Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2010, **20**, 74–76

Mendeleev
Communications

Chlorides of isomeric C_{78} fullerenes: $C_{78}(1)Cl_{30}$, $C_{78}(2)Cl_{30}$, and $C_{78}(2)Cl_{18}$

Erhard Kemnitz[a] **and Sergey I. Troyanov***[b]

[a] *Institute of Chemistry, Humboldt University, 12489 Berlin, Germany*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.*
Fax: +7 495 939 1240; e-mail: stroyano@thermo.chem.msu.ru

DOI: 10.1016/j.mencom.2010.03.003

Addition patterns of isomeric $C_{78}(1)Cl_{30}$ and $C_{78}(2)Cl_{30}$ respectively show striking differences, which concern the formation of extended *vs.* small ring aromatic systems, the presence *vs.* the absence of triple Cl···Cl contacts and chlorinated sites of triple hexagon junctions.

In recent years, many individual fullerene chlorides have been synthesized and structurally investigated showing unexpected features of fullerene reactivities. Some lower fullerene chlorides (for example, $C_{60}Cl_6$ and $C_{70}Cl_{10}$) can be obtained by chlorination of fullerene solutions in organic solvents.[1] A mixture of titanium tetrachloride and bromine can serve as a mild chlorinating agent for the synthesis of fullerene chlorides with 'middle' chlorine contents such as $C_{70}Cl_{16}$,[2] $C_{76}Cl_{18}$,[3] $C_{78}Cl_{18}$,[4,5] and $C_{80}Cl_{12}$.[6] All individual higher chlorides such as $C_{60}Cl_{28}$,[7] $C_{60}Cl_{30}$,[7,8] $C_{70}Cl_{28}$,[9] $C_{78}(2)Cl_{30}$,[10] and $C_{90}Cl_{32}$[11] were prepared by reactions of fullerenes with inorganic chlorides (ICl, PCl_5, $SbCl_5$, VCl_4) at elevated temperatures.

Fullerene chlorides $C_{78}Cl_{18}$ obtained by reaction of individual fullerene isomers $C_{78}(2)$, $C_{78}(3)$,[4(*a*)] and $C_{78}(5)$[4(*b*)] or isomers mixture $C_{78}(2+3)$[5(*a*)] with a solution of bromine in $TiCl_4$ were structurally investigated revealing similar molecular structures. The only higher chloride of C_{78}, $C_{78}(2)Cl_{30}$, was prepared by chlorination of the $C_{78}(2)$ isomer with $SbCl_5$. Here we report a structural characterization of a higher chloride of $C_{78}(1)$, $C_{78}(1)Cl_{30}$, a new crystal modification of $C_{78}(2)Cl_{30}$, and $C_{78}(2)Cl_{18}$, prepared by reactions of C_{78} with VCl_4 or $VOCl_3$.

Fullerene C_{78} was separated from a higher fullerene mixture (MER Corp.) by recycling HPLC using a Cosmosil Buckyprep column (10 mm i.d. × 250 mm, Nacalai Tesque Inc.) and toluene as the eluent (4.6 ml min^{-1} flow rate, 290 nm). UV-VIS spectrum showed an agreement with the published spectra for isomer C_{2v}-$C_{78}(2)$.[12] However, admixtures of other isomers of C_{78}, D_3-$C_{78}(1)$ and C_{2v}-$C_{78}(3)$ were not excluded due to small differences in retention times of these isomers and relatively low sensitivity of the UV-VIS spectral identification.[12,13]

Approximately 0.3 mg of C_{78} was placed into a glass ampoule and 0.3 ml VCl_4 was added. The ampoule was cooled, evacuated, and sealed. Heating the ampoule at 240 °C for 3–4 days yielded yellow crystals which, after ampoule opening, were separated by decanting VCl_4 and washing with conc. HCl. Under close examination, crystals of two shapes were detected. X-ray diffraction study with the use of synchrotron radiation showed that rectangle plates represent the known molecular structure of $C_{78}(2)Cl_{30}$,[10] however, in a different crystalline form.[†] X-ray diffraction analysis of minor rhombus-like plates[†] showed their being $C_{78}(1)Cl_{30}$, *i.e.*, the chloride of D_3-C_{78} (D_3-C_{78} was obviously an admixture in the starting C_{78} sample). This is not very surprising because even recycling HPLC in toluene does not provide full separation of C_{78} isomers.[12] More interesting is the fact that, despite the same composition, the both compounds formed separate crystalline phases.

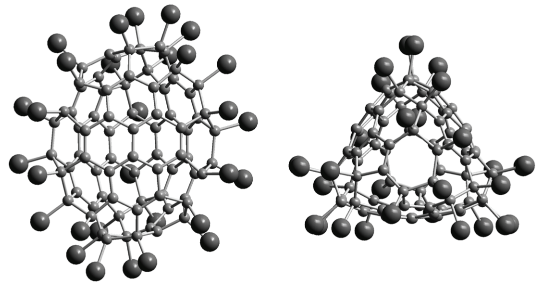

Figure 1 Molecular structure of $C_{78}(1)Cl_{30}$. Left projection is in the direction of a non-crystallographic two-fold axis.

In another experiment, C_{78} reacted with $VOCl_3$ in an ampoule at 240 °C for 5 days. After ampoule opening and washing with HCl and water, a small amount of orange crystals was obtained. X-ray single crystal analysis indicated,[†] for the first sight, the known structure of $C_{78}(2)Cl_{18}$.[4(*a*)] However, a closer inspection of interatomic distances revealed small but important differences, which are discussed below.

[†] *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BL14.2 at the BESSY storage ring (PSF at the Free University of Berlin, Germany) using a MAR225 CCD detector, $\lambda = 0.9050$ Å. Structures were solved by direct methods with SHELXS and refined with SHELXL.

$C_{78}(1)Cl_{30}\cdot 0.5Cl_2$: monoclinic, space group *C2/c*, $a = 24.2126(4)$, $b = 14.8108(3)$ and $c = 37.2468(5)$ Å, $\beta = 108.8042(6)°$, $V = 12644.1(4)$ Å^3, $Z = 8$. Anisotropic refinement with 12005 reflections and 1010 parameters to $wR_2 = 0.130$ and $R_1 = 0.054$ for 11984 reflections with $I > 2\sigma(I)$.

$C_{78}(2)Cl_{30}\cdot 0.03Cl_2$: tetragonal, space group $I\bar{4}$, $a = 34.144(3)$ and $c = 12.693(1)$ Å, $V = 14498(2)$ Å^3, $Z = 8$. Refinement (C isotropic) with 8394 reflections and 586 parameters to $wR_2 = 0.383$ and $R_1 = 0.147$ for 7833 reflections with $I > 2\sigma(I)$; radiation damage resulted in a complete crystal decay in *ca.* an hour.

$C_{78}(2)Cl_{18}$: hexagonal, space group $P6_3/m$, $a = 12.9339(6)$ and $c = 18.650(1)$ Å, $V = 2701.9(2)$ Å^3, $Z = 2$. Anisotropic refinement with 1711 reflections and 158 parameters yielded a conventional $R_1 = 0.058$ for 1497 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.146$ for all reflections. A statistical overlap of three orientations of the C_2-$C_{78}(2)Cl_{18}$ molecule resulted in averaging to trigonal symmetry and disorder of three C atoms between the positions with 0.33/0.67(3) occupancies.

CCDC 752686–752688 contain 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

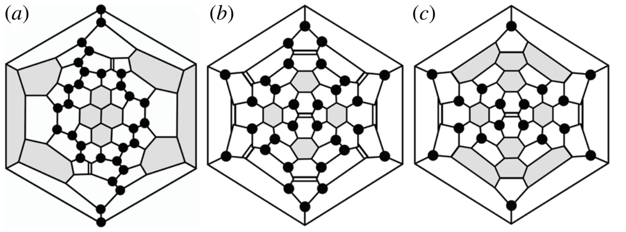

Figure 2 Schlegel diagrams of (*a*) $C_{78}(1)Cl_{30}$, (*b*) $C_{78}(2)Cl_{30}$ and (*c*) $C_{78}(1)Cl_{18}$. Black circles denote the positions of attached Cl atoms. Aromatic systems are shown in grey.

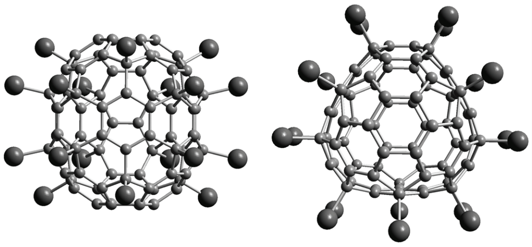

Figure 4 Molecular structure of $C_{78}(2)Cl_{18}$. Left projection is shown in the direction of a non-crystallographic two-fold axis.

The molecular structure of $C_{78}(1)Cl_{30}$ (Figure 1) is the most striking finding of this work. This is due to large differences in addition patterns of the two isomeric molecules, $C_{78}Cl_{30}$, containing carbon cages of $C_{78}(1)$ and $C_{78}(2)$ isomers. The C_2-$C_{78}(1)Cl_{30}$ molecule shows a very irregular distribution of thirty Cl atoms in the addition pattern with two similar chains of Cl atoms attached exclusively in *ortho* positions to each other. There is also a branch of each chain where three *ortho* Cl···Cl contacts come together. Such triple Cl···Cl contacts were previously believed to destabilize the structures of fullerene chlorides thus explaining the formation of only simple Cl···Cl chains exemplified in the known structures of $C_{60}Cl_{28}$,[7] $C_{60}Cl_{30}$,[8(*a*)] $C_{70}Cl_{28}$,[9] $C_{76}Cl_{18}$,[3] and $C_{90}Cl_{32}$.[11] Probably, the energetically unfavourable existence of triple Cl···Cl contacts in the addition pattern of $C_{78}(1)Cl_{30}$ is compensated by the formation of three extended aromatic systems, one pyrene- and two phenanthrene-like fragments, on the fullerene cage [Figure 2(*a*)]. Flattening of these fragments accounts for a roughly triangle-prismatic form of the carbon cage. Note that two Cl atoms are bound to the carbon atoms at triple hexagon junctions (THJ) which are usually less suitable for attachments to fullerenes. This kind of attachments has been observed in the only structure of $C_{70}Cl_{28}$,[9] whereas THJ additions of F atoms and CF_3 groups have been found respectively in overcrowded structures of $C_{70}F_{38}$[14] and $C_{94}(CF_3)_{20}$.[15]

In contrast, in the structure of $C_{78}(2)Cl_{30}$ known from the recent study[10] and also obtained in this work, thirty chlorine atoms are rather uniformly distributed on the $C_{78}(2)$ fullerene cage thus resulting in the formation of only aromatic (benzenoid) rings and isolated double C–C bonds [Figures 2(*b*) and 3]. Therefore, the C_{78} cage in $C_{78}(2)Cl_{30}$ is characterized by a more common egg-like shape. Structural differences of $C_{78}(1)Cl_{30}$ and $C_{78}(2)Cl_{30}$ molecules clearly demonstrate strong distinctions between two isomers of C_{78} in respect of stereochemistry of addition. Some differences between D_3- and C_{2v}-C_{78} were established earlier in multiple cyclopropanation by the Bingel reaction.[16] As has been reported recently, a difference in the photochemical reactivity of these two isomers of C_{78} towards disilirane can even be used for isomer separation by using a silylation–oxidative desilylation procedure.[17]

Although the synthesis of $C_{78}(2)Cl_{30}\cdot 0.03Cl_2$ using VCl_4 as chlorinating agent produced the same molecular structure as the chlorination of $C_{78}(2)$ with $SbCl_5$, their crystalline forms are different. In spite of the fact that the form II (from VCl_4) contains less Cl_2 solvate molecules than form I (*ca.* one solvate Cl_2 molecule per formula), its density is much lower caused by the loose packing of molecules in the crystal. Due to the poor fixation in the crystal, all atoms have large thermal displacement parameters. In addition, a dramatic radiation damage of crystals has been observed for form II during the data collection. Rather different shape of the $C_{78}(1)Cl_{30}$ and $C_{78}(2)Cl_{30}$ molecules made it possible a simultaneous crystallization of both compounds as separate phases.

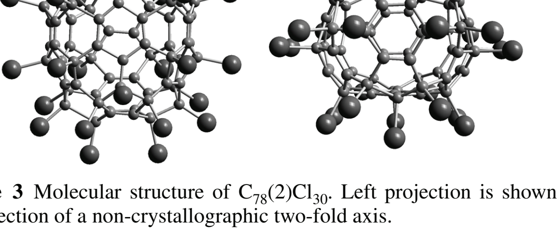

Figure 3 Molecular structure of $C_{78}(2)Cl_{30}$. Left projection is shown in the direction of a non-crystallographic two-fold axis.

Compound $C_{78}(2)Cl_{18}$ (Figure 4), prepared in this work by chlorination of C_{78} with $VOCl_3$ might be an intermediate at chlorination to the higher chloride, $C_{78}Cl_{30}$, by using stronger chlorinating agents such as $SbCl_5$ or VCl_4. This assumption is supported by the fact that all eighteen Cl atoms of $C_{78}(2)Cl_{18}$ retain their positions in the structure of $C_{78}(2)Cl_{30}$ [compare Figures 2(*b*) and 2(*c*)]. In spite of structure disordering around a three-fold axis, C_{78} cage assignment as isomer 2 is unambiguous because of the 0.33/0.67 ratio between parallel and perpendicular orientations of the three C=C bonds in the equatorial belt of the cage.

C–C bond distance relations in the $C_{78}(1)Cl_{30}$ molecule are determined by the existence of long chains of sp^3 hybridized C atoms. All C(sp^3)–C(sp^3) bonds within the chains are strongly elongated ranging between 1.54 and 1.68 Å, 5:6 C–C bonds being the longest (average of 1.63 Å). Most C–C bond lengths within the aromatic fragments are between 1.40 and 1.43 Å. There are also two nearly isolated C–C bonds with a double bond character (1.34 Å). As expected, chlorinated C atoms in THJ positions exhibit the lowest pyramidalization angle of 16.7°, whereas such angles at all other chlorinated carbons are in the range of 17.4–22.1° (average of 19.9°). In contrast, most C–C bonds in the $C_{78}(2)Cl_{30}$ molecule belong either to isolated double (average of 1.33 Å) or aromatic (average of 1.40 Å) bonds, whereas few C(sp^3)–C(sp^3) bonds are all of the 5:6 type (average of 1.60 Å).[10]

All C–Cl distances in the $C_{78}(1)Cl_{30}$ molecule lie in the range of 1.763(3)–1.812(3) Å (average of 1.792 Å) that is very close to the values found in the structure of $C_{78}(2)Cl_{30}$, 1.78–1.81 Å (average of 1.795 Å). Very similar C–Cl distances are found in the structure of $C_{78}(2)Cl_{18}$, 1.808(4)–1.816(4) Å (average of 1.813 Å). Remarkably, for the structure with the same formula, $C_{78}(2)Cl_{18}$, and symmetry, significantly longer C–Cl bonds, 1.845–1.874 Å, have been reported earlier.[4(*a*)] Similarly elongated C–Cl distances have been also found in all other $C_{78}Cl_{18}$ structures irrelevant of the cage isomer 2, 3, or 5.[4] The difference concerns the synthesis method, namely, a chlorinating agent used in the reaction with fullerene. Whereas $VOCl_3$ was used in this work, all $C_{78}Cl_{18}$ chlorides described in refs. 4 and 5(*a*) were obtained by the use of $TiCl_4$–Br_2 mixtures.

Systematic investigation of the reactions of C_{60} with $TiCl_4$–Br_2 mixtures revealed that the compounds obtained, $C_{60}Hal_n$, are characterized by the presence of mixed Cl/Br sites, the Cl/Br ratios being decreased as the concentration of Br_2 increased.[5(*b*)] For this reason, C–Hal bonds were elongated relative to the reference values in real fullerene chlorides (1.77–1.81 Å)[7,8,10,11] dependent on the relative bromine content. The case of $C_{78}(2)Cl_{18}$ is especially instructive because the two compounds, one obtained in this work from the bromine free system and the other one prepared by the reaction of C_{78} with a $TiCl_4$–Br_2 mixture, are isotypic thus allowing their detailed comparison. A close inspection of the C–C bond lengths did not reveal any remarkable discrepancies with an averaged difference of 0.009 Å. In contrast, three crystallographically independent C–Cl bonds differ significantly, those reported[4(*a*)] being on average by 0.05 Å longer. This resulted in small but noticeable differences in unit cell parameters (by *ca.* 0.8%) and unit cell volumes (by 47 Å^3). Therefore, we conclude that $C_{78}(2)Cl_{18}$ reported in ref. 4(*a*) actually should be formulated as $C_{78}(2)Hal_{18}$ with Hal mostly being Cl but with a small part substituted by Br. Therefore, apparent elongation of C–Cl bonds is due to the presence of mixed Cl/Br sites in the crystal structure.

In summary, chlorination of C_{78} with VCl_4 and $VOCl_3$ resulted in $C_{78}(1)Cl_{30}$, $C_{78}(2)Cl_{30}$, and $C_{78}(2)Cl_{18}$. Crystallographic study revealed significant differences in structures of higher chlorides of C_{78} isomers 1 and 2 containing aromatic fragments respectively as extended and small-ring systems. Structural study of $C_{78}(2)Cl_{18}$ and its comparison with the compounds of virtually the same composition reported earlier leads to the conclusion that the latter contain bromine due to the use of a $TiCl_4$–Br_2 mixture in the synthesis.

This work was supported in part by the Russian Foundation for Basic Research (grant nos. 09-03-00433 and 09-03-91337) and the Deutsche Forschungsgemeinschaft (Ke 489/26-2).

References

1 (*a*) 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; (*b*) R. Taylor, G. J. Langley, A. G. Avent, T. J. S. Dennis, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1029.

2 S. I. Troyanov and A. A. Popov, *Angew. Chem. Int. Ed.*, 2005, **44**, 4215.

3 K. S. Simeonov, K. Yu. Amsharov and M. Jansen, *Angew. Chem. Int. Ed.*, 2007, **46**, 8419.

4 (*a*) K. S. Simeonov, K. Yu. Amsharov and M. Jansen, *Chem.-Eur. J.*, 2008, **14**, 9585; (*b*) K. S. Simeonov, K. Yu. Amsharov, E. Krokos and M. Jansen, *Angew. Chem. Int. Ed.*, 2008, **47**, 6283.

5 (*a*) A. V. Burtzev, E. Kemnitz and S. I. Troyanov, *Crystallogr. Rep.*, 2008, **53**, 639; (*b*) S. I. Troyanov, A. V. Burtzev and E. Kemnitz, *Crystallogr. Rep.*, 2009, **54**, 242.

6 K. S. Simeonov, K. Yu. Amsharov and M. Jansen, *Chem.-Eur. J.*, 2009, **15**, 1812.

7 S. I. Troyanov, N. B. Shustova, A. A. Popov, L. N. Sidorov and E. Kemnitz, *Angew. Chem. Int. Ed.*, 2005, **44**, 432.

8 (*a*) P. A. Troshin, R. N. Lubovskaya, I. N. Ioffe, N. B. Shustova, E. Kemnitz and S. I. Troyanov, *Angew. Chem. Int. Ed.*, 2005, **44**, 234; (*b*) P. A. Troshin, A. Łapiński, A. Bogucki, M. Połomska and R. N. Lyubovskaya, *Carbon*, 2006, **44**, 2770.

9 S. I. Troyanov, N. B. Shustova, I. N. Ioffe, A. P. Turnbull and E. Kemnitz, *Chem. Commun.*, 2005, 72.

10 S. I. Troyanov, N. B. Tamm, C. Chen, S. Yang and E. Kemnitz, *Z. Anorg. Allg. Chem.*, 2009, **635**, 1783.

11 E. Kemnitz and S. I. Troyanov, *Angew. Chem. Int. Ed.*, 2009, **48**, 2584.

12 F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, L. Chao and M. M. Alvarez, *Science*, 1991, **254**, 1768.

13 K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho and Y. Achiba, *Nature*, 1992, **357**, 142.

14 (*a*) P. B. Hitchcock, A. G. Avent, N. Martsinovich, P. A. Troshin and R. Taylor, *Chem. Commun.*, 2005, 75; (*b*) P. B. Hitchcock, A. G. Avent, N. Martsinovich, P. A. Troshin and R. Taylor, *Org. Lett.*, 2005, **7**, 1975.

15 N. B. Tamm, L. N. Sidorov, E. Kemnitz and S. I. Troyanov, *Angew. Chem. Int. Ed.*, 2009, **48**, 9102.

16 A. Herrmann and F. Diederich, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1679.

17 A. H. Han, T. Wakahara, Y. Maeda, T. Akasaka, M. Fujitska, O. Ito, K. Yamamoto, M. Kako, K. Kobayashi and S. Nagase, *New J. Chem.*, 2009, **33**, 497.

Received: 28th December 2009; Com. 09/3444