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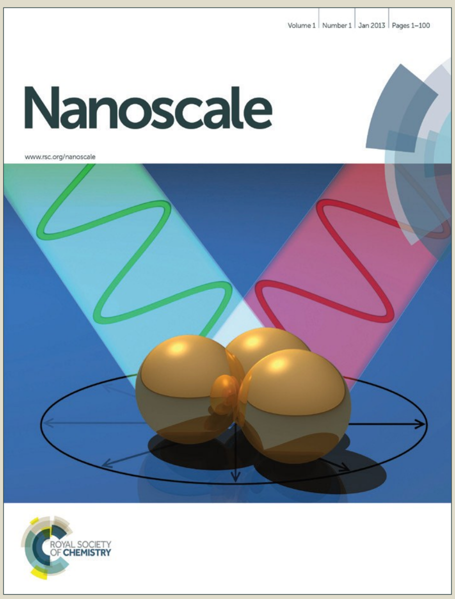

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ARTICLE

$Sc_{20}C_{60}$: A Volleyballene

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An exceptionally stable hollow cage containing 20 scandium atoms and 60 carbon atoms has been identified. This $Sc_{20}C_{60}$ molecular cluster has a T_h point group symmetry and a volleyball-like shape that we refer to below as "*Volleyballene*". Electronic structure analysis shows that the formation of delocalized π bonds between Sc atoms and neighboring pentagonal rings made of carbon atoms is crucial for stabilizing the cage structure. A relatively large HOMO-LUMO gap (~1.4eV) was found. The results of vibrational frequency analysis and molecular dynamics simulations both demonstrate that this *Volleyballene* molecule is exceptionally stable.

Since the experimental observation of C_{60}[1], many very interesting structures have been proposed, such as the metallo-carbohedrenes (Met-Cars) M_8C_{12} (*M*=Ti, V, Zr, Hf, *et al*)[2,3], Au_{20}[4], Au_{32}[5], Au_{42}[6], *M*@Si_n (*M*=Transition Metals; *n*=14,15,16)[7], Eu@Si_{20}[8], Eu_2@Si_{30}[9], B_{80}[10], and $B_{40}^{-/0}$ [11]. Here we describe the structure and stability, and predict the existence of a hollow cage molecule, $Sc_{20}C_{60}$, which has 60 carbon atoms moulded into pentagons, plus 20 scandium atoms locked in octagons, an arrangement that resembles the panels of a volleyball, that we refer to below as "*Volleyballene*". This *Volleyballene* will be the first buckyball to be spiked with scandium atoms.[12]

There is a growing interest in exploring the structure and energetics of metal-carbon clusters because they have unique properties and a wide variety of applications in nanoscale materials[13]. The first Met-Car was characterized during the course of studying the dehydrogenation reactions of hydrocarbons with transition-metal atoms and clusters. In a series of studies, other species with the same stoichiometry were also observed to be stable[14]. Since that time, there have been many studies to determine the geometric and electronic structures of Met-Cars,[15-17] which may be promising candidates for new materials[18,19]. In this study, we have found an exceptionally stable hollow cage, *Volleyballene* $Sc_{20}C_{60}$. It has a T_h point group symmetry and robust stability, as summarized in Table 1. The calculations were performed at three different levels, GGA/PBE, GGA/PW91, and GGA/BLYP. It was found that the *Volleyballenes* $Sc_{20}C_{60}$ obtained are of uniform shapes and similar structural parameters. In the following analyses and electronic structure calculations, the GGA/PBE was employed.

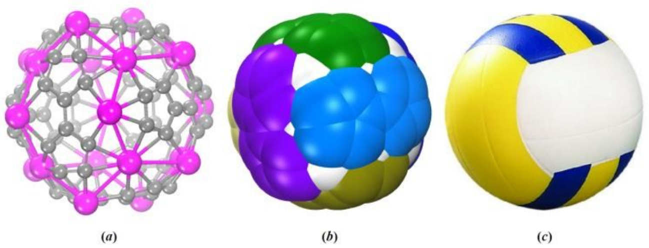

Figure 1. The configurations of the *Volleyballene* $Sc_{20}C_{60}$ viewed in (a) ball and stick model (Large ball: Sc atom; small ball: C atom) and (b) CPK style. Part (c) shows a volleyball.

Figure 1 shows the configuration of *Volleyballene* $Sc_{20}C_{60}$. It may be viewed as consisting of six Sc_8C_{10} subunits joined together in a crisscross pattern, similar to the pattern of a volleyball. In this structure, there are 12 pentagonal rings made of carbon atoms (C-pentagons) and 6 octagonal rings of scandium atoms (Sc-octagons). Every group of two C-pentagons is surrounded by one Sc-octagon to give a Sc_8C_{10} subunit.

The 20 Sc atoms link to form 12 suture lines, and the average Sc-Sc distance is 3.222 Å. For the C-pentagons, the lengths of the C-C bonds lie in the range 1.434-1.466 Å. Along with a 1.463 Å C-C bond connecting the two C-pentagons, the average C-C bond length is found to be 1.446 Å. All these C-C bond lengths in the *Volleyballene* $Sc_{20}C_{60}$ fall between the lengths of a typical C-C single bond (1.54 Å) and C-C double bond (1.34 Å), which may be the result of equalization of the chemical bonds as in 1,3-butadiene. The average Sc-C bond length is 2.248 Å and.

The following aspects of the stability of the *Volleyballene* $Sc_{20}C_{60}$ were investigated: the relative stability, the bonding character, the vibrational frequency and the molecular dynamics, the latter through ensemble simulations.

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Table 1. Summary of the calculated results for the *Volleyballene* $Sc_{20}C_{60}$ at the PBE, PW91, and BLYP levels. The data include the symmetry (Sym.), the C-C bond length ($d_{C\text{-}C}$), the Sc-C bond length ($d_{Sc\text{-}C}$), the distance between the Sc atoms ($d_{Sc\text{-}Sc}$), the binding energy per atom (E_b), the energy band gap (E_g), and the charge transfer from the Sc atom (Q_{Sc}). The units of distance, energy, and charge are Å, eV/atom, and *e*, respectively.

	Sym.	$d_{C\text{-}C}$	$d_{Sc\text{-}C}$	$d_{Sc\text{-}Sc}$	E_b	E_g	Q_{Sc}
PBE	T_h	1.446	2.248	3.222	6.446	1.471	0.604
PW91	T_h	1.446	2.456	3.219	6.331	1.459	0.612
BLYP	T_h	1.453	2.269	3.229	6.234	1.332	0.693

In order to investigate the relative stability of the *Volleyballene* molecule, we first constructed five other molecular structures with different combinations of 12 C-pentagons and 20 Sc atoms. Calculations were carried out within the same framework as described below. After energy minimization, it was found that the optimized structures all showed relatively large deformations and did not retain their original topologies. Figure 2 shows three typical cage-like geometries (*a-c*) examined before and after optimizations. Closer observation of these configurations indicated that although the overall configurations were not viable, one or more Sc_8C_{10} subunit usually appeared, which further suggests that the Sc_8C_{10} subunit is very stable. In addition, several configurations with C_{60} fullerene and 20 Sc atoms were constructed. In the optimized structures, the Sc atoms tended to cluster on the surface of C_{60}, but the binding energies of these structures were distinctly higher than that of the *Volleyballene* $Sc_{20}C_{60}$. Figure 3 shows three typical initial and optimized configurations. Beneath each isomer is listed the relative energy (ΔE) with respect to *Volleyballene*. In addition, several other isomers of $Sc_{20}C_{60}$ that arose during the high-temperature dynamic simulations were considered, but again no lower-energy structures were found (*see* Figure S3 in the Supporting Information). As a result, it appears that the *Volleyballene* $Sc_{20}C_{60}$ is energetically favoured compared to many other possible configurations.

Next, the bonding character of *Volleyballene* $Sc_{20}C_{60}$ was investigated by analyzing its deformation electron density, as shown in Figs. 4*b* and 4*c* where the molecule is viewed from above Sc_8C_{10} subunit and the suture line, respectively. The deformation density shows electron transfer from the Sc to the C atoms, and Mülliken analysis shows a charge transfer of ~0.6e away from each Sc atom to nearby C atoms. The transferred electrons, especially from the Sc 3d state, are delocalized mainly around the Sc-C bonds. Depending on the coordination, both the Sc atoms and C atoms may each be divided into two types, Sc^{I}, Sc^{II} and C^{I}, C^{II} (*see* Fig. 4*a*). For more detailed bond lengths and bond angles see Section VII of the Supporting Information. To understand the chemical bonding, the natural bonding orbital (NBO)[20] analysis was employed. The results of the natural population analysis are in accordance with those of Mülliken analysis. It also shows an average of ~0.5*e* charge transfer. For the Sc^{I} atoms, there are two nearest-neighbor Sc atoms, while the Sc^{II} atoms have

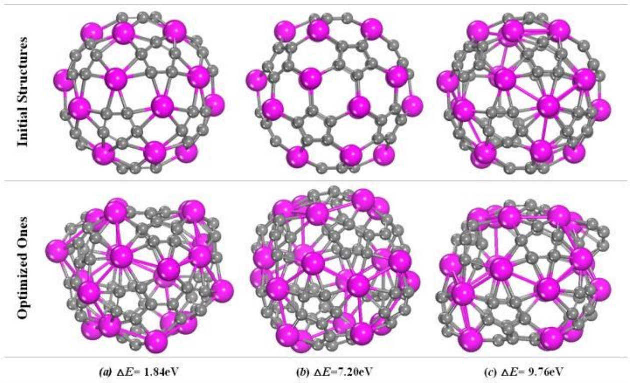

Figure 2. Selected typical initial and optimized configurations of $Sc_{20}C_{60}$ clusters constructed with different combinations of 12 C-pentagons and 20 Sc atoms. Beneath each isomer is listed the relative energy (ΔE) with respect to *Volleyballene* $Sc_{20}C_{60}$. Key: large ball, Sc atom; small ball, C atom.

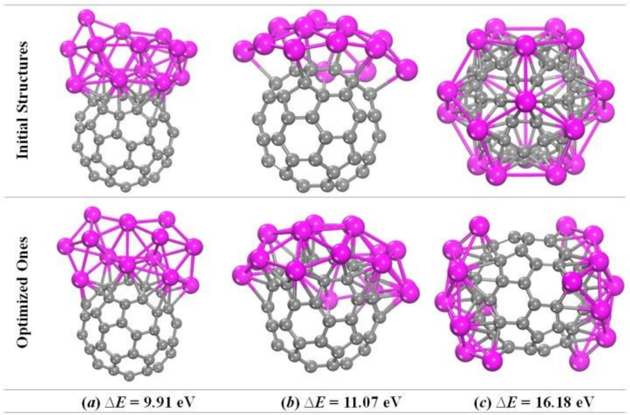

Figure 3. Selected typical initial and optimized configurations of $Sc_{20}C_{60}$ clusters, which were constructed with C_{60} fullerene and 20 Sc atoms.

three nearest-neighbor Sc atoms. Both C^{I} and C^{II} atoms are characterized by sp^2 hybridization and each has three σ bonds (*see* Figure S8 in the Supporting Information). For the C^{I} atoms that have three neighboring C atoms, σ bonds form between all four C atoms. The C^{II} atoms are neighbors to a pair of Sc atoms and two C atoms. Two of the three orbital lobes point towards the two neighboring C atoms, and the third lobe points towards the center point of the line joining the two Sc atoms. This stabilizes the Sc_8C_{10} subunit. For the Sc^{II} atoms, there is a chiral, depleted state with three petals pointing towards the three neighboring C-C bonds, which strengthens the link between the Sc_8C_{10} subunits.

The stability of *Volleyballene* $Sc_{20}C_{60}$ was confirmed using vibrational frequency analysis. The calculated frequencies were in the range 80.1-1389.5 cm^{-1} and there were no imaginary frequencies. More detailed information is shown in Figure S2 where it may be seen that the two highest intensity frequencies were found to be 468.9 and 472.3 cm^{-1}. We also calculated the Raman spectrum. Here, a temperature of 300 K was assumed, and 488.0 nm incident light was selected for the calculations, in order to simulate a realistic Raman spectrum that can be compared to experimental results. The results are shown in Fig. 5 and more detailed data are listed in Section III of the Supporting Information. All these results show that the *Volleyballene* $Sc_{20}C_{60}$ molecule is a statically stable isomer.

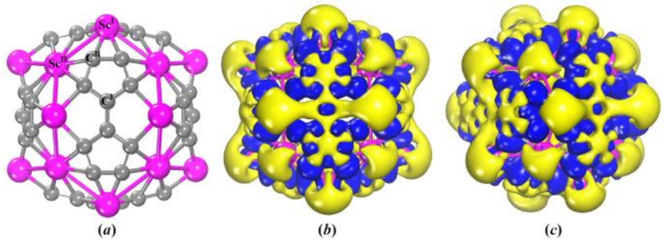

Figure 4. Structure (*a*) and deformation electron densities viewed from the top of a Sc_8C_{10} subunit (*b*) and from the suture line (c) for *Volleyballene* $Sc_{20}C_{60}$. The isosurface is taken to be 0.030 e/Å^3.

In addition, to test the thermodynamic stability of the $Sc_{20}C_{60}$ *Volleyballene, ab initio* molecular dynamics simulations were carried out with both the constant-energy, constant-volume (NVE) ensemble, and the constant-temperature, constant-volume (NVT) ensemble. For the NVE ensemble, the total simulation time was set to be 2.0 *ps* with a time step of 1.0 *fs* at initial temperatures of 1000, 1400, 2000, and 2400 K. The results of the NVE simulations showed that the structure of *Volleyballene* retained its original topological structure over the course of a 2.0 *ps* dynamic simulation at an initial temperature of 2400 K, equal to a ~1200 K effective temperature. For the NVT ensemble, the Gaussian thermostat[21] was chosen, and the total run time was set to be 1.0 *ps* with a time step of 1.0 *fs* at temperatures of T = 800 and 1000 K. The NVT dynamical simulations also indicated that the *Volleyballene* $Sc_{20}C_{60}$ retained its original topological structure up to a temperature of 1000 K. For more details see Section V of the Supporting Information. These results indicate that $Sc_{20}C_{60}$ *Volleyballene* has good thermodynamic stability.

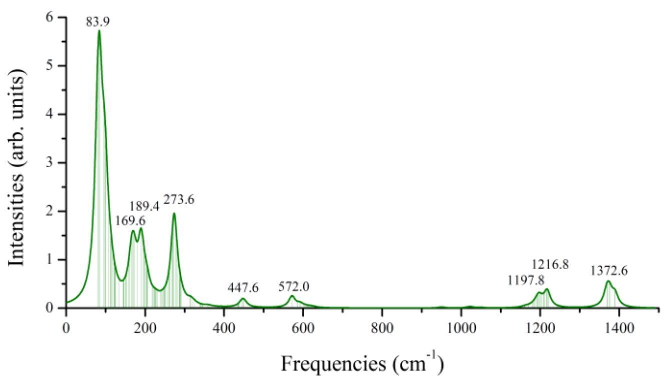

Figure 5. Simulate Raman spectrum for the *Volleyballene* $Sc_{20}C_{60}$ with a 300 K temperature and 488.0 nm incident light. The Lorentzian smearing is set to be 20.00 cm^{-1}. The labels present the frequencies corresponding to the peaks of the intensities.

Considering further the origin of the stability of this molecule, it is natural to explore the electronic structure of *Volleyballene*. To this end, we calculated the frontier molecular orbitals, as shown in Figure 6. From the contours of the HOMO and LUMO orbitals, it may be seen that the HOMO orbitals are mostly localized on the C atoms and Sc^{I} atoms. There are obvious *p-d* hybridization characteristics. As for the LUMO, the energy level features show that the LUMO orbital is doubly degenerate. On the Sc atom, there are obvious *d*-orbital characteristics, with d_{z^2}-like orbitals for Sc^{II} atoms and other *d*-like ($d_{x^2-y^2}$, d_{xy}, d_{yz}, d_{xz}) orbitals for Sc^{I}. The LUMO orbital hybridization is predominantly *sp-d* hybridization. All these results demonstrate that the hybridization between Sc *d* orbitals and C *p* orbitals stabilizes the cage structure.

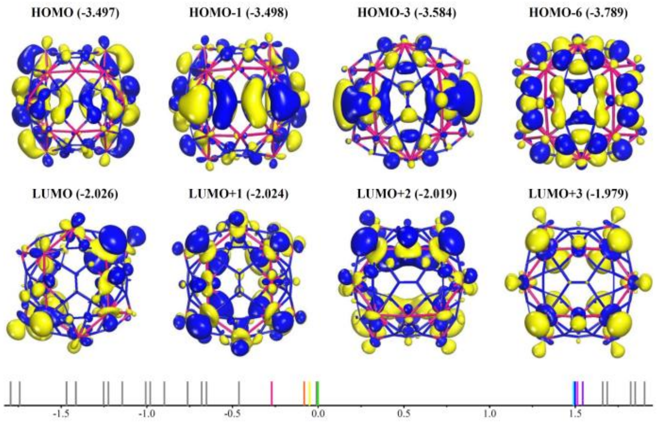

Figure 6. Selected frontier orbitals for *Volleyballene* $Sc_{20}C_{60}$. The values in brackets are eigenvalues in eV. Below is the schematic diagram of orbital energy levels near the HOMO and LUMO orbitals and the inside color lines correspond the above orbitals, ie. red: HOMO-6, orange: HOMO-3, yellow: HOMO-1, green: HOMO, cyan: LUMO, blue: LUMO+1, magenta: LUMO+2, and violet: LUMO+3. The iso-surface is set to be 0.015 e/Å^3.

From the point of view of the electron shell structures[22,23], the stability of *Volleyballene* $Sc_{20}C_{60}$ can also be understood by using the closed shell model of metal clusters. Here, each Sc atom contributes one valence electron and each C atom contributes four electrons resulting in a total of 260*e*, which falls in the range of magic numbers (260±4) describing spherical shell closures in sodium clusters[24]. For the *Volleyballene* $Sc_{20}C_{60}$, a relatively large HOMO-LUMO gap of 1.471 eV was observed at the GGA-PBE level. The *Volleyballene* $Sc_{20}C_{60}$ should therefore be an exotic buckyballene variant with exceedingly high chemical stability.

Conclusions

In conclusion, we have identified a volleyball-like molecular cluster, *Volleyballene* $Sc_{20}C_{60}$, which is energetically and dynamically stable. More importantly, this structure possesses relatively high symmetry (T_h) and a hollow internal space that could potentially hold a large atom that might be able to modify its electronic structure. An example would be a rare-earth atom to control the magnetic moment. With its exceedingly high stability, the *Volleyballene* $Sc_{20}C_{60}$ molecule, if it can be synthesized, may be able to accommodate other atoms or molecules for the purpose of studying fundamental chemistry.

Theoretical Methods

This new, low-lying $Sc_{20}C_{60}$ molecule was obtained within the framework of spin-polarized density functional theory (DFT). The exchange-correlation interaction was treated within the generalized gradient approximation (GGA) using three different functionals, the Perdue-Burke-Ernzerhof correlation (PBE),[25] Perdew-Wang exchange-correlation (PW91),[26] and Becke exchange plus Lee-Yang-Parr correlation (BLYP)[27] to facilitate comparison. A double-numerical polarized (DNP) basis set[28] was chosen to carry out the electronic structure calculations with unrestricted symmetry. For Sc, the core electrons were treated using the DFT semi-core pseudopotentials (DSPP) [29], and the C atoms were treated as in the all-electron case. The binding energy was calculated using the expression $E_b=E(Sc_{20}C_{60})-20E(Sc)-60E(C)$, in which $E(Sc_{20}C_{60})$ is the total energy of the optimized $Sc_{20}C_{60}$ cluster, and E(Sc) and E(C) are the energies of the Sc atom and the C atom, respectively.

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30 (*a*) Forget Buckyballs, Here Comes *Volleyballene*, MIT Technology Review, 2015, February 18; (*b*) Buckyball variant resembles a volleyball, Physics Today, News Picks of Daily Edition, 2015, February 19; (*c*) *Volleyballene*, World Wide Words 2015, **910**, March 07.

