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Sc₂@C₆₆ Revisited: An Endohedral Fullerene with Scandium Ions Nestled within Two Unsaturated Linear Triquinanes

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S Supporting Information

ABSTRACT: The geometries of fullerenes are governed by the isolated pentagon rule (IPR), which states that stable fullerenes have each of their 12 pentagons surrounded by five hexagons. At the dawn of fullerene science, it was widely believed that the IPR would also be applicable for endohedral fullerenes. In 2000, that idea was altered by the discovery of the first non-IPR fullerenes, Sc₂@C₆₆ and Sc₃N@C₆₈. The structural data for Sc₂@C₆₆ were interpreted to indicate the presence of a pair of doubly fused pentagons. However, that structure has remained a long-standing mystery, since it is thermodynamically unfavorable. Here, we demonstrate definitively that Sc₂@C₆₆ does not have the structure that was long believed to be but a brand new type. 2D NMR spectroscopic and single-crystal X-ray analyses disclose that Sc₂@C₆₆ has a C_{2v}(4059)-C₆₆ cage containing two sets of unsaturated linear triquinanes (ULTs), in which three pentagons abut one another and two scandium ions are located within the folds of each of the ULT units.

The discovery of the fullerene C₆₀ in 1985¹ triggered the evolution of synthetic carbon allotropes from fullerenes to carbon nanotubes² and graphene³ in the field of nanotechnology.⁴ Now, fullerenes have become materials of broad interest as molecular allotropes of carbon because of their uniform molecular nature and their unique and unprecedented properties. The extraordinary physical and chemical properties of the large family of fullerenes are governed by the carbon network geometry. To be a closed cage, fullerenes comprised of only hexagons and pentagons must contain 12 carbon pentagons as specified by Euler's polyhedral formula. Therefore, the topological placement of 12 pentagons in carbon cages plays a crucial role in their molecular shapes and properties. Kroto proposed a rule for determining the stability of fullerenes, stating that stable fullerenes are those in which all pentagons are surrounded by five hexagons.⁵ The formation of

fused pentagons increases local steric strain caused by enforced bond angles accompanied by higher pyramidalization of the carbon atoms. In addition, a fused-pentagon patch must be antiaromatic. The isolated pentagon rule (IPR) was also discovered independently and simultaneously justified theoretically by a group in Galveston, Texas.⁶ At the dawn of fullerene science, it was widely believed that the IPR would also be applicable for endohedral fullerenes. However, two papers published in 2000 described the discovery of non-IPR fullerenes, Sc₂@C₆₆⁷ and Sc₃N@C₆₈,⁸ by two independent research groups. On the basis of ¹³C NMR data, the structure of Sc₃N@C₆₈ was proposed to involve one of the 11 non-IPR isomers with 3-fold symmetry. Theoretical work narrowed down the possibilities to one of two D₃ isomers. The one with the less flattened shape, isomer 6140, was preferred and was later verified by single-crystal X-ray diffraction (XRD).⁹ The molecular structure of Sc₂@C₆₆ was examined using ¹³C NMR spectroscopy and MEM (maximum-entropy method)/Rietveld analysis with synchrotron X-ray powder diffraction data.^{7,10} The results were interpreted to indicate that Sc₂@C₆₆ possessed a C_{2v}(4348)-C₆₆ cage that contained two sets of doubly fused pentagons (pentalene units). The encaged metal atoms were situated over the centers of the fused-pentagon moieties of the fullerene cage, indicating that metal coordination plays an important role in the stabilization of fused-pentagon structures, as suggested theoretically.¹¹ Additionally, it was noteworthy that two scandium atoms were encaged as a dimer with a Sc–Sc distance of 2.87(9) Å. These results demonstrated that fused pentagons could be important structural elements in endohedral fullerenes and led to the discovery of many more endohedrals that did not follow the IPR.¹²

However, the identification of Sc₂@C₆₆ as Sc₂@C_{2v}(4348)-C₆₆ with the two scandium ions in close proximity has been controversial. Since the encaged scandium atoms are positively charged as a consequence of the electron transfer to the carbon

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cage, they should repel one another, as seen in other dimetallofullerenes.¹³ In fact, computational calculations suggested that the formation of a scandium dimer was unfavorable. Furthermore, $\text{Sc}_2@C_{2v}(4348)-C_{66}$ did not correspond to the thermodynamically favorable isomer, while the $\text{Sc}_2@C_{2v}(4059)-C_{66}$ isomer was proposed as the most stable and one that better explained the original ^{13}C NMR data.¹⁴ Therefore, the structure of $\text{Sc}_2@C_{66}$ has persisted as a long-standing mystery in fullerene science.

This report describes the definitive structural characterization of the fullerene, $\text{Sc}_2@C_{66}$, using two-dimensional (2D) “incredible natural abundance double quantum transfer experiment” (INADEQUATE) NMR spectroscopy and single-crystal XRD. First, we prepared a ^{13}C -enriched $\text{Sc}_2@C_{66}$ sample using the electric-arc vaporization method with a graphite rod packed with ^{13}C -enriched amorphous carbon and ScNi_2 . Subsequent multistage high-performance liquid chromatography (HPLC) afforded isolation of 12% ^{13}C -enriched $\text{Sc}_2@C_{66}$. The ^{13}C NMR spectrum of our sample exhibited a total of 19 distinct lines, of which 14 lines (named a, b, f, g, h, i, j, k, m, n, o, q, r, and s) have equal intensities and 5 lines (named c, d, e, l, and p) have half intensities, a resonance pattern which is consistent with C_{2v} symmetry for the cage. These ^{13}C chemical shifts are identical to those reported previously by Shinohara and his co-workers in 2000.⁷ Thus, the NMR data indicate that $\text{Sc}_2@C_{66}$ utilizes one of the eight structural isomers of C_{66} with C_{2v} symmetry (Figure 1a).

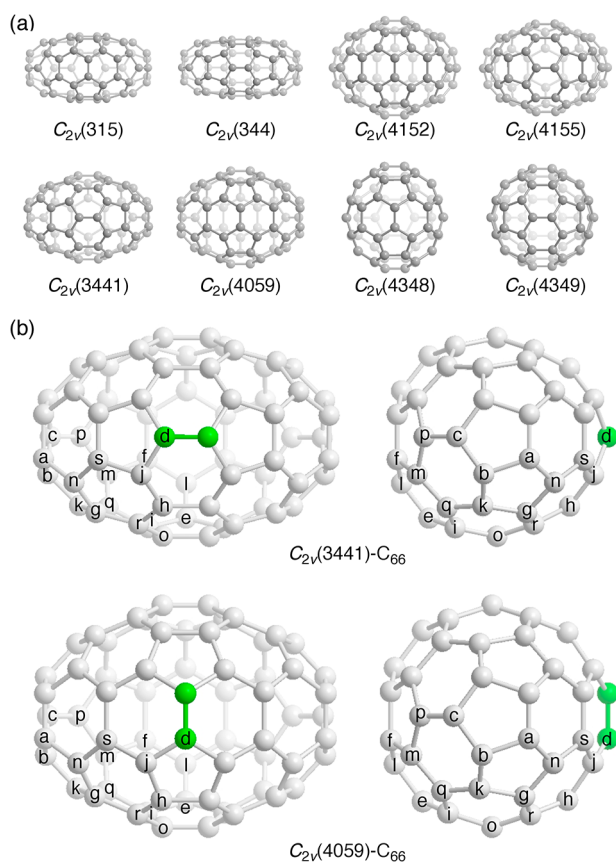


Figure 1. (a) Eight C_{2v} isomers of C_{66} . (b) Assignment of the ^{13}C chemical shifts for the 2D NMR-satisfied candidates $C_{2v}(3441)-C_{66}$ and $C_{2v}(4059)-C_{66}$ (two respective orthogonal views are shown).

Second, we performed 2D-INADEQUATE¹⁵ NMR measurements on the ^{13}C -enriched $\text{Sc}_2@C_{66}$ sample to unveil the bond connectivity in the C_{66} cage. Figure 2 shows the 2D-

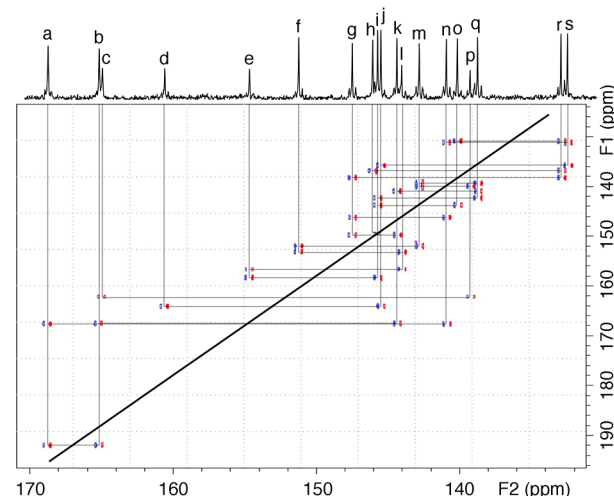


Figure 2. 125 MHz 2D INADEQUATE NMR spectrum of ^{13}C -enriched $\text{Sc}_2@C_{66}$ in CS_2 (acetone- d_6 in capillary as the lock solvent).

INADEQUATE NMR spectrum of ^{13}C -enriched $\text{Sc}_2@C_{66}$, in which each coupled pair of the nuclei gives a pair of peaks in the same vertical coordinate, and each peak appears at the two respective chemical shifts in the horizontal coordinate. On the spectrum, 21 cross-peaks were observed clearly. The observed bond connectivity is presented in Supporting Information Figure S3. The correlation reveals the existence of two contiguous hexagons composed of e–l–f–m–q–i–e and q–i–o–r–g–k–q sequences. In addition, a pentagon composed of the g–k–b–a–n–g sequence adjoins the latter hexagon. Furthermore, a sequential bond connectivity of f–m–p–c was found. In this regard, the carbons named c, d, e, l, and p must be located on the first or second mirror plane because these five carbon signals have half intensities. These observations rule out the six isomers ($C_{2v}(315)$, $C_{2v}(344)$, $C_{2v}(4152)$, $C_{2v}(4155)$, $C_{2v}(4348)$ the cage originally proposed,⁷ and $C_{2v}(4349)$) from eight possible $C_{2v}-C_{66}$ cages (see Figure 1a). However, 2D-INADEQUATE NMR spectroscopy cannot distinguish the $C_{2v}(3441)$ and $C_{2v}(4059)$ cages in principle because they have the same bond connectivity. In fact, the $C_{2v}(3441)$ structure can be generated by a Stone–Wales transformation of a C_2 unit between two abutting hexagons (shown as green in Figure 1b) on the $C_{2v}(4059)$ cage. Nevertheless, the 2D-INADEQUATE NMR data provide spectroscopic evidence that $\text{Sc}_2@C_{66}$ possesses either the $C_{2v}(3441)-C_{66}$ or the $C_{2v}(4059)-C_{66}$ cage and definitely not the $C_{2v}(4348)-C_{66}$ isomer as originally proposed. In these cage structures, the chemical shifts of all carbon atoms can be assigned (see Figure 1b). There are 23 total nonequivalent bonds, of which two correlations, b–c and h–j, are not observed clearly. The correlation signal of two strongly coupled spins consists of two larger inner peaks and two smaller outer peaks, their position and relative intensity depending on the chemical shift difference and the coupling constant J_{CC} . For h–j correlation, the inner peaks are clearly visible, and the outer peaks are hidden in the noise. For b–c bond correlation, only the right inner peak seems to be visible, and the left inner peak and the outer peaks seem to be hidden in the noise. The position of this peak was suggested by a

simulated INADEQUATE NMR spectrum (see Supporting Information Figure S4). The intensity of this correlation signal was much reduced due to the strong coupling and also due to the longer relaxation times of these spins.

Conclusive structural elucidation was accomplished by single-crystal XRD. Black crystals of $4(\text{Sc}_2@C_{2v}(4059)\text{-C}_{66})\cdot 1.42(m\text{-xylene})\cdot 1.00(\text{CS}_2)\cdot 0.58(n\text{-hexane})$ suitable for data collection were obtained by gradual diffusion of *n*-hexane into a solution of $\text{Sc}_2@C_{66}$ in $\text{CS}_2/m\text{-xylene}$. Figure 3 shows the X-ray

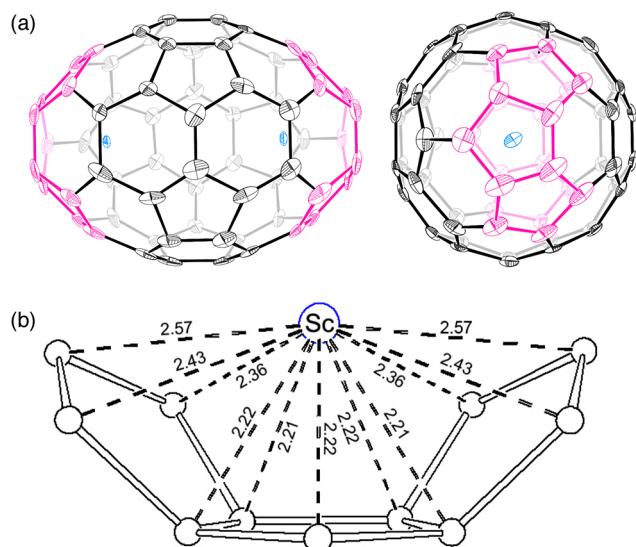


Figure 3. Single-crystal X-ray crystallographic data on $\text{Sc}_2@C_{2v}(4059)\text{-C}_{66}$. (a) Two orthogonal views of the ORTEP plot of a $\text{Sc}_2@C_{2v}(4059)\text{-C}_{66}$ molecule at 90 K with thermal ellipsoids shown at the 30% probability level. Solvate molecules have been omitted for clarity. The ULT moieties are highlighted in pink. (b) Sc-ULT coordination in $\text{Sc}_2@C_{2v}(4059)\text{-C}_{66}$ with the averaged Sc-C atom distances (in Å).

structure of $\text{Sc}_2@C_{2v}(4059)\text{-C}_{66}$. Definitively, the cage structure of this endohedral was determined to be $C_{2v}(4059)\text{-C}_{66}$, contrary to previous reports.^{7,10} The X-ray results show perfect agreement with the 2D INADEQUATE NMR assignment as well as with the theoretical prediction that $C_{2v}(4059)\text{-C}_{66}$ was the preferred cage isomer.¹⁴ Remarkably, there exist two sets of sp^2 -hybridized, unsaturated linear triquinanes (ULTs) within the cage framework.¹⁶ The averaged C-C bond lengths in the central pentagon of the ULT moiety are between 1.42–1.47 Å, showing the similarity with the cyclopentadienyl ligands in metallocenes.¹⁷

The two engaged scandium ions do not form a dimer. Instead, they are located at opposite ends of the cage with an average, nonbonded Sc...Sc distance of 4.90 Å, which shows good agreement with the calculated value (4.93 Å).¹⁴ The scandium atoms are situated over the centers of the ULTs. Figure 3b presents the Sc-ULT coordination geometry in $\text{Sc}_2@C_{2v}(4059)\text{-C}_{66}$. The central pentagon of the ULT moiety is closest to the Sc ion with its Sc-C bond lengths falling in a narrow range, 2.21–2.22 Å. These distances are shorter than those in $\text{Sc}(\eta^5\text{-Cp}^*)(\text{SiH}_2\text{SiPh}_3)$ (2.46–2.51 Å).¹⁷ The other pentagons in the ULT moiety also face the scandium ion closely, with the Sc-C bond lengths in the range 2.21–2.57 Å.

To gain insight into the aromaticity of the ULT structure of $\text{Sc}_2@C_{2v}(4059)\text{-C}_{66}$, nucleus-independent chemical shift (NICS)^{18,19} calculations were performed at the B3LYP^{20–22} level of theory using basis sets of 6-311+G for Sc and 6-31G(d)

for C atoms. The obtained NICS values for each pentagon of the ULT moiety are shown in Figure 4. Interestingly, all the

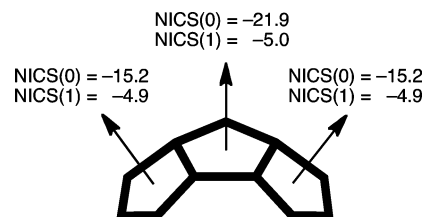


Figure 4. NICS values (in ppm) for each pentagon of the ULT moiety calculated at the B3LYP/6-311+G for Sc and 6-31G(d) for C atoms.

values of the three pentagons are negative, indicating the presence of an induced diatropic ring current. This is the opposite situation to the case of empty C_{66} , where the NICS(0) and NICS(1) values of the central pentagon of the ULT moiety are +1.8 and +2.8 ppm, respectively. In this context, the encapsulation of scandium atoms leads to the increase of the diatropic character of the ULT moieties.

In conclusion, we present compelling evidence that shows that the only known isomer of $\text{Sc}_2@C_{66}$ is $\text{Sc}_2@C_{2v}(4059)\text{-C}_{66}$, which involves two unconventional ULT structures, with the two scandium ions widely separated and nestled within these ULT units. Our identification of $\text{Sc}_2@C_{66}$ as $\text{Sc}_2@C_{2v}(4059)\text{-C}_{66}$ shows that new motifs in carbon cage geometry continue to be discovered and calls attention to the unsaturated linear triquinane unit, whose aromaticity and coordination chemistry deserve further study.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details, additional spectroscopic and crystallographic information, and CIF data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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