

M@C50 as Higher Intermediates towards Large Endohedral Metallofullerenes: Theoretical Characterization, Aromatic and Bonding Properties from Relativistic DFT Calculations

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In recent years, endohedral metallofullerenes involving the C50 cages have been observed experimentally to encapsulate several metal atoms. This is the last step in a bottom-up growing mechanism to produce the most commonly observed large metallofullerenes. Nonetheless, currently, there is a lack of theoretical rationalization of such compounds. We now report, for the first time, a comprehensive theoretical study extending the experimentally known M@C50 species to endohedral group 3 and 4 elements using dispersion-corrected density functional theory. For C50 fullerene, isomers Cs (266) and D5h (271) are the most energetically favorable cages to host these metals, despite being far from the ground state of neutral C50 fullerene. Interestingly, properties of these endohedral compounds are highly comparable to those of the tri- and tetra-anions of the correspondent hollow fullerene cages. It is found that metal-cage binding energies larger than -5 eV are directly related to relative abundances experimentally measured for the group 3 endohedral metallofullerenes. In addition, hypothetical group 4 metallofullerenes are also expected to be stable. Our results show that the resulting metal atoms transfer charge to the cage, to partially covalent-ionic compounds, which is the nature of the metal encapsulation within the C50 cage, where the ionic bond character increases for the heavier elements. In all cases, highest occupied molecular orbital-lowest unoccupied molecular orbital gaps smaller than 0.4 eV are found, in accordance with the high reactivity imposed by the need for further growth. Aromaticity NICS(0)iso indices reveal that some carbon rings close to the enclosed metal M are not fully aromatic and some are even antiaromatic, even though hollow C50 fullerene cages are fully aromatic. Thus, the

stabilities of the endohedral M@C50 compounds are not fully ruled by the aromatic character of the carbon cage but instead by the energy characteristics of the metal-cage interactions, which are fully characterized by means of energy decomposition analyses. Such results can be useful to guide further experimental explorative synthetic efforts toward more diverse metal species encapsulated within the higher intermediate C50 cage, which can be extended to other intermediate species already experimentally detected. © 2018 American Chemical Society.