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Mendeleev Commun., 2024, **34**, 734–736
Mendeleev Communications

Structural study of minor C_{84} isomers as chlorofullerenes, $C_{84}(11)Cl_{22}$, $C_{84}(14)Cl_{22}$, $C_{84}(16)Cl_{22}$, and $C_{84}(16)Cl_{24}$

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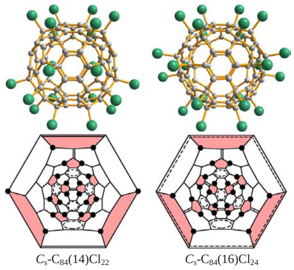
DOI: 10.1016/j.mencom.2024.09.035

Chlorofullerenes $C_{84}Cl_{22,24}$ were obtained by chlorination of minor C_{84} isomers mixture with VCl_4 at 330 °C. An X-ray crystallographic study with the use of synchrotron radiation revealed the presence of $C_{84}(11)Cl_{22}$, $C_{84}(14)Cl_{22}$, $C_{84}(16)Cl_{22}$, and $C_{84}(16)Cl_{24}$ in the same crystal.



C_s-$C_{84}(14)Cl_{22}$ C_s-$C_{84}(16)Cl_{24}$

Keywords: higher fullerenes, C_{84}, chlorination, minor isomers, structure elucidation.

As compared with C_{60} and C_{70}, the chemistry of higher fullerenes is much less developed because of their small abundance in the fullerene soot and the existence of structural isomers. Fullerene C_{84} has 24 topologically possible isomers obeying the Isolated-Pentagon Rule (IPR).[1] The isolation of two major (nos. 22 and 23)[2] and most minor IPR C_{84} isomers (nos. 4, 5, 11, 14, 16, 19, and 24)[3,4] was accomplished by chromatographic separation (HPLC) of C_{84} fraction followed by ^{13}C NMR spectroscopy supported by theoretical consideration (isomer numbering is according to the spiral algorithm[1]).[5–8] The use of direct determination of fullerene cage structures by X-ray crystallography is hampered due to librational mobility of nonfunctionalized fullerene molecules in the solid state.[9] Among IPR isomers of C_{84}, the carbon cage connectivity of the only 'naked' $C_{84}(14)$ was confirmed by X-ray study of its cocrystals with Ag(TPP) (TPP – tetraphenylporphyrin).[10,11] The crystallographic confirmation of some other C_{84} isomers was achieved by X-ray studies of exohedral derivatives, mainly with perfluoroalkyl and chloro addends, of major $C_{84}(22)$ and $C_{84}(23)$ as well as several minor isomers, nos. 4, 5, 11, 16, 18, and 24.[12–20] Note that no exohedral derivative of $C_{84}(14)$ and no chlorofullerenes of $C_{84}(16)$ have been reported so far. The former assumption about the presence of isomers $C_{84}(14)$ and $C_{84}(16)$ as admixtures in the structure of $C_{84}(11)Cl_{22}$[16] did not find confirmation in the subsequent reinvestigation of this compound.[19] Herein, we present the results of the X-ray crystallographic study of chlorofullerenes with minor C_{84} isomers, $C_{84}(11)Cl_{22}$, $C_{84}(14)Cl_{22}$, $C_{84}(16)Cl_{22}$, and $C_{84}(16)Cl_{24}$, which are contained in the same crystal packing. The similarity of the chlorination patterns of $C_{84}Cl_{22}$ and its difference from that of $C_{84}(16)Cl_{24}$ are discussed in detail.

The reaction of the compositionally pure but isomerically mixed C_{84} sample (0.5–1.0 mg) with an excess of VCl_4 was carried out in thick-walled glass ampule at 330 °C for 5 d. After ampule cooling and opening, the reaction product was washed out with dilute HCl and water, leaving orange-colored, fine-crystalline residue of chlorinated C_{84}. Tiny, needle-shaped crystals were studied by X-ray diffraction with the use of synchrotron radiation.[†]

The results of the structural investigation are unusual in that the huge crystal structure contains four different C_{84} chlorofullerene molecules located in four crystallographically independent sites. All four $C_{84}Cl_n$ units denoted with letters A, B, C, and D are disordered due to superposition of two or four chlorofullerene molecules. The disordered molecules of the types A and B have the stoichiometric composition $C_{84}Cl_{22}$, both exhibiting two Stone–Wales (SW) crosses in the cage structure. The appearance of SW crosses, which is a typical phenomenon for chloro derivatives of higher fullerenes, occurs because of the superposition of two similar carbon cages differing by the orientation of only one C–C bond. The topological analysis of the units A and B, both containing two SW crosses, established the presence of three isomeric chlorofullerene molecules, C_1-$C_{84}(11)Cl_{22}$ (in two orientations), C_s-$C_{84}(14)Cl_{22}$, and C_s-$C_{84}(16)Cl_{22}$, with the same positions of 22 Cl atoms. The refinement of the occupancies of C atoms belonging to SW crosses allowed one to obtain relative abundance of isomeric chlorofullerenes with the carbon cages of $C_{84}(11)$, $C_{84}(14)$, and $C_{84}(16)$ as 49.3 : 38.3 : 12.4 in molecule A and 46.4 : 40.7 : 12.9 in molecule B. The disordered molecule $C_{84}Cl_{22}$ of the type C contains only one SW cross which corresponds to the superposition of $C_{84}(11)Cl_{22}$ and $C_{84}(14)Cl_{22}$ in the refined ratio

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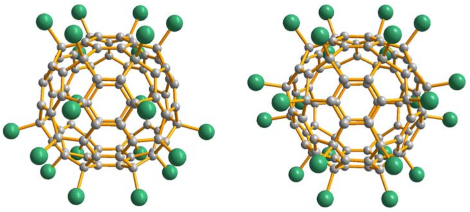
[†] *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, PSF, Berlin, Germany) using a MAR225 CCD detector ($\lambda = 0.89844$ Å). The crystal structure was solved by SHELXD and refined with SHELXL. $3\,C_{84}Cl_{22}\cdot 0.5\,C_{84}Cl_{24}\cdot 1.4\,Cl_2$, triclinic, $P\bar{1}$, $a = 12.703(1)$, $b = 31.312(2)$ and $c = 32.674(2)$ Å, $\alpha = 78.719(2)$, $\beta = 79.536(6)$ and $\gamma = 84.770(4)°$, $V = 12512.4(15)$ Å^3, $Z = 2$. The refinement with 47482 reflections and 3518 parameters converged to $wR_2 = 0.313$ and $R_1 = 0.099$ for 29407 reflections with $I > 2\sigma(I)$.

CCDC 2339487 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



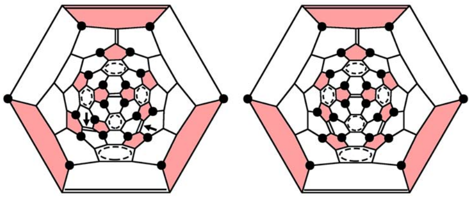
C_s-C_{84}(14)Cl_{22} C_s-C_{84}(16)Cl_{24}

Figure 1 Molecular structures of C_s-C_{84}(14)Cl_{22} and C_s-C_{84}(16)Cl_{24}. Both C_s-symmetrical molecules are viewed parallel to their mirror planes.

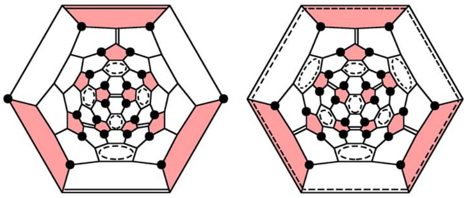
of 39.5 : 60.5. The molecule of the type D, C_s-C_{84}(16)Cl_{24}, represented by its half in the asymmetric unit, is disordered around an inversion center. The average contents of isomeric carbon cages C_{84}(11) : C_{84}(14) : C_{84}(16) in the crystal under investigation is calculated to be 38.6 : 39.9 : 21.5. Note that the relative abundance of isomer C_{84}(11) found in the crystal does not correspond to the statement in ref. 3 that this isomer is most abundant among minor isomers of C_{84}.

The presence of three minor C_{84} isomers nos. 11, 14, and 16 in the same crystal can be accounted for by rather close retention times during chromatographic separation of C_{84} fraction in toluene.[3] Two other minor isomers, C_{84}(4) and C_{84}(5), are known to elute much later, just before (or together with) isomers of C_{86}.[3] The crystallographic results of this work are important because they confirm the previously reported data concerning the structure of C_{84}(11)Cl_{22} and reveal the addition pattern of the first derivative of C_{84}(14) and the first chloro derivatives of C_{84}(16), C_{84}(16)Cl_{22} and C_{84}(16)Cl_{24}, in addition to the structures of C_{84}(16)(C_2F_5)$_{12}$ (two isomers) reported presiously.[15,16] The views of the C_s-C_{84}(14)Cl_{22} and C_s-C_{84}(16)Cl_{24} molecules are presented in Figure 1. It can be seen that the attachments of Cl atoms in both molecules retains the mirror symmetry of the corresponding C_{84} carbon cages.

The chlorination patterns of four $C_{84}Cl_n$ molecules incorporated in the same crystal are shown as Schlegel diagrams in Figure 2. All three $C_{84}Cl_{22}$ molecules are characterized by the same pattern of 22 Cl atoms on the carbon cages featuring the attachment exclusively in *para*-C_6Cl_2 hexagons. Small differences in the structures concern the orientation of one or two C–C bonds of the carbon cage. The same outer shape of three isomeric $C_{84}Cl_{22}$ molecules results in their ability to substitute each other in the crystal packing observed in isomerically mixed molecules of types A, B, and C. Despite of some differences in the carbon cage connectivities, $C_{84}Cl_{22}$ molecules possess very similar system of stabilizing structural fragments, six isolated C=C bonds and five benzenoid rings.



C_s-C_{84}(11)Cl_{22} C_s-C_{84}(14)Cl_{22}



C_s-C_{84}(16)Cl_{22} C_s-C_{84}(16)Cl_{24}

Figure 2 Schlegel diagrams of four $C_{84}Cl_n$ molecules present in the crystal packing. Cage pentagons are shown with red color. Black circles designate the attachment position of Cl atoms. The location of isolated C=C bonds and benzenoid rings on the carbon cage is indicated by double lines and dashed ovals, respectively. Left and right arrows on the Schlegel diagram of C_1-C_{84}(11)Cl_{22} indicate the positions of C–C bonds the rotation of which transforms the C_2-C_{84}(11) carbon cage in isomers C_s-C_{84}(14) and C_s-C_{84}(16), respectively.

The chlorination pattern of molecule D, C_{84}(16)Cl_{24}, differs considerably from that of C_{84}(16)Cl_{22}. Note that in several known cases, the attachment of two Cl atoms proceeds by simple addition without changes in the starting chlorofullerene. The closest example is the structures of C_{84}(11)Cl_{20} and C_{84}(11)Cl_{22}, the former being a substructure of the latter.[19] The other examples of structure/substructure relationships were reported for chlorofullerene pairs $C_{60}Cl_{28,30}$,[21] $C_{70}Cl_{26,28}$,[22] C_{96}(144)$Cl_{22,24}$,[23] *etc*. A comparison of the addition patterns of C_s-C_{84}(16)Cl_{22} and C_s-C_{84}(16)Cl_{24} demonstrates significant differences, especially in the central region of the Schlegel diagram, however with retaining of the attachment principle in *para*-C_6Cl_2 hexagons. In particular, six isolated C=C bonds in C_s-C_{84}(16)Cl_{24} are arranged in a different way and the number of benzenoid rings is increased to eight *vs*. five in the C_s-C_{84}(16)Cl_{22} molecule. Thus, each attached Cl atom in C_s-C_{84}(16)Cl_{24} participates in the isolation of one C=C bond and two benzenoid rings on the carbon cage similarly to the recently reported structure of D_{2d}-C_{84}(23)Cl_{24}.[20]

The chlorination enthalpy [per one Cl atom E(Cl)] for three isomeric $C_{84}Cl_{22}$ molecules was calculated theoretically (DFT),[24–26] resulting in close values of ΔE(Cl) relative to D_{3d}-$C_{60}Cl_{30}$ taken as a standard: 7.5, 7.2, and 7.1 kJ mol^{-1} for isomeric C_{84}(11)Cl_{22}, C_{84}(14)Cl_{22}, and C_{84}(16)Cl_{22}, respectively. Remarkably, the ΔE(Cl) for C_s-C_{84}(16)Cl_{24} was calculated to be much larger, 9.7 kJ mol^{-1} in spite of the general trend of decreasing ΔE(Cl) values with increasing number of attached Cl atoms. The considerable increase in the thermodynamic stability of C_s-C_{84}(16)Cl_{24} compared to that of C_{84}(11,14,16)Cl_{22} is due to the large number of benzenoid rings (eight *vs*. five) on the C_{84} carbon cage. Note that virtually the same value of ΔE(Cl), 9.6 kJ mol^{-1}, was calculated for D_{2d}-C_{84}(23)Cl_{24} also containing six isolated C=C bonds and eight benzenoid rings as stabilizing structural fragments on the carbon cage.[20] Moreover, both $C_{84}Cl_{24}$ chlorofullerenes possess the same arrangement of 24 Cl atoms whereas the differences concern the orientation of only two C=C bonds on the carbon cage.

In summary, the X-ray structure determination of C_{84} chlorofullerene revealed the presence of four $C_{84}Cl_n$ molecules, three of which are disordered superposition of $C_{84}Cl_{22}$ units, containing the carbon cages of minor isomers, C_2-C_{84}(11), C_s-C_{84}(14), and C_s-C_{84}(16). The fourth molecule is represented by the disordered but isomerically pure C_{84}(16)Cl_{24}. While the chlorofullerene C_1-C_{84}(11)Cl_{22} was reported previously, chloro derivatives of C_{84}(14) and C_{84}(16) are structurally characterized for the first time. Theoretical calculations of chlorination enthalpy revealed a significantly higher value for C_s-C_{84}(16)Cl_{24} as compared with the values for $C_{84}Cl_{22}$ molecules which was accounted for by the larger number of stabilizing structural fragments in the former molecule.

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Received: 28th March 2024; Com. 24/7438