

Supporting Information

Synthesis, Mass Spectroscopy Detection, and Density Functional Theory Investigations of the Fullerenols $\text{Gd@C}_{82}\text{O}_x(\text{OH})_y$ ($x = 0, 3$; $y = 8, 16, 24, 36, 44$)

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Mass spectra of Gd@C₈₂ endohedral complex

Carbon condensate containing Gd@C₈₂ was synthesized in high frequency arc discharge plasma by spraying of graphite electrodes with axial holes of 3 mm in diameter. The electrodes contained a mixture of Gd₂O₃ powder and graphite in the ratio 1:1 by weight. A fullerene mixture was separated from the carbon condensate in a Soxhlet apparatus by carbon disulfide. A mixture of Gd@C₈₂ and higher fullerenes was isolated from the solution using TiCl₄ Lewis acid. After that, the sample was dried and redissolved in toluene and Gd@C₈₂ endohedral complex was isolated from the solution using high-performance Agilent Technologies 1200 Series chromatograph (Cosmosil Buckyprep M column; toluene flow 5 ml/min). By treatment with acid HNO₃ and further washing in distilled water, O and OH groups were attached to the isolated Gd@C₈₂. Bruker BIFLEX TM III MALDI-TOF mass spectrometer was used to obtain a mass spectrum of the endohedral complex (Figure S1). It was found that the only one Gd@C₈₂ endohedral complex has been detected in the mass spectrum, which signal clearly stands out against the background of broadband noise.

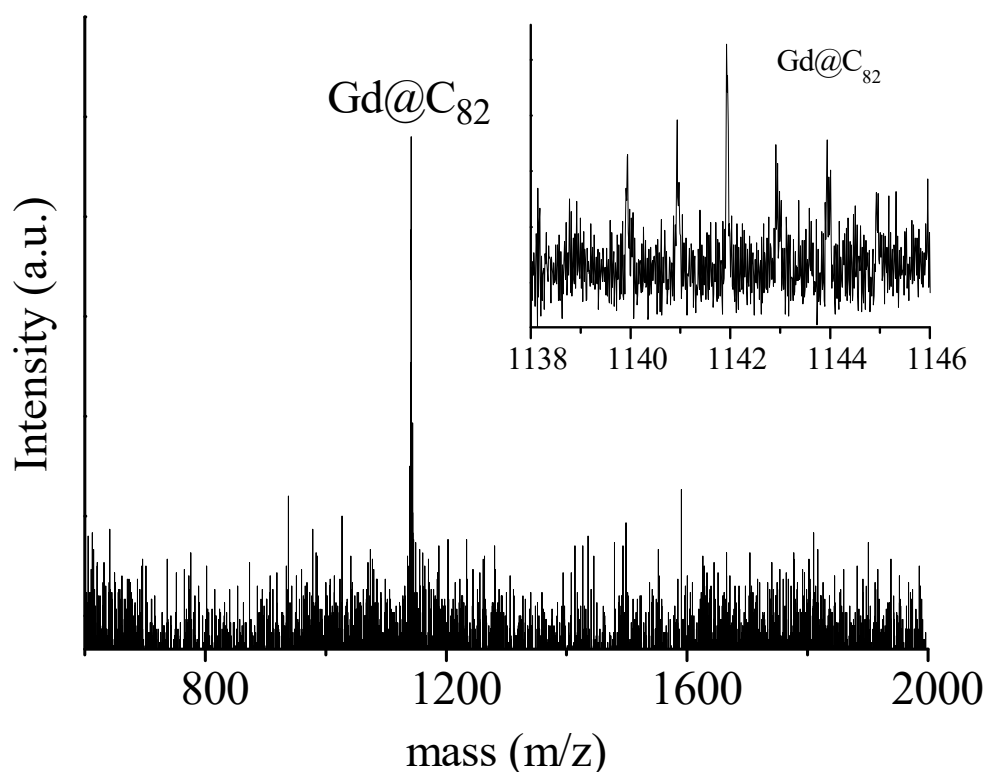


Figure S1. Mass spectrum of the chromatographic fraction with Gd@C₈₂ (positive mode)

Solvation models and Structural Models of Gd Endohedral Complexes of Fullerenoles

Both Polarizable continuum model (PCM) and Universal solvation model based on density (SMD) methods [1] were tested to take into account solvation and spectral properties (HOMO-LUMO gaps, energy differences between isomers, e.t.c.) in fullerenole endohedral complexes. It was found that SMD model is more suitable for description of $\text{Gd}@C_{82}\text{O}_3(\text{OH})_y$ fullerenoles in water solutions because the SMD model parameters allow one to tune the results more precisely than PCM one. So, the SMD approach was used in the study to take into account the solvation effects.

Fullerenole molecules with 8, 16, 24, 36, and 44 hydroxyl groups either symmetrically or asymmetrically distributed over C_{82} cage were designed and calculated. It was found that in contrast with asymmetrical ones, optimization of symmetrical fullerenoles mostly returns stable structures without SCF convergency problems. So, finally symmetrically distributed OH groups over the $\text{Gd}@C_{82}$ were employed to develop the atomistic models of different fullerenols and to calculate their atomic and electronic structures (Figure 1c). The closed asymmetrical distribution of hydroxyl groups caused dramatic changes of hybridization of carbon atoms in C_{82} cage and it led to breakdown of the carbon lattice with amorphization of the C_{82} structure, which directly contradicted with the mass-spectrometry data.

- [1] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem.* **2009**, *113*, 6378-96.

Electronic and solvation properties of $\text{Gd}@\text{C}_{82}\text{O}_3(\text{OH})_y$ fullerenols

Table S1. Energy of solvation of $\text{Gd}@\text{C}_{82}\text{O}_3(\text{OH})_y$, $\text{C}_{82}\text{O}_3(\text{OH})_y$ and $\text{C}_{82}\text{O}_8(\text{OH})_y$

| Energy of solvation | Complexes | | | | |
|---------------------|--|---|---|---|---|
| | $\text{C}_{82}\text{O}_x(\text{OH})_y$ | | | | |
| E, kJ/mol | $\text{C}_{82}\text{O}_3(\text{OH})_8$ | $\text{C}_{82}\text{O}_3(\text{OH})_{16}$ | $\text{C}_{82}\text{O}_3(\text{OH})_{24}$ | $\text{C}_{82}\text{O}_3(\text{OH})_{36}$ | $\text{C}_{82}\text{O}_3(\text{OH})_{44}$ |
| | 213 | 344 | 402 | - | - |
| E, kJ/mol | $\text{C}_{82}\text{O}_8(\text{OH})_8$ | $\text{C}_{82}\text{O}_8(\text{OH})_{16}$ | $\text{C}_{82}\text{O}_8(\text{OH})_{24}$ | $\text{C}_{82}\text{O}_8(\text{OH})_{36}$ | $\text{C}_{82}\text{O}_8(\text{OH})_{44}$ |
| | 165 | 242 | 298 | 258 | 288 |
| | $\text{Gd}@\text{C}_{82}\text{O}_x(\text{OH})_y$ | | | | |
| E, kJ/mol | $\text{Gd}@\text{C}_{82}\text{O}_3(\text{OH})_8$ | $\text{Gd}@\text{C}_{82}\text{O}_3(\text{OH})_{16}$ | $\text{Gd}@\text{C}_{82}\text{O}_3(\text{OH})_{24}$ | $\text{Gd}@\text{C}_{82}\text{O}_3(\text{OH})_{36}$ | $\text{Gd}@\text{C}_{82}\text{O}_3(\text{OH})_{44}$ |
| | 712 | 793 | 730 | - | - |

Energy of solvation calculated at MN15/def(2)-TZVP level of theory.

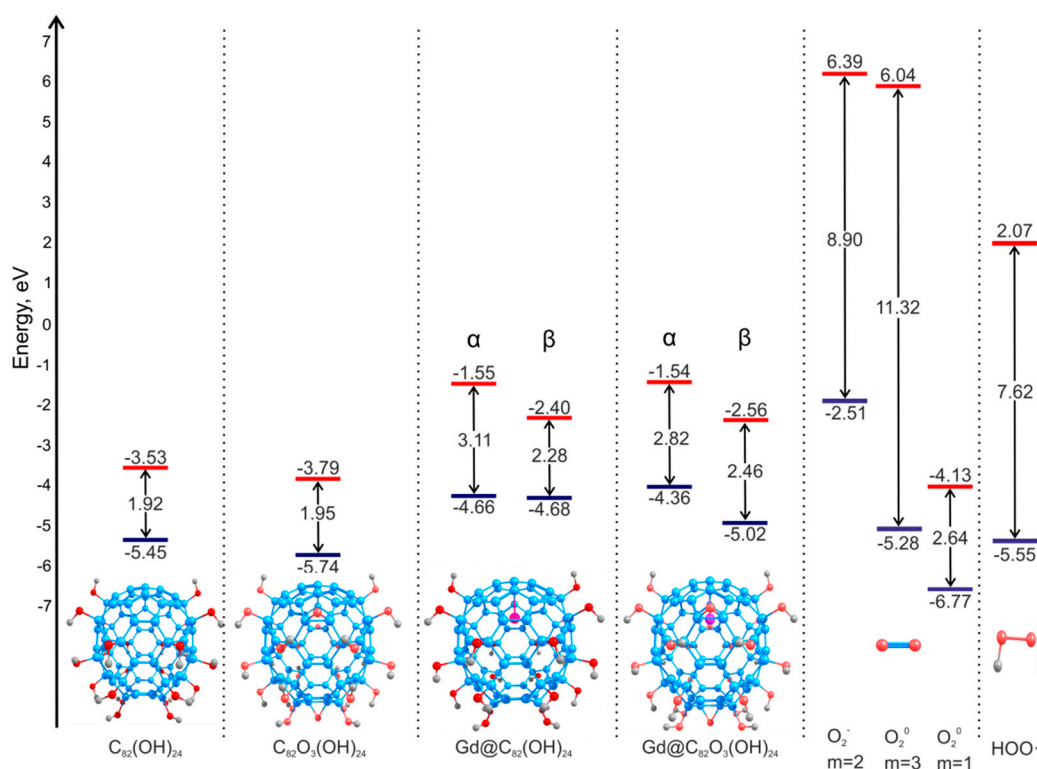


Figure S2. Diagram of the boundary molecular orbitals of $\text{C}_{82}\text{O}_x(\text{OH})_{24}$, $\text{Gd}@\text{C}_{82}\text{O}_x(\text{OH})_{24}$ ($x = 0, 3$), O_2^0 ($m = 1, 3$), O_2^- ($m = 2$), and HOO^\bullet in the solvent (H_2O). The HOMO and LUMO levels are shown in blue and red color, respectively. The number between the HOMO and LUMO is the energy gap ($\Delta E_{\text{HOMO-LUMO}}$, eV).

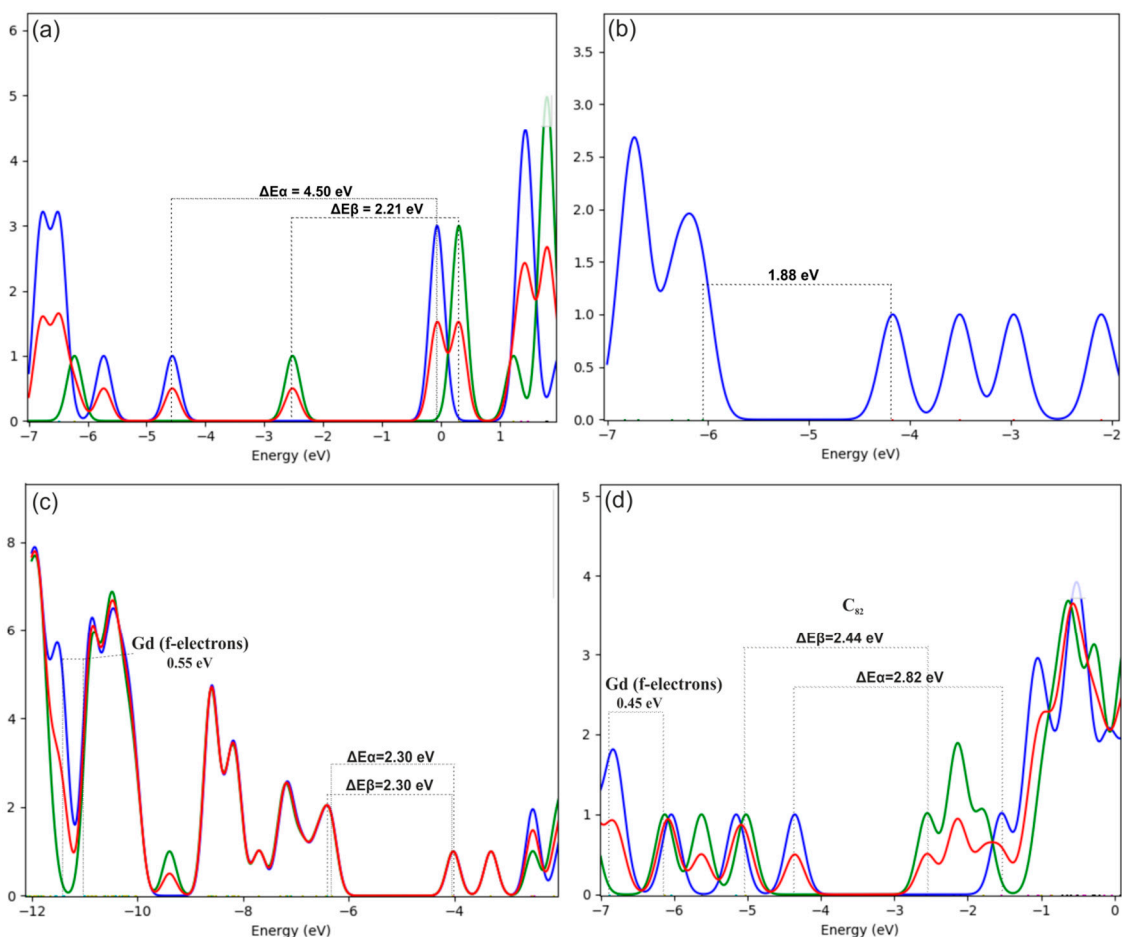


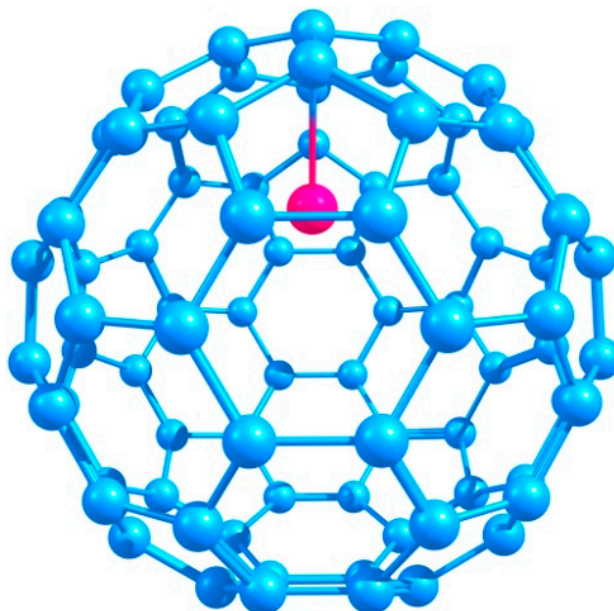
Figure S3. Densities of states of $\text{Gd@C}_{82}\text{O}_x(\text{OH})_y$. TDOS is total density of states, PDOS is partial density of states. Gd, C_{82} and Gd@C_{82} were calculated in gas phase, $\text{Gd@C}_{82}\text{O}_3(\text{OH})_{24}$ in water solvent. (a) Gd: TDOS is shown in red color and multiplied by 0.5, PDOS of α - β -channels are shown in blue and green colors, respectively; (b) C_{82} : TDOS is shown in blue color; (c) Gd@C_{82} : TDOS is shown in red color and multiplied by 0.5, PDOS of α - β -channels are shown in blue and green colors; (d) $\text{Gd@C}_{82}\text{O}_3(\text{OH})_{24}$: TDOS is shown in red color and multiplied by 0.5, PDOS of α - β -channels are shown in blue and green colors. Dotted line shows HOMO-LUMO energy gap ΔE .

Total (TDOS) and partial (PDOS) density of states (DOS) of free-standing Gd atom, free-standing C_{82} fullerene, Gd@C_{82} and $\text{Gd@C}_{82}\text{O}_3(\text{OH})_{24}$ endohedral complexes are presented in Figure S2. For free-standing gadolinium, the energy ranges from -4.56 to -0.06 eV ($\Delta E = 4.50$ eV) for α electrons and from -2.52 to -0.31 eV ($\Delta E = 2.21$ eV) for β electrons. The energy for C_{82} fullerene lies between -6.05 and -4.17 eV ($\Delta E = 1.88$ eV) of TDOS. The partial density of states of α electrons of Gd@C_{82} ranges from -6.31 to -4.01 eV ($\Delta E = 2.30$ eV) and the PDOS of β electrons, from -6.32 to -4.02 eV ($\Delta E = 2.30$ eV). In addition, the PDOS of 7 electrons are lower in energy in the range from -11.00 to -11.55 eV ($\Delta E = 0.55$ eV). α and β PDOS of $\text{Gd@C}_{82}\text{O}_3(\text{OH})_{24}$ shifts upward in energy relative to Gd@C_{82} to the energy range from -4.36 to -1.54 eV ($\Delta E = 2.82$ eV) and from -5.02 to -2.56 eV ($\Delta E = 2.44$ eV), respectively. Gd 4f-electrons shift to the energy range from -6.44 to -6.89 eV ($\Delta E = 0.45$ eV).

Cartesian coordinates

Atomic Cartesian coordinates of complexes under investigation (in Å: X, Y, Z) are presented below. Equilibrium ground states calculated at MN15/def(2)-TZVP level of theory. Carbon, gadolinium, oxygen, and hydrogen atoms are shown in blue, fuchsia, red, and gray colors, respectively.

Gd@C₈₂

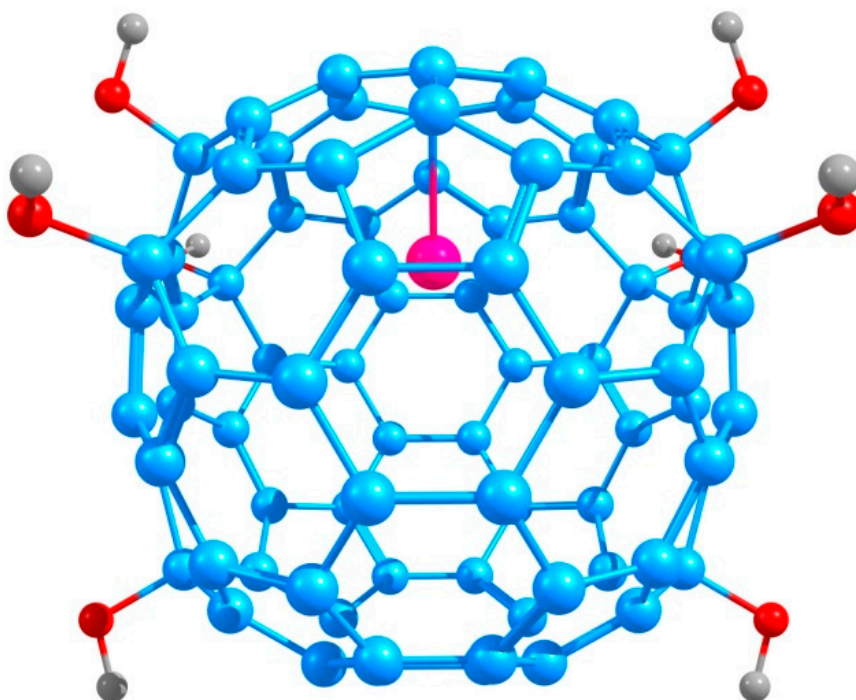
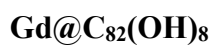


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| C | -3.094894033 | 1.162021867 | 2.194492657 |
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| C | -3.688302750 | -1.464488370 | -0.200486973 |
| C | 3.688302750 | 1.464488370 | -0.200486973 |

| | | | |
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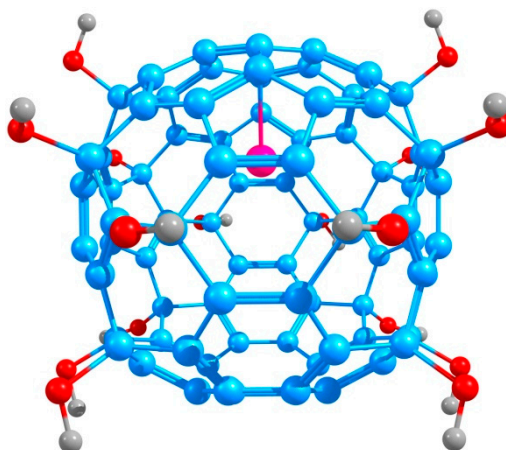
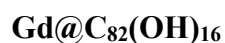
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| | | | |
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| O | 3.315443016 | -4.479947527 | -1.548925661 |
| H | 4.183189503 | 4.152693794 | -1.839989480 |
| H | -4.183189503 | -4.152693794 | -1.839989480 |
| H | -4.183189503 | 4.152693794 | -1.839989480 |
| H | 4.183189503 | -4.152693794 | -1.839989480 |
| Gd | 0.000000000 | 0.000000000 | -1.246774078 |



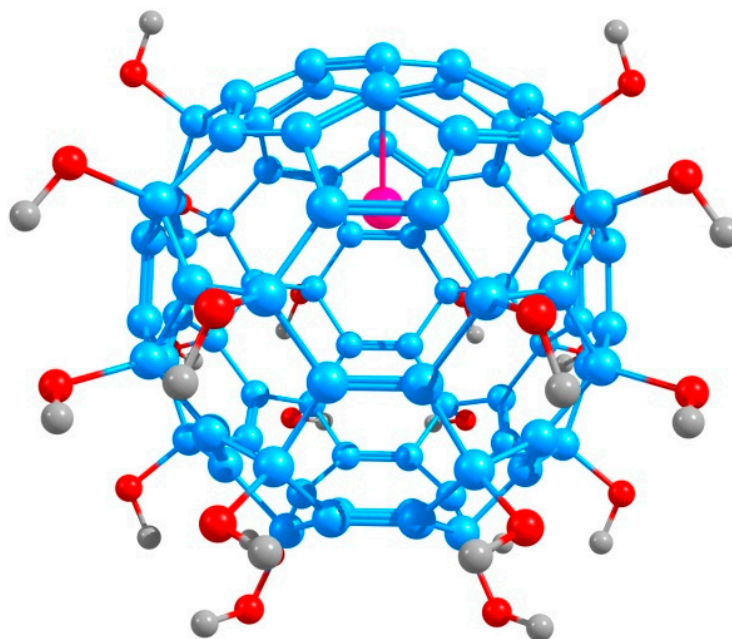
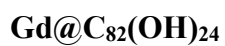
MN15/def(2)-TZVP//H₂O//Ground state

| | | | |
|---|--------------|--------------|--------------|
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| C | -2.622286343 | 0.000000000 | 2.962445604 |
| C | 3.043089804 | -1.148753907 | 2.239730096 |
| C | -3.043089804 | 1.148753907 | 2.239730096 |
| C | -3.043089804 | -1.148753907 | 2.239730096 |
| C | 3.043089804 | 1.148753907 | 2.239730096 |
| C | 3.748267862 | -0.690810050 | 1.063610012 |
| C | -3.748267862 | 0.690810050 | 1.063610012 |
| C | -3.748267862 | -0.690810050 | 1.063610012 |
| C | 3.748267862 | 0.690810050 | 1.063610012 |
| C | 2.547379489 | -3.378939751 | 1.270661847 |
| C | -2.547379489 | 3.378939751 | 1.270661847 |
| C | -2.547379489 | -3.378939751 | 1.270661847 |
| C | 2.547379489 | 3.378939751 | 1.270661847 |
| C | 4.061172987 | -1.559070190 | -0.125582987 |
| C | -4.061172987 | 1.559070190 | -0.125582987 |
| C | -4.061172987 | -1.559070190 | -0.125582987 |
| C | 4.061172987 | 1.559070190 | -0.125582987 |
| C | 3.104187004 | -2.748376630 | -0.027452622 |
| C | -3.104187004 | 2.748376630 | -0.027452622 |
| C | -3.104187004 | -2.748376630 | -0.027452622 |
| C | 3.104187004 | 2.748376630 | -0.027452622 |
| C | 2.303598679 | -2.340281745 | 2.329461121 |

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|---|--------------|--------------|--------------|
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| C | -2.303598679 | -2.340281745 | 2.329461121 |
| C | 2.303598679 | 2.340281745 | 2.329461121 |
| C | 2.410895704 | -3.245807026 | -1.065877848 |
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| C | 2.410895704 | 3.245807026 | -1.065877848 |
| C | 3.724151119 | -0.727088191 | -1.395768446 |
| C | -3.724151119 | 0.727088191 | -1.395768446 |
| C | -3.724151119 | -0.727088191 | -1.395768446 |
| C | 3.724151119 | 0.727088191 | -1.395768446 |
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| C | 2.586594128 | 2.824837753 | -2.476758051 |
| C | 3.127166701 | -1.391055433 | -2.466070473 |
| C | -3.127166701 | 1.391055433 | -2.466070473 |
| C | -3.127166701 | -1.391055433 | -2.466070473 |
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| C | 2.397280113 | -0.684169724 | -3.442827599 |
| C | -2.397280113 | 0.684169724 | -3.442827599 |
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| C | 1.216495226 | -2.651012124 | -3.141164825 |
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| C | 1.181049948 | -3.909622438 | -0.610760881 |
| C | -1.181049948 | 3.909622438 | -0.610760881 |
| C | -1.181049948 | -3.909622438 | -0.610760881 |
| C | 1.181049948 | 3.909622438 | -0.610760881 |

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|---|--------------|--------------|--------------|
| C | 1.194990067 | -3.912886098 | 0.791211361 |
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| C | -1.194990067 | -3.912886098 | 0.791211361 |
| C | 1.194990067 | 3.912886098 | 0.791211361 |
| C | 1.180352043 | -2.400027046 | 3.154694551 |
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| C | 1.430864075 | 0.000000000 | 3.719682396 |
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| C | 0.000000000 | -0.717333292 | -4.147634691 |
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| C | 0.000000000 | -3.509143171 | -2.854132144 |
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| C | 0.000000000 | -3.911729279 | -1.366085778 |
| C | 0.000000000 | 3.911729279 | -1.366085778 |
| C | 0.000000000 | -3.861485352 | 1.518440159 |
| C | 0.000000000 | 3.861485352 | 1.518440159 |
| C | 0.000000000 | -3.366128185 | 2.951280746 |
| C | 0.000000000 | 3.366128185 | 2.951280746 |
| O | 0.000000000 | -4.743873851 | -3.589025275 |
| O | 0.000000000 | 4.743873851 | -3.589025275 |
| H | 0.000000000 | -4.511039931 | -4.532654123 |
| H | 0.000000000 | 4.511039931 | -4.532654123 |
| O | 0.000000000 | -4.477130289 | 3.825782694 |
| O | 0.000000000 | 4.477130289 | 3.825782694 |
| H | 0.000000000 | -4.141772296 | 4.738208773 |
| H | 0.000000000 | 4.141772296 | 4.738208773 |
| O | 3.391437787 | -4.398018973 | 1.768436984 |
| O | -3.391437787 | 4.398018973 | 1.768436984 |
| O | -3.391437787 | -4.398018973 | 1.768436984 |

| | | | |
|----|--------------|--------------|--------------|
| O | 3.391437787 | 4.398018973 | 1.768436984 |
| H | 3.911417230 | -4.545064960 | 1.526865024 |
| H | -3.911417230 | 4.545064960 | 1.526865024 |
| H | -3.911417230 | -4.545064960 | 1.526865024 |
| H | 3.911417230 | 4.545064960 | 1.526865024 |
| O | 3.438356357 | -3.728544298 | -3.162264295 |
| O | -3.438356357 | 3.728544298 | -3.162264295 |
| O | -3.438356357 | -3.728544298 | -3.162264295 |
| O | 3.438356357 | 3.728544298 | -3.162264295 |
| H | 3.184485134 | -4.031842168 | -3.728267818 |
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| H | 3.184485134 | 4.031842168 | -3.728267818 |
| O | 5.407072769 | -2.009061079 | -0.131308299 |
| O | -5.407072769 | 2.009061079 | -0.131308299 |
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| O | 5.407072769 | 2.009061079 | -0.131308299 |
| H | 5.890035857 | -1.572053017 | -0.272227665 |
| H | -5.890035857 | 1.572053017 | -0.272227665 |
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| Gd | 0.000000000 | 0.000000000 | 1.387462556 |



MN15/def(2)-TZVP//H₂O//Ground state

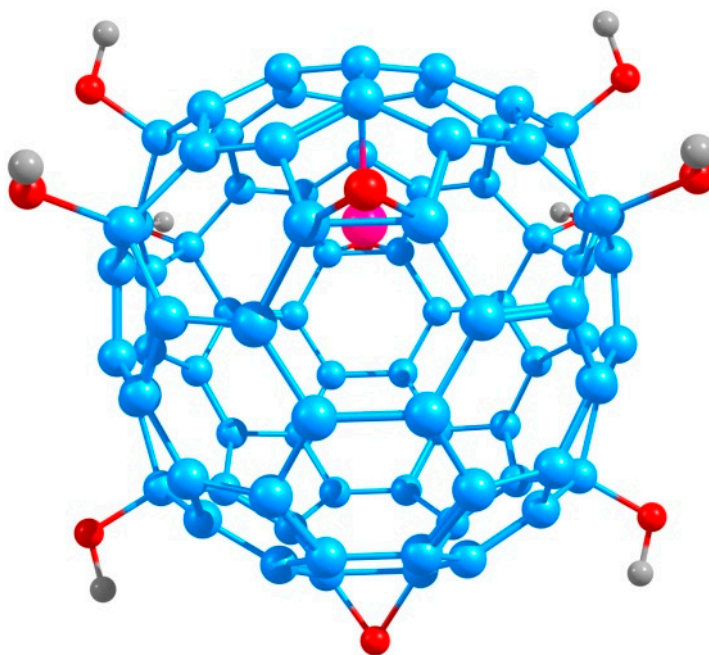
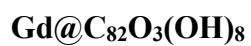
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| C | 3.057833756 | -1.155930311 | 2.594017143 |
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| C | -3.057833756 | -1.155930311 | 2.594017143 |
| C | -3.777026204 | 0.699395195 | 1.446271998 |
| C | 3.777026204 | -0.699395195 | 1.446271998 |
| C | 3.777026204 | 0.699395195 | 1.446271998 |
| C | -3.777026204 | -0.699395195 | 1.446271998 |
| C | -2.537842509 | 3.375264287 | 1.591970708 |
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| C | 2.537842509 | 3.375264287 | 1.591970708 |
| C | -2.537842509 | -3.375264287 | 1.591970708 |
| C | -3.969607682 | 1.525085901 | 0.212168636 |
| C | 3.969607682 | -1.525085901 | 0.212168636 |
| C | 3.969607682 | 1.525085901 | 0.212168636 |
| C | -3.969607682 | -1.525085901 | 0.212168636 |
| C | -3.044945297 | 2.707751826 | 0.329463757 |
| C | 3.044945297 | -2.707751826 | 0.329463757 |

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|---|--------------|--------------|--------------|
| C | 3.044945297 | 2.707751826 | 0.329463757 |
| C | -3.044945297 | -2.707751826 | 0.329463757 |
| C | -2.314476317 | 2.371728191 | 2.692963302 |
| C | 2.314476317 | -2.371728191 | 2.692963302 |
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| C | -3.603324195 | 0.675495579 | -1.023514942 |
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| C | -2.531513529 | 3.486154408 | -0.840494216 |
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| C | -2.531513529 | -3.486154408 | -0.840494216 |
| C | -2.326361805 | 2.576034244 | -1.994438287 |
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| C | -2.450260810 | 0.664024668 | -3.277009823 |
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| C | -2.450260810 | -0.664024668 | -3.277009823 |
| C | -1.208813202 | 2.541383483 | -2.728139147 |
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| C | 1.208813202 | 2.541383483 | -2.728139147 |
| C | -1.208813202 | -2.541383483 | -2.728139147 |
| C | -1.282514999 | 1.480687744 | -3.808818887 |
| C | 1.282514999 | -1.480687744 | -3.808818887 |
| C | 1.282514999 | 1.480687744 | -3.808818887 |
| C | -1.282514999 | -1.480687744 | -3.808818887 |
| C | -1.184471553 | 3.928819350 | -0.317076536 |

| | | | |
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| C | 1.184471553 | -3.928819350 | -0.317076536 |
| C | 1.184471553 | 3.928819350 | -0.317076536 |
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| C | -1.189116227 | 3.875767740 | 1.081764285 |
| C | 1.189116227 | -3.875767740 | 1.081764285 |
| C | 1.189116227 | 3.875767740 | 1.081764285 |
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| C | -1.183545533 | 2.417237059 | 3.481169510 |
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| C | -0.709654463 | 1.228216493 | 4.147038259 |
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| C | -1.424570788 | 0.000000000 | 4.062975181 |
| C | 1.424570788 | 0.000000000 | 4.062975181 |
| C | 0.000000000 | 0.670284769 | -3.853820771 |
| C | 0.000000000 | -0.670284769 | -3.853820771 |
| C | 0.000000000 | 3.425990101 | -2.516313771 |
| C | 0.000000000 | -3.425990101 | -2.516313771 |
| C | 0.000000000 | 3.903776283 | -1.060507403 |
| C | 0.000000000 | -3.903776283 | -1.060507403 |
| C | 0.000000000 | 3.825227776 | 1.812693796 |
| C | 0.000000000 | -3.825227776 | 1.812693796 |
| C | 0.000000000 | 3.370094052 | 3.258583875 |
| C | 0.000000000 | -3.370094052 | 3.258583875 |
| O | 0.000000000 | 4.516835289 | -3.421326416 |
| O | 0.000000000 | -4.516835289 | -3.421326416 |
| H | 0.000000000 | 4.149324890 | -4.324243946 |
| H | 0.000000000 | -4.149324890 | -4.324243946 |
| O | 0.000000000 | 4.517639545 | 4.091830353 |
| O | 0.000000000 | -4.517639545 | 4.091830353 |
| H | 0.000000000 | 4.213438263 | 5.014759730 |
| H | 0.000000000 | -4.213438263 | 5.014759730 |

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|---|--------------|--------------|--------------|
| O | -3.404724887 | 4.416961813 | 2.019720795 |
| O | 3.404724887 | -4.416961813 | 2.019720795 |
| O | 3.404724887 | 4.416961813 | 2.019720795 |
| O | -3.404724887 | -4.416961813 | 2.019720795 |
| H | -3.624574884 | 4.943856379 | 1.229704702 |
| H | 3.624574884 | -4.943856379 | 1.229704702 |
| H | 3.624574884 | 4.943856379 | 1.229704702 |
| H | -3.624574884 | -4.943856379 | 1.229704702 |
| O | -3.356552143 | 4.608600393 | -1.142502040 |
| O | 3.356552143 | -4.608600393 | -1.142502040 |
| O | 3.356552143 | 4.608600393 | -1.142502040 |
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| H | -4.215635545 | 4.268950186 | -1.451453445 |
| H | 4.215635545 | -4.268950186 | -1.451453445 |
| H | 4.215635545 | 4.268950186 | -1.451453445 |
| H | -4.215635545 | -4.268950186 | -1.451453445 |
| O | -4.491225395 | 2.037304169 | -2.809403598 |
| O | 4.491225395 | -2.037304169 | -2.809403598 |
| O | 4.491225395 | 2.037304169 | -2.809403598 |
| O | -4.491225395 | -2.037304169 | -2.809403598 |
| H | -5.124034468 | 1.319809319 | -2.992117695 |
| H | 5.124034468 | -1.319809319 | -2.992117695 |
| H | 5.124034468 | 1.319809319 | -2.992117695 |
| H | -5.124034468 | -1.319809319 | -2.992117695 |
| O | -5.328072454 | 1.969246541 | 0.058408092 |
| O | 5.328072454 | -1.969246541 | 0.058408092 |
| O | 5.328072454 | 1.969246541 | 0.058408092 |
| O | -5.328072454 | -1.969246541 | 0.058408092 |
| H | -5.413560808 | 2.325515220 | -0.845490987 |
| H | 5.413560808 | -2.325515220 | -0.845490987 |
| H | 5.413560808 | 2.325515220 | -0.845490987 |
| H | -5.413560808 | -2.325515220 | -0.845490987 |
| O | -1.475879928 | 2.070803046 | -5.080522762 |
| O | 1.475879928 | -2.070803046 | -5.080522762 |
| O | 1.475879928 | 2.070803046 | -5.080522762 |

| | | | |
|----|--------------|--------------|--------------|
| O | -1.475879928 | -2.070803046 | -5.080522762 |
| H | -2.253008701 | 2.654139209 | -5.025499839 |
| H | 2.253008701 | -2.654139209 | -5.025499839 |
| H | 2.253008701 | 2.654139209 | -5.025499839 |
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| Gd | 0.000000000 | 0.000000000 | 1.752189709 |



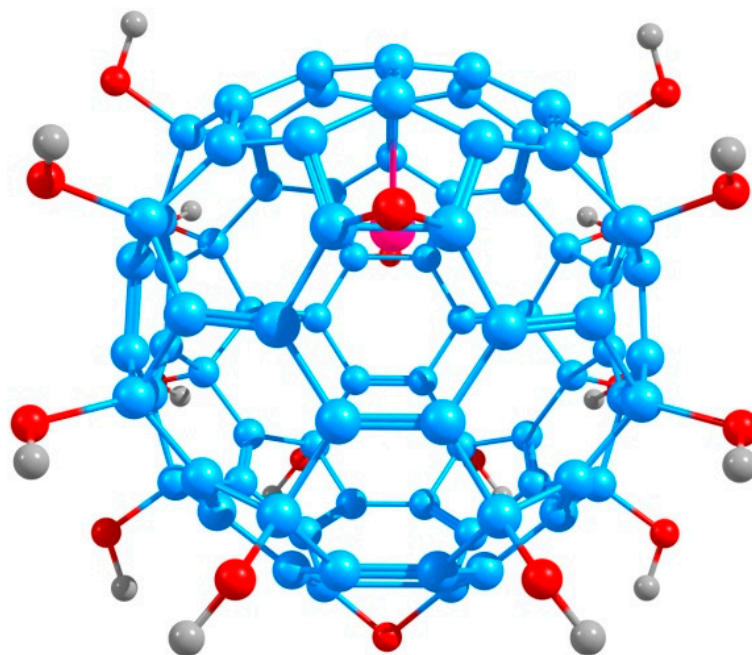
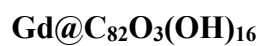
MN15/def(2)-TZVP//H₂O//Ground state

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| C | -3.089491994 | -1.175381000 | -2.173770467 |
| C | 3.089491994 | 1.175381000 | -2.173770467 |
| C | 3.089491994 | -1.175381000 | -2.173770467 |
| C | -3.089491994 | 1.175381000 | -2.173770467 |
| C | -3.932355992 | -0.751617431 | -1.013415963 |
| C | 3.932355992 | 0.751617431 | -1.013415963 |
| C | 3.932355992 | -0.751617431 | -1.013415963 |
| C | -3.932355992 | 0.751617431 | -1.013415963 |
| C | -2.562643995 | -3.390024107 | -1.132845018 |
| C | 2.562643995 | 3.390024107 | -1.132845018 |
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| C | -2.562643995 | 3.390024107 | -1.132845018 |
| C | -3.719448493 | 1.479987324 | 0.255600149 |
| C | 3.719448493 | -1.479987324 | 0.255600149 |
| C | 3.719448493 | 1.479987324 | 0.255600149 |
| C | -3.719448493 | -1.479987324 | 0.255600149 |
| C | -3.099136994 | 2.724135720 | 0.151965493 |
| C | 3.099136994 | -2.724135720 | 0.151965493 |

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| C | 3.099136994 | 2.724135720 | 0.151965493 |
| C | -3.099136994 | -2.724135720 | 0.151965493 |
| C | -2.336072996 | -2.345959115 | -2.209778151 |
| C | 2.336072996 | 2.345959115 | -2.209778151 |
| C | 2.336072996 | -2.345959115 | -2.209778151 |
| C | -2.336072996 | 2.345959115 | -2.209778151 |
| C | -3.663378493 | -0.736513613 | 1.497465232 |
| C | 3.663378493 | 0.736513613 | 1.497465232 |
| C | 3.663378493 | -0.736513613 | 1.497465232 |
| C | -3.663378493 | 0.736513613 | 1.497465232 |
| C | -2.399325495 | -3.267863921 | 1.252785829 |
| C | 2.399325495 | 3.267863921 | 1.252785829 |
| C | 2.399325495 | -3.267863921 | 1.252785829 |
| C | -2.399325495 | 3.267863921 | 1.252785829 |
| C | -2.389444995 | 2.630763666 | 2.469258122 |
| C | 2.389444995 | -2.630763666 | 2.469258122 |
| C | 2.389444995 | 2.630763666 | 2.469258122 |
| C | -2.389444995 | -2.630763666 | 2.469258122 |
| C | -3.083408494 | -1.387175304 | 2.613754158 |
| C | 3.083408494 | 1.387175304 | 2.613754158 |
| C | 3.083408494 | -1.387175304 | 2.613754158 |
| C | -3.083408494 | 1.387175304 | 2.613754158 |
| C | -2.383538995 | -0.687808198 | 3.657061543 |
| C | 2.383538995 | 0.687808198 | 3.657061543 |
| C | 2.383538995 | -0.687808198 | 3.657061543 |
| C | -2.383538995 | 0.687808198 | 3.657061543 |
| C | -1.209258998 | -2.631964606 | 3.312835336 |
| C | 1.209258998 | 2.631964606 | 3.312835336 |
| C | 1.209258998 | -2.631964606 | 3.312835336 |
| C | -1.209258998 | 2.631964606 | 3.312835336 |
| C | -1.220616498 | -1.461706644 | 4.052184615 |
| C | 1.220616498 | 1.461706644 | 4.052184615 |
| C | 1.220616498 | -1.461706644 | 4.052184615 |
| C | -1.220616498 | 1.461706644 | 4.052184615 |
| C | -1.178695998 | -3.901693650 | 0.773914650 |

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|---|--------------|--------------|--------------|
| C | 1.178695998 | 3.901693650 | 0.773914650 |
| C | 1.178695998 | -3.901693650 | 0.773914650 |
| C | -1.178695998 | 3.901693650 | 0.773914650 |
| C | -1.193558498 | -3.859558085 | -0.631835129 |
| C | 1.193558498 | 3.859558085 | -0.631835129 |
| C | 1.193558498 | -3.859558085 | -0.631835129 |
| C | -1.193558498 | 3.859558085 | -0.631835129 |
| C | -1.180165998 | -2.400124946 | -3.020635406 |
| C | 1.180165998 | 2.400124946 | -3.020635406 |
| C | 1.180165998 | -2.400124946 | -3.020635406 |
| C | -1.180165998 | 2.400124946 | -3.020635406 |
| C | -0.727589499 | -1.233838279 | -3.677640124 |
| C | 0.727589499 | 1.233838279 | -3.677640124 |
| C | 0.727589499 | -1.233838279 | -3.677640124 |
| C | -0.727589499 | 1.233838279 | -3.677640124 |
| C | -1.443088997 | 0.000000000 | -3.610295673 |
| C | 1.443088997 | 0.000000000 | -3.610295673 |
| C | 0.000000000 | -0.791870131 | 4.543365067 |
| C | 0.000000000 | 0.791870131 | 4.543365067 |
| C | 0.000000000 | 3.514356509 | 3.036078180 |
| C | 0.000000000 | -3.514356509 | 3.036078180 |
| C | 0.000000000 | -3.894526444 | 1.535290009 |
| C | 0.000000000 | 3.894526444 | 1.535290009 |
| C | 0.000000000 | -3.819331596 | -1.362198180 |
| C | 0.000000000 | 3.819331596 | -1.362198180 |
| C | 0.000000000 | 3.367684791 | -2.807226694 |
| C | 0.000000000 | -3.367684791 | -2.807226694 |
| O | 0.000000000 | -4.729094117 | 3.759540875 |
| O | 0.000000000 | 4.729094117 | 3.759540875 |
| H | 0.000000000 | 4.514575748 | 4.704917283 |
| H | 0.000000000 | -4.514575748 | 4.704917283 |
| O | 0.000000000 | -4.487930641 | -3.647722410 |
| O | 0.000000000 | 4.487930641 | -3.647722410 |
| H | 0.000000000 | -4.191042518 | -4.570024359 |
| H | 0.000000000 | 4.191042518 | -4.570024359 |

| | | | |
|----|--------------|--------------|--------------|
| O | -3.317836494 | -4.483679645 | -1.581447525 |
| O | 3.317836494 | 4.483679645 | -1.581447525 |
| O | 3.317836494 | -4.483679645 | -1.581447525 |
| O | -3.317836494 | 4.483679645 | -1.581447525 |
| H | -4.220056992 | -4.186492494 | -1.770802247 |
| H | 4.220056992 | 4.186492494 | -1.770802247 |
| H | 4.220056992 | -4.186492494 | -1.770802247 |
| H | -4.220056992 | 4.186492494 | -1.770802247 |
| O | -5.095010990 | 0.000000000 | -1.291810563 |
| O | 5.095010990 | 0.000000000 | -1.291810563 |
| O | 0.000000000 | 0.000000000 | 5.703410474 |
| Gd | 0.000000000 | 0.000000000 | -1.302107873 |



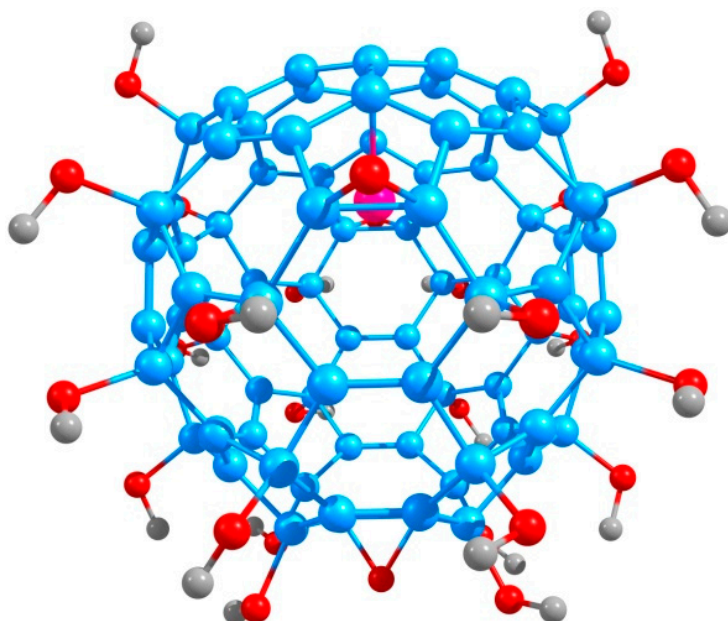
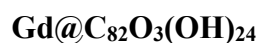
MN15/def(2)-TZVP//H₂O//Ground state

| | | | |
|---|--------------|--------------|--------------|
| C | 2.621718813 | 0.000000000 | 3.106564816 |
| C | -2.621718813 | 0.000000000 | 3.106564816 |
| C | 3.075627098 | -1.178852273 | 2.451502964 |
| C | -3.075627098 | 1.178852273 | 2.451502964 |
| C | -3.075627098 | -1.178852273 | 2.451502964 |
| C | 3.075627098 | 1.178852273 | 2.451502964 |
| C | 3.785098694 | -0.748160918 | 1.232768539 |
| C | -3.785098694 | 0.748160918 | 1.232768539 |
| C | -3.785098694 | -0.748160918 | 1.232768539 |
| C | 3.785098694 | 0.748160918 | 1.232768539 |
| C | 2.543754341 | -3.394741777 | 1.396180664 |
| C | -2.543754341 | 3.394741777 | 1.396180664 |
| C | -2.543754341 | -3.394741777 | 1.396180664 |
| C | 2.543754341 | 3.394741777 | 1.396180664 |
| C | 3.511879345 | -1.476196471 | -0.021485682 |
| C | -3.511879345 | 1.476196471 | -0.021485682 |
| C | -3.511879345 | -1.476196471 | -0.021485682 |
| C | 3.511879345 | 1.476196471 | -0.021485682 |
| C | 3.045314754 | -2.741683356 | 0.096419961 |
| C | -3.045314754 | 2.741683356 | 0.096419961 |

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|---|--------------|--------------|--------------|
| C | -3.045314754 | -2.741683356 | 0.096419961 |
| C | 3.045314754 | 2.741683356 | 0.096419961 |
| C | 2.302944855 | -2.360176058 | 2.481838433 |
| C | -2.302944855 | 2.360176058 | 2.481838433 |
| C | -2.302944855 | -2.360176058 | 2.481838433 |
| C | 2.302944855 | 2.360176058 | 2.481838433 |
| C | 3.456839482 | -0.683796565 | -1.274267018 |
| C | -3.456839482 | 0.683796565 | -1.274267018 |
| C | -3.456839482 | -0.683796565 | -1.274267018 |
| C | 3.456839482 | 0.683796565 | -1.274267018 |
| C | 2.546642787 | -3.558407220 | -1.070976806 |
| C | -2.546642787 | 3.558407220 | -1.070976806 |
| C | -2.546642787 | -3.558407220 | -1.070976806 |
| C | 2.546642787 | 3.558407220 | -1.070976806 |
| C | 2.337114557 | -2.658508185 | -2.234270344 |
| C | -2.337114557 | 2.658508185 | -2.234270344 |
| C | -2.337114557 | -2.658508185 | -2.234270344 |
| C | 2.337114557 | 2.658508185 | -2.234270344 |
| C | 3.225442934 | -1.472258887 | -2.563099791 |
| C | -3.225442934 | 1.472258887 | -2.563099791 |
| C | -3.225442934 | -1.472258887 | -2.563099791 |
| C | 3.225442934 | 1.472258887 | -2.563099791 |
| C | 2.332947737 | -0.698144693 | -3.556372570 |
| C | -2.332947737 | 0.698144693 | -3.556372570 |
| C | -2.332947737 | -0.698144693 | -3.556372570 |
| C | 2.332947737 | 0.698144693 | -3.556372570 |
| C | 1.204870122 | -2.641357216 | -2.948598068 |
| C | -1.204870122 | 2.641357216 | -2.948598068 |
| C | -1.204870122 | -2.641357216 | -2.948598068 |
| C | 1.204870122 | 2.641357216 | -2.948598068 |
| C | 1.203982309 | -1.491497102 | -3.857592318 |
| C | -1.203982309 | 1.491497102 | -3.857592318 |
| C | -1.203982309 | -1.491497102 | -3.857592318 |
| C | 1.203982309 | 1.491497102 | -3.857592318 |
| C | 1.191416508 | -3.965350038 | -0.523106760 |

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|---|--------------|--------------|--------------|
| C | -1.191416508 | 3.965350038 | -0.523106760 |
| C | -1.191416508 | -3.965350038 | -0.523106760 |
| C | 1.191416508 | 3.965350038 | -0.523106760 |
| C | 1.192784904 | -3.883471596 | 0.875905033 |
| C | -1.192784904 | 3.883471596 | 0.875905033 |
| C | -1.192784904 | -3.883471596 | 0.875905033 |
| C | 1.192784904 | 3.883471596 | 0.875905033 |
| C | 1.180122550 | -2.430722877 | 3.293005606 |
| C | -1.180122550 | 2.430722877 | 3.293005606 |
| C | -1.180122550 | -2.430722877 | 3.293005606 |
| C | 1.180122550 | 2.430722877 | 3.293005606 |
| C | 0.711807083 | -1.233575929 | 3.951582842 |
| C | -0.711807083 | 1.233575929 | 3.951582842 |
| C | -0.711807083 | -1.233575929 | 3.951582842 |
| C | 0.711807083 | 1.233575929 | 3.951582842 |
| C | 1.421824669 | 0.000000000 | 3.878196351 |
| C | -1.421824669 | 0.000000000 | 3.878196351 |
| C | 0.000000000 | -1.064215989 | -4.432245190 |
| C | 0.000000000 | 1.064215989 | -4.432245190 |
| C | 0.000000000 | -3.533516374 | -2.725171163 |
| C | 0.000000000 | 3.533516374 | -2.725171163 |
| C | 0.000000000 | -3.957372391 | -1.256471607 |
| C | 0.000000000 | 3.957372391 | -1.256471607 |
| C | 0.000000000 | -3.816297532 | 1.600951710 |
| C | 0.000000000 | 3.816297532 | 1.600951710 |
| C | 0.000000000 | -3.369621114 | 3.049907494 |
| C | 0.000000000 | 3.369621114 | 3.049907494 |
| O | 0.000000000 | -4.671966257 | -3.561689242 |
| O | 0.000000000 | 4.671966257 | -3.561689242 |
| H | 0.000000000 | -4.379154295 | -4.489187974 |
| H | 0.000000000 | 4.379154295 | -4.489187974 |
| O | 0.000000000 | -4.546073776 | 3.856820293 |
| O | 0.000000000 | 4.546073776 | 3.856820293 |
| H | 0.000000000 | -4.256171711 | 4.784094147 |
| H | 0.000000000 | 4.256171711 | 4.784094147 |

| | | | |
|----|--------------|--------------|--------------|
| O | 3.329300859 | -4.490734736 | 1.818357353 |
| O | -3.329300859 | 4.490734736 | 1.818357353 |
| O | -3.329300859 | -4.490734736 | 1.818357353 |
| O | 3.329300859 | 4.490734736 | 1.818357353 |
| H | 4.167353888 | -4.140210630 | 2.164207039 |
| H | -4.167353888 | 4.140210630 | 2.164207039 |
| H | -4.167353888 | -4.140210630 | 2.164207039 |
| H | 4.167353888 | 4.140210630 | 2.164207039 |
| O | 5.001750340 | 0.000000000 | 1.339935586 |
| O | -5.001750340 | 0.000000000 | 1.339935586 |
| O | 0.000000000 | 0.000000000 | -5.317409506 |
| O | 3.358189619 | -4.684075248 | -1.342018597 |
| O | -3.358189619 | 4.684075248 | -1.342018597 |
| O | -3.358189619 | -4.684075248 | -1.342018597 |
| O | 3.358189619 | 4.684075248 | -1.342018597 |
| H | 4.203836979 | -4.358117524 | -1.696081360 |
| H | -4.203836979 | 4.358117524 | -1.696081360 |
| H | -4.203836979 | -4.358117524 | -1.696081360 |
| H | 4.203836979 | 4.358117524 | -1.696081360 |
| O | 4.496257437 | -1.846138674 | -3.050419450 |
| O | -4.496257437 | 1.846138674 | -3.050419450 |
| O | -4.496257437 | -1.846138674 | -3.050419450 |
| O | 4.496257437 | 1.846138674 | -3.050419450 |
| H | 4.372582209 | -2.445653436 | -3.806619360 |
| H | -4.372582209 | 2.445653436 | -3.806619360 |
| H | -4.372582209 | -2.445653436 | -3.806619360 |
| H | 4.372582209 | 2.445653436 | -3.806619360 |
| Gd | 0.000000000 | 0.000000000 | 1.532155982 |



MN15/def(2)-TZVP//H₂O//Ground state

| | | | |
|---|--------------|--------------|--------------|
| C | -2.625404200 | -0.389511810 | -3.459398260 |
| C | 2.659248040 | -0.300919370 | -3.401324180 |
| C | -3.073256990 | -1.495575510 | -2.681717900 |
| C | 3.078355850 | 0.949555930 | -2.859398990 |
| C | 3.132388820 | -1.387414510 | -2.621883450 |
| C | -3.101732220 | 0.845642760 | -2.929818910 |
| C | -3.928077350 | -0.953798880 | -1.589039610 |
| C | 3.921760650 | 0.660147460 | -1.670675690 |
| C | 3.951723290 | -0.821502560 | -1.509062850 |
| C | -3.945231830 | 0.528470720 | -1.749218170 |
| C | -2.480493950 | -3.538339210 | -1.390184900 |
| C | 2.498497150 | 3.240698580 | -2.085708190 |
| C | 2.609274410 | -3.430873990 | -1.331007590 |
| C | -2.596554670 | 3.152036770 | -2.131809260 |
| C | -3.973643310 | -1.610227400 | -0.216907480 |
| C | 3.965046800 | 1.611145540 | -0.480309700 |
| C | 3.996326300 | -1.478062120 | -0.137588430 |
| C | -4.028232020 | 1.468202710 | -0.554169550 |
| C | -3.003022040 | -2.749397240 | -0.213532040 |
| C | 3.022566260 | 2.750475320 | -0.752302850 |

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|---|--------------|--------------|--------------|
| C | 3.030369660 | -2.598355990 | -0.156007730 |
| C | -3.116625610 | 2.633868510 | -0.807769130 |
| C | -2.267579550 | -2.639382960 | -2.578199840 |
| C | 2.306951980 | 2.097441080 | -3.045996550 |
| C | 2.403521880 | -2.584001280 | -2.562418940 |
| C | -2.356249480 | 2.020573650 | -3.096260310 |
| C | -3.619636160 | -0.604982910 | 0.902284840 |
| C | 3.575237680 | 0.875152960 | 0.822889740 |
| C | 3.599991780 | -0.472397490 | 0.963451900 |
| C | -3.627848170 | 0.738660740 | 0.754168000 |
| C | -2.491513940 | -3.387018190 | 1.037431770 |
| C | 2.453584960 | 3.619462910 | 0.323885500 |
| C | 2.569096110 | -3.283500890 | 1.066515500 |
| C | -2.606472880 | 3.528084280 | 0.276908770 |
| C | -2.299619170 | -2.354112070 | 2.083147440 |
| C | 2.228483190 | 2.827964440 | 1.556966440 |
| C | 2.317946270 | -2.265034890 | 2.104537610 |
| C | -2.376299160 | 2.742255500 | 1.511221570 |
| C | -3.284121610 | -1.229330220 | 2.263381340 |
| C | 3.210586700 | 1.780277770 | 2.002707850 |
| C | 3.259794380 | -1.112495280 | 2.318234520 |
| C | -3.327171460 | 1.663516530 | 1.944872420 |
| C | -2.436062470 | -0.317509870 | 3.133326620 |
| C | 2.349723190 | 1.082813370 | 3.040839360 |
| C | 2.370961540 | -0.234817320 | 3.184378020 |
| C | -2.462879730 | 1.000506610 | 3.001655550 |
| C | -1.202926080 | -2.248043700 | 2.843533160 |
| C | 1.121604230 | 2.900367290 | 2.305272080 |
| C | 1.194215430 | -2.184754800 | 2.834014600 |
| C | -1.276239790 | 2.839279990 | 2.264524720 |
| C | -1.329461950 | -1.091425940 | 3.818591340 |
| C | 1.225778810 | 1.983399140 | 3.512359130 |
| C | 1.258423450 | -1.048298000 | 3.826045540 |
| C | -1.363875390 | 1.937347130 | 3.476567300 |
| C | -1.137461620 | -3.865119950 | 0.570310400 |

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|---|--------------|--------------|--------------|
| C | 1.108208580 | 3.973453800 | -0.264325230 |
| C | 1.237033510 | -3.825344270 | 0.601778150 |
| C | -1.264160050 | 3.934260010 | -0.286299390 |
| C | -1.127008090 | -3.953642600 | -0.819983930 |
| C | 1.127230450 | 3.750405220 | -1.643701460 |
| C | 1.254011780 | -3.900309940 | -0.802417630 |
| C | -1.251230420 | 3.711924120 | -1.665794850 |
| C | -1.111315980 | -2.765058010 | -3.356099160 |
| C | 1.163530380 | 2.036026860 | -3.851655850 |
| C | 1.261816200 | -2.743039410 | -3.363041370 |
| C | -1.197385970 | 1.999352810 | -3.873525320 |
| C | -0.664274900 | -1.664781610 | -4.124377370 |
| C | 0.727367230 | 0.789314680 | -4.353301430 |
| C | 0.780452380 | -1.651148220 | -4.132518160 |
| C | -0.710434600 | 0.766422390 | -4.368616510 |
| C | -1.407878630 | -0.454068630 | -4.190039910 |
| C | 1.463163580 | -0.408429860 | -4.157379210 |
| C | -0.044544550 | -0.269272260 | 3.966075840 |
| C | -0.062806100 | 1.208091660 | 3.803108300 |
| C | 0.024131380 | -3.128199450 | 2.723681680 |
| C | -0.096276090 | 3.733580350 | 1.967040230 |
| C | 0.046111150 | -3.744463510 | 1.321370000 |
| C | -0.085653190 | 4.020196760 | 0.462413330 |
| C | 0.078451530 | -3.963347770 | -1.542878090 |
| C | -0.053195190 | 3.601476800 | -2.371228740 |
| C | 0.083174440 | -3.674594660 | -3.026153160 |
| C | -0.032679990 | 2.988089060 | -3.750714090 |
| O | 0.054330010 | -4.128871400 | 3.732496720 |
| O | -0.154554770 | 4.938209090 | 2.708599760 |
| H | 0.351601390 | -3.713005360 | 4.561205120 |
| H | -0.327345770 | 4.717284530 | 3.641163150 |
| O | 0.086982220 | -4.905060110 | -3.730984510 |
| O | -0.040126540 | 4.033930120 | -4.705329770 |
| H | 0.081610090 | -4.705365800 | -4.682324640 |
| H | -0.024392920 | 3.632714080 | -5.590426580 |

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|---|--------------|--------------|--------------|
| O | -3.326285550 | -4.625820730 | -1.728998360 |
| O | 3.322180330 | 4.242719330 | -2.654578980 |
| O | 3.468928230 | -4.543723390 | -1.641612510 |
| O | -3.453187740 | 4.124861170 | -2.701602300 |
| H | -3.518567720 | -5.107316820 | -0.903214670 |
| H | 3.489083790 | 4.909490980 | -1.963825840 |
| H | 3.757567990 | -4.881200270 | -0.774391780 |
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| O | -3.321480960 | -4.467455140 | 1.455054740 |
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| O | 3.411816570 | -4.358460770 | 1.552755250 |
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| H | 0.843831830 | 3.215363840 | 4.986734520 |
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| H | -2.428499520 | 3.265256150 | 4.443637850 |
| Gd | -0.027696265 | -0.200455853 | -1.984064038 |