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Mixed chlorotrifluoromethyl fullerene $C_{60}(CF_3)_{12}Cl_{12}$

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A mixed chlorothifluoromethyl derivative of [60]fullerene, $C_{60}(CF_3)_{12}Cl_{12}$, was prepared by the chlorination of $C_{60}(CF_3)_{12}$ with $SbCl_5$ at 280 °C.

Fullerene chloride, $C_{60}Cl_6$, reported in 1993, was among the first derivatives obtained after the discovery of fullerenes.[1] Other chlorides such as $C_{60}Cl_{24}$, $C_{60}Cl_{28}$ and $C_{60}Cl_{30}$ were synthesised recently by the reaction of fullerenes with inorganic chlorides ($SbCl_5$, VCl_4, PCl_5, ICl *etc.*).[2] The preparation, though as a mixture, of trifluoromethylated fullerenes was first reported in 1993.[3] Since then, a large variety of $C_{60}(CF_3)_n$ compounds with $n = 2$–18 were synthesised by the reaction of C_{60} with compounds easily releasing CF_3 radicals on heating. Their molecular structures were unambiguously characterised by X-ray diffraction studies.[4–6] The compound S_6-$C_{60}(CF_3)_{12}$ is prominent among others in that its synthesis can be carried out with a high selectivity and its crystalline form is negligibly soluble in most organic solvents.[7]

Here, we report the first preparation of a mixed chlorotrifluoromethyl derivative of fullerene, $C_{60}(CF_3)_{12}Cl_{12}$, accomplished by the chlorination of S_6-$C_{60}(CF_3)_{12}$ with $SbCl_5$. The crystal and molecular structures of the new compound were elucidated by X-ray crystallography.

Crystalline S_6-$C_{60}(CF_3)_{12}$ was prepared by the known method using an ampoule reaction of C_{60} with CF_3I.[7] The reaction product was washed out with toluene to remove the traces of other $C_{60}(CF_3)_n$ compounds. It was placed in a two-section glass ampoule together with excess liquid $SbCl_5$. The ampoule was evacuated at cooling, sealed off, and then heated in a tube furnace at 270–280 °C for 24 h. At cooling, light yellow crystals were formed, which were separated from remaining $SbCl_5$ and a small amount of $SbCl_3$ by their condensation in the other (cooled) section of the ampoule. The isolated compound $C_{60}(CF_3)_{12}Cl_{12}$ (30 mg, 90% yield) was structurally characterised by single-crystal X-ray diffraction analysis.† Its IR spectrum is essentially different from that of the starting compound apart for the positions of some IR bands at 1150–1300 cm^{-1} due to the presence of CF_3 groups (Figure 1). The compound is stable in air; it is practically insoluble in most organic solvents. The thermal stability of the compound is high. According to thermogravimetric analysis in an inert atmosphere at 1 bar, it decomposes at 360–415 °C with evolution of chlorine immediately followed by sublimation of the remaining $C_{60}(CF_3)_{12}$ at 415–490 °C thus resulting in a complete mass loss.

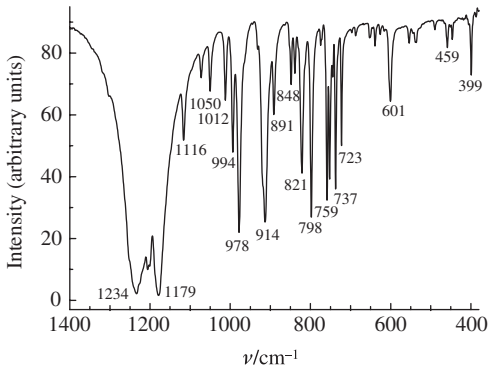

Figure 1 IR spectrum of $C_{60}(CF_3)Cl_{12}$ in a KBr pellet.

X-ray crystallography revealed that the molecular structure of the new compound retains the addition pattern of CF_3 groups

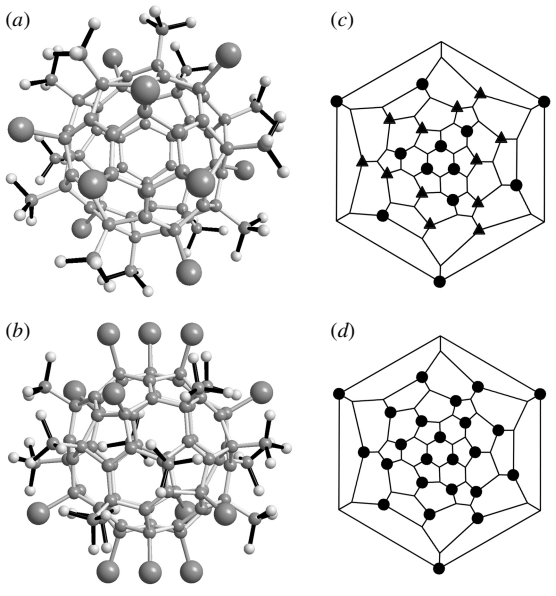

Figure 2 S_6-$C_{60}(CF_3)Cl_{12}$ molecule viewed along the axes (*a*) *c* and (*b*) *b*; (*c*) Schlegel diagrams for S_6-$C_{60}(CF_3)Cl_{12}$ (triangles and circles denote CF_3 groups and Cl atoms, respectively) and (*d*) $C_{60}X_{24}$ (circles denote halogen atoms X = Cl or Br).

† *Crystal data*: $C_{60}(CF_3)_{12}Cl_{12}$, crystal dimensions 0.4×0.4×0.2 mm, $M = 1974.12$, trigonal, space group $R\bar{3}c$, $a = 13.371(2)$, $c = 59.129(11)$ Å, $V = 9155(3)$ Å^3, $\mu = 0.709$ mm^{-1}, $Z = 6$. Data collection was performed with an IPDS (Stoe) at 170 K (MoKα, $\lambda = 0.71073$ Å). Reflections collected 25515, independent 2626, $R_{int} = 0.037$. Structure solution with SHELXS97[11] and structure refinement with SHELXL97.[12] Anisotropic refinement with 190 parameters yielded a conventional $R_1(F) = 0.039$ for 2364 reflections with $I > 2\sigma(I)$ and $wR_2(F^2) = 0.104$ for all reflections. One of two independent Cl atoms is disordered between two positions with occupancies 0.80 and 0.20, respectively.

CCDC 671037 contains 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, 2008.

in the starting S_6-$C_{60}(CF_3)_{12}$, whereas 12 Cl atoms are attached in the way that no *ortho* contacts are present between CF_3 groups and Cl atoms or between the latter (Figure 2). The $C_{60}(CF_3)_{12}Cl_{12}$ molecule possesses S_6 symmetry with an independent part of 1/6 of the whole molecule (10 cage carbons, 2 CF_3 groups and 2 Cl atoms). The positions of 12 CF_3 groups and 12 Cl atoms on fullerene cage closely resemble the well-known addition pattern of T_h-$C_{60}X_{24}$ (X = Br[8] or Cl[2(a),9]). Thus, 18 isolated double C=C bonds are present on the fullerene cage with an average bond length of 1.331 Å. The C–C bonds of the sp^3–sp^2 type are essentially longer. Average cage C–C bond lengths with the sp^3 atom bonded to Cl are slightly shorter (1.513 Å) than those with the sp^3 atom bonded to the CF_3 group (1.530 Å). In either of the two bond groups, C–C bonds of the 6:6 type are slightly shorter that those of the 5:6 type. C–CF_3 and C–Cl bond lengths are 1.558 and 1.813 Å, respectively.

The molecular packing in a crystal of $C_{60}(CF_3)_{12}Cl_{12}$ differs dramatically from that of S_6-$C_{60}(CF_3)_{12}$. Whereas the latter is built of linear chains of molecules obviously attracted by stacking interaction between empty cage hexagons,[7,10] molecular layers can be recognised in the former (Figure 3, left). Approximately close-packed layers with an intralayer fullerene–fullerene distance of 13.37 Å (the parameter a) are packed together in the *ABC* sequence, *i.e.*, forming distorted *ccp* arrangement; the interlayer distance is 1/6 of the parameter c (9.86 Å), and the interlayer fullerene–fullerene distance is 10.58 Å. The *ABC* sequence is, however, not entirely exact because the molecules in the forth layer, though exactly below those in the first layer, are mirrored by the c glide plane in the structure (Figure 3, right).

Note that our attempts to prepare the mixed CF_3-Cl derivatives by the reverse method, *i.e.*, by the trifluoromethylation of fullerene chloride were unsuccessful. The ampoule reaction between D_{3d}-$C_{60}Cl_{30}$ and CF_3I resulted in a mixture of compounds part of which contained some Cl atoms in addition to many CF_3 groups per fullerene cage according to negative-ion MALDI analysis. However, HPLC separation did not result in the isolation of individual compounds in a crystalline form so that the structures of these compounds with low Cl contents remain unknown. The attempts to brominate S_6-$C_{60}(CF_3)_{12}$ failed. No changes were observed after the contact of S_6-$C_{60}(CF_3)_{12}$ with neat bromine for several weeks.

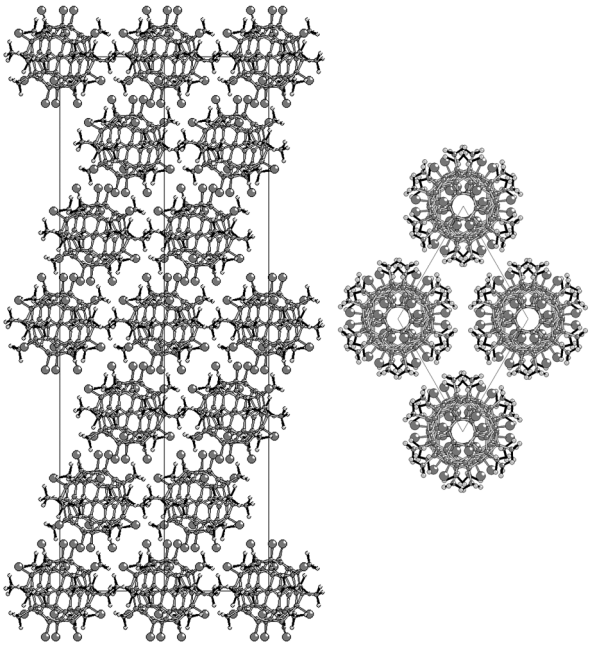

Figure 3 Cross-section of the molecular packing in the crystal structure of S_6-$C_{60}(CF_3)Cl_{12}$ by the (110) plane (left); view along the axis c with molecules only from two layers at $z = 0$ and $z = 0.5$ (right).

In conclusion, the chlorination of trifluoromethylated fullerene with $SbCl_5$ resulted in the mixed CF_3-Cl derivative $C_{60}(CF_3)_{12}Cl_{12}$. Similar reactions applied to other trifluoromethyl derivatives of C_{60} or C_{70} are expected to result in the synthesis of CF_3-Cl compounds provided that the starting CF_3 compounds are available in sufficient amounts.

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