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Crystal structure of $C_{60}Cl_6$ prepared by a reaction of C_{60} with $POCl_3$

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$C_{60}Cl_6$ was prepared using $POCl_3$ as a chlorinating agent; crystal structure determination revealed that the $C_{60}Cl_6$ molecules are packed in slightly corrugated layers, which are arranged in the ABAC sequence.

Halogenated fullerenes are of considerable interest because they are prospective precursors for the derivatization of fullerenes. Chlorofullerenes were poorly investigated in comparison with other halogenated fullerenes. Chlorinated derivatives of C_{60} such as $C_{60}Cl_{24}$ (T_h),[1] $C_{60}Cl_{28}$ (C_1),[2] $C_{60}Cl_{30}$ (C_2)[2] and $C_{60}Cl_{30}$ (D_{3d})[3] have been synthesised and structurally characterised by single-crystal X-ray crystallography. The synthesis of $C_{60}Cl_6$ was reported,[4] and this chloride was used for the preparation of organic derivatives of C_{60}.[5–8] However, the reaction of C_{60} and ICl in benzene[4] produced a variety of phenylated by-products in addition to the chloride $C_{60}Cl_6$.[9] Recently, an improved synthesis of $C_{60}Cl_6$ was reported, which allowed the preparation of pure compound without arylated by-products.[10] Although the preparation of $C_{60}Cl_6$ was described previously,[4,10,11] the addition of six chlorine atoms to the fullerene cage could be only deduced based on the data of ^{13}C NMR spectroscopy and, indirectly, on the structure of the substitution products. Here, we report the preparation of $C_{60}Cl_6$ by the chlorination of C_{60} with $POCl_3$ and the investigation of its crystal structure by single-crystal X-ray crystallography.

C_{60} (20–30 mg, Term-USA, 99.5%) and an excess of $POCl_3$ (~2 g, Aldrich, 99%) were sealed in a glass ampoule and heated at 100–150 °C for two to eight weeks. Then, the ampoule was opened and an excess of phosphorus oxytrichloride was removed by washing with 15% HCl followed by drying the product *in vacuo* over phosphorus pentaoxide during two days. The obtained product contained a mixture of red- and black-coloured crystals as thin plates and needles, respectively. Two types of crystals were separated under microscope yielding *ca.* 1 mg of each phase, which were used for recording IR spectra (KBr pellets, 2 cm^{-1} resolution on a 200 Nicolet spectrometer). Analysis of the IR spectra revealed that the red crystals were pure $C_{60}Cl_6$ as determined by the comparison with the published IR spectrum [Figure 1(*b*),(*c*)].[4,9] The IR spectrum of the black crystals [Figure 1(*a*)] was a superposition of those for C_{60} (ref. 12) and $POCl_3$ (the band at 580 cm^{-1} *viz.* 590 cm^{-1} in ref. 13) thus indicating the formation of a solvate of [60]fullerene with phosphorus oxytrichloride.†

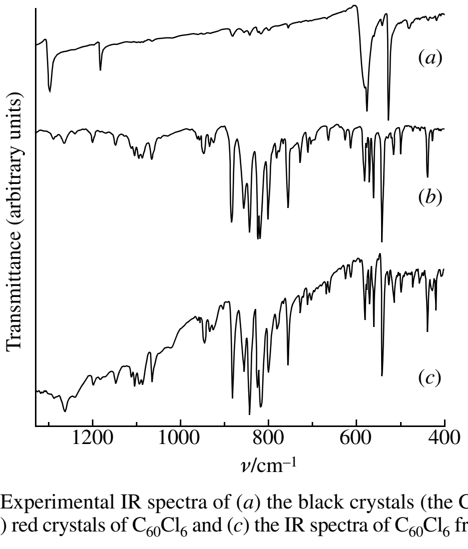

Figure 1 Experimental IR spectra of (*a*) the black crystals (the $C_{60}{\cdot}POCl_3$ solvate), (*b*) red crystals of $C_{60}Cl_6$ and (*c*) the IR spectra of $C_{60}Cl_6$ from ref. 4.

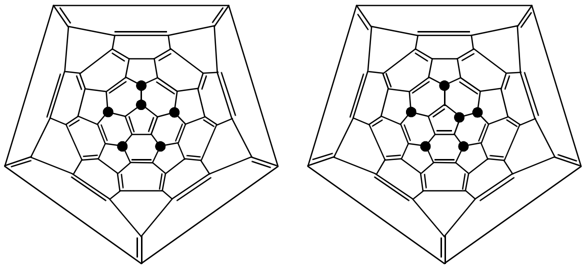

Figure 2 Schlegel diagrams showing two overlapping positions rotated with respect to one another by *ca.* 72° for each independent $C_{60}Cl_6$ molecule.

Note that the formation of the both types of crystals was also observed in experiments which were carried out at room temperature for 8–10 weeks; however, the amount of the red crystals was significantly lower in these cases. Another interesting observation concerns the fact that the formation of $C_{60}Cl_6$ took place neither at room temperature nor on heating even for 8–10 weeks, if $POCl_3$ purified by distillation was used. Trace amounts of Fe and Ti were detected by EDX analysis of the non-purified $POCl_3$ sample after hydrolysis. The ion-chromatographic analysis of the non-distilled $POCl_3$ sample dissolved in water revealed the presence of *ca.* 1% phosphorus(III) as the phoshite anion, whereas the distilled $POCl_3$ sample was free from this impurity.

An X-ray single-crystal diffraction study was carried out for the red crystal of $C_{60}Cl_6$ (0.10×0.08×0.01 mm) using synchrotron radiation.‡ The asymmetric unit contains two independent $C_{60}Cl_6$ molecules. Each of them is strongly disordered mainly due to the overlap of two positions rotated relative to one another by *ca.* 72°, as shown in Figure 2. Since the $C_{60}Cl_6$ molecule is far

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† The unit cell of black crystals was determined by means of single-crystal X-ray crystallography: orthorhombic, $a = 10.020(2)$, $b = 16.184(2)$ and $c = 19.383(3)$Å, $V = 3143.2(8)$ Å^3. Taking $Z = 4$, the independent volume, 786 Å^3, is consistent with the 1:1 ratio, *i.e.* the composition of $C_{60}{\cdot}POCl_3$.

‡ *Crystal data*: $C_{60}Cl_6$, $M = 933.36$, orthorhombic, space group *Pbca*, $a = 17.207(2)$ Å, $b = 39.875(6)$ Å and $c = 19.539(3)$ Å, $V = 13406(3)$ Å^3, $\mu = 0.568$ mm^{-1}, $Z = 16$. Synchrotron X-ray data were measured at the Swiss-Norwegian Beam Lines at the European Synchrotron Radiation Facility, Grenoble, France. The data were collected at 100 K using a MAR345 image plate detector, $\lambda = 0.7000$ Å. Reflections collected 55770, independent 13268. Some chlorine atoms were found to be disordered between two positions. Crystal structure determination and refinement were additionally complicated by strong diffuse scattering observed as modulated rods propagating through the Bragg reflections in the b^* direction. Pronounced diffuse scattering obscures extraction of the Bragg intensities thus not allowing us to obtain a precise geometry of the molecule. Anisotropic refinement with 1284 parameters yielded a conventional $R_1(F) = 0.197$ for 11775 reflections with $I > 2\sigma(I)$ and $wR_2(F^2) = 0.393$ for all reflections.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 616739. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

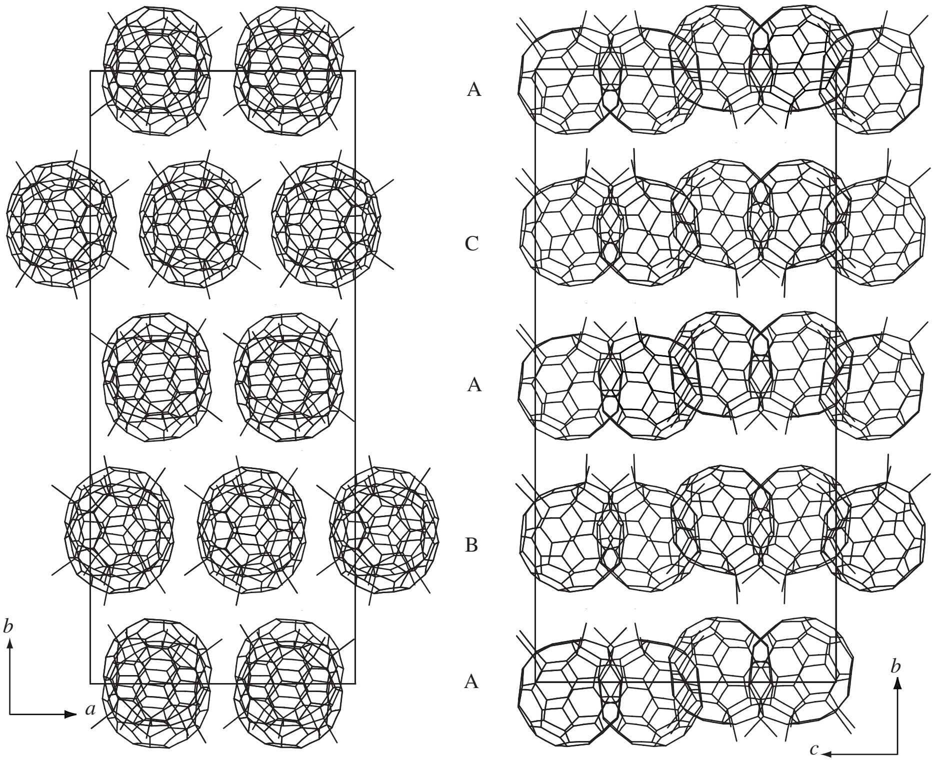

Figure 3 Packing of $C_{60}Cl_6$ molecules in the crystal structure. Only the main components of disordered molecules are shown.

from obeying the C_5 symmetry, the overlap of most atoms in the region of a skew-pyramidal attachment of Cl atoms is not perfect. The packing mode of the molecules in a crystal can be described as weakly corrugated closed-packed layers of the $C_{60}Cl_6$ molecules, which are parallel to the *ac* plane (Figure 3, right). In the layer, every $C_{60}Cl_6$ molecule is surrounded by six others, four of which are disposed at a distance of 9.88 Å and two others at 9.75 Å. Note that the top Cl atoms (in the central pentagons on Schlegel diagrams, Figure 2) always protrude outward the layer in the direction of the interlayer space. The layers are stacked in the *b* direction in the ABAC sequence (Figure 3, top). The positional disorder of the protruding Cl atoms in the interlayer space results in faults in the layer sequence manifested as diffuse rods along *b**. A modulation of diffracted intensity along the rods indicates a non-random distribution of stacking faults. Apparently, this is the main reason for the occurrence of a modulated diffuse scattering in the diffraction pattern.

A comparison between packing modes in $C_{60}Cl_6$ and $C_{60}Br_6$ (ref. 14) revealed a similar way of packing with layers of $C_{60}Br_6$ molecules and the sixth Br atoms (on tops of skew pyramids) protruding into the interlayer space. However, there is only one crystallographically independent $C_{60}Br_6$ molecule so that the packing is much more simple (AB) as compared with the crystal structure of $C_{60}Cl_6$.

In conclusion, the ampoule reaction of C_{60} with liquid $POCl_3$ results in the formation of $C_{60}Cl_6$ (in low yield) and $C_{60}{\cdot}POCl_3$. Single-crystal X-ray crystallography revealed the presence of the ABAC packing of $C_{60}Cl_6$ layers characterised by faults in the layer sequence.

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