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Communication

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Capturing C_{84} Isomers as Chlorides and Pentafluoroethyl Derivatives: $C_{84}Cl_{22}$ and $C_{84}(C_2F_5)_{12}$

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Supporting Information

ABSTRACT: A mixture of higher fullerenes $C_{76}-C_{96}$ was pentafluoroethylated with C_2F_5I at 250 °C affording a mixture of C_2F_5 derivatives. After separation with high-performance liquid chromatography, the second C_2F_5 derivative of $C_{84}(16)$, $C_{84}(C_2F_5)_{12}$, was investigated by X-ray crystallography and compared with the known isomer in terms of addition patterns and formation energies. Chlorination of a C_{84} isomeric mixture with VCl_4 at 350−400 °C resulted in the formation of $C_{84}Cl_{22}$. X-ray diffraction study revealed the superposition of several $C_{84}Cl_{22}$ molecules with different isomeric C_{84} cages but the same chlorination pattern.

Structural characterization of higher fullerenes, which typically is accomplished by means of ^{13}C NMR spectroscopy, is not fully reliable in some cases.[1] Derivatization of higher fullerenes, followed by the separation of derivatives and the use of direct methods for their characterization, appeared to be rather effective, as illustrated by some examples for $C_{76}-C_{96}$.[2]

C_{84}, the most abundant higher fullerene, has 24 possible isomers obeying the isolated pentagon rule.[3] A relatively high abundance and the richness of the isomeric composition led to a large number of experimental and theoretical studies on C_{84}. Two major C_{84} isomers, 22 and 23 (the numbering is based on the spiral algorithm[3]), were shown to be more abundant in the 2:1 ratio to one another.[4] Several minor isomers (4, 5, 11, 14, 16, and 18) have also been found in the usual fullerene mixture.[1a,b,2b,c] In particular, two C_{84} isomers, $C_s(a)$ and $C_s(b)$, were reported several times, although their assignment as isomers 14 and 16 (or reverse) was not fully unambiguous.[1a,b] Later, isomer $C_s(b)$ was proven to represent isomer 14 according to an X-ray crystallographic study of its cocrystal with silver tetraphenylporphyrin.[5] On the other hand, the cage connectivity of isomer 16 has been confirmed by structural investigation of its pentafluoroethyl derivative, $C_{84}(C_2F_5)_{12}$-I.[2c] Recently, the cage connectivity of isomer $C_{84}(5)$ has been confirmed by X-ray crystallography of its chlorides, $C_{84}Cl_{20}$ and $C_{84}Cl_{32}$, and trifluoromethyl derivative, $C_{84}(CF_3)_{16}$.[6]

In this communication, we report the synthesis, isolation, and X-ray crystallographic study of a new C_2F_5 derivative of C_{84} (isomer 16) and the chloride of C_{84}, $C_{84}Cl_{22}$, which contains several C_{84} carbon cages. The discussion concerns the addition patterns of the derivatives, their relative stabilities, and the cocrystallization phenomenon in the case of chlorides.

A mixture of higher fullerenes $C_{76}-C_{96}$ with a higher abundance of C_{84} (15 mg, MER Corp.) was pentafluoroethylated in a glass ampule with an excess of C_2F_5I (98%, Apollo) at 250 °C as described elsewhere.[2c] According to matrix-assisted laser desorption ionization mass spectrometry (MALDI MS) analysis, the mixture of C_2F_5 derivatives contained mainly $C_{76}(C_2F_5)_{10,12}$, $C_{78}(C_2F_5)_{10}$ and $C_{84}(C_2F_5)_{12}$. The product was dissolved in hexane and subjected to high-performance liquid chromatography (HPLC) separation using a Cosmosil Buckyprep column (10 mm i.d. × 25 cm, Nacalai Tesque Inc.) and hexane as the eluent (4.6 mL min^{-1}), monitored at 290 nm. In addition to the fraction containing known individual isomers of $C_{78}(C_2F_5)_{10}$,[7] $C_{84}(C_2F_5)_{12}$,[2c] and $C_{96}(C_2F_5)_{12}$,[2e] a new fraction with $C_{84}(C_2F_5)_{12}$ eluted at 8.7 min has been isolated and gave crystals after slow evaporation of the solvent. A single-crystal X-ray diffraction study with the use of synchrotron radiation (Table 1) revealed the molecular structure of $C_{84}(C_2F_5)_{12}$ with a carbon cage of isomer $C_{84}(16)$ shown in Figure 1.

This is the second case of capturing isomer $C_{84}(16)$ as a derivative with 12 attached C_2F_5 groups. Both isomeric molecules, $C_{84}(16)(C_2F_5)_{12}$-I (retention time 6.9 min at the same HPLC conditions)[2c] and $C_{84}(16)(C_2F_5)_{12}$-II, have in common that 12 C_2F_5 groups are attached by one per each cage pentagon (Figure 2). However, the comparison of the addition patterns reveals significant differences because only three C_2F_5 groups are attached in the same positions on the cage. In $C_{84}(16)(C_2F_5)_{12}$-II, all C_2F_5 groups are arranged in para positions in p-$C_6(C_2F_5)_2$ hexagons, with seven such hexagons sharing common edges, whereas two others are isolated. Therefore, the addition pattern of $C_{84}(16)(C_2F_5)_{12}$-II can be abbreviated as p^7,p,p. In $C_{84}(16)(C_2F_5)_{12}$-I, most C_2F_5 groups are arranged in p-$C_6(C_2F_5)_2$ hexagons, whereas one group is isolated on the fullerene cage. The abbreviated notation is p^5,p^2,p,i. While the formation of chains of edge-sharing p-$C_6(R^F)_2$ hexagons (R^F = CF_3, C_2F_5, C_3F_7) is a usual feature of the addition patterns of perfluoroalkylated fullerenes, isolated R^F groups on a fullerene cage are rare with only a few known examples in the molecules of $C_{70}(CF_3)_{10}$,[8a] $C_{70}(C_2F_5)_{10}$,[8b] and $C_{84}(23)(C_2F_5)_{12}$.[2c]

The cage of $C_{84}(16)$ possesses a coronene subunit, which is not functionalized in the $C_{84}(16)(C_2F_5)_{12}$-II molecule, thus resulting in a flattened region of the carbon cage (Figure 1, right). In contrast, the coronene subunit of isomer I has two attached C_2F_5 groups. In spite of significant differences in the

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Table 1. Selected Crystallographic Data of $C_{84}(C_2F_5)_{12}$-II and $C_{84}Cl_{22}$[a]

	$C_{84}(16)(C_2F_5)_{12}$-II	$C_{84}Cl_{22}\cdot 0.16Cl_2$
empirical formula	$C_{108}F_{60}$	$C_{84}Cl_{22.33}$
formula weight	2437.08	1800.44
cryst size/mm	0.03 × 0.02 × 0.02	0.05 × 0.02 × 0.01
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1/m$
a/Å	13.388(1)	12.830(1)
b/Å	23.356(2)	18.301(1)
c/Å	13.546(1)	13.385(1)
β/deg	110.329(2)	95.182(6)
V/Å^3	3971.9(5)	3130.0(4)
Z	2	2
D_{calc}/g cm^{-3}	2.038	1.910
λ/Å	0.905	0.843
reflns measd	30 908	52 102
unique data	13 650	8348
no. of param	1513	538
R1	0.103	0.049
wR2	0.252	0.137

[a] Data collection was performed on a MAR225 CCD detector at 100 K using synchrotron radiation at the BESSY storage ring (BL14.2, PSF of the Free University of Berlin, Berlin, Germany).

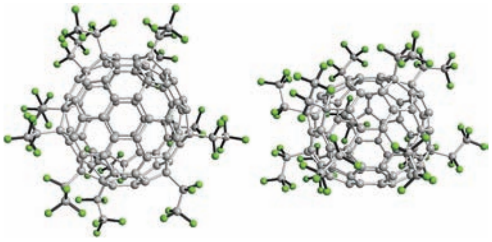

Figure 1. Two projections of $C_{84}(16)(C_2F_5)_{12}$-II. Color code: C, gray; F, green. A nonfunctionalized coronene subunit is at the center and at the bottom in the left and right projections, respectively.

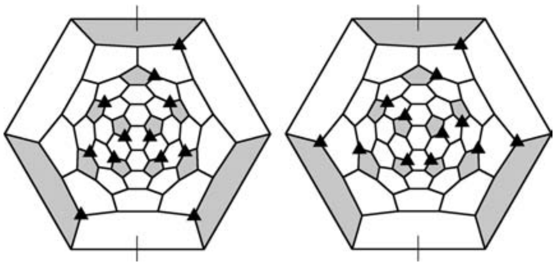

Figure 2. Schlegel diagrams of $C_{84}(16)(C_2F_5)_{12}$-I (left) and -II (right). Cage pentagons are shaded. Black triangles denote the positions of the attached C_2F_5 groups.

addition patterns of isomers I and II, the latter is only 5.1 kJ mol^{-1} more stable according to density functional theory calculations.

In other experiments, we performed chlorination of the C_{84} fraction isolated from a C_{76}−C_{96} mixture by HPLC in toluene/*o*-dichlorobenzene.[9] A total of 1−2 mg of C_{84} was chlorinated with VCl_4 in a glass ampule at 350−400 °C for 4 days. Only one type of yellow, needlelike crystals was found in the reaction product. An X-ray diffraction study with the use of synchrotron radiation revealed the structure of $C_{84}Cl_{22}$ (Table 1).

The $C_{84}Cl_{22}$ molecule adopts the crystallographic mirror symmetry and contains two C−C crosses that resulted from the formal disorder of two C−C bonds (Figure 3). The presence of C−C crosses is due to an overlap of similar $C_{84}Cl_{22}$ molecules in the same crystallographic site. Most simple interpretation of the disorder suggests that overlapped C_{84} cages correspond to isomers 14 (gray and violet C atoms) and 16 (gray and blue C atoms) in the ratio of 0.68/0.32(1). However, the simultaneous presence of the third isomeric cage, $C_{84}(11)$ (gray, two violet, and two blue C atoms) is also possible, which would imply a statistical overlap of two asymmetric (enantiomeric) molecules in equal quantities. Therefore, besides $C_{84}(14)$, C_{84} cages 16 and 11 can be present in different relative proportions to one another. All three minor C_{84} isomers were previously found in fullerene soot and confirmed by diffraction methods.[1b,2b,c]

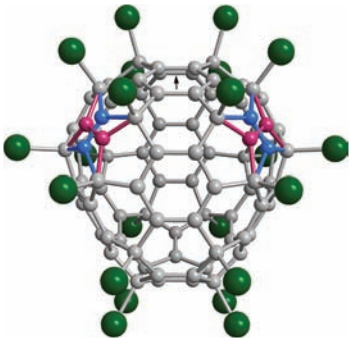

Figure 3. C_s-symmetrical molecule of $C_{84}Cl_{22}$ with two crosses of C−C bonds. Formal disorder may result from an overlap of $C_{84}(14)Cl_{22}$ (gray and violet C atoms and C−C bonds) and $C_{84}(16)Cl_{22}$ (gray and blue C atoms and bonds). In both molecules, Cl atoms (green) are attached in the same positions. The C−C bond indicated by the arrow is slightly disordered.

In fact, there is a small disorder (12%) of one more C−C bond, which is indicated by the arrow in Figure 3, that results in the additional C−C cross on a mirror plane (not shown). This implies the presence of a small admixture of $C_{84}Cl_{22}$ molecule(s) with a carbon cage of $C_{84}(12)$, -(15), or -(17). None of these C_{84} cages has been detected previously. From three possible additional cages, isomer $C_{84}(17)$ seems to be less probable because of its higher relative formation energy.[10]

Schlegel diagrams in Figure 4 demonstrate that possible isomeric $C_{84}(14)Cl_{22}$ and $C_{84}(16)Cl_{22}$ molecules differ in the orientation of only two isolated C−C bonds. A rotation of only one such bond on either side results in $C_{84}(11)Cl_{22}$. The arrow indicates the bond that is slightly disordered, thus suggesting

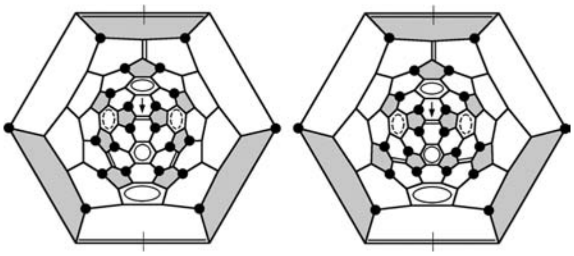

Figure 4. Schlegel diagrams of $C_{84}(14)Cl_{22}$ (left) and $C_{84}(16)Cl_{22}$ (right). Cage pentagons are shown in gray. Black circles denote attached Cl atoms. Isolated benzenoid rings and C=C bonds are also indicated. The arrow indicates the additionally disordered C−C bond.

the presence of additional C_{84} cages. In all possible cases, the positions of 22 Cl atoms remain the same on the fullerene cages, thus enabling cocrystallization of several $C_{84}Cl_{22}$ chlorides with different C_{84} cages. Similar cocrystallization phenomena also accompanied by the formation of C−C bond crosses are well documented for the pairs of cages formally connected by one Stone−Wales rearrangement such as C_{78}(2) and -(3),[11a,b] C_{84}(22) and -(23),[2a] and C_{90}(34) and -(46).[11c] In the latter example, the C_{90}(34) cage has been detected for the first time. It has been later confirmed in an isomerically pure derivative, $C_{90}(34)Cl_{32}$.[2d]

The addition patterns of $C_{84}Cl_{22}$ molecules are characterized by Cl attachments only in para positions in C_6Cl_2 hexagons, as in the above case of $C_{84}(16)(C_2F_5)_{12}$-II. However, because of the smaller size of a Cl atom compared with a C_2F_5 group, as many as 10 pentagons have two attached Cl atoms. The multiattachment of Cl atoms is accompanied by the formation of stabilizing substructures on the fullerene cage such as isolated benzenoid rings and isolated double C−C bonds (see Figure 4). Averaged C−C bond lengths in isolated (or nearly isolated) benzenoid rings lie within a narrow range of 1.39−1.40 Å; the averaged length of isolated double C−C bonds is 1.32 Å.

A somewhat unusual stoichiometry of the $C_{84}Cl_{22}$ molecules can be understood from detailed consideration of their chlorination patterns. As a rule, the use of such a strong chlorinating agent as VCl_4 results in the formation of deeper chlorinated molecules such as $C_{60}Cl_{24}$,[12a] C_2-$C_{60}Cl_{30}$,[12b] $C_{70}Cl_{28}$,[12c] $C_{78}Cl_{30}$,[12d] and $C_{90}Cl_{24}$.[2d] Therefore, one could have expected to observe the addition of at least 24 Cl atoms, i.e., two per each pentagon, to the C_{84} cages as well under the conditions employed. The insusceptibility of the $C_{84}Cl_{22}$ molecules to further chlorination can be attributed to the fact that any possible addition of the second Cl atoms in the two singly chlorinated pentagons would result in a biradical electronic shell. Otherwise, energetically unfavorable additions to C atoms at triple hexagon junctions must be involved.

Theoretical calculations have established that the relative formation energies of all experimentally confirmed minor C_{84} isomers lie up to 16 kcal mol^{-1} higher than those of the major isomers (22 and 23).[10] It is well documented that fullerene mixtures produced by the arc-discharge process always contain C_{84}(11), -(14), and -(16) as admixtures to the two main isomers 22 and 23.[1a,b,2c,5] Notably, three minor C_{84} isomers as well as three additional C_{84} cages (12, 15, and 17) can be formally interconverted by one or two Stone−Wales rearrangements.[3] These relationships indirectly support the suggestions about Stone−Wales rearrangements taking place during the fullerene synthesis.[13]

In summary, the present study has significantly contributed to the chemistry of the most abundant higher fullerene, C_{84}. Pentafluoroethylation of a fullerene mixture resulted in isolation of the second isomer of $C_{84}(16)(C_2F_5)_{12}$, allowing the discussion of the addition patterns with 12-fold C_2F_5 attachments (one per each pentagon). Chlorination of a C_{84} isomer mixture followed by a crystallographic study of $C_{84}Cl_{22}$ revealed an interesting case of cocrystallization of several molecules possibly containing carbon cages of new C_{84} isomers. The resistance of $C_{84}Cl_{22}$ to further chlorination was accounted for by the instability of $C_{84}Cl_{24}$ structures with two Cl atoms per each cage pentagon. Synthesis and investigation of new derivatives of C_{84} are currently under way in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. 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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