

Th@C₈₆, Th@C₈₂, Th@C₈₀, and Th@C₇₆: role of thorium encapsulation in determining spherical aromatic and bonding properties on medium-sized endohedral metallofullerenes

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Abstract

Thorium encapsulated metallofullerenes (Th-EMFs) with external C₇₆, C₈₀, C₈₂, and C₈₆ cages have been synthesized, with the ¹³C-NMR spectrum recorded for Th@C₈₂. Here, we explore computationally the chemical bonding, NMR and spherical aromaticity of Th@C₈₂ and related thorium-encapsulated metallofullerenes. Our results show that these Th-EMFs are new examples of spherical aromatic structures, representing interesting low-symmetry exceptions to the Hirsch 2(N + 1)² rule of spherical aromaticity. Their electronic structures are based on π-electron counts of 80, 84, 86, and 90, respectively, with a shell structure ranging from S₂P₆D₁₀F₁₄G₁₈H₂₂I₈ to S₂P₆D₁₀F₁₄G₁₈H₂₂I₁₈, where the partially filled I-shell remains as a frontier orbital. Their behavior is comparable to that of the spherical aromatic alkali-C₆₀- phases, which in addition to the favorable endohedral Th-fullerene bonding account for their particular abundance exhibiting the ability to sustain a long-range shielding cone as a result of the favorable metal-cage bonding. This rationalization of such species as neutral spherical aromatic EMFs suggests the possibility of an extensive series of aromatic fullerenes with nuclearity larger than C₆₀ buckminsterfullerene as stable building blocks towards nanostructured metal-organic materials.