

Pyramidalization of Gd₃N inside a C₈₀ cage. The synthesis and structure of Gd₃N@C₈₀

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The X-ray crystal structure of Gd₃N@C₈₀•Ni^{II}-(OEP)•1.5(benzene) shows that the Gd₃N unit within the I_h C₈₀ cage is pyramidal, whereas Sc₃N@C₈₀, Sc₃N@C₇₈, Sc₃N@C₆₈, Lu₃N@C₈₀ and Sc₂ErN@C₈₀ have planar M₃N units.

Chelated gadolinium complexes dominate the field of magnetic resonance imaging (MRI) contrast agents due to the high magnetic moment of Gd³⁺.¹ Recent developments have shown that gadolinium ions encapsulated within fullerene cages, which are also subsequently functionalized to impart water solubility, are also effective MRI relaxation agents even though water molecules cannot directly coordinate the Gd³⁺ ions.^{2,3} The recent discovery of the M₃N@C₈₀ family of endohedrals, which contain planar M₃N units, by Dorn and coworkers suggests that it should be possible to obtain Gd₃N@C₈₀, which would contain three paramagnetic Gd³⁺ ions within a single cage.⁴ However, will three such large ions fit within the cage and what will be the structure of the Gd₃N unit within the cage? For comparison, computations by Kobayashi *et al.* have suggested that the La₃N unit in the hypothetical La₃N@C₈₀ will be pyramidal with the N atom 1.10 Å out of the La₃ plane.⁵

Carbon soot containing Gd₃N@C₈₀ was produced in an electric-arc fullerene reactor as described earlier⁴ with graphite rods packed with 3 mole % Gd₂O₃. The resulting soot was extracted with *o*-xylene, and the filtered extract was purified by HPLC. The chromatogram of the initial extract is shown in Fig. 1. The Gd₃N@C₈₀ fraction eluting between 37 and 41 min was collected and further purified on a 20 mm × 250 mm BuckyPrep column with *o*-xylene as eluent.

To ascertain its purity, the isolated sample of Gd₃N@C₈₀ was injected into a Buckyclutcher column (10 mm × 250 mm, Regis) to demonstrate the absence of other fullerene peaks. The HPLC trace for the purified sample is shown in Fig. 2.

The mass spectrum of this sample, which is shown in Fig. 3, reveals the expected isotope pattern for Gd₃N@C₈₀ at *m/z* = 1446.

In order to obtain suitably ordered crystals of Gd₃N@C₈₀ we allowed a benzene solution of Ni^{II}(OEP) (OEP is the dianion of octaethylporphyrin) to slowly diffuse into a benzene solution of the endohedral. As we have previously shown, co-crystallization of endohedral fullerenes with M^{II}(OEP) is a useful method of crystallization that produces sufficient orientational order of the fullerene for single crystal X-ray diffraction.^{4,6} The structural results obtained from black crystals of Gd₃N@C₈₀•(NiC₃₆H₄₄N₄)•1.5(C₆H₆) are shown in Fig. 4. The Ni^{II}(OEP) molecule resides on a mirror plane.

Eighty carbon atoms with 0.50 occupancy form the fullerene cage, which has non-crystallographic I_h symmetry. Since the crystallographic mirror plane does not coincide with any of the mirror planes of the fullerene, the crystal symmetry produces a second orientation of the cage. Only one orientation is shown in Fig. 4. The contents of the cage are also disordered with respect to

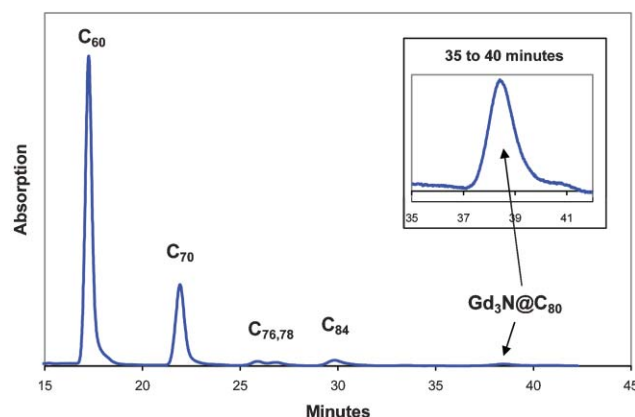


Fig. 1 HPLC chromatogram of extract on a PBB column with 1 mL injection volume, 6 mL min⁻¹ of *o*-xylene, and 360 nm UV detection.

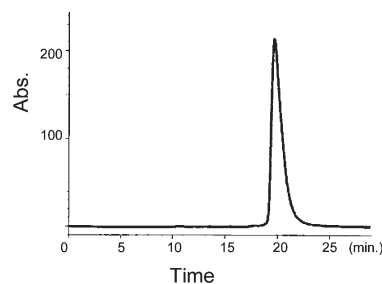


Fig. 2 HPLC chromatogram of purified Gd₃N@C₈₀ on a Buckyclutcher column with 100 µL injection volume, 1 mL min⁻¹ of chloroform, and 360 nm UV detection.

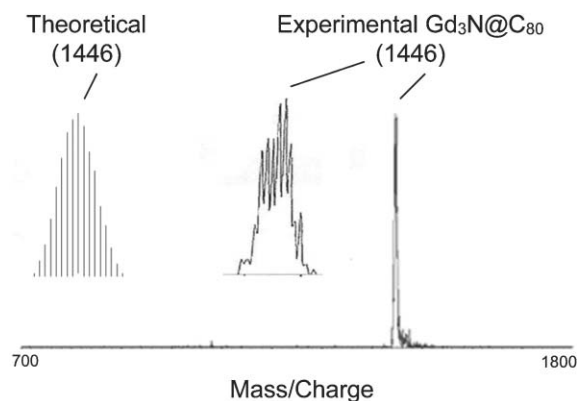


Fig. 3 MALDI-TOF mass spectrum of purified Gd₃N@C₈₀.

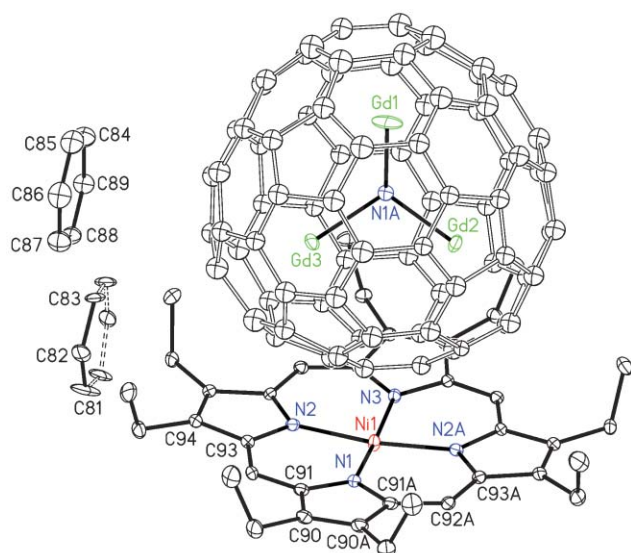


Fig. 4 A view of $\text{Gd}_3\text{N}@C_{80}(\text{NiC}_{36}\text{H}_{44}\text{N}_4)\cdot 1.5(\text{C}_6\text{H}_6)$.

the mirror plane. In addition there is severe disorder in the Gd positions, which is a consequence of multiple shallow potential minima. Fig. 5 shows the major set of three gadolinium atoms (Gd1, Gd2, and Gd3), each with a refined occupancy of 0.4098(12) vs. 0.50 for full occupancy, and anisotropic thermal parameters. The refinement included five other gadolinium atoms with freely refined occupancies ranging from 0.020(2) to 0.034(2) and isotropic thermal parameters which are not included in Fig. 5. The central nitrogen atom is disordered over two sites, N1a and N1b with refined occupancies of 0.309(9) and 0.191(9), respectively. Only N1a is shown in Fig. 5.

As Fig. 5 shows, the gadolinium atoms are positioned over the centers of hexagons in the fullerene cage. The three Gd-to-ring-center distances are similar: 2.050 Å for Gd1, 2.001 Å for Gd2, and 1.952 Å for Gd3. The Gd_3N unit is pyramidal with N1a 0.522(8) Å out of the Gd_3 plane. Likewise, at the minor site, N1b is 0.463 Å from the Gd_3 plane. Despite significant variations in the cage size and geometry in the endohedral fullerenes, $\text{Sc}_3\text{N}@C_{80}$,⁴ $\text{Sc}_3\text{N}@C_{78}$,⁶ and $\text{Sc}_3\text{N}@C_{68}$,⁷ the Sc_3N unit remains planar in each. Similarly, the somewhat larger ErSc_2N and Lu_3N units in $\text{ErSc}_2\text{N}@C_{80}$ and $\text{Lu}_3\text{N}@C_{80}$ are also planar.^{8,9} The differences in pyramidalization of the nitrogen atom in these endohedrals may be simply a result of the variations in the sizes of the metals involved. Gd^{3+} (ionic radius 1.08 Å) is significantly larger than either Sc^{3+} (ionic radius 0.88 Å) or Lu^{3+} (ionic radius 1.00 Å).†

Notes and references

† Crystal data: A black parallelepiped of $\text{Gd}_3\text{N}@C_{80}(\text{NiC}_{36}\text{H}_{44}\text{N}_4)\cdot 1.5(\text{C}_6\text{H}_6)$ was obtained by diffusion of a benzene solution of $\text{Ni}^{\text{II}}(\text{OEP})$ into a benzene solution of $\text{Gd}_3\text{N}@C_{80}$ and formed in the monoclinic space group $C2/m$ with $a = 25.2636(6)$, $b = 15.0802(6)$, $c = 19.7261(5)$ Å, $\beta = 95.098(2)$ at 12(2) K with $Z = 4$. Refinement of 12415 reflections, and 633

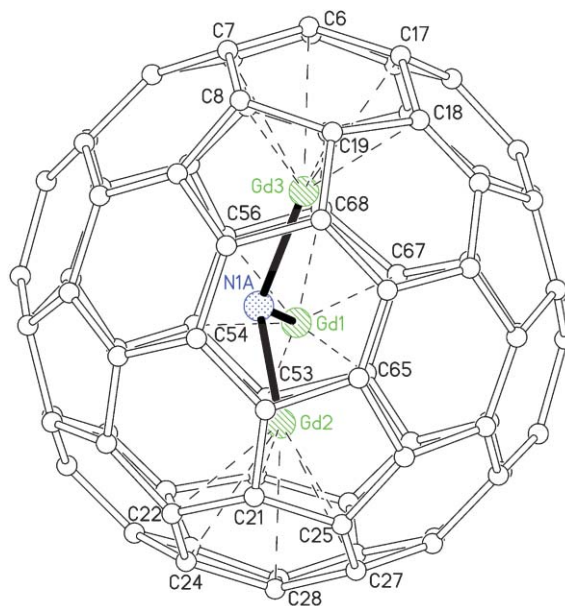


Fig. 5 A view of $\text{Gd}_3\text{N}@C_{80}$ that emphasizes the pyramidal nature of the Gd_3N group. Selected distances; Gd1–N1a, 2.038(8), Gd2–N1a, 2.085(4), Gd3–N1a, 2.117(5), ranges of Gd–C distances: Gd1–C53, 2.344(13) to Gd1–C68, 2.600(14); Gd2–C21, 2.402(10) to Gd2–C28, 2.482(12); Gd3–C7, 2.439(12) to Gd3–C18, 2.481(18) Å. Selected angles; Gd1–N1a–Gd2, 111.6(2); Gd1–N1a–Gd3, 119.7(3); Gd2–N1a–Gd3, 110.3(3)°.

parameters, yielded $wR_2 = 0.198$ for all data and a conventional $R_1 = 0.063$ based on 8409 reflections with $I > 2\sigma(I)$. The largest peak and hole in the final difference map are 2.327 and -1.443 eÅ^{-3} . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. CCDC 247597. See <http://www.rsc.org/suppdata/cc/b4/b412338g/> for crystallographic data in .cif or other electronic format.

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