Inorganic Chemistry

Communication

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Trifluoromethyl and Chloro Derivatives of a Higher Fullerene D_2-$C_{80}(2)$: $C_{80}(CF_3)_{12}$ and $C_{80}Cl_{28}$

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S *Supporting Information*

ABSTRACT: Two derivatives of the low-abundant D_2-C_{80} (isomer 2), $C_{80}(CF_3)_{12}$ and $C_{80}Cl_{28}$, have been synthesized, isolated, and structurally characterized by single-crystal X-ray crystallography. Notably, the addition pattern of $C_{80}(CF_3)_{12}$ is the same as that of the known $C_{80}Cl_{12}$. The molecule of $C_{80}Cl_{28}$ contains very short (1.33 Å) and very long (up to 1.62 Å) C−C bonds in its carbon cage.

Higher fullerenes have generally much lower abundances in the fullerene soot than C_{60} and C_{70}. Among higher fullerenes, C_{80} belongs to those of smallest abundance, especially in comparison with its neighbors, C_{76}, C_{78}, and C_{84}. This results in the fact that the investigation on the chemistry of C_{80} is very scarce so far. There are seven topologically possible isolated pentagon rule (IPR) isomers of C_{80}.[1] In the pristine form, isomers 1 (D_{5d}) and 2 (D_2) have lower formation energies, indicating their higher stability, whereas other isomers show much lower stability according to theoretical calculations.[2]

Experimentally, isolation of a C_{80} fraction by high-performance liquid chromatography (HPLC) from the fullerene extract allowed identification of D_2-$C_{80}(2)$ by ^{13}C NMR spectroscopy as the most abundant C_{80} species.[3a] Later on, the lower-abundant D_{5d}-$C_{80}(1)$ was also isolated by multistage HPLC.[3b] The cage connectivity of D_2-$C_{80}(2)$ has been confirmed by X-ray crystallography of $C_{80}Cl_{12}$ obtained by chlorination with a ($TiCl_4$ + Br_2) mixture.[4] Moreover, the presence of an elusive, nonsoluble C_{2v}-$C_{80}(5)$ was established by a ^{19}F NMR study of its trifluoromethyl derivative, $C_{80}(5)(CF_3)_{12}$.[5] It is worth noting that the relative stability of C_{80} isomers changes dramatically in endohedral derivatives because of charge transfer from the encaged metal to the cage. Therefore, many endohedral fullerenes with D_{5h}-$C_{80}(6)$ and I_h-$C_{80}(7)$ cages, especially with rare-earth metal or its nitride clusters (M_3N) inside, have been synthesized, isolated, and structurally investigated as pristine and exohedrally derivatized compounds.[6]

Herein we report the synthesis and single-crystal X-ray structures of two new D_2-$C_{80}(2)$ derivatives, $C_{80}(CF_3)_{12}$ and $C_{80}Cl_{28}$. The addition patterns of both derivatives are discussed in comparison with one another and the only so far known $C_{80}(2)$ derivative, $C_{80}Cl_{12}$.

Syntheses of the CF_3 derivatives of higher fullerenes were performed by trifluoromethylation of a C_{76}/C_{96} mixture (40 mg, MER Corp.) with CF_3I in quartz ampules at 560 °C (see refs 6d and 7 for more details). The trifluoromethylation product was separated by two-step HPLC using a Buckyprep column (Nakalai Tesque, 10 mm i.d. × 250 mm) with toluene/hexane as the eluents, monitored at 290 nm. The toluene fraction eluted between 2.9 and 3.4 min at a flow rate of 4.6 mL min^{-1} was further separated in hexane at a flow rate of 2.3 mL min^{-1}. The hexane fraction eluted at 18.1 min contained $C_{80}(CF_3)_{12}$ species according to mass spectrometric analysis. Slow concentration of the hexane solution afforded small crystals of $C_{80}(CF_3)_{12}$, which were studied by X-ray diffraction using synchrotron radiation.[8]

Syntheses of C_{80} chlorides were performed using a pure C_{80} fraction as the starting material, which was isolated by multistep HPLC. Isolated C_{80} (ca. 0.05 mg) reacted with excess VCl_4 in glass ampules at 330 or 350 °C. The reaction at 330 °C for 4 days gave crystals of known $C_{80}(2)Cl_{12}$, as was revealed by an X-ray diffraction study. The reaction at 350 °C for 24 days afforded crystalline $C_{80}(2)Cl_{28}$, according to single-crystal X-ray crystallography.[8] Note that the reaction times given above correspond to the formation of crystals of suitable (but very small) sizes, whereas low-crystalline chlorides of the same compositions form earlier during the synthesis.

In the crystal structure of $C_{80}(CF_3)_{12}$, there are two crystallographically independent, but chemically identical, $C_{80}(CF_3)_{12}$ molecules with idealized D_2 symmetry (Figure 1a), which retain the symmetry of the pristine D_2-$C_{80}(2)$ cage. Significantly, the addition pattern in D_2-$C_{80}(CF_3)_{12}$ is the same as that in the known D_2-$C_{80}Cl_{12}$ molecule in spite of the considerable differences in the sizes of a CF_3 group and a Cl atom. Usually, CF_3 and chloro derivatives of fullerenes with the same stoichiometry possess rather different addition patterns, as exemplified by the structure pairs of $C_{70}(CF_3)_{16}$[9a] versus $C_{70}Cl_{16}$[10a] and $C_{76}(1)(CF_3)_{18}$[9b] versus $C_{76}(1)Cl_{18}$.[10b]

Obviously, the addend attachments in both D_2-$C_{80}(CF_3)_{12}$ and D_2-$C_{80}Cl_{12}$ molecules are governed by the same factors. First, all 12 groups/atoms are uniformly distributed on the fullerene cage with an attachment of one group/atom per each pentagon (see the Schlegel diagram in Figure 2a). Second, the

Received: February 11, 2013
Published: April 8, 2013

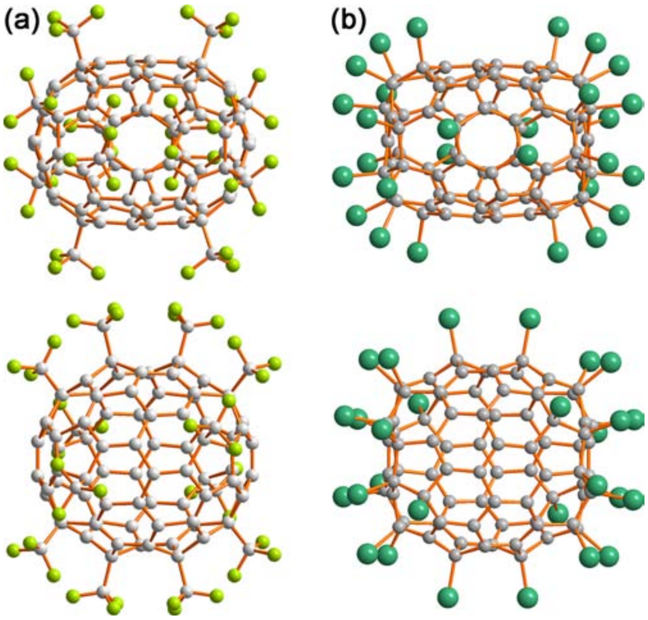

Figure 1. Projections of D_2-$C_{80}(CF_3)_{12}$ and D_2-$C_{80}Cl_{28}$ molecules along two of three 2-fold axes.

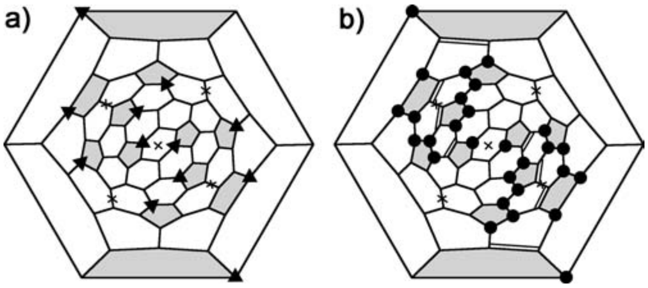

Figure 2. Schlegel diagrams of the $C_{80}(2)(CF_3/Cl)_{12}$ (a) and D_2-$C_{80}(2)Cl_{28}$ (b) molecules. Cage pentagons are highlighted in gray. Black triangles and circles denote respectively the positions of attached CF_3 groups and Cl atoms. Crosses in the centers of the hexagons or in the middle of C−C bonds indicate the positions of the 2-fold axes.

attachment of groups/atoms releases the strain in the cage due to the attachment in positions of double-hexagon junctions (DHJs), which results in flattening at the neighboring positions of triple-hexagon junctions (THJs), as discussed for the structure of D_2-$C_{80}Cl_{12}$ previously.[4] Pyramidalization angles of these THJ atoms drop from 6.6−7.9° in the pristine $C_{80}(2)$ to 2.5−5.4° in D_2-$C_{80}(CF_3)_{12}$ (3.1−5.1° in D_2-$C_{80}Cl_{12}$[4]). At the same time, the DHJ positions, which belong to interpentagonal C−C bonds (ICCBs), remain unoccupied, thus preventing addition in adjacent (ortho) positions.

Another important feature of this addition pattern is that all additions occur in para positions in cage hexagons, thus forming two para chains of six addends each. Further extension of these six-membered para chains is hampered because all para continuation positions are of the THJ type. Probably, this circumstance is responsible for an enhanced stability of D_2-$C_{80}(2)Cl_{12}$ and $C_{80}(2)(CF_3)_{12}$ molecules to further derivatization, thus enabling isolation of these compounds. A similar arrangement of 12 attached CF_3 groups in two para chains was observed in D_2-$C_{84}(CF_3)_{12}$, thus accounting for its inertness to further trifluoromethylation.[7] The shortest C−C bonds on the carbon cage [average length of 1.350 Å in both independent D_2-$C_{80}(CF_3)_{12}$ molecules] are ICCBs in para $C_6(CF_3)_2$ hexagons.

It is remarkable that both $C_{80}(2)Cl_{12}$ and $C_{80}(2)Cl_{28}$ were obtained in this work by using the same chlorination agent, VCl_4, under similar reaction conditions but for different reaction times. Previously, D_2-$C_{80}(2)Cl_{12}$ was synthesized by chlorination of $C_{80}(2)$ with a $TiCl_4$ + Br_2 mixture, the chlorination power of which is much lower (although dependent on the Br_2 concentration[11a]) than that of VCl_4. For example, the fullerene chlorides synthesized by chlorination of C_{60}, C_{70}, D_2-C_{76}, and C_{2v}-C_{78} with a $TiCl_4$ + Br_2 mixture are known to be $C_{60}Cl_6$,[11a] $C_{70}Cl_{16}$,[10a] $C_{76}Cl_{18}$,[10b] and $C_{78}Cl_{18}$,[11b] respectively, whereas the corresponding chlorides obtained with VCl_4 are C_2-$C_{60}Cl_{30}$,[11c] $C_{70}Cl_{28}$,[11d] $C_{76}Cl_{34}$,[11e] and $C_{78}Cl_{30}$.[11f] Therefore, isolation of D_2-$C_{80}Cl_{12}$ in the reaction with VCl_4 evidences a rather high stability of this molecule against further chlorination because of the peculiarities of its addition pattern discussed above.

A reaction of $C_{80}(2)$ with VCl_4 for a longer reaction time resulted in further chlorination under formation of a higher chloride, $C_{80}(2)Cl_{28}$ (Figure 1b). The chlorination pattern of a D_2-$C_{80}Cl_{28}$ molecule (Figure 2b) contains eight positions in common with D_2-$C_{80}Cl_{12}$, thus suggesting not only simple addition but also Cl atom migration on the fullerene cage during chlorination. Similar phenomena, i.e., substantial changes of the attachment positions in the course of chlorination ("chlorine dance") have been reported earlier for high-temperature chlorination of C_{60}[12] and C_{76}.[11e]

The chlorination pattern of D_2-$C_{80}Cl_{28}$ is characterized by the attachments exclusively in DHJ positions. Four cage pentagons (around the central inner and outer hexagons in Figure 2b) have one attached Cl atom each, whereas each of the other eight pentagons possesses three added Cl atoms. The chlorinated sites contribute to the formation of butadiene-like fragments and nearly isolated C═C bonds on the fullerene cage. In two independent molecules, the average bond lengths of double and single C−C bonds in C═C−C═C fragments are 1.330 and 1.420 Å, respectively, whereas nearly isolated C═C bonds have an average length of 1.347 Å. The longest C−C bonds are found in four six-membered chains with adjacently attached Cl atoms. Starting from a pentagon containing the C═C bond of a butadiene-like fragment, five C−C bonds along the chain have average lengths of 1.580, 1.616, 1.551, 1.592, and 1.614 Å, respectively. Note that the less elongated, middle C−C bond is of the 6:6 type, whereas all others are common edges of a pentagon and a hexagon (5:6). The C−Cl bond lengths lie in the range of 1.781(4)−1.822(4) Å with an average value of 1.800 Å. According to density functional theory (DFT) calculations,[12,13] the average C−Cl bond energies in two chlorides, D_2-$C_{80}(2)Cl_{12}$ and D_2-$C_{80}(2)Cl_{28}$, are respectively 10.5 and 1.2 kJ mol^{-1} higher than that in D_{3d}-$C_{60}Cl_{30}$.[14] These relations reflect a usual monotonic decrease of the C−Cl bond energy with an increase in the number of Cl atoms attached to a fullerene cage regardless of its size.[11e,15]

The carbon cages of both D_2-$C_{80}(CF_3)_{12}$ and D_2-$C_{80}Cl_{28}$ molecules have the shapes of flattened ellipsoids with more planar regions containing most THJ sites (Figure 1). The molecular packing diagrams in two crystal structures are shown in Figure 3. Interestingly, two crystallographically independent molecules in the crystal structure of D_2-$C_{80}(2)(CF_3)_{12}$ lie on different 2-fold axes, which are parallel to the *a* and *b* directions, respectively. The 2-fold axis parallel to the *a* direction passes

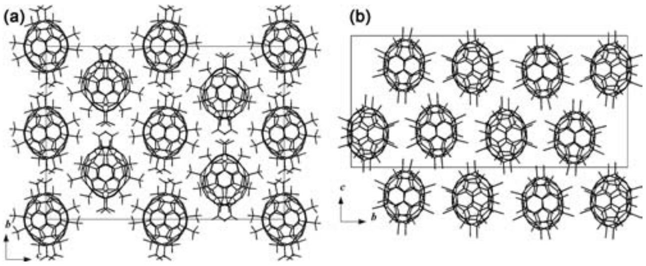

Figure 3. Packing motifs in the crystal structures of D_2-$C_{80}(2)(CF_3)_{12}$ (a) and D_2-$C_{80}Cl_{28}$ (b). Two different $C_{80}(2)(CF_3)_{12}$ molecules lie on 2-fold axes along *a* and parallel to *b*, respectively. Both independent $C_{80}Cl_{28}$ molecules are in general positions.

through the middles of the opposite C−C bonds, whereas the axis parallel to *b* goes through the centers of the opposite cage hexagons. Interestingly, a very large, channel-like void is present because of the partial loss of hexane during storage, but the packing of fullerene molecules remained intact.

In the crystal structure of $C_{80}Cl_{28}$, both crystallographically independent molecules with idealized D_2 symmetry are in general positions. A 2-fold axis of the one D_2-$C_{80}Cl_{28}$ molecule is oriented nearly parallel to the *a* direction, whereas the other independent molecule shows no special orientation relative to the crystallographic axes. The shortest intermolecular Cl···Cl distances are in the range of 3.00−3.40 Å.

In summary, two new derivatives of a low-abundant higher fullerene D_2-$C_{80}(2)$, D_2-$C_{80}(CF_3)_{12}$ and D_2-$C_{80}Cl_{28}$, have been synthesized, isolated, and structurally elucidated by X-ray crystallography. The addition pattern of D_2-$C_{80}(CF_3)_{12}$ was found to be identical with that of the known D_2-$C_{80}Cl_{12}$, which is a rare case for CF_3 and chloro derivatives of fullerenes with the same stoichiometry. The carbon cage of the D_2-$C_{80}Cl_{28}$ molecule contains fragments with short C═C bonds as well as chains of very elongated C−C bonds. Thus, the use of derivatization enables a study of the chemistry of higher fullerenes, even for those with very low abundances.

■ 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.

■ ACKNOWLEDGMENTS

This work was supported, in part, by the Russian Foundation for Basic Research (Grants 12-03-00324, 13-03-91332, and 13-03-91162), the Deutsche Forschungsgemeinschaft (Grant Ke 489/39-1), the NSFC (Grant 21132007), and "100 Talents Programme of CAS", National Basic Research Program of China (Grant 2010CB923300).

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(8) Synchrotron X-ray data were collected at 100 K at BL14.2 at the BESSY storage ring using a MAR225 CCD detector, $\lambda = 0.88561$ or 0.87933 Å. $C_{80}(CF_3)_{12}$, $M_w = 1788.92$: orthorhombic, $C222_1$, $a = 15.345(1)$ Å, $b = 26.997(1)$ Å, $c = 37.335(2)$ Å, $V = 15466.7(14)$ Å^3, $Z = 8$. There are two halves of $C_{80}(CF_3)_{12}$ molecules in the asymmetric unit; the peak of the residual electron density is located in the large, channel-like void. After using *SQUEEZE*, refinement with 17066 reflections and 1153 parameters yielded a conventional R1(*F*) = 0.049 for 15257 reflections with $I > 2\sigma(I)$ and wR2(F^2) = 0.128 for all reflections. $C_{80}Cl_{28.12}\cdot 0.017Cl_2$, $M_w = 1958.89$: monoclinic, $P2_1/n$, $a = 14.511(1)$ Å, $b = 43.534(3)$ Å, $c = 20.824(1)$ Å, $\beta = 99.786(8)°$, $V = 13006.9(14)$ Å^3, $Z = 8$. There are two $C_{80}Cl_{28}$ molecules in the asymmetric unit. Anisotropic refinement with 28520 reflections and 1972 parameters yielded a conventional R1(*F*) = 0.063 for 26748 reflections with $I > 2\sigma(I)$ and wR2(F^2) = 0.147.

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