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Giant Fullerenes

Chlorination of IPR C_{100} Fullerene Affords Unconventional $C_{96}Cl_{20}$ with a Nonclassical Cage Containing Three Heptagons**

Shangfeng Yang, Song Wang, Erhard Kemnitz,* and Sergey I. Troyanov**

Abstract: *Chlorination of C_{100} fullerene with a mixture of VCl_4 and $SbCl_5$ afforded $C_{96}Cl_{20}$ with a strongly unconventional structure. In contrast to the classical fullerenes containing only hexagonal and pentagonal rings, the C_{96} cage contains three heptagonal rings and, therefore, should be classified as a fullerene with a nonclassical cage (NCC). There are several types of pentagon fusions in the C_{96} cage including pentagon pairs and pentagon triples. The three-step pathway from isolated-pentagon-rule (IPR) C_{100} to C_{96}(NCC-3hp) includes two C_2 losses, which create two cage heptagons, and one Stone–Wales rotation under formation of the third heptagon. Structural reconstruction established C_{100} isomer no. 18 from 450 topologically possible IPR isomers as the starting C_{100} fullerene. Until now, no pristine C_{100} isomers have been confirmed based on the experimental results.*

The development of the chemistry of the higher fullerenes is hampered by their low abundance in the fullerene soot (except C_{84}) and the existence of many cage isomers. For the higher fullerenes in the range of C_{76}–C_{96}, it was still possible to isolate individual IPR (isolated pentagon rule) isomers in quantities sufficient for ^{13}C NMR study (C_{76}–C_{84})[1] or for cocrystallization with metal porphyrins (C_{86}–C_{96}).[2] In the case of even larger (giant) fullerenes, HPLC isolation generally provides much smaller quantities, which sometimes amount to several dozens of micrograms. Therefore, the isolation and structural study of giant empty fullerenes still remain quite challenging. Two recent reports are devoted to the characterization of chlorinated giant empty fullerenes such as two isomers of C_{104}[3] and nonclassical, heptagon-containing C_{102} resulting from a chlorination-promoted transformation of IPR $C_{102}(19)$[4] (numbering according to the spiral algorithm[5]). On the other hand, giant endohedral fullerenes such as $Dy_2@C_{100}$,[6] $La_2@C_{100}(450)$,[7] and $Sm_2@C_{104}(822)$[8] have been also isolated and characterized.

Up to now, empty fullerene C_{100} has been registered only by mass spectrometry. Theoretical calculations suggested that several of altogether 450 IPR isomers of C_{100} are more stable than others and, therefore, can be present in the fullerene soot. Among them, isomer D_2-$C_{100}(449)$ was found to be the most stable according to the calculations performed by different methods.[9] The sets of next stable C_{100} isomers found in three theoretical studies[9a–c] are different, most probably due to the use of the selection and cutoffs for subsequent high-level calculations,[9b,c] whereas all 450 IPR isomers have been systematically calculated in Ref. [9a].

Herein we report the isolation and structural characterization of an unprecedented chlorinated C_{96} fullerene with a nonclassical cage (NCC) containing three heptagons, C_{96}(NCC-3hp)Cl_{20}. The reconstruction of the pathway revealed that C_{96}(NCC-3hp) is a result of a three-step transformation, including two C_2 losses and one Stone–Wales (SW) rearrangement of the starting IPR $C_{100}(18)$, the first isomer of pristine C_{100} evidenced by experimental results.

The fullerene soot was synthesized by the Krätschmer–Huffman DC arc-discharging method with an undoped graphite rod under He pressure of 400 mbar. The extracted fullerene mixture was subjected to HPLC separation in toluene using a preparative 5PYE column. The fraction eluting between 41.4 and 44.6 min was further separated with a semipreparative Buckyprep column and the main subfractions were then subjected to recycling HPLC with a semipreparative Buckyprep-M column. According to mass spectrometric analyses, three subfractions collected after several separation cycles contained mixtures with a prevailing abundance of C_{100} (see the Supporting Information for more details). The most pure C_{100} subfraction was used as the starting material for chlorination.

Around 0.02 mg of C_{100} was placed into a glass ampoule and approximately 0.4 mL of VCl_4 and a drop of $SbCl_5$ were added. The ampoule was evacuated, sealed off, and heated at 350–360 °C for roughly four weeks. After the ampoule was cooled and opened, the reaction product was washed with conc. HCl and water to remove excess $SbCl_5$ and VCl_4 leaving small orange-colored crystals. Single-crystal X-ray diffraction

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[*] Prof. Dr. S.-F. Yang, S. Wang
Hefei National Laboratory
for Physical Sciences at Microscale
CAS Key Laboratory of Materials for Energy Conversion
Department of Materials Science and Engineering
University of Science and Technology of China
Hefei 230026 (China)
E-mail: sfyang@ustc.edu.cn

Prof. Dr. E. Kemnitz
Institute of Chemistry, Humboldt University Berlin
Brook-Taylor-Strasse2, 12489 Berlin (Germany)
E-mail: erhard.kemnitz@chemie.hu-berlin.de

Prof. Dr. S. I. Troyanov
Department of Chemistry, Moscow State University
119991 Moscow, Leninskie gory (Russia)
E-mail: stroyano@thermo.chem.msu.ru

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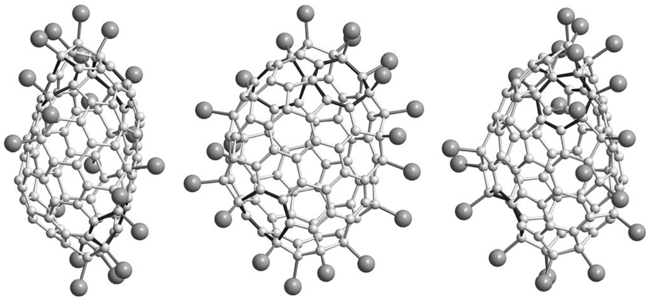

Figure 1. Three projections of the C_1-C_{96}(NCC-3hp)Cl_{20} molecule with heptagon rings highlighted in black. The left projection is along the former C_2 axis of the starting C_{100}, the middle one shows the relative positions of three cage heptagons, whereas the third one demonstrates a concave cage region due to the removal of a C_2 unit.

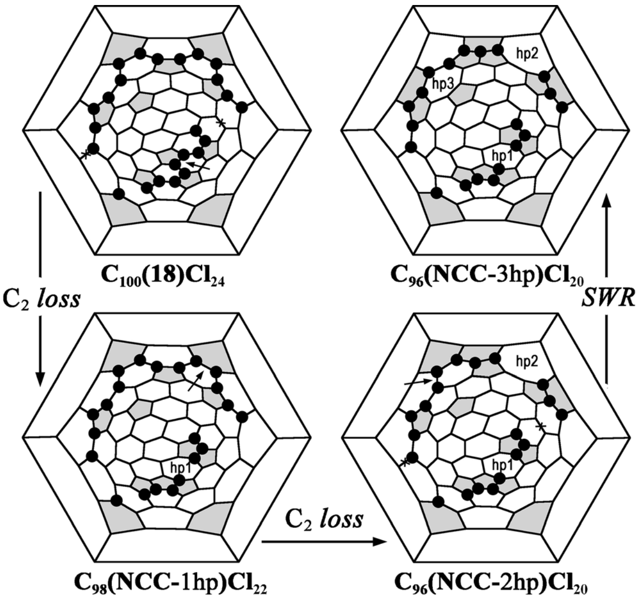

Figure 2. Schlegel diagram representation of a three-step pathway from IPR C_{100}(18)Cl_{24} via C_{98}(NCC-1hp)Cl_{22} and C_{96}(NCC-2hp)Cl_{20} to the experimentally determined C_{96}(NCC-3hp)Cl_{20}. Pentagons are shown in gray, and heptagons are labeled hp1, hp2, and hp3. Small arrows show the position of the bonds that are removed or rotated in the next step. The positions of the twofold axes of the carbon cages in C_{100}(18)Cl_{24} and C_{96}(NCC-2hp)Cl_{20} are marked with +. SWR = Stone–Wales rearrangement.

using synchrotron radiation revealed the formation of C_{96} fullerene chloride.[10]

The crystallographic results revealed that the obtained C_{96} chloride, $C_{96}Cl_{20}$, possesses a very unusual molecular structure featuring the presence of three heptagonal rings (hp) in its carbon cage (Figure 1) and, therefore should be designated as a “nonclassical carbon cage“ (NCC) in contrast to ”classical“ fullerenes containing only five- and six-membered rings. Significantly, although the possible role of heptagons in high-temperature fullerene synthesis and their formation by the loss of C_2 moieties have been intensely discussed in the literature,[11,12] so far the experimentally confirmed NCC fullerene derivatives including $C_{58}F_{18}$ and $C_{58}F_{17}(CF_3)$,[13] $C_{68}Cl_6$,[12] $C_{84}Cl_{32}$,[14] and $C_{88}Cl_{22/24}$[15] all contain only one heptagon in the carbon cage.

As a consequence of the Euler theorem, the carbon cage of C_{96}(NCC-3hp)Cl_{20} contains 15 pentagons (versus 12 pentagons in all classical fullerenes), most of which are fused forming three pentagon pairs, one sequentially fused triple, and one directly fused triple (see the top right Schlegel diagram in Figure 2). As a result, the C_{96}(NCC-3hp)Cl_{20} molecule as a whole has a rather irregular shape because the areas of pentagon fusion are protruding, whereas the regions with heptagons are concave (see Figure 1).

The attachment of 20 Cl atoms on the C_{96}(NCC-3hp) cage is quite nonuniform; the structure features a long nine-membered chain of adjacent additions together with shorter, three- and four-membered chains (Figure 2). It is known that a pentagon fusion in fullerene cages results in additional strain which can be relieved by exohedral chlorination.[16] Indeed, all common edges of fused pentagon pairs are chlorinated. In the sequentially fused triple of pentagons three vertices of two common edges are chlorinated in accordance with the rule formulated previously for such pentagon arrangements.[17] Finally, in the directly fused pentagon triple only three of four vertices of fusion are chlorinated in contrast to the only known example for lower non-IPR fullerene, $C_{64}Cl_4$[18] (see discussion below). Noteworthy, in spite of the involvement of Cl atoms in adjacent attachments, two cage pentagons are not chlorinated. Similarly, two unoccupied pentagons in chlorinated higher fullerenes with more than 12 attached Cl atoms have been reported for $C_{88}(17)Cl_{16}$[19] and $C_{104}(258)Cl_{16}$.[3]

The most interesting question arises about the origin of the C_{96}(NCC-3hp) cage because neither non-IPR nor non-classical empty fullerenes can be present in the starting material. Because the starting fraction of C_{100} was compositionally rather pure (see the Supporting Information), the pathway from IPR C_{100} to C_{96}(NCC-3hp) cage should be sought. It follows from the previous cases of IPR fullerene shrinkage that heptagonal rings can be formed by the elimination of 5:6 C−C bonds from the cage.[13–15] Obviously, two such eliminations are responsible for the formation of two heptagons, whereas the third heptagon should be created by a different way. It can be assumed that the third heptagon is obtained by a Stone–Wales rotation of a 6:6 C−C bond, which connects a pentagon with a hexagon. Such transformations have never been reported for fullerenes, but a similar rotation of a 6:6 bond in a pyrene-like fragment (four hexagons) is widely discussed as a mechanism creating so-called Stone–Wales defects in nanotubes and graphene (two pentagons and two heptagons).[20] A reconstruction of a possible pathway from C_{100} to C_{96}(NCC-3hp) revealed that only three transformation steps (in any order) are necessary, including two C_2 losses and one SW rotation of the type discussed above.

Figure 2 shows a possible three-step pathway with C_2 losses occurring first, followed by the SW rotation. The starting IPR C_{100} cage corresponds to isomer 18,[5] whereas the final and intermediate NCC cages can be properly designated with their spiral codes (see the Supporting Information).

It should be noted that the attachment positions in the starting and intermediate chlorinated fullerenes in Figure 2 are given somewhat arbitrarily. In fact, some positions, especially those in triple hexagon junctions (THJs) could be chlorinated in next steps, where THJs change to junctions of two hexagons and one pentagon (HHP). Most probably, a C_2 moiety is removed from the cage as a chlorinated species (C_2Cl_n).[14,15] The driving force of the C_2 losses and heptagon generation is the simultaneous formation of chlorinated sites at pentagon–pentagon adjacencies of fused pentagon pairs and within pentagon triples. The two C_2 losses from the C_2-C_{100}(18) cage are symmetrically related and that produces C_{96}(NCC-2hp)Cl_{20} containing the carbon cage with twofold symmetry.

Apparently, the SW rotation of a chlorinated C–C bond in the third step accompanied by the creation of the third heptagon (hp3) is driven by the formation of additional chlorinated pentagon–pentagon junctions, in particular, the directly fused pentagon triple. DFT calculations revealed this transformation to be strongly (103 kJ mol^{-1}) exothermic.[21] The SW rotation proceeds without formation of new chlorinated sites, so that one vertex of the resulting directly fused pentagon triple remains nonchlorinated. Interestingly, the cage regions of heptagons 1 and 2, which were formed by C_2 abstraction, are pronouncedly concave (see Figure 1), whereas heptagon 3, which resulted from the SW rotation, is only slightly twisted. Average pyramidalization angles at sp^3 sites (defined as the average Cl-C-C angle minus 109.5°)[17] are $-0.7°$ (THJ), $+0.2°$ (HHP), $+2.8°$ (PPH), and 4.2° (PPHp and PPP), where HHP, PPH, PPHp, and PPP designate the junctions of pentagons (P), hexagons (H), and heptagons (Hp).

The C_2-C_{100}(18) isomer can be confidently considered to be the starting IPR cage because 1) it is achievable by the shortest reconstruction path from the experimentally determined C_{96}(NCC-3hp) cage and 2) IPR–IPR transformations do not occur at the relatively low reaction temperatures of 350–360 °C used in the present study. Furthermore, C_2-C_{100}(18) isomer ranks second in stability among all 450 IPR C_{100} isomers and possesses a large HOMO–LUMO gap according to theoretical calculations.[9a] A high probability of the presence of C_{100}(18) in the fullerene soot is additionally supported by the fact that its relative content in the equilibrium mixture of C_{100} isomers is rather high over a wide temperature range as revealed by the calculation of Gibbs energies.[9a] The absence of C_{100}(18) among the most stable C_{100} isomers in other theoretical studies[9b,c] might be due to the incompleteness of the isomer sets used in the calculations.

DFT calculations of the formation energies of IPR and NCC C_{96} fullerenes and C_{96}(NCC-3hp)Cl_{20} allowed us to estimate the average energy of C–Cl bonds (chlorination enthalpy of the parent fullerene per one Cl atom).[21] As expected, the C_{96}(NCC-3hp) fullerene is energetically extremely unfavorable being 696 kJ mol^{-1} less stable than the most stable IPR D_2-C_{96}(183). However, the C_{96}(NCC-3hp)Cl_{20} molecule is very stable; its C–Cl bond energy is 42 kJ mol^{-1} higher than that in D_{3d}-$C_{60}Cl_{30}$,[22] apparently, due to the contribution from chlorinated pentagon–pentagon adjacencies, in particular, the triply fused pentagons. For comparison, the value for the non-IPR $^{\#18917}C_{76}Cl_{24}$ containing five pairs of fused pentagons is still higher (55 kJ mol^{-1}) because of additional stabilization due to the presence of the flattened coronene fragments on the unfunctionalized part of the C_{76} cage.[23] In contrast, the average C–Cl bond energy in the IPR $C_{96}(183)Cl_{24}$ molecule[24] is only 1.8 kJ mol^{-1} higher than that in D_{3d}-$C_{60}Cl_{30}$; this is in accord with the empirical rule that the C–Cl bond energy slightly decreases with the increasing number of Cl attachments.[19,24]

In contrast to the empty C_{100} fullerenes, of which the lowest-energy isomers possess numbers 449 and 18, the endohedral C_{100} fullerenes have a fully different stability order. Thus, IPR isomer D_5-C_{100}(450) was theoretically predicted to be the most favorable C_{100} cage for the endohedral fullerenes incorporating two lanthanide atoms, which are able to donate up to six electrons to the carbon cage.[25] This assumption was later confirmed by the isolation and structure determination of $La_2@C_{100}$(450).[7] Note that empty C_{100}(450) is 395th in the stability row ranking and possesses a virtually zero HOMO–LUMO gap according to theoretical calculations.[9a]

In summary, the significance of the findings of this work for the fundamental fullerene chemistry is threefold. First, a chlorinated nonclassical C_{96} fullerene featuring, for the first time, three heptagons and sequentially/directly fused pentagon triples has been isolated and structurally characterized. Second, a new transformation path to heptagons, a Stone–Wales rearrangement, has been shown to proceed in the course of chlorination under relatively mild conditions. Third, the presence of the first IPR isomer of empty C_{100} fullerene, C_2-C_{100}(18), in the arc-discharge fullerene soot has been proposed on the basis of the experimental structural data. Thus, chlorination followed by a single-crystal X-ray diffraction study proved to be a powerful means of investigating higher fullerenes available only in extremely small quantities. Structural studies on the derivatives of other C_{100} isomers are underway in our laboratories.

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[10] Synchrotron X-ray data were collected at 100 K on a MAR225 CCD detector on BL14.2 at the BESSY II electron storage ring (Berlin, Germany) ($\lambda = 0.8856$ Å). $C_{96}Cl_{20}O_{0.16}$: monoclinic, $C2/c$, $a = 14.229(1)$, $b = 25.921(2)$, $c = 33.971(3)$ Å, $\beta = 93.904(9)°$, $V = 12500.4(17)$ Å^3, $Z = 8$, $R_1/wR_2 = 0.093/0.223$ for 5724/11894 reflections and 1084 parameters. There is a small admixture of the oxidized molecule at the same crystallographic site. CCDC 972412 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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