

Intermediates for Larger Endohedral Metallofullerenes: Theoretical Characterization of M@C44 Species

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Endohedral metallofullerenes M@C44 containing several different endohedral species have been considered as intermediates in the path to form larger species. Such compounds containing interstitial atoms of groups 3 and 4, recently detected in experiments, are studied theoretically for the first time. Calculations carried out at a dispersion-corrected density functional theory level agree admirably well with experimental data for C44 and its endohedral compounds. The most suitable C44 isomer to form endohedral compounds is the D2 (89) isomer. The binding energy between the endohedral atom and the cage is a good indicator of the abundance found in synthesis. The properties of the endohedral compounds of C44-D2 (89) can be compared directly with those of the tri- and tetraanions of empty C44. In addition, the electron-richest regions in all of them are the four triple sequentially fused pentagon units. The centroids of the central pentagons of each such unit are approximately disposed in a seesaw structure around the endohedral atom. This structural feature of C44-D2 (89) accounts for the preferential bonding in almost all cases of these to the endohedral atom. A detailed study of the metal-cage bonding highlights the partially ionic and covalent character of their interaction. The ionic nature of the metal-cage bonding increases for the heavier endohedral atoms. Endohedral species containing group 3 metals are expected to be more reactive than those containing group 4 metals according to their highest occupied molecular orbital-lowest unoccupied molecular orbital gaps. The cage aromaticity evaluated by the NICS(0)iso indices indicates that this property does not play a crucial role in the stabilization of the endohedral species. The evaluated behavior and properties of intermediate M@C44 species can be useful to extend and understand the encapsulation processes of elements as the size of the cage increases

toward larger fullerenes. © 2017 American Chemical Society.