Synthesis, Separation and Structure Elucidation of a Missing C$_{60}$ Chloride: C_{2v}-C$_{60}$Cl$_8$

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Dedicated to Professor Heribert Offermanns on the occasion of his 75th birthday

The so far missing chloro analog of the bromofullerene C_{2v}-C$_{60}$Br$_8$ has been synthesized by reaction of C$_{60}$ fullerene with iodine monochloride. The title compound has been separated by means of HPLC, and its molecular structure has been unambiguously determined by single-crystal X-ray analysis. A facile synthesis of C_s-C$_{60}$Cl$_6$ and C_{2v}-C$_{60}$Cl$_8$ in preparative amounts is presented.

Key words: Chlorinated Fullerenes, Crystal Structure, Iodine Monochloride

Introduction

The family of fullerenes is offering stunning opportunities for chemical research, including promising vistas for potential applications, *e. g.* as functional materials [1 – 3]. In the first place, the pristine fullerenes need to be synthesized, isolated and characterized with respect to their individual structural, electronic and physical properties. Next, the virtually innumerable options for derivatization deserve to be explored. The most versatile procedure in this context is halogenation [4 – 6]. Among the halofullerenes the chloro derivatives are the ones targeted most. They represent versatile syntons because their stabilities and solubilities best fulfill the requirements for subsequent derivatization. Importantly, the chlorination of pristine fullerenes is frequently regioselective and effective for the synthesis of various C$_{60}$ chlorides and chlorinated higher fullerenes [4 – 17]. As an alternative to postsynthetic chlorination, the *in-situ* chlorination during conventional fullerene synthesis has demonstrated rich potential for stabilizing unstable fullerenes, allowing access to exotic fullerene cages that do not obey the isolated−pentagon rule (non-IPR fullerenes) [18 – 28]. A closer inspection of the chlorination patterns has revealed some unexpected systematics, even allowing for predicting site selectivities for fullerene chlorination [10, 27, 29]. To a certain extent, these regularities are reflected by numerous bromo and chloro derivatives of fullerenes displaying identical halogenation patterns. However, the chlorine analog of one of the first isolated and characterized bromofullerenes, C$_{60}$Br$_8$ [30 – 34], had thus far escaped discovery. Here we report on the synthesis and isolation of C$_{60}$Cl$_8$ in pure form, and its structure determination in a solvate crystal.

Results and Discussion

The first selective chlorination of a fullerene was demonstrated for the synthesis of C_s-C$_{60}$Cl$_6$ utilizing iodine monochloride as a chlorinating agent [35]. Later, the reaction conditions were optimized, and it was shown that C$_{60}$Cl$_6$ can be obtained by reaction with ICl in chlorobenzene with more than 90 % purity [36]. It has also been found that the selectivity of the chlorination is extremely sensitive to the temperature, the solvent used, the concentration of reagents, and the time of reaction. Thus utilizing ICl as a chlorinating agent, several chloro derivatives C$_{60}$Cl$_2$ [37], C$_{60}$Cl$_4$ [37], C$_{60}$Cl$_{10}$ [37], C$_{60}$Cl$_{12}$ [38], C$_{60}$Cl$_{28}$ [39], and C$_{60}$Cl$_{30}$ [40] were obtained and characterized. The chlorination of higher fullerenes using ICl has also been reported and found to be selective [15, 41, 42]. On the other hand, the high selectivity of chlorination is often overemphasized, and the reaction frequently results in the formation of a complex mixture which requires further HPLC purification. Recently the chlo-

rination of C_{60} with iodine monochloride in chlorobenzene was studied in great detail [37]. It was shown that besides readily formed $C_{60}Cl_6$ a mixture of various chlorofullerenes $C_{60}Cl_n$, with n ranging from 2 to 12 can be obtained depending on the reaction time and the molar ratio of C_{60} to ICl. The utilized synthetic procedure requires removal of all volatiles "immediately" after the addition of ICl under reduced pressure which usually takes several minutes. The main drawbacks of the approach are difficulties connected with controlling the evaporation time which greatly depends on the amount of solvent and on the equipment used. As a consequence important reaction conditions such as the concentration of reagents and the time of the reaction cannot be managed properly. Moreover the reaction cannot be carried out at low temperature and the process is difficult to scale-up. To avoid the above mentioned drawbacks we have modified the original procedure. Instead of the evaporation step the reaction mixture was diluted with hexane, which leads to immediate quenching of the reaction and precipitation of the products. Using this improved protocol $C_{60}Cl_6$ can be easily obtained by reaction of C_{60} and ICl in chlorobenzene at 25 °C in a few minutes. Notably, the synthesis is characterized by high reproducibility and can be easily scaled up. According to HPLC analysis, the purity of $C_{60}Cl_6$ obtained is essentially the same as reported for the product synthesized by the original protocol with solvent evaporation (95 %) [36]. A slight increase in the selectivity of $C_{60}Cl_6$ formation was observed when the reaction was carried out at 0 °C (Fig. 1a). In contrast to the low temperature synthesis, reactions at 50 and 80 °C result in noticeable formation of an additional chlorofullerene as indicated by subsequent HPLC analysis (Fig. 1b). Small amounts of the same compound (as can be concluded from equal retention time and UV/Vis spectral identity) can also be found in the products of the low-temperature synthesis (Fig. 1a). Importantly in this case the new chlorofullerene is formed in very small amounts and coelutes with several other unknown chlorofullerenes preventing its easy separation (previously this fraction was assigned to a mixture of $C_{60}Cl_8/C_{60}Cl_{10}$ based on LDI-MS analysis [36]). In contrast, the synthesis at higher temperatures yields the new chlorofullerene as the second dominating product after $C_{60}Cl_6$. The compound eluted as an individual isomer as indicated by the symmetrical shape of the corresponding peak in the HPLC chromatogram (Fig. 1b). Further, it was shown that
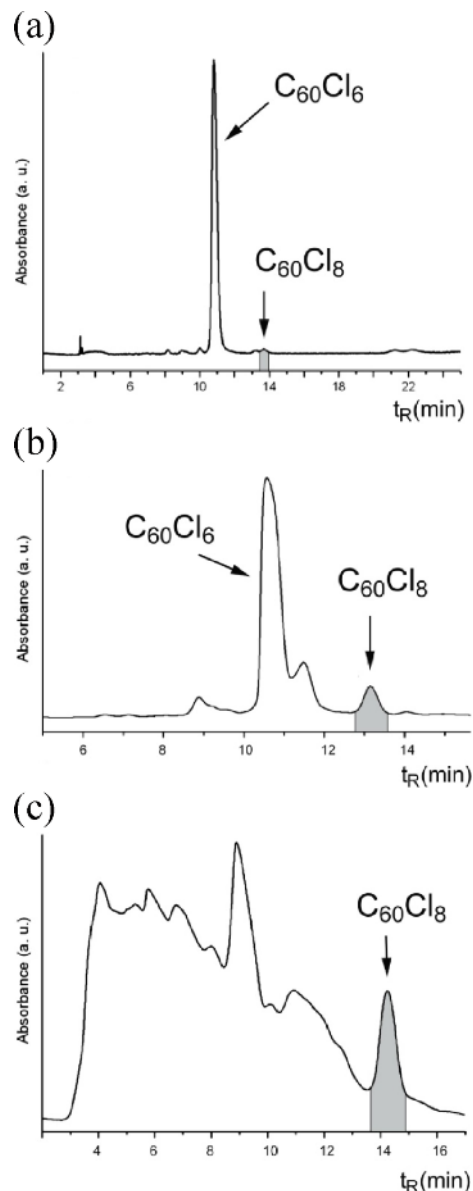

Fig. 1. HPLC traces of samples containing $C_{60}Cl_8$ prepared in this work by chlorination of C_{60} fullerene with iodine monochloride. The fractions containing $C_{60}Cl_8$ (2,5,8,10,15,18,24,27-$C_{60}Cl_8$) are highlighted in grey; a) reaction conditions: chlorobenzene, ICl (25 eq.), 0 °C, 3 h. HPLC conditions: 5PYE column, toluene-hexane 4 : 1 v/v, 1 mL min^{-1}, 25 °C, 300 nm detection; b) reaction conditions: chlorobenzene, ICl (25 eq.), 50 °C, 10 min. HPLC conditions: 5PYE column, toluene-hexane 4 : 1 v/v, 1 mL min^{-1}, 25 °C, 300 nm detection; c) reaction conditions: *o*-dichlorobenzene, ICl (30 eq.), 25 °C, 3 h. HPLC conditions: Buckyprep column, toluene, 4 mL min^{-1}, 25 °C, 300 nm detection.

the newly formed compound is not a product of further chlorination of $C_{60}Cl_6$ since no formation of this chlorofullerene was observed during chlorination of HPLC-purified $C_{60}Cl_6$. These results demonstrate that the formation of $C_{60}Cl_6$ and the new chlorofullerene are two independent processes, which thus represent a classic case of two kinetically controlled concurrent reactions. Thus, at low temperatures only one product is formed, whereas an increase of the reaction temperature reduces the selectivity and both processes take place with comparable probability.

The same compound (as indicated by UV/Vis spectra identity) has also been observed in the reaction of C_{60} with ICl in *o*-dichlorobenzene at 25 °C. Although a very complex mixture of chlorofullerenes is formed in this case the target compound can be rather easily separated (Fig. 1c). Notably, in both cases (synthesis in chlorobenzene at 50 °C and synthesis in *o*-dichlorobenzene at 25 °C) effective purification of the title compound can be achieved in just one HPLC step, which is suitable for preparative separation.

The corresponding chlorofullerene was obtained in mg scale after preparative HPLC separation, enabling its further characterization. The compound was found to be stable in the solid state as well as in toluene solution (in air, dark), evidenced by the absence of any degradation products after storage for several months. The LDI-MS analysis was found to be uninformative since under these conditions all chlorine atoms are stripped and only a single peak at $m/z = 720.0$ corresponding to the pristine C_{60} can be observed. C_{60} chloride was analyzed using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix which is known to be the best to prevent fragmentation of chlorofullerenes [36]. In MALDI experiments with DCTB the chlorinated species $C_{60}Cl_9^-$, $C_{60}Cl_7^-$ and $C_{60}Cl_5^-$ were detected, indicating that the most probable composition of the separated chlorofullerene is $C_{60}Cl_8$ (*trans*-chlorination and loss of chlorine under MALDI conditions are typical for chlorofullerenes [36]). The presence of a low-intensity signal corresponding to $C_{60}Cl_{11}$ could arise from trace amounts of $C_{60}Cl_{10}$, although the formation of this ion from $C_{60}Cl_8$ cannot be excluded. The UV/Vis and MALDI-MS spectra of the purified sample are presented in Fig. 2.

The new chlorofullerene was crystallized by slow evaporation of a toluene-hexane solution resulting in small orange crystals. The quality of the crystal allowed to collect a good single-crystal diffraction data set and to reliably determine the crystal structure, presenting all atoms of the chlorofullerene in ordered and fixed positions. Highly disordered solvent molecules occupying the tunnel-like voids were modeled with partially occupied carbon positions. The presence of disordered solvent molecules is the reason for the high *R* value. Fortunately, this disorder did not impair the identification of the connectivity of chlorofullerene. Despite the high *R* value, the quality of the data has allowed for refining all carbon and chlorine positions in C_{60} chloride without any restraints. The structure determination and refinement revealed the chlorofullerene $C_{2v}-C_{60}Cl_8$ (2,5,8,10,15,18,24,27-$C_{60}Cl_8$) with an addition pattern previously found in the brominated analog 2,5,8,10,15,18,24,27-$C_{60}Br_8$ [30 – 34]. The Schlegel diagram and ORTEP projection are presented in Fig. 3.

The title compound crystallizes in the monoclinic space group $P2/n$ with $Z = 2$ forming numerous short intermolecular C···C and Cl···Cl contacts, which are rather typical for chlorinated fullerenes [7 – 10]. Each $C_{60}Cl_8$ molecule is involved in six short Cl···Cl contacts (3.28 – 3.40 Å) with neighboring molecules, thus formally forming a 2D network in the (010) plane as presented in Fig. 4. The corresponding "layers" are stacked in an AA sequence producing tunnellike voids
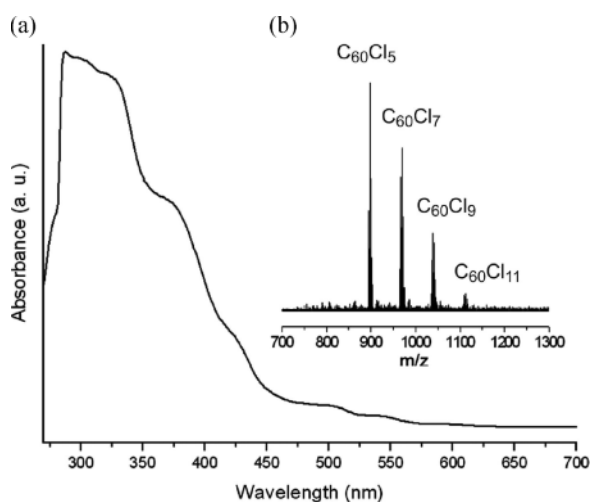

Fig. 2. a) UV/Vis spectrum of 2,5,8,10,15,18,24,27-$C_{60}Cl_8$ (toluene); b) MALDI mass spectrum of purified $C_{60}Cl_8$ (DCTB as a matrix, negative mode).
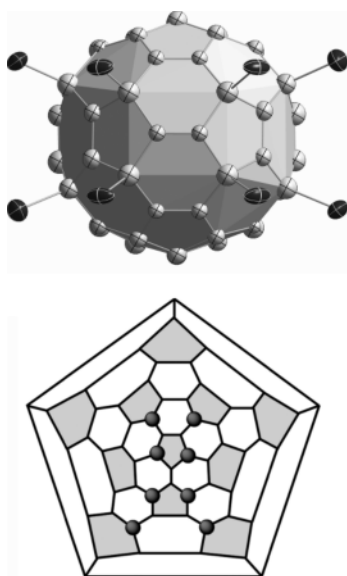
Fig. 3. Molecular structure and Schlegel diagram of 2,5,8,10,15,18,24,27-$C_{60}Cl_8$; (top) ORTEP plot of C_{2v}-$C_{60}Cl_8$. The carbon atoms are given in grey, the chlorine atoms in black. Displacement ellipsoids are set at 30% probability level; (bottom) The Schlegel diagram of $C_{60}Cl_8$ showing the chlorination pattern. Black circles correspond to chlorine atoms, pentagons are highlighted in grey.
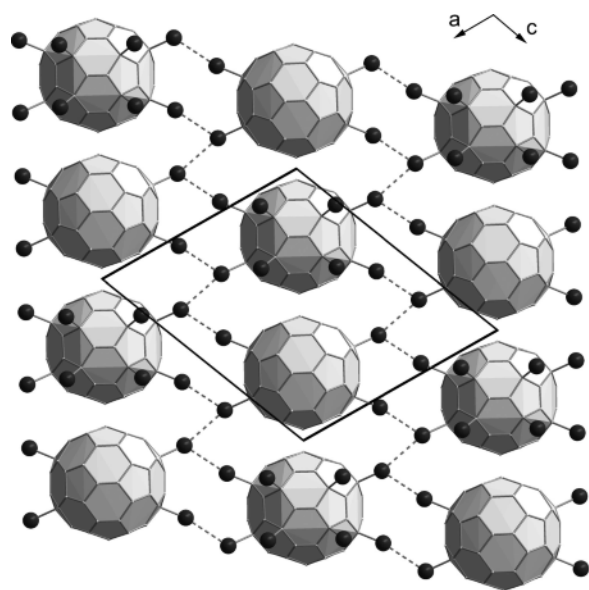

Fig. 4. Crystal structure of 2,5,8,10,15,18,24,27-$C_{60}Cl_8\cdot Sol_x$ projected onto (010) showing short two- and three-centered Cl···Cl contacts (represented by dashed lines). The unit cell is highlighted by black lines. The chlorine atoms are represented as black circles. The disordered solvent molecules (Sol) are omitted for clarity.
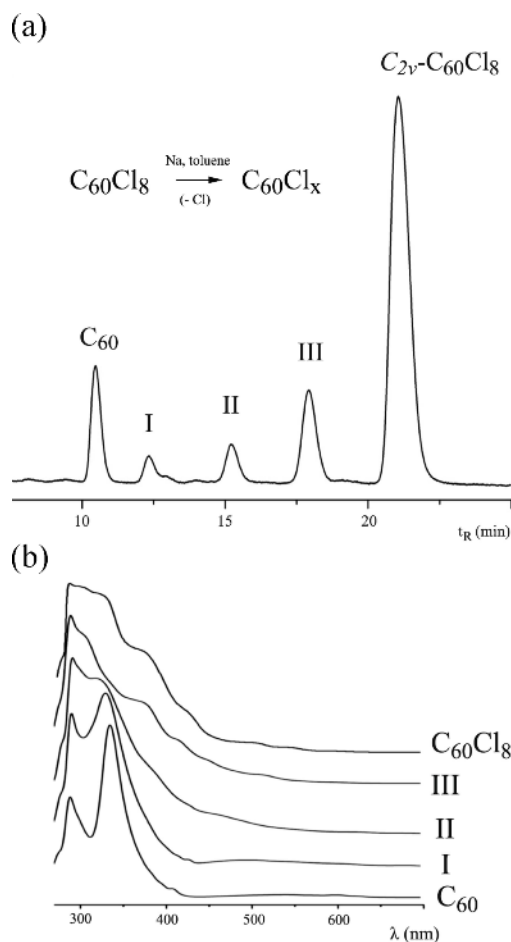

Fig. 5. Stepwise dechlorination of $C_{60}Cl_8$ by reaction with metallic Na in toluene; a) HPLC profile showing the formation of several unconventional chlorofullerenes (**I**, **II** and **III**) and prestine C_{60} fullerene. (Buckyprep, toluene/hexane, 7 : 3 v/v); b) UV/Vis spectra of starting $C_{60}Cl_8$ and corresponding dechlorination products.

along [101], which are filled with disordered solvent molecules.

Due to its high molecular symmetry, the discovered C_{2v}-$C_{60}Cl_8$ represents a prospective synton for further modification. Since the molecule possesses only two non-equivalent chlorine atoms, the selective transformation of $C_{60}Cl_8$ into various C_{60} fullerene derivatives seems to be very promising. Moreover, $C_{2v}-C_{60}Cl_8$ provides opportunities for the synthesis of new chlorofullerenes by its further chlorination or dechlorination. In a test experiment it was found that a stepwise dechlorination takes place upon reaction of the

title $C_{60}Cl_8$ with metallic Na in toluene. In this case the formation of new chlorofullerenes with an unconventional chlorination pattern has been monitored by HPLC-UV/Vis analysis (Fig. 5).

Conclusion

Summarizing, experimental evidence of the missing C_{2v}-$C_{60}Cl_8$ has been provided for the first time. The compound has been synthesized, separated and unambiguously characterized by single-crystal X-ray analysis. It was shown that the formation of $C_{60}Cl_6$ and of the title $C_{60}Cl_8$ from C_{60} and ICl are two concurrent kinetically controlled processes. The optimal conditions for synthesis and separation of the new chlorofullerene C_{2v}-$C_{60}Cl_8$ are presented. Due to its high symmetry, the new $C_{60}Cl_8$ chlorofullerene represents an attractive synton for further modification. The possibility of stepwise dechlorination of chlorofullerenes has been demonstrated for the first time.

Experimental Section

General information

C_{60} fullerene (MER, 99.9%), iodine monochloride (Merck), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (Fluka) and the reagent-grade solvents chlorobenzene (Acros organics), *o*-dichlorobenzene (Sigma-Aldrich) and hexane (Roth), were used as received. HPLC-grade toluene (Fisher Scientific) and hexane (Fisher Scientific) were used for HPLC separation. HPLC analysis was performed on a Shimadzu CBM-20A (SPD-M20A DAD detector) equipped with a 4.6 mm × 250 mm Cosmosil 5PYE column. For preparative separation a 10 mm × 250 mm Cosmosil Buckyprep column was used.

Synthesis

2,5,8,10,15,18,24,27-$C_{60}Cl_8$

Method A: 310 mg (0.1 mL, 25 equiv.) of ICl was added to a solution of 55 mg of C_{60} in 20 mL chlorobenzene at 50 °C. After stirring for 5 min at 50 °C the reaction mixture was poured in 100 mL of cooled hexane (−20 °C) and kept at −20 °C for 10 min. The precipitate formed was filtered off and washed with small amounts of hexane resulting in an orange crystalline powder (50–60 mg). Pure $C_{60}Cl_8$ was obtained after HPLC separation (see main text).

Method B: 250 mg of C_{60} was dissolved in 30 mL of *o*-dichlorobenzene, and 1.7 g (30 equiv.) of ICl was added. The mixture was stirred at 25 °C for 10 min, and the solvent

and excess ICl were removed at room temperature under vacuum over 3 h. The resulting products were redissolved in dichloromethane und the solvent evaporated again. The resulting red-brown solid was dissolved in toluene and filtered through a micro filter before HPLC separation. Pure $C_{60}Cl_8$ was obtained after HPLC separation (see main text). UV/Vis (toluene): $\lambda_{max} = 278, 287, 304, 324, 371, 422, 500, 544$ nm.

1,6,9,12,15,18-$C_{60}Cl_6$

310 mg (0.1 mL, 25 equiv.) of ICl was added to a solution of 55 mg of C_{60} in 20 mL chlorobenzene at 0 °C. The reaction mixture was stirred for 3 h at 0 °C, poured in 100 mL of cooled hexane (−20 °C) and kept for additional 30 min at −20 °C. The precipitate formed was filtered off and washed with small amounts of hexane resulting in an orange crystalline powder (62 mg, 87%). The estimated purity of the $C_{60}Cl_6$ obtained was about 95% (HPLC analysis). Spectroscopic data were found to be in agreement with those previously reported [36].

Dechlorination of 2,5,8,10,15,18,24,27-$C_{60}Cl_8$

Small amounts (0.5 – 1 mg) of HPLC-purified $C_{60}Cl_8$ were dissolved in 20 mL of dry toluene. A small piece of freshly cut sodium metal (5 – 10 mg) was added, and the mixture was stirred at room temperature for 1 h (argon atmosphere). The solution was filtered through micro filter and analyzed by means of HPLC (see main text).

Table 1. Crystal structure data for $C_{60}Cl_8$.

Formula	$C_{60}Cl_8 \cdot (Sol)_x$
Formula weight	1154.33
Color and shape	orange block
Crystal size, mm^3	$0.1 \times 0.1 \times 0.1$
Temperature, K	100(2)
Crystal system	monoclinic
Space group, Z	$P2/n$, 2
a, Å	13.60(2)
b, Å	10.947(19)
c, Å	15.69(3)
β, deg	111.767(19)
V, Å^3	3874 (6)
D_{calcd}, g cm^{-3}	1.89
Absorption coefficient, mm^{-1}	0.6
Diffractometer	Smart APEX II, Bruker AXS
Radiation; λ, Å	MoK_α; 0.71073
$2\theta_{max}$, deg	38
hkl range	$\pm12, \pm9, \pm14$
Absorption correction	multi-scan, SADABS
Reflections collected / independent	1725 / 1020
No. of ref. parameters	228
R_1 / $wR_2(F^2)$ [$F^2 > 2\ \sigma(F^2)$]	0.1528 / 0.3769
R$_1$ / wR_2 (all data)	0.2246 / 0.4260
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.803 / −0.451

Crystal structure determination of
2,5,8,10,15,18,24,27-$C_{60}Cl_8$

X-Ray measurements were performed with a Smart APEX II diffractometer (Bruker AXS) with MoK_α radiation ($\lambda = 0.71073$ Å) at 100 K. For data reduction the Bruker Suite software package was used, and SADABS was applied for absorption correction [43, 44]. The structure was determined by Direct Methods and refined by full-matrix least-squares fitting using the SHELXTL software package [45]. All atomic positions and displacement parameters of all chlorine atoms were refined freely. All carbon atoms of the fullerene cage were refined isotropically. Selected crystallographic parameters are listed in Table 1.

CCDC 890613 contains the supplementary crystallographic data for this paper. This 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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