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Crystallographic Characterization of the Structure of the Endohedral Fullerene {$Er_2@C_{82}$ Isomer I} with C_s Cage Symmetry and Multiple Sites for Erbium along a Band of Ten Contiguous Hexagons

Marilyn M. Olmstead,[‡] Ana de Bettencourt-Dias,[‡] S. Stevenson,[#] Harry C. Dorn,[§]* and
Alan L. Balch[‡]*

Department of Chemistry, University of California, Davis, California 95616, Luna Nanomaterials,
2851 Commerce Street, Blacksburg, Virginia 24060, and Department of Chemistry,
Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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After the discovery that {$La@C_{82}$} was uniquely stable and soluble in organic solvents,[1] endohedral fullerenes with C_{82} cages have become particularly numerous.[2] The C_{82} fullerene cage is large enough to encapsulate one, two, or three metal atoms. 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 obey the isolated pentagon rule.[3] For isolated empty cage C_{82}, analysis of the ^{13}C NMR spectrum reveals that the dominant isomer present has C_2 symmetry, while two other fullerenes are present in minor amounts.[4] However, for most C_{82} containing endohedrals, the specific cage isomer is frequently unknown. Moreover, theoretical calculations indicate that the stability of the C_{82} cage isomers depends markedly upon the negative charge that resides on the cage.[5]

Here we present a structural study of one isomer of {$Er_2@C_{82}$} that allows us to examine the positioning of the two metal atoms within the cage with the more crowded environments found in the interior of the metallonitrides: {$Sc_3N@C_{80}$},[6] {$Sc_2ErN@C_{80}$},[7] and {$Sc_3N@C_{78}$}.[8] Three isomers of {$Er_2@C_{82}$} have been previously separated and characterized by chromatographic retention time, UV/vis spectroscopy, and mass spectrometry,[9] and similar results have been reported later from another laboratory.[10] For the present study, a sample of {$Er_2@C_{82}$} was obtained as a byproduct of the preparation of {$Er_3N@C_{80}$},[7] and separated chromatographically as described previously. The elution time and the UV/vis spectrum of the purified sample indicated that it consisted of the previously identified Isomer I of {$Er_2@C_{82}$}.

Black crystals of {$Er_2@C_{82}$ Isomer I}·{Co^{II}(OEP)}·1.4(C_6H_6)·0.3($CHCl_3$) were obtained by slow diffusion of solutions of {Co^{II}(OEP)} in chloroform and {$Er_2@C_{82}$ Isomer I} in benzene together.[11] Figure 1 shows a drawing of the individual molecular components as determined by single-crystal X-ray diffraction at 113 K.[12] The dimensions of the nonfullerene components are entirely normal. As usual with structures of this type, the fullerene resides near the cobalt porphyrin with its eight ethyl groups surrounding the fullerene. The C_{82} cage is identified specifically as the C_s(82:6) isomer from the crystallographic data. The carbon atoms of the C_{82} cage were individually identified and refined with only a constraint that required the two halves of the cage to possess similar bond lengths. Although the carbon cage is well ordered at 113 K, the erbium atoms are disordered. There are two prominent sites with 0.350 site-occupancy. These sites are the two shown in Figure 1. The distance between these two sites is 3.641(2) Å. This distance is greater than twice the metallic radius (3.522 Å) of erbium and greater than the Er−Er separation (3.262 Å) calculated for an isomer of {$Er_2@C_{82}$} with C_{2v} cage symmetry.[13] Since the erbium atoms will have given up charge to the fullerene, the size of the erbium cations will be even smaller than that found in metallic erbium. These two erbium atoms reside near the walls of the fullerene cage. Er1 is positioned over the carbon atoms at a 6:6 ring junction with Er−C distances of 2.31(2) and 2.30(3) Å. Er2 resides over a 6:5 ring junction with Er−C distances of 2.36(2) and 2.387(18) Å. In contrast, the erbium atom in {$Sc_2ErN@C_{80}$} sits over a carbon atom of the cage while in {$Sc_3N@C_{78}$} the scandium atoms are positioned over the centers of C═C bonds at 6:6 ring junctions. The closest Er−C distances in {$Sc_2ErN@C_{80}$} are 2.22 and 2.20 Å. For further comparison with traditional organo−erbium complexes, the Er−C distance in $Ph_3Er(THF)_3$ is 2.412 Å,[14] and the Er−C distance in (η^5-C_5H_5)$_2$$Er_2$($\mu$-Cl)$_2$ is 2.59 Å.[15] However, in traditional organometallics, the metal centers are more heavily ligated than is the case with {$Sc_2ErN@C_{80}$} where much of the metal ion is exposed, much like the case in gas-phase $M(C_6H_6)^+$ species.[16]

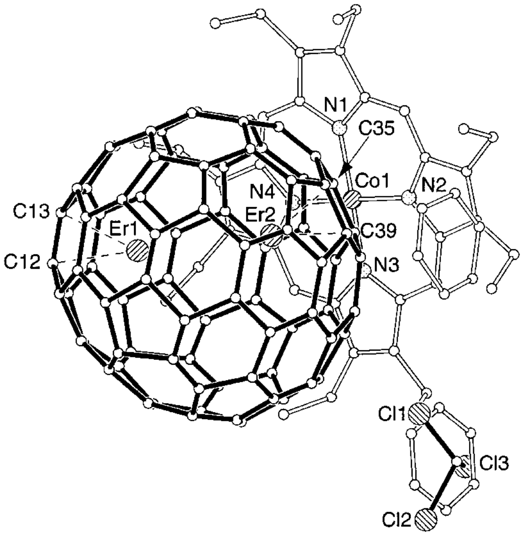

Figure 1. A view of the components within {$Er_2@C_{82}$ Isomer I}·{Co^{II}(OEP)}·1.4(C_6H_6)·0.3($CHCl_3$). Only the two Er sites with highest occupancy are shown. The group of molecules is drawn so that the noncrystallographic mirror plane of the fullerene is nearly parallel to the page.

The remaining electron density within the cage of {$Er_2@C_{82}$ Isomer I} has been modeled with individual erbium atoms. Twenty-one additional sites have been identified with occupancies ranging from 0.138 to 0.011. Figure 2 shows two orthogonal views of the molecule and shows the locations of all 23 erbium sites within the cage. The sum of the occupancies of all these erbium sites is 1.83.

[‡] University of California.
[#] Luna Nanomaterials.
[§] Virginia Polytechnic Institute and State University.

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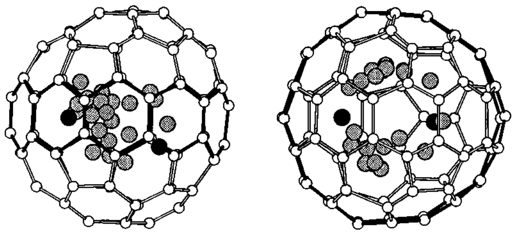

Figure 2. Two orthogonal views of the $\{Er_2@C_{82}$ Isomer I$\}$ molecule with all 23 erbium sites shown as hatched circles or solid circles for the two most highly occupied sites. Solid lines denote the band of 10 contiguous hexagons.

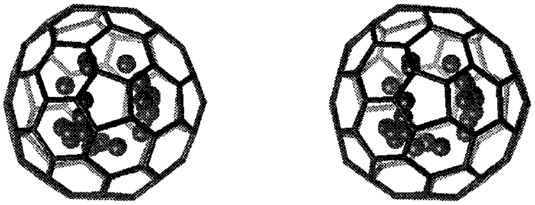

Figure 3. A stereoscopic view of $\{Er_2@C_{82}$ Isomer I$\}$.

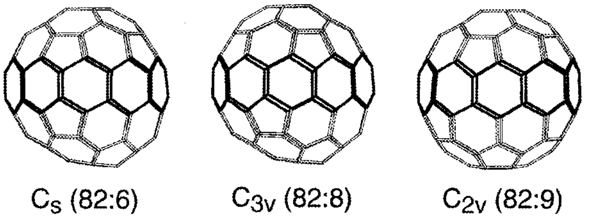

Figure 4. Views of the three IPR (isolated pentagon rule) isomers of the C_{82} cage that have bands of 10 contiguous hexagons. These bands are shown with solid lines connecting the atoms. For the C_{2v} (82:9) isomer there are two equivalent bands while for C_{3v} (82:8) there are three equivalent bands. However, only one band is highlighted in each drawing.

Consequently, there is additional electron density within the cage that has not been modeled and which shows up as small difference peaks after final refinement. As seen in Figure 2, the erbium sites all reside near the walls of the fullerene. Moreover they cluster near a band of 10 contiguous hexagons that encircles the carbon cage. This band is highlighted in Figure 2 by the use of solid lines connecting the carbon atoms within the band. Figure 3 shows a stereoview of the molecule.

Since the erbium atoms cluster near the band of 10 adjoining hexagons seen in Figure 2, we examined the structures of the other eight C_{82} isomers to determine whether this structural feature was found in any of these other isomers. As seen in Figure 4, two other isomers of C_{82} (C_{3v}(82:8) and C_{2v}(82:9)) have a similar band of 10 contiguous hexagons. It is tempting to speculate that the other two known isomers of $\{Er_2@C_{82}\}$ have these cage structures with analogous bands of 10 hexagons.

The observation that the erbium atoms are scattered over many sites within the cage at 113 K is consistent with previous calculations that indicate that the electrostatic potentials inside anionic fullerene cages are relatively flat.[17,18] At room temperature, it is likely that the erbium atoms are able to move free within the fullerene cage and that upon cooling they are distributed among many similar sites along the walls of the fullerene. NMR evidence for the motion of metal atoms within the fullerene cage of $\{La_2@C_{80}\}$ has been presented previously.[19] Since we have seen no correlation between pairs of erbium sites in the model we have developed, the concept of a unique Er−Er distance inside the fullerene should be replaced by the idea that the two erbium atoms (or ions) operate independently and are generally widely separated within the cage.

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Supporting Information Available: Figures of the mass and electronic spectra of the $\{Er_2@C_{82}$ Isomer I$\}$ sample used in this work and details of X-ray crystallographic data collection and structure refinement, tables and atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions for $\{Er_2@C_{82}$ Isomer I$\}\cdot\{Co^{II}(OEP)\}\cdot 1.4(C_6H_6)\cdot 0.3(CHCl_3)$ (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystals of $\{Er_2@C_{82}\}\cdot\{Co^{II}(OEP)\}\cdot 1.4(C_6H_6)\cdot 0.3(CHCl_3)$ were obtained by layering a green solution of ca. 0.5 mg of $\{Er_2@C_{82}\}$ in 0.5 mL of benzene over a red solution of 2.5 mg of $\{Co^{II}(OEP)\}$ in 1.5 mL of chloroform. The two solutions were allowed to diffuse together over a 5 day period and gradually black crystals formed. Crystal data for $\{Er_2@C_{82}\}\cdot\{Co^{II}(OEP)\}\cdot 1.4(C_6H_6)\cdot 0.3(CHCl_3)$:_black parallelepiped, 0.01 × 0.01 × 0.02 mm^3, triclinic, space group $P1$, $a = 17.756(3)$ Å, $b = 14.818(3)$ Å, $c = 19.881(4)$ Å, $\alpha = 86.28(3)°$, $\beta = 86.83(3)°$, $\gamma = 61.74(3)°$, $V = 3819.4(13)$ Å^3, ? = 0.77490 Å, $Z = 2$, $D_c = 1.788$ Mg m^{-3}; μ(16 keV) = 2.492 mm^{-1}; ω scans, $2\Phi_{max} = 27.38°$; $T = 113(2)$ K.; 20346 reflections collected; 12169 independent ($R_{int} = 0.046$) included in the refinement; min/max transmission = 0.973/0.981; Patterson and difference Fourier methods solution (SHELXS-97, Sheldrick, 1990); full-matrix least squares based on F^2 (SHELXL-97; Sheldrick, 1998); $R1 = 0.161$, $wR = 0.428$ for all data; conventional $R1 = 0.148$ computed for 10278 observed data ($>2\ \sigma(I)$) with 92 restraints and 919 parameters. Distance restraints that preserved the noncrystallographic 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), which is funded by the U.S. Department of Energy and the National Institute of Health. The diffractometer employed a Huber Kappa goniometer and 345 mm MAR image plate. The monochromator was a double-crystal “pin-post” type. 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.
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