Molecular Structure of Endohedral Metallofullerene Ce$_2$@$D_{5h}$-C$_{80}$

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M$_2$@C$_{80}$ (M=La, Ce) is the most abundantly yielded species of endohedral dimetallofullerenes. Their cage structures have been characterized to possess either $I_h$ or $D_{5h}$ symmetry by means of NMR, closely resembling those of nitride cluster fullerenes M$_3$N@C$_{80}$. On the other hand, their structural features concerning the endohedral part, including the endohedral dynamics and the cage deformation induced by endohedral clusters, are crucial for understanding their unique electrical and chemical properties. Thus, a closer inspect on their structures via X-ray crystallography method is highly necessary.

Up to now, as compared to the rich crystallographic studies on M$_3$N@C$_{80}$ (M=Sc, Tb, Tm, Lu), M$_2$@C$_{80}$, especially its $D_{5h}$ isomer, has been rarely studied. Herein we for the first time report on the crystallographic characterization of Ce$_2$@$D_{5h}$-C$_{80}$ and related DFT-calculation results. In fact, Ce$_2$@$D_{5h}$-C$_{80}$ forms cocrystal with Ni$^{II}$ (octaethylporphyrin) (OEP) in the space group $C2/m$ with $Z=4$. Accordingly, two crystallographic structures of Ce$_2$@$D_{5h}$-C$_{80}$ (Figure 1) are rationally constructed with an R value of 0.08, between which the difference relies only on the orientations of Ce$_2$ cluster. DFT-calculations reveal that the structure drawn in the right is 49.8 Kcal/mol more stable than the left one at B3LYP/6-31G(d)/CEP-31G level. Thus, when the Ce$_2$ cluster is within a plane surrounded by the band of ten contiguous hexagons of $D_{5h}$-C$_{80}$ cage, the molecule is more stabilized. Also, detailed analysis demonstrates that the Ce$_2$ cluster is either approaching to a pyracylene unit of $D_{5h}$-C$_{80}$ cage with the Ce-C distance ranging from 2.287 Å to 2.944 Å, indicative of stronger interaction between them.

\[ \text{Figure 1. Views of two crystallographic structures of Ce}_2@D_{5h}\text{-C}_{80}. \]