gd@C_{2v}(9)-C_{82} with nickel^{II} octaethylporphyrin [Ni^{II}(OEP)] reveal that the Gd^{3+} cation is off-center, being located under a hexagonal ring along the 2-fold axis of the C_{2v}(9)-C_{82} cage. This result is in sharp contrast to that of a previous study, showing that Gd@C_{2v}(9)-C_{82} has an anomalous endohedral structure, with the metal being positioned over a [6,6] bond, which is opposite to the hexagonal ring along the C_2 axis (*Phys. Rev. B* **2004**, *69*, 113412). In agreement with theoretical calculations and related studies, it is conclusive that the single rare-earth metal in M@C_{2v}(9)-C_{82} always tends to coordinate with the hexagonal ring along the 2-fold axis, instead of interacting with the [6,6] bond on the other end, regardless of the type of metal atom.



INTRODUCTION

Endohedral metallofullerenes (EMFs), which are fullerenes with metal atoms or metallic clusters trapped inside the spacious cage cavity, have continued to attract wide interest because of their unique structures and fascinating properties, as a result of the electron transfer from the endohedral metallic species to the carbon cage.[1] Accordingly, vast potential applications are anticipated for EMFs in biomedicine, photovoltaics, and materials sciences.[1] It has been of particular interest to know the structure of EMFs, including the cage symmetry and the location/motion of the internal metals because it is assumed that the formation mechanism and intrinsic properties of EMFs, especially their chemical reactivity, are closely associated with these structural issues.[2,3]

Ever since the first solvent extraction of La@C_{82} in 1991,[4] M@C_{82} (M = group 3 metals and lanthanides) are viewed as prototypes of EMFs, partially because of their relatively easy availability.[1] Although it had been assumed in the very beginning of EMF research that the La atom is encapsulated inside the most stable C_2(3) isomer of C_{82}, results of a further theoretical study suggested that the C_{2v}(9)-C_{82} cage should be more preferred by the metal cation because three electrons are transferred from the metal to the cage.[5] That prediction was verified by ^{13}C NMR spectrometry performed on the anions of M@C_{82} (M = Y, La, Ce, and Pr).[6] More recently, the single-crystal X-ray crystallographic results of the M@C_{82} derivatives (M = Y, La, and Ce) confirmed the C_{2v}(9)-C_{82} cage structure unambiguously.[7]

Regarding the metal position inside M@C_{82}, however, it is difficult for NMR spectrometry to give definite conclusions.[2a] Studies using synchrotron-radiation (SR) powder diffraction coupled with Rietveld analysis and the maximum entropy method (MEM) of Sc@C_{82} and La@C_{82} showed great success in the very beginning of EMF research, which not only confirmed the C_{2v}(9)-C_{82} cage structure but also revealed that the metal atom is not in the center of the cage but is located under a hexagonal ring of the C_{2v}(9)-C_{82} cage along the C_2 axis (Figure 1a),[8] as theoretically predicted.[5] The above conclusion was further corroborated by both theoretical calculations and other experimental results, including single-crystal X-ray crystallographic analyses of the corresponding derivatives of M@C_{82} (M = Y, La, and Ce), but in the latter case, the metal position was evidently changed upon chemical modification of the cage.[7] However, for Gd@C_{82} and Eu@C_{82}, the SR/Rietveld/MEM results indicated an anomalous endohedral structure in which the metal atom is situated above a [6,6] bond along the C_2 axis on the opposite side of the C_{2v}(9)-C_{82} cage (Figure 1b).[9] Such an anomalous position of the metal has stimulated considerable interest, both theoretically and experimentally. However, a theoretical study of the structure of M@C_{82} (M = Gd and Eu) revealed that the metal could not find an energy minimum at the position proposed by the SR/Rietveld/MEM method (cf. Figure 1b).[10] In addition, an X-ray absorption near-edge structure study of Gd@C_{82} indicated that the Gd atom should coordinate with the hexagonal ring along the axis but not with the opposite [6,6] bond.[11] Very recently, single-crystal X-ray analysis of a derivative of Gd@C_{82}, namely, Gd@C_{82}(Ad) (Ad = adamantylidene), confirmed that Gd@C_{82} should also have a normal endohedral structure like other M@

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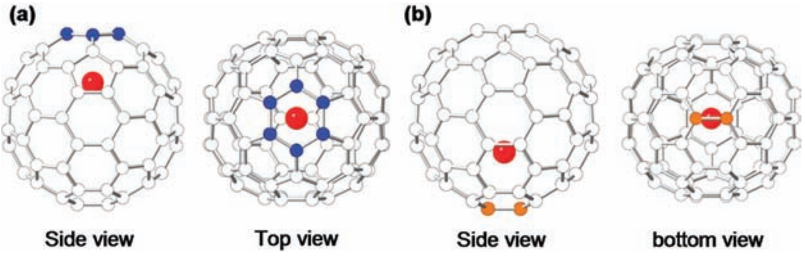

Figure 1. Different endohedral structures of M@C_{2v}(9)-C_{82} proposed by the SR/Rietveld/MEM method: (a) M = Sc and La; (b) M = Gd and Eu.

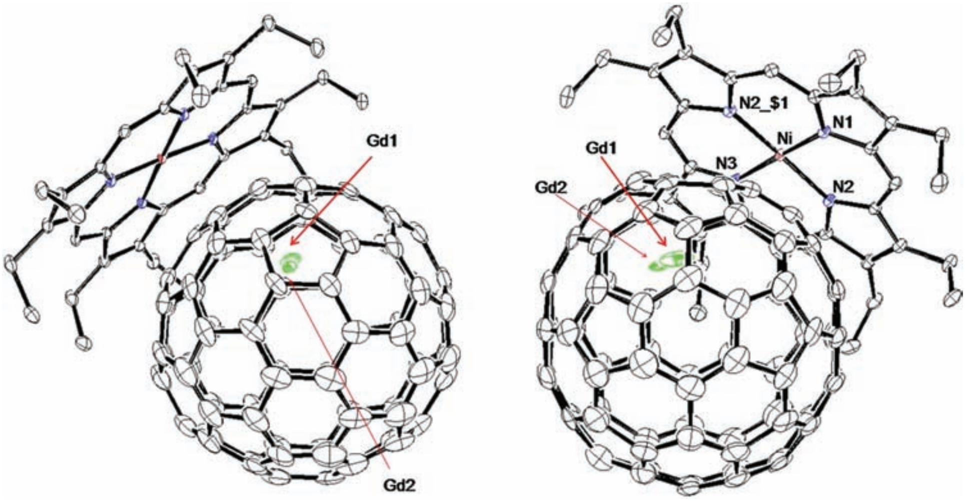

Figure 2. Orthogonal views of the endohedral fullerene and Ni^{II}(OEP) molecules in Gd@C_{82}·Ni^{II}(OEP)·0.6$CHCl_3$·1.4C_6H_6 showing 30% thermal probability. Only one cage orientation and the two major Gd sites are shown; solvent molecules and H atoms are omitted for clarity. Symmetry code: $1 = +*x*, −*y*, +*z*.

C_{82} (M = Sc, Y, La, and Ce) with the Gd atom located under a hexagonal ring, instead of sitting above the opposite [6,6] bond along the C_2 axis.[12] However, because the exohedral modification of Gd@C_{82} breaks a C−C bond on the cage and therefore invariably changes the position of the internal metal, the metal environment is certainly different from that in the pristine EMFs;[1f,g] it is particularly necessary to obtain the definitive structure of pristine Gd@C_{82}, which is the final solution to the debate presented above.

This report describes the single-crystal X-ray crystallographic results of pristine Gd@C_{82}, which is cocrystallized with Ni^{II}(OEP) (OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin) to hinder free rotation of the spherical EMF molecule in the crystal lattice.[3] In agreement with theoretical calculations, it is finally concluded that Gd@C_{2v}(9)-C_{82} also has a normal endohedral structure that is consistent with that shown in Figure 1a but not the structure of Figure 1b proposed by the SR/MEM/Rietveld method.

■ EXPERIMENTAL SECTION

Black crystalline rods of Gd@C_{2v}(9)-C_{82}/Ni^{II}(OEP) were obtained by layering a 0.5 mL benzene solution containing ca. 0.5 mg of Gd@C_{2v}(9)-C_{82} over a red chloroform solution of Ni^{II}(OEP) in a glass tube (diameter 0.7 mm). Over a period of several weeks, the two solutions diffused together and black crystals formed at the bottom of the tube. Several crystals were checked with a Bruker APEX-II machine equipped with a liquid-nitrogen low-temperature apparatus providing a constant temperature at 90 K. Finally, a piece of crystal with dimensions of 0.33 mm × 0.23 mm × 0.08 mm was found suitable for the X-ray diffraction measurement and presented all of the data for additional structural analyses.

■ RESULTS AND DISCUSSION

Similar to several reported crystallographic studies of EMF/Ni^{II}(OEP) cocrystals,[3] the asymmetric unit of Gd@C_{82}·Ni^{II}(OEP)·0.6$CHCl_3$·1.4C_6H_6 consists of half of the porphyrin molecule and halves of the fullerene, whereas the cell cavities are filled with benzene and chloroform molecules. The well-ordered nickel porphyrin is present on the crystallographic mirror plane that bisects N1, Ni, and N3. Consequently, a whole Ni^{II}(OEP) molecule is readily obtainable by combining the existing half with its mirror image. However, the C_{82} cage resides in such a fashion that none of its symmetric elements is coincident with the crystallographic mirror plane. Two quarter molecules of the fullerene cage are distinguished, and a complete C_{82} cage is only obtainable by combining one of the quarter C_{82} units with the mirror image of the other. Accordingly, the occupancy of both cages has to be set as 0.50.

Disorder also exists in the positions of the guest solvents and the endohedral metal cation. One disordered chloroform with an occupancy of 0.36 exists in a general position together with a benzene molecule whose occupancy is 0.64, whereas the other chloroform with an occupancy of 0.24 shares the position on the crystallographic mirror plane with another benzene with 0.76 occupancy. Inside the cage, four sites of the Gd cation are also identified with occupancy values of 0.21 for Gd1, 0.19 for Gd2, 0.07 for Gd3, and 0.03 for Gd4. Because all of them are within a small area close to the cage, this indicates that the metal cation is oscillating inside.[14] This is consistent with the tremendous observations of the motional behavior of metals inside EMF cages.

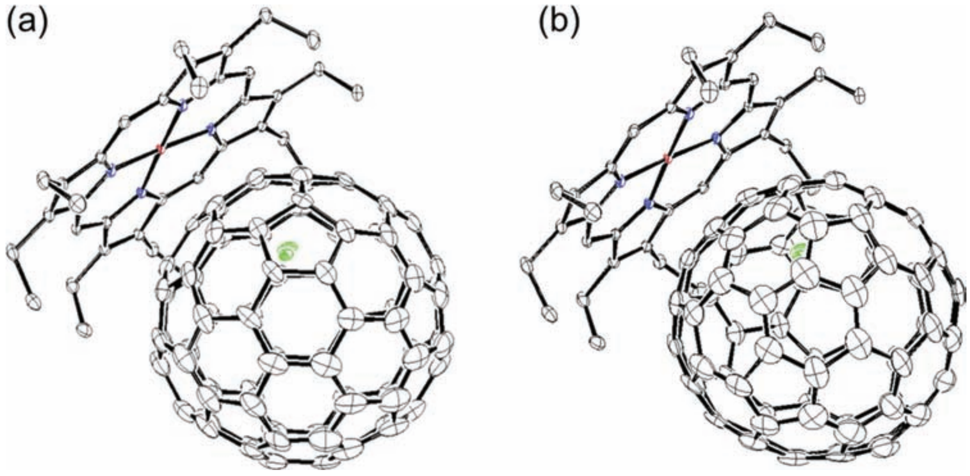

Figure 3. X-ray structures of Gd@C_{2v}(9)-C_{82} showing the major metal position (Gd1) encapsulated in (a) one cage orientation in which the metal is under a hexagonal ring along the C_2 axis. This structure is designated as conformation A; (b) the other cage orientation, which is the mirror image of the cage in part a, is designated as conformation B. Thermal ellipsoids are set at the 30% probability level.

Figure 2 portrays the molecular structure of the endofullerene and its relation to the nickel porphyrin. For clarity, only one cage orientation and the two major Gd sites with occupancies of 0.21 (Gd1) and 0.19 (Gd2) are included and solvent molecules are omitted. The cage structure is C_{2v}(9)-C_{82}, as was already pointed out both experimentally and theoretically using numerous methods.[5−7] It is apparent from Figure 2 that a relatively flat region of the cage closely approaches the porphyrin plane, which consists of Ni, four N atoms, and the adjacent C atoms, indicating a shape-matching $\pi-\pi$ interaction. It is noteworthy that the interaction parts in both cage orientations involve a common cage carbon (C1; Figure S1 in the Supporting Information), which resides on the crystallographic mirror. The shortest cage−Ni distance (Ni−C1) is 2.783 Å, which is similar to the corresponding results derived from the X-ray data of metal nitride cluster fullerenes with Ni^{II}(OEP).[13]

Because of the disorder of the cage, two different relationships between the metal and the cage can be deduced from the X-ray results. Figure 3a displays the conformation of one cage orientation encapsulating the major metal Gd1 (conformation A); in Figure 3b, the metal is encapsulated inside the second cage orientation, which is actually the mirror image of the former one (conformation B). In conformation A, the metal is localized under a hexagonal ring along the C_2 axis, as in the situation found previously for M@C_{2v}(9)-C_{82} (M = Sc and La); cf. Figure 1a, while in conformation B, the metal is more likely under a [5,6]-bond junction apart from the symmetric axis of the cage.

The possibility of conformation B is finally excluded by theoretical calculations. All calculations were conducted using the *Gaussian 09* program package.[15] Geometry optimization was performed using the density functional theory with the recently introduced M06-2X functional,[16] the 3-21G basis set[17] for the C atom, and the SDD basis set[18] (with the SDD effective core potential) for Ni and Gd atoms (the M06-2X/3-21G∼SDD level). Because all metal positions are mutually close, it is reasonable to consider only the major one: Gd1. The two possible configurations of the endohedral derived from the X-ray data, as was already shown in Figure 3, are considered: conformation A, where the metal (Gd1) is under the hexagonal ring, and conformation B, with the metal encapsulated in the mirror image. Our calculation results reveal that conformation A (Figure 3a) corresponds to a reasonable energy minimum: it remains almost unchanged during geometry optimization (Figure 4). In sharp contrast, conformation B (Figure 3b) is about 50 kcal/mol less stable: no energy minimum could be found around the area of the metal. Accordingly, it is conclusive that conformation A corresponds to the real situation of the metal in Gd@C_{2v}(9)-C_{82}; that is, the metal is located under the hexagonal ring along the C_2 axis of the cage but does not sit over the opposite [6,6] bond.

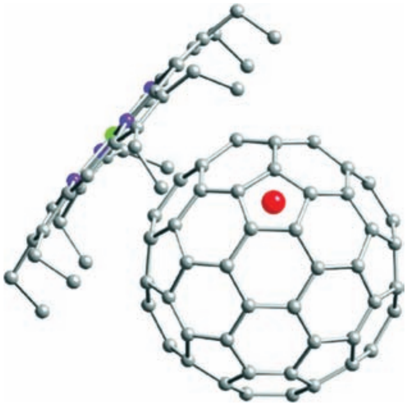

Figure 4. Theoretically optimized structure of Gd@C_{2v}(9)-C_{82} with Ni^{II}(OEP).

■ CONCLUSION

In summary, we have presented solid crystallographic X-ray results of the pristine Gd@C_{2v}(9)-C_{82}, for which a controversial SR X-ray study of a powder sample coupled with Rietveld/MEM analyses proposed an anomalous location of the endohedral metal. Our accurate single-crystal X-ray elucidation of its cocrystal with Ni^{II}(OEP) reveals that the Gd atom is located under a hexagonal ring along the C_2 axis, excluding the possibility of the anomalous endohedral structure. Our results have clarified the long debate about the anomalous structure of Gd@C_{2v}(9)-C_{82}, indicating that Eu@C_{2v}(9)-C_{82} should also bear a regular endohedral structure.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, complete citations of refs 6a, 6b, 7c, 12, and 15, spectroscopic data of Gd@C_{82}, experimental details of the cocrystallization process, X-ray structures, a photograph of single crystals, HPLC profiles, mass and UV−vis−NIR spectra, and X-ray data at 90 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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