Ti$_2$C$_{80}$ is more likely a titanium carbide endohedral metallofullerene (Ti$_2$C$_2$)@C$_{78}$†

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We show by means of density functional calculations that the previously synthesized metallofullerene Ti$_2$C$_{80}$ does not take the form of Ti$_2$@C$_{80}$, but is a titanium carbide endohedral metallofullerene, Ti$_2$C$_2$@C$_{78}$, that has a C$_{78}$$^{6-}$ (D$_{3h}$) cage which follows faithfully the stable closed-shell electronic rule.

Endohedral metallofullerenes that encapsulate a metal atom or cluster inside hollow carbon cages have received extensive attention in the past two decades owing to their fascinating structural and electronic properties.[1] Electron transfer occurs from the encapsulated metal or clusters to the fullerene cages, resulting in negatively charged carbon cages adopting preferentially stable closed-shell electronic configurations.[2,3] As such, the number of electrons transferred is a key factor that controls the stability of the otherwise unstable fullerene cages. This is exemplified by Sc$_2$@C$_{66}$,[4] Sc$_3$N@C$_{68}$[5] and La$_2$@C$_{72}$,[6] where the carbon cages even violate the well-known isolated pentagon rule (IPR)[3] and are certainly unstable in their empty neutral forms. However, exceptions[7] to the aforementioned stable closed-shell electronic rule seem available, *e.g.*, the recently synthesized Ti$_2$C$_{80}$.[8] In Ti$_2$C$_{80}$, the two Ti atoms were believed to be encapsulated in a C$_{80}$ (D$_{5h}$) or C$_{80}$ (I$_h$) cage with a total of four electrons transferred to the carbon cages,[8] although clear cut evidence is available that both C$_{80}$ cages prefer to accept six electrons to attain a closed-shell electronic configuration.[9] Here we show by means of density functional calculations that the Ti$_2$C$_{80}$ is not in the form of Ti$_2$@C$_{80}$ (Fig. 1), but that it is actually a titanium carbide endohedral metallofullerene, Ti$_2$C$_2$@C$_{78}$ (Fig. 2), that has a C$_{78}$$^{6-}$ (D$_{3h}$) cage[9,10] that follows faithfully the stable closed-shell electronic rule.

All calculations were carried out with the hybrid density functional theory at the B3LYP level[11] using the Gaussian 98 program.[12] Two basis set–RECP (relativistic effective core potential) combinations were used. The first, denoted DZ, is the combination of the split-valence 3-21G basis set[13] for C with the small core RECP, plus the valence double-ζ basis set (denoted LanL2DZ)[14] for Ti. The second, denoted DZP, combines the split-valence d-polarized 6-31G* basis set[15] for C with the LanL2DZ set for Ti. The geometries of all Ti$_2$C$_{80}$ isomers concerned were first optimized at the B3LYP/DZ level; the geometries of key structures
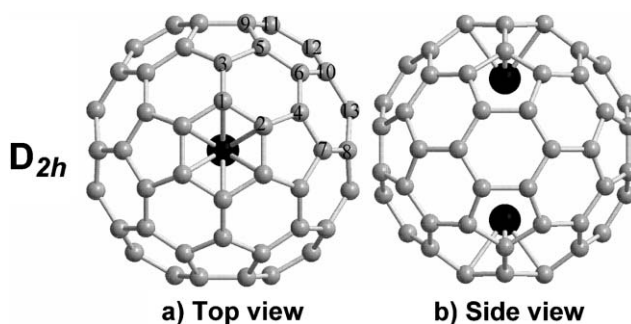
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† Electronic Supplementary Information (ESI) available: Cartesian coordinates and energies of the optimized Ti$_2$@C$_{80}$ and Ti$_2$C$_2$@C$_{78}$, and electron isodensity surfaces of selected molecular orbitals of Ti$_2$@C$_{80}$ and Ti$_2$C$_2$@C$_{78}$. See http://dx.doi.org/10.1039/b507855e
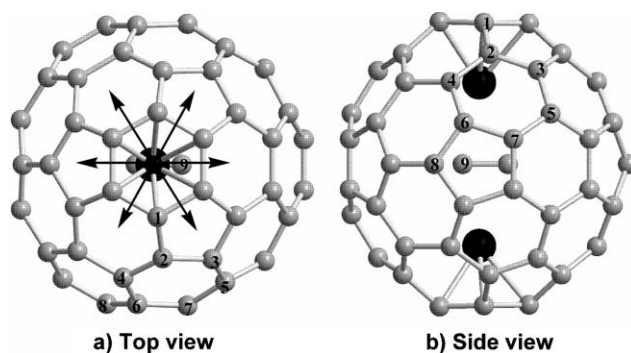

Fig. 1 (a) Top view and (b) side view of the B3LYP/DZP-optimized D$_{2h}$-symmetric geometry of singlet state Ti$_2$@C$_{80}$, in which the carbon cage is the I$_h$(7 : 7) IPR isomer of C$_{80}$. The shortest C–Ti distances are 2.20 Å.

Fig. 2 (a) Top view and (b) side view of the B3LYP/DZP-optimized static C$_{2v}$-symmetric geometry of singlet state Ti$_2$C$_2$@C$_{78}$, in which the carbon cage is the D$_{3h}$(5 : 5) IPR isomer of C$_{78}$. The average Ti–C1 and Ti–C9 distances are 2.20 and 2.38 Å, respectively. The optimal C–C bond length for the central acetylide C$_2$$^{2-}$ group is 1.27 Å.

were reoptimized at the B3LYP/DZP level. Similar combinations of theoretical method and basis sets have been shown to be reasonable at predicting the geometries of metallofullerenes such as La$_2$@C$_{72}$,[6] La$_2$@C$_{80}$[9] and Sc$_3$N@C$_{80}$.[16] NMR chemical shielding tensors were evaluated by employing the gauge-independent atomic orbital (GIAO) method.[17] Based on the computed chemical shielding tensors, theoretical ^{13}C NMR chemical shifts were calculated relative to C$_{60}$ and converted to the TMS (tetramethylsilane) scale using the experimental value for C$_{60}$ (142.5 ppm).[18] The GIAO-B3LYP/DZP theory proved to be sufficiently accurate at reproducing ^{13}C NMR chemical shifts of fullerenes such as C$_{60}$, C$_{70}$, C$_{76}$ and C$_{78}$,[19] and metallofullerenes such as Sc$_3$N@C$_{80}$[16] and Sc$_2$@C$_{66}$.[20]

In the experimental ^{13}C NMR characterization of pure Ti$_2$C$_{80}$,[8] Cao *et al.* found a total of eight ^{13}C NMR chemical shifts ranging from 130 to 145 ppm, and proposed that their sample was a mixture of two Ti$_2$@C$_{80}$ isomers of I$_h$ and D$_{5h}$ symmetric C$_{80}$ cages in a ratio of 1 : 3. Hence, we chose the I$_h$ (7 : 7) IPR isomer of C$_{80}$ to investigate the structures of Ti$_2$@C$_{80}$. The encapsulation of two equivalent metal atoms in the C$_{80}$ (I$_h$) cage leads to several highly symmetric structures, including those of D$_{5d}$, D$_{2h}$ and D$_{3d}$ symmetries.[9] Geometry optimizations of these high symmetry isomers in a singlet state were performed at the B3LYP/DZ level. The singlet D$_{2h}$ structure (Fig. 1) appears to be the most stable by 20.1 kcal mol^{-1}, compared to the singlet D$_{5d}$ structure. The shortest C–Ti bond length in the singlet D$_{2h}$ structure (2.24 Å) is much shorter than that (2.35 Å) in titanocenes,[21] implying stronger Ti–cage covalent bonding in Ti$_2$@C$_{80}$. Even shorter C–Ti bond lengths (~ 2.20 Å) were predicted by the more sophisticated B3LYP/DZP optimizations. A detailed analysis of its molecular orbitals (Fig. S1, ESI†) indicates that the Ti$_2$@C$_{80}$ can be described as Ti$_2^{6+}$@C$_{80}^{6-}$, but that the presence of strong covalent dative bonding between Ti^{3+} and C$_{80}^{6-}$ results in back-donation of charge from the negatively charged cage to the cations. The relatively strong Ti–cage covalent bonding should prohibit free rotation of the Ti$_2$ unit in the carbon cage at room temperature, and consequently Ti$_2$@C$_{80}$ with a C$_{80}$ (I$_h$) cage would show thirteen ^{13}C NMR signals, not the expected two lines.[8] In addition, single-point B3LYP/DZP calculations revealed that the triplet state of D$_{2h}$ symmetric Ti$_2$@C$_{80}$ is 14.0 kcal mol^{-1} lower in energy than its singlet state, with one spin-unpaired electron localized on each Ti atom. Hence Ti$_2$@C$_{80}$, preferentially adopting an open-shell electronic configuration, should be paramagnetic in nature and consequently should not have detectable signals in its NMR spectrum at all. Instead, the other structural model, which is diamagnetic, should be proposed to account for the experimental ^{13}C NMR spectrum of Ti$_2$C$_{80}$.

We then inferred that the synthesized Ti$_2$C$_{80}$ should adopt a different structure model, *i.e.* Ti$_2$C$_2$@C$_{78}$, with a C$_{78}$ cage of D$_{3h}$ symmetry (Fig. 2). This structural model is based on the following considerations. Firstly, a D$_{3h}$-symmetric C$_{78}$ cage would show eight ^{13}C NMR signals.[10] Secondly, the C$_{78}$ cage can accept up to six electrons,[10] whereas the encapsulated Ti$_2$C$_2$ cluster can be hexavalent consisting of two Ti^{4+} cations and a C$_2^{2-}$ group; the whole structure would thus have a diamagnetic closed-shell electronic configuration.

Fig. 2 depicts the static C$_{2v}$-symmetric geometry of Ti$_2$C$_2$@C$_{78}$, optimized at the B3LYP/DZP level. The averaged Ti–C1 and Ti–C9 distances are 2.20 and 2.38 Å respectively, indicating that the Ti–cage bonding is much stronger than the Ti–acetylide bonding. The Ti$_2$C$_2$@C$_{78}$ can be viewed as Ti$_2^{8+}$C$_2^{2-}$@C$_{78}^{6-}$ with covalent dative bonding between the Ti^{4+} cations and the C$_{78}^{6-}$ cage, as well as ionic Ti^{4+}–acetylide interactions (Fig. S2, ESI†). The weaker ionic Ti–acetylide interaction allows rapid (free) rotation of the acetylide group around the C$_3$ axis of the C$_{78}$ cage with a small rotation barrier of about 0.1 kcal mol^{-1}, estimated at the B3LYP/DZ level. Thus at room temperature, the C$_{78}$ cage in Ti$_2$C$_2$@C$_{78}$ should maintain a D$_{3h}$ symmetry over a long timescale due to the constant rotation of the encapsulated acetylide group.

Table 1 lists the ^{13}C NMR chemical shifts of Ti$_2$C$_2$@C$_{78}$, predicted by GIAO-B3LYP/DZP calculations, along with the experimental data[8] for Ti$_2$C$_{80}$. The good agreement between the theoretical ^{13}C NMR chemical shifts and the experimental data convinces us that the metallofullerene Ti$_2$C$_{80}$, synthesized by Cao *et al.*, is not Ti$_2$@C$_{80}$, but is most likely in the form Ti$_2$C$_2$@C$_{78}$. For the acetylide carbon atoms in Ti$_2$C$_2$@C$_{78}$, the calculated ^{13}C NMR chemical shift is 288.5 ppm, much higher than that (92 ppm) observed for Sc$_2$C$_2$@C$_{84}$.[22] Unfortunately, this signal was not observed experimentally,[8] due probably to the spin–rotation interaction[9,23] at room temperature.

In summary, we have shown theoretically that the previously synthesized metallofullerene Ti$_2$C$_{80}$ does not take the form of Ti$_2$@C$_{80}$, but is most likely a titanium carbide endohedral metallofullerene, Ti$_2$C$_2$@C$_{78}$. Hence, Ti$_2$C$_{80}$ is the smallest metal carbide endohedral fullerene disclosed so far; other metal carbide endohedral fullerenes including Sc$_2$C$_2$@C$_{84}$[22] and Y$_2$C$_2$@C$_{82}$.[23] The present work shows that care should be taken during the structural determination of metallofullerenes with large carbon cages, especially such dimetallofullerenes as Sc$_2$C$_{82}$,[24] Sc$_2$C$_{84}$,[24,25] Ti$_2$C$_{84}$[26] and Hf$_2$C$_{80}$,[27] in that their simple endohedral forms, M$_2$@C$_n$, may not fulfil the stable closed-shell electronic rule. To attain stable closed-shell electronic configurations, it is likely that some of these dimetallofullerenes will form M$_2$C$_2$@C$_{n-2}$ cages, as implied by high-resolution ion mobility measurements on Sc metallofullerenes.[24]

Table 1 Theoretical and experimental ^{13}C NMR chemical shifts (in ppm) of Ti$_2$C$_2$@C$_{78}$

Theory/ppm[a,b]	Experiment/ppm[c]	Site[d]
128.6	129.8	C1
130.5	130.5	C2
133.5	131.6	C5
137.4	136.4	C4
139.8	138.9	C3
141.0	140.4	C6
142.5	141.6	C7
143.6	144.3	C8

[a] The chemical shifts of equivalent isomeric sites were averaged to obtain the value. [b] The predicted ^{13}C NMR chemical shift for the acetylide C atoms is 288.5 ppm. [c] Data extracted from ref. 8. [d] See Fig. 2 for the definition of the carbon sites.

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