Preparation and crystallographic characterization of $C_{60}Cl_{24}$†

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$C_{60}Cl_{24}$ has been synthesized by the chlorination of C_{60} with VCl_4 or $C_{60}Br_{24}$ with $SbCl_5$; the X-ray single crystal structure of $C_{60}Cl_{24}\cdot 2Br_2$ confirmed the molecular T_h symmetry in good agreement with the IR data and theoretical calculations.

The chlorination of fullerenes has been intensively studied since the early 1990s because these compounds are important synthons for further derivatization of fullerenes. However, reliable data were only obtained for the chlorofullerenes $C_{60}Cl_6$ and $C_{70}Cl_{10}$, which were characterized using ^{13}C NMR spectroscopy.[1,2] Quite recently, a new chloride of C_{60}, D_{3d}–$C_{60}Cl_{30}$, was obtained and its molecular structure was determined by X-ray crystallography.[3]

To date, there have been some reports about the preparation of samples of composition $C_{60}Cl_{24}$. Heating of C_{60} in a chlorine flow was claimed to yield $C_{60}Cl_{24}$.[4,5] The composition of these samples was determined only by means of elemental analysis and/or thermogravimetry. In another synthetic study, the product of UV irradiation of a solution of [60]fullerene in carbon tetrachloride saturated with chlorine was suggested to contain $C_{60}Cl_{24}$ based on FAB mass spectrometric data.[6] Though $C_{60}Cl_{24}$ was proposed to be isostructural to T_h–$C_{60}Br_{24}$, no redundant proof for the molecular structure of $C_{60}Cl_{24}$ was actually obtained. Moreover, whenever spectroscopic data for $C_{60}Cl_{24}$ were presented,[4,7] the presence of broad unresolved bands ruled out the formation of an individual compound, at least with T_h molecular symmetry.

In our recent study, we reported the high yield synthesis of $C_{60}Cl_{24}$ and suggested that it had T_h molecular symmetry by comparison of the experimental and calculated IR spectra.[8] Here, we confirm that the chlorination of C_{60} using VCl_4 or $C_{60}Br_{24}$ using $SbCl_5$ produces T_h–$C_{60}Cl_{24}$ which is unambiguously evidenced by an X-ray single-crystal structure investigation.

$C_{60}Cl_{24}$ samples were prepared with the use of $SbCl_5$ or VCl_4 as described previously.[8] Typically, chlorination of C_{60} (50 mg) by excess VCl_4 (2 ml) was performed at 160 °C in a glass ampoule over 7 days. When the starting reagents were $C_{60}Br_{24}$ (50 mg) and $SbCl_5$ (2 ml), the ampoules were heated at 140 °C for 14 days. The inorganic components of the reaction mixtures such as excess $SbCl_5$ or VCl_4, $SbCl_3$ or VCl_3 were removed by washing with 15% HCl followed by drying the product over P_2O_5 yielding yellowish-brown powders. Recrystallization from neat bromine at room temperature resulted in a coarse crystalline material containing very small orange coloured crystals suitable for X-ray investigation.‡

The crystal structure determination for $C_{60}Cl_{24}\cdot 2Br_2$ revealed the molecular symmetry of $C_{60}Cl_{24}$ to be very close to T_h as previously suggested.[8] Accordingly, there are only five different types for C–C and one for C–Cl bonds. The $C_{60}Cl_{24}$ molecule (Fig. 1) within the crystal possesses C_i symmetry only but the deviations of individual bond lengths from their average within each bond type rarely exceed 0.01 Å. Average C–C distances of types a–e labeled on a Schlegel diagram (Fig. 1, bottom) are in

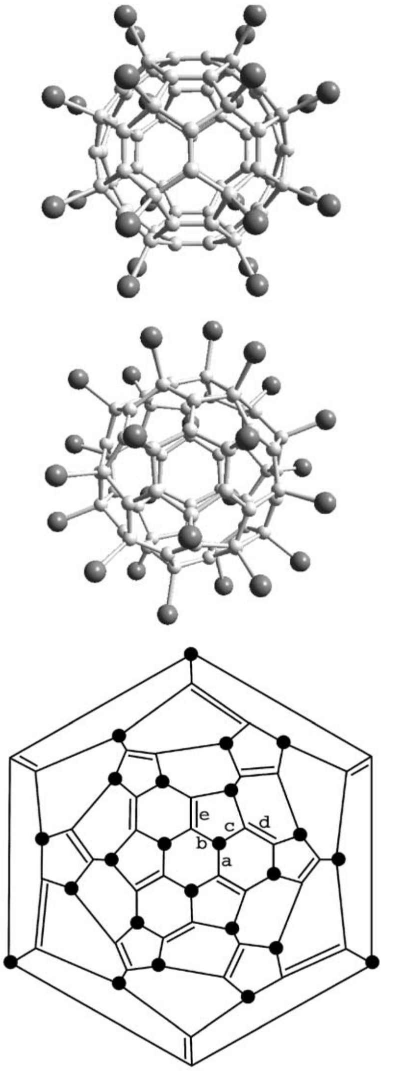

Fig. 1 View of the $C_{60}Cl_{24}$ molecule along the non-crystallographic C_2 and C_3 axes; Schlegel diagram showing location of the chlorines and labeling for independent C–C bond types.

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† Electronic supplementary information (ESI) available: Details of vibrational calculations. See http://www.rsc.org/suppdata/cc/b4/b416341a/
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Table 1 Experimental and calculated bond lengths in $C_{60}Cl_{24}$ (Å)

Bond type[a]	a	b	c	d	e	C—Cl
Exper. (av.)	1.511	1.495	1.522	1.327	1.353	1.840
Calculation 1	1.516	1.495	1.514	1.338	1.349	1.848
Calculation 2	1.513	1.494	1.514	1.326	1.335	1.846

[a] See Schlegel diagram on Fig. 1 for bonds' labeling.

good agreement with the values obtained using PBE/TZ2P (1) and B3LYP/cc-pVTZ(-f) (2) methods (Table 1).§ Both approaches predict bond lengths quite close to the experimentally determined values. However, the difference between d and e type C=C bonds predicted by DFT is half that experimentally determined.

With the exception of C–Hal bonds, geometry parameters of the $C_{60}Cl_{24}$ molecule are very similar to those of T_h–$C_{60}Br_{24}$.[9–11] For example, average bond lengths for single and double C–C bonds are 1.509 and 1.510 Å, 1.344 and 1.346 Å, respectively.[9] The distortions from the spherical shape are also similar in both molecules, the average distances of C atoms from the center of the cage being 3.765 Å for sp^3 C (3.768 Å in $C_{60}Br_{24}$), 3.582 and 3.476 Å for the two types of sp^2 C atoms (3.586 and 3.481 Å in $C_{60}Br_{24}$).[9] The crystal structure of $C_{60}Cl_{24}\cdot 2Br_2$ is isotypic to that of $C_{60}Br_{24}\cdot 2Br_2$ with the same closest cubic packing motifs of pseudospherical $C_{60}X_{24}$ molecules (Fig. 2).[9,10] The Br_2 molecules with a Br–Br distance of 2.271 Å occupy the tetrahedral holes between the host molecules.

Thermal decomposition of $C_{60}Cl_{24}$ into C_{60} and Cl_2 occurs in the temperature range of 280–390 °C with a maximal rate of mass loss at 330 °C. Thus, $C_{60}Cl_{24}$ is much less thermally stable than D_{3d}–$C_{60}Cl_{30}$, which decomposes at 450–500 °C.[3]

The IR spectrum of $C_{60}Cl_{24}$¶ contains main bands at 146w, 373m, 588m, 645m, 732m, 785m, 815s, 881vs, 929s, 958m, 1049w, 1115w, 1240s, 1325w, 1633w, 1670vw, and 1699w cm^{-1} (Fig. 3). Its close analogy with the IR spectrum of $C_{60}Br_{24}$ is an additional confirmation of the T_h symmetry and the bulk isomeric purity of the synthesized chlorofullerene. Theoretical PBE calculations predict a very similar distribution of absorption bands though shifted to lower wave numbers. The scaling of the force field with seven factors allowed us to attain a close agreement between calculated and experimental spectra. It is worth mentioning that these coefficients can be used in calculations of IR spectra of other chlorinated fullerenes.[3,12] A comparison of the IR spectrum presented in this work with spectroscopic data reported previously for samples of similar composition shows that earlier attempts resulted in a mixture of chlorofullerenes instead of pure T_h–$C_{60}Cl_{24}$.[4,7] A close inspection of the IR spectrum presented in the earlier paper[4] showed that $C_{60}Cl_{24}$ was a minor component in the chlorination product containing primarily a mixture of $C_{60}Cl_{28}$[13] and other unidentified chlorofullerenes.

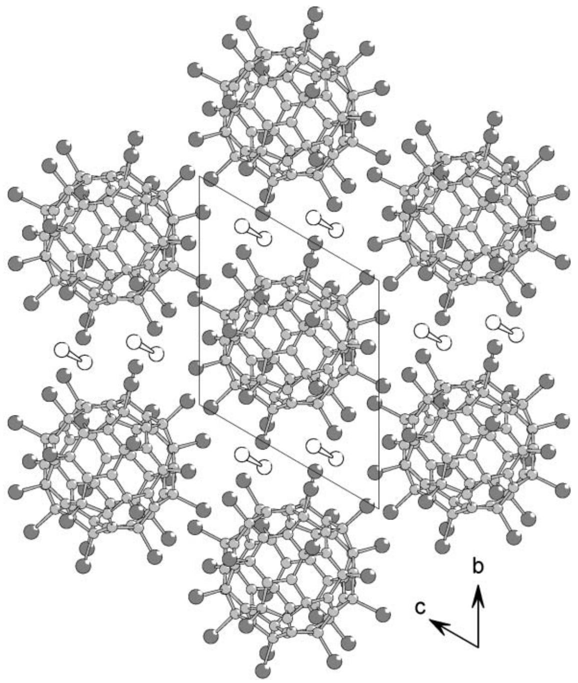

Fig. 2 The packing of $C_{60}Cl_{24}$ molecules with Br_2 molecules occupying the tetrahedral holes between the layers.

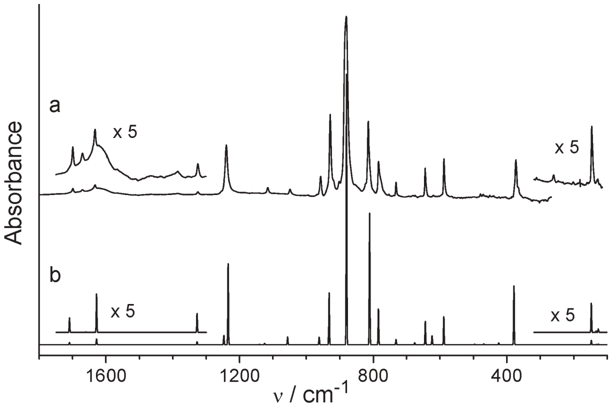

Fig. 3 FT-IR spectrum of $C_{60}Cl_{24}$ (a); IR spectrum calculated after the scaling of the molecule force field (b).

According to comprehensive semiempirical and DFT computations,[14] the T_h isomer of $C_{60}Cl_{24}$ with isolated C–C double bonds and the absence of 1,2 Cl–Cl contacts has the lowest energy among all possible isomers with this composition. It is known, however, that further chlorination of $C_{60}Cl_{24}$ with the same chlorination agents results in the formation of $C_{60}Cl_{28}$ or C_2–$C_{60}Cl_{30}$, the structures of which contain two aromatic six-membered rings along with the chains of chlorinated (sp^3) carbon atoms.[13] Chlorination of $C_{60}Cl_{24}$ with $SbCl_5$ at a higher temperature (*ca.* 300 °C) produces a thermodynamically stable D_{3d} isomer of $C_{60}Cl_{30}$ containing two benzenoid and one trannulene ring in its molecular structure.[3,13]

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Notes and references

‡ *Crystal data*: $C_{60}Cl_{24}\cdot 2Br_2$, triclinic, $P\bar{1}$, a = 12.200(1), b = 12.484(1), c = 12.591(1) Å, α = 60.433(4), β = 62.908(5), γ = 84.406(5)°, V = 1464.8(2) Å^3, D_c = 2.144 g cm^{-1}, Z = 1, T = 100 K. Data were collected on a MAR345 image plate using synchrotron radiation at the BESSY storage ring (λ = 0.9184 Å), PSF BL 14.2 of the Free University of Berlin, Germany. Anisotropic refinement with 4607 reflections and 398 parameters yielded a conventional R_1 (F) = 0.078 for 3922 reflections with $I > 2\sigma(I)$ and wR_2 (F^2) = 0.226 for all reflections. Estimated standard deviations for individual C–C and C–Cl bonds were 0.009 and 0.007 Å, respectively. CCDC 254950. See http://www.rsc.org/suppdata/cc/b4/b416341a/ for crystallographic data in .cif or other electronic format.

§ The program PRIRODA with the implemented original basis set of TZ2P quality (D. N. Laikov, *Chem. Phys. Lett.,* 1997, **281**, 151) and the PBE exchange–correlation functional (J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* 1996, **77**, 3865) were used in the structural and vibrational calculations. DFT calculations of the geometry parameters were also performed at B3LYP/cc-pVTZ(-f) level using a PC GAMESS package (http://classic.chem.msu.su/gran/gamess/index.html). The DISP program package (A. G. Yagola, I. V. Kochikov, G. M. Kuramshina and Y. A. Pentin, *Inverse Problems of Vibrational Spectroscopy*, VSP, Zeist, 1999) was used for solution of vibrational problems and scaling of the force field.†

¶ IR spectra of $C_{60}Cl_{24}$ were measured with 1 cm^{-1} resolution on a Bruker Equinox 55 FT spectrometer in KBr pellets (mid-IR range) and in pellets from the pure substance (far-IR range).

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