

Crystallographic characterization of Isomer 2 of $\text{Er}_2@C_{82}$ and comparison with Isomer 1 of $\text{Er}_2@C_{82}$

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The X-ray crystal structure of (Isomer 2 of $\text{Er}_2@C_{82}$)- $\text{Ni}^{\text{II}}(\text{OEP})\cdot 2(\text{benzene})$ shows that the fullerene cage in Isomer 2 of $\text{Er}_2@C_{82}$ is the C_{3v} isomer (82:8) and that the erbium ions are distributed over 23 interior sites with occupancies ranging from 0.25 to 0.03.

Fullerenes larger than C_{74} can exist in several isomeric forms (*e.g.* 2 for C_{76} , 5 for C_{78} , 7 for C_{80} , 9 for C_{82} , 24 for C_{84} and 450 for C_{100}) that obey the isolated pentagon rule (IPR).¹ The IPR requires that each of the 12 pentagons in a fullerene be surrounded by five hexagons. A number of isomeric fullerenes and endohedral fullerenes have been separated and structurally characterized by ^{13}C NMR spectroscopy.² For example three different isomers of $\text{Er}_2@C_{82}$ have been prepared by the conventional Krätschmer–Huffman arc synthesis using graphite rods doped with Er_2O_3 and separated by chromatography.^{3,4} The structure of the fastest eluting isomer of $\text{Er}_2@C_{82}$ (which has been designated as Isomer 1) has recently been determined by single crystal X-ray diffraction.⁵ The structure reveals that the fullerene cage is the isomer $C_s(82:6)$ ¹ with C_s symmetry. This is one of nine isomeric forms (three different C_2 isomers, three C_s isomers, two C_{3v} isomers, and one C_{2v} isomer) of the C_{82} cage that obey the isolated pentagon rule. There are two prominent erbium sites with 0.35 fractional occupancy and 21 other sites for erbium ions within the well ordered cage. All of these erbium sites are distributed along a set of 10 contiguous hexagons that form a belt about the fullerene. Since two other isomers of C_{82} ($C_{3v}(82:8)$ and $C_{2v}(82:9)$) also have bands of ten contiguous hexagons, we speculated that the other two known isomers of $\{\text{Er}_2@C_{82}\}$ have these particular cage structures. Here we report the crystal structure of another isomer, Isomer 2, the second fastest eluting and most abundant isomer of $\text{Er}_2@C_{82}$. This structure allows the first comparison of structures of two isomeric fullerenes.

Isomer 2 of $\text{Er}_2@C_{82}$ was obtained as a byproduct of the synthesis of $\text{Er}_3\text{N}@C_{80}$ ^{5,6} and purified as described earlier.³ The chromatographic retention time and the UV/Vis spectrum of the sample used in this study were identical to those reported earlier.^{3,4} In order to obtain a suitable crystal of this endohedral fullerene, we co-crystallized it with $\text{Ni}^{\text{II}}(\text{OEP})$ (OEP is the dianion of octaethylporphyrin) by allowing benzene solutions of the two compounds to diffuse together. As we have previously shown, co-crystallization of fullerenes and endohedral fullerenes with various metallo-octaethylporphyrins is an effective means of obtaining samples with enough orientational order in the fullerene portion to be suitable for single crystal X-ray diffraction.^{5–10}

Black crystals of (Isomer 2 of $\text{Er}_2@C_{82}$)- $(\text{NiC}_{36}\text{H}_{44}\text{N}_4)\cdot 2(\text{C}_6\text{H}_6)$ were obtained and the structure of these is shown in Fig. 1.† As is usual with structures of this sort, each porphyrin and its eight ethyl groups make close contact with the endohedral fullerene. However, the closest $\text{Ni}\cdots\text{C}$ distance is 2.836(4) Å, so there is no covalent bond formed between the fullerene and the $\text{Ni}^{\text{II}}(\text{OEP})$ molecule. Benzene molecules also

make close face-to-face contact with the fullerene. Pairs of porphyrins are also positioned to make face-to-face contact with one another. The $\text{Ni}\cdots\text{Ni}'$ distance is 3.459(2) Å, the shortest $\text{Ni}\cdots\text{N}'$ distance is 3.136(6) Å, and the slip distance¹¹ is 1.45 Å.

The fullerene cage in Isomer 2 of $\text{Er}_2@C_{82}$ has C_{3v} symmetry and has been identified as isomer (82:6),¹ which is one of two C_{3v} isomers of C_{82} that obey the IPR. Fig. 2 presents a drawing that compares the shapes of the fullerene cages with C_s symmetry (82:6) in Isomer 1 and C_{3v} symmetry (82:8) in Isomer 2 of $\text{Er}_2@C_{82}$. Both cages have a fairly spherical shape, and both contain bands of 10 contiguous hexagons. However, whereas there is only one such band in isomer (82:6) with C_s symmetry, there are three such bands in the C_{3v} symmetric isomer (82:8). Thus, the earlier suggestion⁵ that the remaining isomers of $\text{Er}_2@C_{82}$ might contain bands of contiguous hexagons has been confirmed for Isomer 2.

However, there is orientational disorder in the position of the C_{82} cage in crystalline (Isomer 2 of $\text{Er}_2@C_{82}$)- $(\text{NiC}_{36}\text{H}_{44}\text{N}_4)\cdot 2(\text{C}_6\text{H}_6)$. Two different orientations have been identified. The predominant orientation has occupancy of 0.60 while the minor orientation has 0.40 site occupancy. Such orientational disorder is common in crystalline fullerenes,^{6,8,9,12,13} but was absent in the structure of (Er₂@C₈₂ Isomer 1)-Co^{II}(OEP)·1.4(C₆H₆)·0.3(CHCl₃).⁵

There is also disorder in the positions of the erbium ions within the fullerene cage. The erbium ions are distributed over 23 different sites with site occupancies ranging from 0.25 to 0.03. The sum of the occupancy factors for all 23 sites was 2.00. Fig. 3 shows a drawing of the predominant orientation of the C_{82} cage and the 23 erbium sites on the inside. The distribution of these sites is different in the two isomers. In Isomer 1 there are

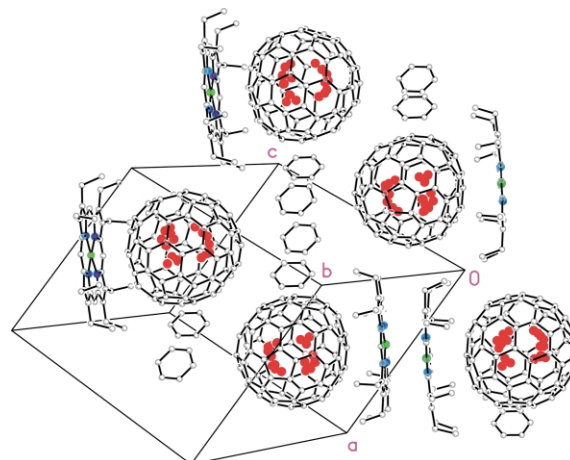


Fig. 1 A perspective view of the structure of (Isomer 2 of $\text{Er}_2@C_{82}$)- $(\text{NiC}_{36}\text{H}_{44}\text{N}_4)\cdot 2(\text{C}_6\text{H}_6)$. Only the major site of the C_{82} cage is shown, but all 23 erbium sites are shown. Erbium ions are red, nickel atoms are green, and nitrogen atoms are blue.

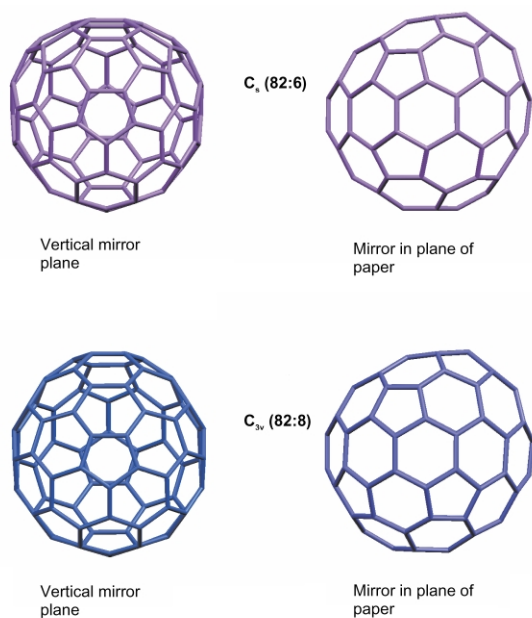


Fig. 2 A comparison of the structures of the C_4 symmetry (82:6) cage found in Isomer **1** of $Er_2@C_{82}$ and the C_{3v} symmetry (82:8) cage found in Isomer **2** of $Er_2@C_{82}$.

two prominent sites with 0.35 occupancy and then 21 minor sites with occupancies of 0.09 or less. In Isomer **2**, the most prominent site has only 0.25 occupancy, but there are two sites with 0.15 occupancy and four sites with 0.14–0.15 occupancy. Since there are three bands of contiguous hexagons in each of the two orientations of the C_{82} cages in Isomer **2** it is not possible to conclude whether the erbium ions congregate along these bands. However, it is clear that the erbium ions do cluster near the walls rather than at the center of the fullerene. The shortest Er–C distances are in the range 2.29 to 2.35 Å. Furthermore, the distribution of erbium ions in Isomer **2** appears to consist of two distinct groups (Fig. 3). Although it was not possible to construct a 1 : 1 mapping of an Er in one set to an Er in the other, it was possible to identify six non-bonded pairs with similar occupancies and distances in the expected range. These distances (in Å) were 3.632(7) Er2···Er12; 3.612(5) Er3···Er13; 3.578(9) Er4···Er14; 3.603(10) Er5···Er15; 3.607(6) Er6···Er16; 3.616(8) Er7···Er17. By comparison, the predominant Er···Er distance in Isomer **1** was 3.641(2) Å.

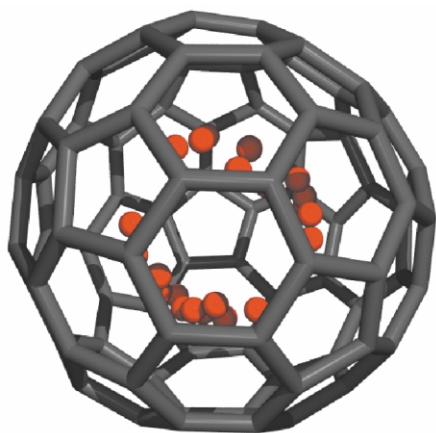


Fig. 3 A drawing of the predominant orientation of the C_{82} cage in Isomer **2** of $Er_2@C_{82}$ with the 23 different erbium sites shown on the inside.

An additional observation relates to the question of whether there is any electrostatic communication between the contents of the ball and the exterior of the ball. As can be seen by inspection of Fig. 1, one of the two groups of disordered erbium ions is closer to the porphyrin (and its Ni atom) while the other group is distant from the porphyrin. Since the fullerene cage itself is expected to be highly negative, there does seem to be a dipolar arrangement which alternates the partial positive and negative charges as well as the repulsive effect between the two groups of positively charged erbium ions in the interior. Similar factors resulted in the orientation of the $ErSc_2N$ unit in crystalline $ErSc_2N@C_{80}(\text{Co}^{\text{II}}(\text{OEP}))\cdot 1.5(\text{C}_6\text{H}_6)\cdot 0.3\text{CHCl}_3$.⁶

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Notes and references

† *Crystal data*: black parallelepipeds of (Isomer **2** of $Er_2@C_{82}$)· $(\text{NiC}_{36}\text{H}_{44}\text{N}_4)\cdot 2(\text{C}_6\text{H}_6)$, that were obtained by diffusion of a benzene solution of Isomer **2** of $Er_2@C_{82}$ into a benzene solution of $\text{Ni}^{\text{II}}(\text{OEP})$, form in the triclinic space group $P1$ with $a = 14.715(3)$, $b = 14.799(3)$, $c = 19.758(4)$ Å, $\alpha = 85.57(3)$, $\beta = 86.06(3)$, $\gamma = 61.82(3)^\circ$ at 160(2) K with $Z = 2$. Refinement of 9533 reflections, 985 parameters, and 439 restraints yielded $wR2 = 0.3070$ for all data and a conventional $R_1 = 0.1234$ based on 8993 reflections with $I > 2\sigma(I)$. The largest peak and hole in the final difference map are 1.330 and $-1.157 \text{ e } \text{Å}^{-3}$. Distance restraints that preserved the non-crystallographic mirror symmetry of the fullerene were applied during refinement but isotropic thermal parameters for the fullerene carbons were freely refined. The data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL), BL 11-1, which is funded by the U.S. Department of Energy and the National Institute of Health. The diffractometer employed a Huber Kappa goniometer and single crystal Si(111) bent monochromator, $\lambda = 0.800$ Å, and a Quantum-315 CCD (ADSC) detector. Final agreement factors are high as a result of additional diffuse occupancy of Er sites within the fullerene as well as thermal motion or disorder in the fullerene cage. CCDC 194258. See <http://www.rsc.org/suppdata/cc/b2/b209270k/> for crystallographic files in CIF or other electronic format.

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