Zeitschrift für Anorganische und
Allgemeine Chemie

Synthesis and Structure of a Highly Chlorinated C₇₈: C₇₈(2)Cl₃₀

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.200900206.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	06-May-2009
Complete List of Authors:	Kemnitz, Erhard; Humboldt-University, Chemistry
Keywords:	Fullerene, C ₇₈ , Cage isomers, Chlorination, Structure elucidation

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43

ARTICLE

DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

Synthesis and Structure of a Highly Chlorinated C₇₈: C₇₈(2)Cl₃₀Sergey I. Troyanov,^[a] Nadezhda B. Tamm,^[a] Chuanbao Chen,^[b] Shangfeng Yang,^[b] and Erhard Kemnitz^{*,[c]}*Dedicated to Prof. Martin Jansen on the Occasion of his 65 birthday*

A Highly chlorinated C₇₈ fullerene, C₇₈(2)Cl₃₀, has been obtained by the reaction of the isomer C₇₈ (2) with SbCl₅ in ampoules at 330–340 °C. Single crystal structure determination revealed that the C_{2v}-C₇₈Cl₃₀ molecule contains only isolated double bonds and aromatic

benzenoid rings in the C₇₈ carbon cage. Therefore, C₇₈Cl₃₀ represents the highest possible chlorination degree for C₇₈ fullerenes **obtained so far**.

- [a] Chemistry Department, Moscow State University, Leninskie Gory, 119991 Moscow, Russia
Fax: +007 494 9391240
E-mail: stroyano@thermo.chem.msu.ru
- [b] Hefei National Laboratory for Physical Sciences at Microscale & Department of Materials Science and Engineering, University of Science and Technology of China (USTC), Hefei 230026, China
- [c] Institute of Chemistry, Humboldt University, Brook-Taylor Str. 2, 12489 Berlin, Germany
Fax: +49 030 20937277
E-mail: erhard.kemnitz@chemie.hu-berlin.de

synthesis and single crystal X-ray study of C₇₈Cl₃₀ which seems to be the highest chloride of C₇₈ fullerene.

Experimental Section

C₇₈ fullerene was separated from toluene extraction of the fullerene soot by a two-step HPLC using a Cosmosil Buckyprep column (10 mm i.d. x 250 mm, Nacalai Tesque Inc.) and toluene as the eluent (5.0 mL min⁻¹ flow rate, 320 nm). Briefly, in the first-step HPLC a mixed fraction comprised of C₇₆ and two isomers of C₇₈ was collected, which was subjected to the second-step recycling HPLC separation. After two cycles, the major isomer of C₇₈ was successfully obtained with the identification and purity confirmed by MALDI-TOF MS analysis. UV-Vis spectrum of the isolated C₇₈ fullerene dissolved in toluene was recorded on a UV-Vis-NIR 3600 spectrometer (Shimadzu, Japan).

Approximately 0.3 mg of C₇₈ (2) was placed into a glass ampoule and 0.3 mL SbCl₅ was added. The ampoule was cooled, evacuated, and sealed off. Heating the ampoule at 330–340 °C for 2–3 days produced orange crystals which, after ampoule opening, were separated by decanting SbCl₅ and washing with conc. HCl.

The data for crystal with dimensions of 0.20×0.15×0.12 mm³ were collected on an IPDS diffractometer (Stoe) at 100 K using graphite monochromatized Mo-K_α-radiation, $\lambda = 0.71073$ Å, $2\theta_{\max} = 58.4^\circ$; $-28 < h, k < 28$, $-43 < l < 43$, $R_{\text{int}} = 0.063$. Structure solution and refinement were performed with SHELXS97 and SHELXL97, respectively. Absorption correction was not applied. Crystal data for C₇₈Cl₃₀·Cl₂: $M = 2071.18$, tetragonal, space group $I \bar{4}$, $a = 20.7619(3)$, $c = 31.4440(6)$ Å, $V = 13554.1(4)$ Å³, $Z = 8$, $D_{\text{calc}} = 2.030$ g cm⁻³, $\mu = 1.333$ mm⁻¹; reflections collected 76817, independent 18284, $wR_2 = 0.067$ for 18274 reflections and 1019 parameters, $R_1 = 0.030$ for 17653 reflections with $I > 2\sigma(I)$. Whereas C₇₈Cl₃₀ molecule is fully ordered, the solvated Cl₂ molecule is highly disordered between several positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-726149. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) _44-1223-336-033; E-Mail: data_request@ccdc.cam.ac.uk].

Introduction

Fullerene halides were among the first structurally investigated fullerene derivatives [1]. On the one hand, they can serve as intermediates for further derivatization of fullerenes. On the other hand, they sometimes facilitate characterization of the connectivity patterns of higher fullerenes. Chlorides of a given fullerene comprise a range of compositions, which lies between those of bromides and fluorides. For example, the known chlorides of C₆₀ contain 6 to 30 attached Cl atoms [2–5], whereas extreme compositions for bromide are C₆₀Br₆ [1] and C₆₀Br₂₄ [6], and those reported for fluorides are C₆₀F₂ and C₆₀F₄₈ [7]. Interestingly, lower chlorides of C₆₀ and C₇₀, C₆₀Cl₆ [2] and C₇₀Cl₁₀ [8], differ significantly in their properties such as solubility, stability and reactivity from the corresponding higher chlorides, C₆₀Cl₃₀ [4, 5] and C₇₀Cl₂₈ [9].

In the last years, remarkable progress has been achieved in synthesis and investigation of chlorides of higher fullerenes. Using the reaction of fullerenes with a mixture of TiCl₄ and bromine, higher fullerenes D₂-C₇₆ (1), three isomers of C₇₈ (C_{2v} (2), C_{2v} (3), and D_{3h} (5)), and D₂-C₈₀ (2) have been selectively chlorinated, respectively, to C₇₆Cl₁₈ [10], C₇₈Cl₁₈ [11, 12], and C₈₀Cl₁₂ [13] in crystalline form thus enabling structural investigation of the connectivity pattern in pristine fullerenes. The chlorinating power of TiCl₄ and Br₂ mixtures depends on the bromine concentration [14, 15], however, on average, it results in the formation of chlorides with lower to middle chlorine content. Higher chlorides can be produced by using stronger chlorinating agents such as Cl₂ or some inorganic chlorides (ICl, SbCl₅ etc.) at higher temperature [16]. For instance, recently chlorination of the mixture of higher fullerenes with SbCl₅ resulted in isolation and structural characterization of C₉₀Cl₃₂ [17]. In this paper, we report the

Results and Discussion

As shown by Wakabayashi et al. [18], fullerene soot production performed at significantly different conditions could result in fullerene mixtures in which C_{78} is represented by three cage isomers, D_3 (1), C_{2v} (2), and C_{2v}' (3), in significantly different ratios. Obviously, these circumstances account for different isomeric compositions of C_{78} as reported by some authors [19, 20]. In our case, the first of two C_{78} fractions is the major isomer and contains mainly the isomer C_{2v} - C_{78} (2) according to UV-Vis spectra, thus resembling the first C_{78} fraction described by Diederich et al. in their report concerning isolation and characterization of C_{78} isomers (1) and (2) [21].

Our X-ray crystallographic study of several single crystals revealed the formation of the same chlorinated derivative of C_{78} , $C_{78}Cl_{30}$ (Fig. 1). The C_{78} carbon cage in $C_{78}Cl_{30}$ can be easily recognized as C_{78} (2) (with the following spiral code: 1,7,9,11,13,24,27,30,32,36,38,40 [22]) due to the presence of only one horizontal C-C bond in the equatorial belt and the presence of a coronene subunit on the opposite side of the cage (Figure 2). The $C_{78}Cl_{30}$ molecule as a whole retains (non-crystallographic) C_{2v} symmetry of the initial C_{78} (2) cage with a two-fold axis passing through the middle point of the central C-C bond and the centre of the coronene subunit.

Insert Figure 1 here

Thirty Cl atoms are attached in 1,2-, 1,3-, and 1,4-positions in carbon hexagons so that the remaining (non-chlorinated) C atoms form either isolated C-C double bonds or aromatic benzenoid rings. There are altogether nine isolated double bonds with an averaged C-C distance of 1.33 Å and five flattened benzenoid rings with averaged C-C distances of 1.39-1.41 Å. Most uniform (1.406 ± 0.006 Å) are C-C bonds in the central hexagon of the coronene subunit; its high aromaticity also becomes apparent in a high planarity of this cage region (Fig. 1, right). Four other aromatic benzenoid rings have one or two edge-sharing pentagons in their cage surroundings; C-C bonds of hexagon-pentagon junctions are the shortest (1.37-1.38 Å) among C-C ring bonds thus resulting in less uniform distribution of bondlengths and, therefore, less flat regions of the cage. Unfortunately, a comparison with bondlengths in a non-functionalized C_{2v} - C_{78} (2) molecule is not possible, because the only available data concern a disordered C_{2v} - C_{78} molecule (due to an overlap of two closely situated molecules) in co-crystals with Cu-tetraphenylporphyrin [23].

It is worth noting that all other reported chlorides of C_{78} were synthesized by chlorination of individual C_{78} isomers or their mixtures with solutions of Br_2 in $TiCl_4$ [11,12,14]. They all have the same composition $C_{78}Cl_{18}$ and are characterized by the same addition pattern of 18 Cl atoms on slightly different C_{78} carbon cages. Bromination of C_{78} (as a by-mixture to C_{70}) produced $C_{78}Br_{18}$ (co-crystals with isomeric cages 2 and 3) possessing the same addition pattern of 18 Br atoms [24]. The attachment of 18 halogen atoms to C_{78} cages results in three isolated bonds and three aromatic benzenoid rings, whereas the remaining cage has larger regions with delocalized C-C bonds. C-C bonds in benzenoid rings

Insert Figure 2 here

are 1.392-1.403 Å long, i.e. they are in the same range as in the $C_{78}Cl_{30}$ molecule. Isolated double bonds in the $C_{78}(2)Cl_{18}$ molecule can not be calculated reliably because of a statistical disorder resulting in a higher D_{3d} molecular symmetry. A comparison of the addition patterns of $C_{78}(2)Cl_{30}$ and $C_{78}(2)Cl_{18}$ [11] (Fig. 2) demonstrates that the latter is a substructure of the former being most probably its precursor in the course of chlorination.

Because of the presence of only isolated double bonds and benzenoid rings and also due to an effective shielding of these fragments by the attached Cl atoms, $C_{78}(2)Cl_{30}$ obviously represents the highest possible degree of chlorination of C_{2v} - C_{78} (2). Chlorination of each isolated double bond would generate triple Cl...Cl contacts, which are known to be avoided due to strong repulsion [5]. Even in the fullerene fluoride $C_{60}F_{48}$, six isolated C-C bonds are effectively shielded making this compound highly stable. Attempts to further fluorinate $C_{60}F_{48}$ result in a cage destruction [24]. Other structurally similar C_{78} isomers except for D_3 - C_{78} (1) would also attach a maximum of 30 Cl atoms with the same addition pattern. Noteworthy, the use of $SbCl_5$ as chlorination agent at elevated temperature seems to facilitate the formation of the highest possible fullerene chloride as already found for the chlorination of C_{60} to $C_{60}Cl_{30}$ [4], C_{70} to $C_{70}Cl_{28}$ [9], and C_{90} (isomers 46 and 34) to $C_{90}Cl_{32}$ [17]. For example, our attempts to further chlorinate $C_{60}Cl_{30}$ or $C_{70}Cl_{28}$ with liquid Cl_2 at ca. 100 °C did not afford compounds with a higher degree of chlorination.

All C-Cl bondlengths lie in the comparatively narrow range of 1.780(3) – 1.812(3) Å (av. 1.795 Å). Six slightly shorter C-Cl bonds (av. 1.782 Å) involve Cl atoms having two 1,2 intramolecular Cl...Cl contacts. These values are in good agreement with averaged C-Cl bondlengths in $C_{60}Cl_{30}$ (1.785 [4] and 1.801 Å [5] for the two isomeric molecules) or $C_{60}Cl_{28}$ (1.789 Å [5]) prepared by chlorination of C_{60} with $SbCl_5$ or ICl. Virtually the same average C-Cl distance, 1.796 Å, has been found in the $C_{90}Cl_{32}$ molecule (in triclinic crystalline modification) obtained by chlorination with $SbCl_5$ [17]. At the same time, all molecules of fullerene chlorides prepared by chlorination with $TiCl_4/Br_2$ mixtures have elongated averaged C-Cl distances: 1.83 Å for $C_{76}Cl_{18}$ [10], 1.84-1.88 Å for $C_{78}Cl_{18}$ with different C_{78} isomeric cages [11], and 1.868 Å for cocrystals of $C_{78}Cl_{18}$ with a mixture of cage isomers 2 and 3 [14]. We suggested in [14] that such an elongation might be due to the presence of a small fraction of Br atoms, that could contribute to the apparent elongation of C-Cl bonds (in fact, C-X, X = Cl, Br). Typical C-Br bondlengths in fullerene bromides ($C_{60}Br_6$ [1, 16], $C_{60}Br_8$ [1, 16], $C_{60}Br_{24}$ [7, 16], and $C_{78}Br_{18}$ [25]) are all about 1.99–2.01 Å. The presence of a few percent of Br in fullerene chlorides can significantly elongate the obtained C-X distances because Br atoms with 35 electrons have larger impact than Cl atoms (17 electrons) on the position of statistically averaged X atoms. In a more recent work [15], we investigated the chlorination of C_{60} with $TiCl_4/Br_2$ systematically by varying the Br_2 content in the “chlorinating” agent. It has been established that the higher the bromine content was, the higher the Br/Cl ratio was found in the obtained crystals of $C_{60}X_6$, $C_{60}X_8$, and $C_{60}X_{24}$ (X = Cl, Br). Noteworthy, Br atoms were not uniformly distributed among the C-X bonds of different types. Therefore, the values for C-Cl (C-X) distances in crystals of fullerene chlorides obtained from systems with even low bromine content must be considered critically due to their possible elongation.

Insert Figure 3 here

Fragments of the packing motifs in crystal structure of $C_{78}Cl_{30} \cdot Cl_2$ are shown in Fig. 3. $C_{78}Cl_{30}$ molecules are packed in approximately hexagonal layers which are oriented diagonally relative to the unit cell axes. Shortest intermolecular Cl...Cl contacts are within 3.13 – 3.42 Å range. Comparatively short intermolecular Cl...Cl distances found in most crystal packings of fullerene chlorides [4,5,10-12,14,17] are most probably due to the very small charge on Cl atoms being nearly zero [26]. Solvated chlorine molecules occupy large tetrahedral holes in the packing of $C_{78}Cl_{30}$ molecules; therefore, they are highly disordered between several positions.

In summary, the highly chlorinated C_{78} fullerene, $C_{78}(2)Cl_{30}$, has been obtained by using $SbCl_5$ as chlorinating agent at elevated temperature. In its molecular structure, the C_{78} carbon cage

contains only isolated double bonds and aromatic benzenoid rings that most probably implies the highest possible chlorination degree achieved for C₇₈ fullerene. Preparation of highly chlorinated fullerene derivatives and determination of their structures may further serve as an effective way to establish connectivity patterns and study the reactivity of higher fullerenes.

Acknowledgments

This work was partially supported by the Russian Foundation for Basic Research (09-03-00433 and 09-03-91337) and the Deutsche Forschungsgemeinschaft (Ke 489/26-2). S. Y. thanks the National Natural Science Foundation of China (20801052).

- [1] P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor, and D. R. M. Walton, *Nature*, **1992**, 357, 479–481.
- [2] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, **1993**, 1230–1232.
- [3] N. B. Shustova, D. Yu., Chernyshov S. I., Troyanov *Mendeleev Commun.* **2006**, 16, 209–210.
- [4] P. A. Troshin, R. N. Lubovskaya, I. N. Ioffe, N. B. Shustova, E. Kemnitz, S. I. Troyanov, *Angew. Chem. Int. Ed.*, **2005**, 44, 234–237.
- [5] S. I. Troyanov, N. B. Shustova, A. A. Popov, L. N. Sidorov, E. Kemnitz, *Angew. Chem. Int. Ed.*, **2005**, 44, 432–435.
- [6] F. N. Tebbe, R. L. Harlow, D. B. Chase, D. L. Torn, G. C. Campbell, J. J. C. Calabrese, N. Herron, R. J. Young, E. Wasserman, *Science*, **1992**, 256, 822–825.
- [7] R. Taylor, *J. Fluorine Chem.* **2004**, 125, 359–368.
- [8] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1995**, 683–684.
- [9] S. I. Troyanov, N. B. Shustova, I. N. Ioffe, A. P. Turnbull, E. Kemnitz, *Chem. Commun.* **2005**, 72–74.
- [10] K. S. Simeonov, K. Yu. Amsharov, M. Jansen, *Angew. Chem. Int. Ed.* **2007**, 46, 8419–8421.
- [11] K. S. Simeonov, K. Yu. Amsharov, M. Jansen, *Chem.–Eur. J.* **2008**, 14, 9585–9590.
- [12] K. S. Simeonov, K. Yu. Amsharov, E. Krokos, M. Jansen, *Angew. Chem. Int. Ed.* **2008**, 47, 6283–6285.
- [13] K. S. Simeonov, K. Yu. Amsharov, M. Jansen, *Chem.–Eur. J.* **2009**, 15, 1812–1815.
- [14] A. V. Burtzev, E. Kemnitz, S. I. Troyanov, *Crystallogr. Rep.* **2008**, 53, 639–644.
- [15] S. I. Troyanov, A. V. Burtzev, E. Kemnitz, *Crystallogr. Rep.* **2009**, 54, 242–249.
- [16] S. I. Troyanov, E. Kemnitz, *Eur. J. Org. Chem.* **2005**, 4951–4962.
- [17] E. Kemnitz, S. I. Troyanov, *Angew. Chem. Int. Ed.* **2009**, 48, 2584–2587.
- [18] T. Wakabayashi, K. Kikuchi, S. Suzuki, H. Shiromaru, Y. Achiba, *J. Phys. Chem.* **1994**, 98, 3090–3091.
- [19] R. Taylor, G. J. Langley, T. J. S. Dennis, H. W. Kroto, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1992**, 1043–1046.
- [20] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, Y. Achiba, *Nature* **1992**, 357, 142–145.
- [21] F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, L. Chao, M. M. Alvarez, *Science* **1991**, 254, 1768–1770.
- [22] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon, Oxford, 1995.
- [23] L. Eppe, K. Yu. Amsharov, M. Jansen, *Fullerenes, Nanotubes Carbon Nanomater.* **2009**, 17, 67–77.
- [24] V. F. Bagryantsev, A. S. Zapol'skii, N. A. Galeva, O. V. Boltalina, L. N. Sidorov, *Russ. J. Inorg. Chem.* **2000**, 45, 1112–1118.
- [25] S. I. Troyanov, E. Kemnitz, *Eur. J. Org. Chem.* **2003**, 3916–3919.
- [26] C. B. Hübschle, St. Scheins, M. Weber, P. Luger, A. Wagner, T. Koritsánszky, S. I. Troyanov, O. V. Boltalina, I. V. Goldt, *Chem. Eur. J.* **2007**, 13, 1910–1920.

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Figure Captions

Figure 1. Top and side projections of the C_{2v} - $C_{78}Cl_{30}$ molecule.

Figure 2. Schlegel diagrams of the $C_{78}Cl_{30}$ and $C_{78}Cl_{18}$ molecules both with C_{78} (2) isomer cage. Aromatic benzenoid fragments are marked with grey color except for largest limiting hexagons in the both Schlegel diagrams.

Figure 3. Packing in the crystal structure of $C_{78}Cl_{30}\cdot Cl_2$ shown within limited depth for clarity (left). Two systems of mutually perpendicular layers can be seen. Separate rods represent some positions of disordered Cl_2 molecules. Packing within the layer (right); the shortest intermolecular $Cl\cdots Cl$ contacts are shown as dashed lines.

Table of Contents text

A Highly chlorinated C_{78} fullerene, $C_{78}(2)Cl_{30}$, has been obtained by the reaction of the isomer C_{78} (2) with $SbCl_5$ in ampoules at 330-340 °C. Single crystal structure determination revealed that the C_{2v} - $C_{78}Cl_{30}$ molecule contains only isolated double bonds and aromatic benzenoid rings in the C_{78} carbon cage thus representing the highest possible chlorination degree for C_{78} fullerenes obtained so far.

Keywords:

Fullerene; C_{78} ; Cage isomers; Chlorination; Structure elucidation

ARTICLE

DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

Synthesis and Structure of a Highly Chlorinated C₇₈: C₇₈(2)Cl₃₀Sergey I. Troyanov,^{*,[a]} Nadezhda B. Tamm,^[a] Chuanbao Chen,^[b] Shangfeng Yang,^[b] and Erhard Kemnitz^{*,[c]}*Dedicated to Prof. Martin Jansen on the Occasion of his 65 birthday*

A Highly chlorinated C₇₈ fullerene, C₇₈(2)Cl₃₀, has been obtained by the reaction of the isomer C₇₈ (2) with SbCl₅ in ampoules at 330–340 °C. Single crystal structure determination revealed that the C_{2v}-C₇₈Cl₃₀ molecule contains only isolated double bonds and aromatic

benzenoid rings in the C₇₈ carbon cage. Therefore, C₇₈Cl₃₀ represents the highest possible chlorination degree for C₇₈ fullerenes obtained so far.

- [a] Chemistry Department, Moscow State University, Leninskie Gory, 119991 Moscow, Russia
Fax: +007 494 9391240
E-mail: stroyano@thermo.chem.msu.ru
- [b] Hefei National Laboratory for Physical Sciences at Microscale & Department of Materials Science and Engineering, University of Science and Technology of China (USTC), Hefei 230026, China
- [c] Institute of Chemistry, Humboldt University, Brook-Taylor Str. 2, 12489 Berlin, Germany
Fax: +49 030 20937277
E-mail: erhard.kemnitz@chemie.hu-berlin.de

synthesis and single crystal X-ray study of C₇₈Cl₃₀ which seems to be the highest chloride of C₇₈ fullerene.

Experimental Section

C₇₈ fullerene was separated from toluene extraction of the fullerene soot by a two-step HPLC using a Cosmosil Buckyprep column (10 mm i.d. x 250 mm, Nacalai Tesque Inc.) and toluene as the eluent (5.0 mL min⁻¹ flow rate, 320 nm). Briefly, in the first-step HPLC a mixed fraction comprised of C₇₆ and two isomers of C₇₈ was collected, which was subjected to the second-step recycling HPLC separation. After two cycles, the major isomer of C₇₈ was successfully obtained with the identification and purity confirmed by MALDI-TOF MS analysis. UV-Vis spectrum of the isolated C₇₈ fullerene dissolved in toluene was recorded on a UV-Vis-NIR 3600 spectrometer (Shimadzu, Japan).

Approximately 0.3 mg of C₇₈ (2) was placed into a glass ampoule and 0.3 mL SbCl₅ was added. The ampoule was cooled, evacuated, and sealed off. Heating the ampoule at 330–340 °C for 2–3 days produced orange crystals which, after ampoule opening, were separated by decanting SbCl₅ and washing with conc. HCl.

The data for crystal with dimensions of 0.20×0.15×0.12 mm³ were collected on an IPDS diffractometer (Stoe) at 100 K using graphite monochromatized Mo-K_α-radiation, λ = 0.71073 Å, 2θ_{max} = 58.4°; -28 < h, k < 28, -43 < l < 43, R_{int} = 0.063. Structure solution and refinement were performed with SHELXS97 and SHELXL97, respectively. Absorption correction was not applied. Crystal data for C₇₈Cl₃₀·Cl₂: M = 2071.18, tetragonal, space group I 4̄, a = 20.7619(3), c = 31.4440(6) Å, V = 13554.1(4) Å³, Z = 8, D_{calc} = 2.030 g cm⁻³, μ = 1.333 mm⁻¹; reflections collected 76817, independent 18284, wR₂ = 0.067 for 18274 reflections and 1019 parameters, R₁ = 0.030 for 17653 reflections with I > 2σ(I). Whereas C₇₈Cl₃₀ molecule is fully ordered, the solvated Cl₂ molecule is highly disordered between several positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-726149. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) _44-1223-336-033; E-Mail: data_request@ccdc.cam.ac.uk].

Introduction

Fullerene halides were among the first structurally investigated fullerene derivatives [1]. On the one hand, they can serve as intermediates for further derivatization of fullerenes. On the other hand, they sometimes facilitate characterization of the connectivity patterns of higher fullerenes. Chlorides of a given fullerene comprise a range of compositions, which lies between those of bromides and fluorides. For example, the known chlorides of C₆₀ contain 6 to 30 attached Cl atoms [2–5], whereas extreme compositions for bromide are C₆₀Br₆ [1] and C₆₀Br₂₄ [6], and those reported for fluorides are C₆₀F₂ and C₆₀F₄₈ [7]. Interestingly, lower chlorides of C₆₀ and C₇₀, C₆₀Cl₆ [2] and C₇₀Cl₁₀ [8], differ significantly in their properties such as solubility, stability and reactivity from the corresponding higher chlorides, C₆₀Cl₃₀ [4, 5] and C₇₀Cl₂₈ [9].

In the last years, remarkable progress has been achieved in synthesis and investigation of chlorides of higher fullerenes. Using the reaction of fullerenes with a mixture of TiCl₄ and bromine, higher fullerenes D₂-C₇₆ (1), three isomers of C₇₈ (C_{2v} (2), C_{2v} (3), and D_{3h} (5)), and D₂-C₈₀ (2) have been selectively chlorinated, respectively, to C₇₆Cl₁₈ [10], C₇₈Cl₁₈ [11, 12], and C₈₀Cl₁₂ [13] in crystalline form thus enabling structural investigation of the connectivity pattern in pristine fullerenes. The chlorinating power of TiCl₄ and Br₂ mixtures depends on the bromine concentration [14, 15], however, on average, it results in the formation of chlorides with lower to middle chlorine content. Higher chlorides can be produced by using stronger chlorinating agents such as Cl₂ or some inorganic chlorides (ICl, SbCl₅ etc.) at higher temperature [16]. For instance, recently chlorination of the mixture of higher fullerenes with SbCl₅ resulted in isolation and structural characterization of C₉₀Cl₃₂ [17]. In this paper, we report the

Results and Discussion

As shown by Wakabayashi et al. [18], fullerene soot production performed at significantly different conditions could result in fullerene mixtures in which C_{78} is represented by three cage isomers, D_3 (1), C_{2v} (2), and C_{2v}' (3), in significantly different ratios. Obviously, these circumstances account for different isomeric compositions of C_{78} as reported by some authors [19, 20]. In our case, the first of two C_{78} fractions is the major isomer and contains mainly the isomer C_{2v} - C_{78} (2) according to UV-Vis spectra, thus resembling the first C_{78} fraction described by Diederich et al. in their report concerning isolation and characterization of C_{78} isomers (1) and (2) [21].

Our X-ray crystallographic study of several single crystals revealed the formation of the same chlorinated derivative of C_{78} , $C_{78}Cl_{30}$ (Fig. 1). The C_{78} carbon cage in $C_{78}Cl_{30}$ can be easily recognized as C_{78} (2) (with the following spiral code: 1,7,9,11,13,24,27,30,32,36,38,40 [22]) due to the presence of only one horizontal C-C bond in the equatorial belt and the presence of a coronene subunit on the opposite side of the cage (Figure 2). The $C_{78}Cl_{30}$ molecule as a whole retains (non-crystallographic) C_{2v} symmetry of the initial C_{78} (2) cage with a two-fold axis passing through the middle point of the central C-C bond and the centre of the coronene subunit.

Insert Figure 1 here

Thirty Cl atoms are attached in 1,2-, 1,3-, and 1,4-positions in carbon hexagons so that the remaining (non-chlorinated) C atoms form either isolated C-C double bonds or aromatic benzenoid rings. There are altogether nine isolated double bonds with an averaged C-C distance of 1.33 Å and five flattened benzenoid rings with averaged C-C distances of 1.39-1.41 Å. Most uniform (1.406 ± 0.006 Å) are C-C bonds in the central hexagon of the coronene subunit; its high aromaticity also becomes apparent in a high planarity of this cage region (Fig. 1, right). Four other aromatic benzenoid rings have one or two edge-sharing pentagons in their cage surroundings; C-C bonds of hexagon-pentagon junctions are the shortest (1.37-1.38 Å) among C-C ring bonds thus resulting in less uniform distribution of bondlengths and, therefore, less flat regions of the cage. Unfortunately, a comparison with bondlengths in a non-functionalized C_{2v} - C_{78} (2) molecule is not possible, because the only available data concern a disordered C_{2v} - C_{78} molecule (due to an overlap of two closely situated molecules) in co-crystals with Cu-tetraphenylporphyrin [23].

It is worth noting that all other reported chlorides of C_{78} were synthesized by chlorination of individual C_{78} isomers or their mixtures with solutions of Br_2 in $TiCl_4$ [11,12,14]. They all have the same composition $C_{78}Cl_{18}$ and are characterized by the same addition pattern of 18 Cl atoms on slightly different C_{78} carbon cages. Bromination of C_{78} (as a by-mixture to C_{70}) produced $C_{78}Br_{18}$ (co-crystals with isomeric cages 2 and 3) possessing the same addition pattern of 18 Br atoms [24]. The attachment of 18 halogen atoms to C_{78} cages results in three isolated bonds and three aromatic benzenoid rings, whereas the remaining cage has larger regions with delocalized C-C bonds. C-C bonds in benzenoid rings

Insert Figure 2 here

are 1.392-1.403 Å long, i.e. they are in the same range as in the $C_{78}Cl_{30}$ molecule. Isolated double bonds in the $C_{78}(2)Cl_{18}$ molecule can not be calculated reliably because of a statistical disorder resulting in a higher D_{3d} molecular symmetry. A comparison of the addition patterns of $C_{78}(2)Cl_{30}$ and $C_{78}(2)Cl_{18}$ [11] (Fig. 2) demonstrates that the latter is a substructure of the former being most probably its precursor in the course of chlorination.

Because of the presence of only isolated double bonds and benzenoid rings and also due to an effective shielding of these fragments by the attached Cl atoms, $C_{78}(2)Cl_{30}$ obviously represents the highest possible degree of chlorination of C_{2v} - C_{78} (2). Chlorination of each isolated double bond would generate triple Cl...Cl contacts, which are known to be avoided due to strong repulsion [5]. Even in the fullerene fluoride $C_{60}F_{48}$, six isolated C-C bonds are effectively shielded making this compound highly stable. Attempts to further fluorinate $C_{60}F_{48}$ result in a cage destruction [24]. Other structurally similar C_{78} isomers except for D_3 - C_{78} (1) would also attach a maximum of 30 Cl atoms with the same addition pattern. Noteworthy, the use of $SbCl_5$ as chlorination agent at elevated temperature seems to facilitate the formation of the highest possible fullerene chloride as already found for the chlorination of C_{60} to $C_{60}Cl_{30}$ [4], C_{70} to $C_{70}Cl_{28}$ [9], and C_{90} (isomers 46 and 34) to $C_{90}Cl_{32}$ [17]. For example, our attempts to further chlorinate $C_{60}Cl_{30}$ or $C_{70}Cl_{28}$ with liquid Cl_2 at ca. 100 °C did not afford compounds with a higher degree of chlorination.

All C-Cl bondlengths lie in the comparatively narrow range of 1.780(3) – 1.812(3) Å (av. 1.795 Å). Six slightly shorter C-Cl bonds (av. 1.782 Å) involve Cl atoms having two 1,2 intramolecular Cl...Cl contacts. These values are in good agreement with averaged C-Cl bondlengths in $C_{60}Cl_{30}$ (1.785 [4] and 1.801 Å [5] for the two isomeric molecules) or $C_{60}Cl_{28}$ (1.789 Å [5]) prepared by chlorination of C_{60} with $SbCl_5$ or ICl . Virtually the same average C-Cl distance, 1.796 Å, has been found in the $C_{90}Cl_{32}$ molecule (in triclinic crystalline modification) obtained by chlorination with $SbCl_5$ [17]. At the same time, all molecules of fullerene chlorides prepared by chlorination with $TiCl_4/Br_2$ mixtures have elongated averaged C-Cl distances: 1.83 Å for $C_{76}Cl_{18}$ [10], 1.84-1.88 Å for $C_{78}Cl_{18}$ with different C_{78} isomeric cages [11], and 1.868 Å for co-crystals of $C_{78}Cl_{18}$ with a mixture of cage isomers 2 and 3 [14]. We suggested in [14] that such an elongation might be due to the presence of a small fraction of Br atoms, that could contribute to the apparent elongation of C-Cl bonds (in fact, C-X, X = Cl, Br). Typical C-Br bondlengths in fullerene bromides ($C_{60}Br_6$ [1, 16], $C_{60}Br_8$ [1, 16], $C_{60}Br_{24}$ [7, 16], and $C_{78}Br_{18}$ [25]) are all about 1.99–2.01 Å. The presence of a few percent of Br in fullerene chlorides can significantly elongate the obtained C-X distances because Br atoms with 35 electrons have larger impact than Cl atoms (17 electrons) on the position of statistically averaged X atoms. In a more recent work [15], we investigated the chlorination of C_{60} with $TiCl_4/Br_2$ systematically by varying the Br_2 content in the “chlorinating” agent. It has been established that the higher the bromine content was, the higher the Br/Cl ratio was found in the obtained crystals of $C_{60}X_6$, $C_{60}X_8$, and $C_{60}X_{24}$ (X = Cl, Br). Noteworthy, Br atoms were not uniformly distributed among the C-X bonds of different types. Therefore, the values for C-Cl (C-X) distances in crystals of fullerene chlorides obtained from systems with even low bromine content must be considered critically due to their possible elongation.

Insert Figure 3 here

Fragments of the packing motifs in crystal structure of $C_{78}Cl_{30} \cdot Cl_2$ are shown in Fig. 3. $C_{78}Cl_{30}$ molecules are packed in approximately hexagonal layers which are oriented diagonally relative to the unit cell axes. Shortest intermolecular Cl...Cl contacts are within 3.13 – 3.42 Å range. Comparatively short intermolecular Cl...Cl distances found in most crystal packings of fullerene chlorides [4,5,10-12,14,17] are most probably due to the very small charge on Cl atoms being nearly zero [26]. Solvated chlorine molecules occupy large tetrahedral holes in the packing of $C_{78}Cl_{30}$ molecules; therefore, they are highly disordered between several positions.

In summary, the highly chlorinated C_{78} fullerene, $C_{78}(2)Cl_{30}$, has been obtained by using $SbCl_5$ as chlorinating agent at elevated temperature. In its molecular structure, the C_{78} carbon cage

contains only isolated double bonds and aromatic benzenoid rings that most probably implies the highest possible chlorination degree achieved for C₇₈ fullerene. Preparation of highly chlorinated fullerene derivatives and determination of their structures may further serve as an effective way to establish connectivity patterns and study the reactivity of higher fullerenes.

Acknowledgments

This work was partially supported by the Russian Foundation for Basic Research (09-03-00433 and 09-03-91337) and the Deutsche Forschungsgemeinschaft (Ke 489/26-2). S. Y. thanks the National Natural Science Foundation of China (20801052).

- [1] P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor, and D. R. M. Walton, *Nature*, **1992**, 357, 479–481.
- [2] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, **1993**, 1230–1232.
- [3] N. B. Shustova, D. Yu., Chernyshov S. I., Troyanov *Mendeleev Commun.* **2006**, 16, 209–210.
- [4] P. A. Troshin, R. N. Lubovskaya, I. N. Ioffe, N. B. Shustova, E. Kemnitz, S. I. Troyanov, *Angew. Chem. Int. Ed.*, **2005**, 44, 234–237.
- [5] S. I. Troyanov, N. B. Shustova, A. A. Popov, L. N. Sidorov, E. Kemnitz, *Angew. Chem. Int. Ed.*, **2005**, 44, 432–435.
- [6] F. N. Tebbe, R. L. Harlow, D. B. Chase, D. L. Torn, G. C. Campbell, J. J. C. Calabrese, N. Herron, R. J. Young, E. Wasserman, *Science*, **1992**, 256, 822–825.
- [7] R. Taylor, *J. Fluorine Chem.* **2004**, 125, 359–368.
- [8] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1995**, 683–684.
- [9] S. I. Troyanov, N. B. Shustova, I. N. Ioffe, A. P. Turnbull, E. Kemnitz, *Chem. Commun.* **2005**, 72–74.
- [10] K. S. Simeonov, K. Yu. Amsharov, M. Jansen, *Angew. Chem. Int. Ed.* **2007**, 46, 8419–8421.
- [11] K. S. Simeonov, K. Yu. Amsharov, M. Jansen, *Chem.–Eur. J.* **2008**, 14, 9585–9590.
- [12] K. S. Simeonov, K. Yu. Amsharov, E. Krokos, M. Jansen, *Angew. Chem. Int. Ed.* **2008**, 47, 6283–6285.
- [13] K. S. Simeonov, K. Yu. Amsharov, M. Jansen, *Chem.–Eur. J.* **2009**, 15, 1812–1815.
- [14] A. V. Burtzev, E. Kemnitz, S. I. Troyanov, *Crystallogr. Rep.* **2008**, 53, 639–644.
- [15] S. I. Troyanov, A. V. Burtzev, E. Kemnitz, *Crystallogr. Rep.* **2009**, 54, 242–249.
- [16] S. I. Troyanov, E. Kemnitz, *Eur. J. Org. Chem.* **2005**, 4951–4962.
- [17] E. Kemnitz, S. I. Troyanov, *Angew. Chem. Int. Ed.* **2009**, 48, 2584–2587.
- [18] T. Wakabayashi, K. Kikuchi, S. Suzuki, H. Shiromaru, Y. Achiba, *J. Phys. Chem.* **1994**, 98, 3090–3091.
- [19] R. Taylor, G. J. Langley, T. J. S. Dennis, H. W. Kroto, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1992**, 1043–1046.
- [20] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, Y. Achiba, *Nature* **1992**, 357, 142–145.
- [21] F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, L. Chao, M. M. Alvarez, *Science* **1991**, 254, 1768–1770.
- [22] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon, Oxford, 1995.
- [23] L. Eppe, K. Yu. Amsharov, M. Jansen, *Fullerenes, Nanotubes Carbon Nanomater.* **2009**, 17, 67–77.
- [24] V. F. Bagryantsev, A. S. Zapol'skii, N. A. Galeva, O. V. Boltalina, L. N. Sidorov, *Russ. J. Inorg. Chem.* **2000**, 45, 1112–1118.
- [25] S. I. Troyanov, E. Kemnitz, *Eur. J. Org. Chem.* **2003**, 3916–3919.
- [26] C. B. Hübschle, St. Scheins, M. Weber, P. Luger, A. Wagner, T. Koritsánszky, S. I. Troyanov, O. V. Boltalina, I. V. Goldt, *Chem. Eur. J.* **2007**, 13, 1910–1920.

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Figure Captions

Figure 1. Top and side projections of the C_{2v} - $C_{78}Cl_{30}$ molecule.

Figure 2. Schlegel diagrams of the $C_{78}Cl_{30}$ and $C_{78}Cl_{18}$ molecules both with C_{78} (2) isomer cage. Aromatic benzenoid fragments are marked with grey color except for largest limiting hexagons in the both Schlegel diagrams.

Figure 3. Packing in the crystal structure of $C_{78}Cl_{30} \cdot Cl_2$ shown within limited depth for clarity (left). Two systems of mutually perpendicular layers can be seen. Separate rods represent some positions of disordered Cl_2 molecules. Packing within the layer (right); the shortest intermolecular $Cl \cdots Cl$ contacts are shown as dashed lines.

Table of Contents text

A Highly chlorinated C_{78} fullerene, $C_{78}(2)Cl_{30}$, has been obtained by the reaction of the isomer C_{78} (2) with $SbCl_5$ in ampoules at 330-340 °C. Single crystal structure determination revealed that the C_{2v} - $C_{78}Cl_{30}$ molecule contains only isolated double bonds and aromatic benzenoid rings in the C_{78} carbon cage thus representing the highest possible chlorination degree for C_{78} fullerenes obtained so far.

Keywords:

Fullerene; C_{78} ; Cage isomers; Chlorination; Structure elucidation