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Synthesis and structures of C_{60} fullerene chlorides

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Systematic study of chlorination of fullerene C_{60} with inorganic chlorides $SbCl_5$, VCl_4, $MoCl_5$, and $KICl_4$ was carried out. Higher chlorofullerenes, *viz.*, T_h-$C_{60}Cl_{24}$, $C_{60}Cl_{28}$, C_2-$C_{60}Cl_{30}$, and D_{3d}-$C_{60}Cl_{30}$, can be prepared depending on the temperature and time of chlorination. The molecular and crystal structures of $C_{60}Cl_{24} \cdot VOCl_3$, $C_{60}Cl_{30} \cdot 2CS_2$, and $C_{60}Cl_{30}O_{1.22}$ were determined by single-crystal X-ray diffraction. Fullerenes $C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$ were shown to be only kinetically stable, whereas D_{3d}-$C_{60}Cl_{30}$ is a thermodynamically stable product. Transformations of less chlorinated fullerenes into more chlorinated products are accompanied by substantial changes in the addition patterns.

Key words: fullerene, X-ray crystallography, chlorination, synchrotron radiation, fullerene chlorides, IR spectroscopy, chlorinating reagents, density functional theory, antimony pentachloride, aromaticity, vanadium tetrachloride, trannulene, molybdenum pentachloride, thermal stability, potassium tetrachloroiodate, vanadium oxotrichloride.

Until recently, fullerene chlorides have been studied in much less detail than fluorides or bromides. Numerous fluorofullerenes with the composition $C_{60}F_n$ (n = 2—48) are known,[1] whereas data for fluorinated fullerene C_{70} are scarce.[2,3] Properties of fullerene bromides have not been adequately studied because of their low thermostability and poor solubility. However, reliable structural data have been obtained for many of them ($C_{60}Br_6$, $C_{60}Br_8$, $C_{60}Br_{24}$, $C_{70}Br_{10}$, and $C_{78}Br_{18}$).[4—6]

Until recently, the published data for chlorofullerenes have been contradictory. The reaction of solid fullerene C_{60} with liquid chlorine at −36 °C afforded[7] mixtures of chlorides with molecular formulas $C_{60}Cl_{12-15}$. Chlorination of fullerene C_{60} in a flow of chlorine at 250 °C produced[8] a sample, whose composition corresponded to $C_{60}Cl_{24}$ (elemental analysis data). The IR spectrum of this sample contained broad absorption bands, which was indicative of the formation of a mixture of chlorides rather than an individual compound. An assumption[9] that the product prepared in a flow of chlorine at 325 °C is isostructural with the bromide T_h-$C_{60}Br_{24}$ was not confirmed experimentally because only broad absorption bands were observed in the IR spectra. A product with the composition $C_{60}Cl_{24}$, which was also synthesized by direct chlorination of fullerene, was studied based on electronic absorption spectra, which demonstrated[10] that the geometry of this chloride cannot be described by the molecular symmetry T_h.

The chlorination product formed upon UV irradiation of a solution of fullerene C_{60} in CCl_4 contained chlorofullerene $C_{60}Cl_{24}$, as followed from mass-spectrometric analysis.[11] However, no evidence was presented that it was pure $C_{60}Cl_{24}$ that has been synthesized. MALDI mass-spectrometric studies of reaction products prepared by UV irradiation of a mixture of C_{60} with liquid chlorine revealed[12] several higher chlorofullerenes containing up to 32 chlorine atoms per C_{60} fullerene cage.

Reliable data on the composition and addition patterns are available for two chlorofullerenes, *viz.*, $C_{60}Cl_6$ [13] and $C_{70}Cl_{10}$,[14] which were prepared by the reactions of C_{60} or C_{70}, respectively, with iodine monochloride in benzene and were characterized by ^{13}C NMR spectroscopy. However, it should be noted that phenyl derivatives of fullerenes are formed as by-products.[15] Rather recently,[16] the reactions of C_{60} with ICl, ICl_3, and $KICl_4$ in 1,2-dichlorobenzene have been examined. The preparation of chlorofullerenes with compositions ranging from $C_{60}Cl_6$ to $C_{60}Cl_{26}$ was reported, but these chlorides were not adequately characterized as individual compounds. In 2005, we succeeded in synthesizing individual higher fullerene C_{60} chlorides, *viz.*, $C_{60}Cl_{24}$,[17] $C_{60}Cl_{28}$,[18] and $C_{60}Cl_{30}$ (two isomers),[18,19] by virtue of the use of new chlorinating agents ($SbCl_5$ and VCl_4). The molecular structures of these fullerene chlorides have been established by X-ray diffraction analysis.

In the present study, we systematically investigated the reactions of C_{60} with inorganic chlorides of elements with variable oxidation states, examined interconversions of fullerene chlorides, and determined the structures of two solvates, *viz.*, $C_{60}Cl_{24} \cdot VOCl_3$ and $C_{60}Cl_{30} \cdot 2CS_2$, and oxochloride $C_{60}Cl_{30}O_2$ by X-ray diffraction.

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Experimental

Experiments were carried out with fullerene C_{60} (99.98%, TERMUSA). Fullerene bromide was synthesized according to a known procedure.[20] The purity of the reaction products was estimated by comparing the IR spectra of the samples with the literature data. Molybdenum pentachloride (98%, Aldrich), iodine monochloride (98%, Aldrich), and vanadium(v) oxochloride (99%, Aldrich) were used without preliminary purification. Antimony pentachloride (99%, Aldrich) was distilled under a chlorine atmosphere. Potassium tetrachloroiodate was prepared from $KIBr_2$ in a flow of chlorine at room temperature.[21] The purity of the sample was checked by powder X-ray diffraction analysis. Vanadium tetrachloride was synthesized by chlorination of metallic vanadium at 300—350 °C followed by distillation in a flow of chlorine at 152—154 °C.

Chorination of fullerene or its bromide with an excess of a chlorinating reagent was carried out in two-compartment glass tubes both at room temperature and in the temperature range of 100—300 °C. Fullerene (30 mg) and a large excess of a chlorinating agent were placed in the tube, this was cooled with liquid nitrogen, evacuated, and sealed. After completion of the reaction, the excess of the chlorinating agent and its reduction products (in the case of $SbCl_5$ and ICl) were distilled off by cooling one compartment of the tube with liquid nitrogen. Excess $MoCl_5$, VCl_4, $VOCl_3$, and $KICl_4$ were removed by washing with 15% HCl, and the products were kept for 2 days in a desiccator over P_2O_5.

After removal of inorganic chlorides, the percentage of carbon and chlorine in the samples was determined by elemental analysis. The IR spectra of the samples (KBr pellets) were recorded on a 200 NICOLET spectrometer in the region of 400—4000 cm^{-1}. Thermographic study of fullerene chlorides was carried out in an inert atmosphere on a STA 409 C Skimmer® (NETZSCH) thermoanalyzer with mass-spectrometric analysis of the gas phase.

Geometry optimization of the molecules and calculations of their IR spectra were carried out using the PRIRODA program[22] with the PBE functional[23] and the TZ2P triple-zeta basis set. The relative energies of isomers were also calculated by the B3LYP method[24] with the cc-pVTZ(-f) basis set using the PC GAMESS program package.[25]

Compounds prepared as small crystals were recrystallized to prepare crystals suitable for X-ray diffraction study. Tiny crystals of $C_{60}Cl_{24}$ that have been obtained with the use of $VOCl_3$ were studied using synchrotron radiation at the BL14.2 beamline (λ = 0.9100 Å) on the BESSY storage ring (PSF Laboratory, Free University, Berlin, Germany). Crystals of the solvate $C_{60}Cl_{30} \cdot 2CS_2$ (prepared by recrystallization of $C_{60}Cl_{30}$ from carbon disulfide) and mixed crystals of oxide $C_{60}Cl_{30}O_2$ and $C_{60}Cl_{30}$ were studied on an IPDS (Stoe) single-crystal diffractometer equipped with an area detector (MoKα radiation, graphite monochromator, λ = 0.71073 Å). Crystallographic calculations were carried out using the SHELXS97[26] and SHELXL97 program packages.[27] Crystallographic data and details of data collection and structure refinement are given in Table 1. Complete crystallographic data were deposited with the Cambridge Structural Database (refcodes CCDC 260207—260209).

Results and Discussion

Synthesis of chlorofullerenes

The published data show that no individual chlorofullerenes could be obtained by chlorination of fullerene C_{60} with gaseous or liquid chlorine. Earlier,[28] we have

Table 1. Crystallographic data and details of data collection and refinement

Parameter	Characteristic		
Molecular formula	$C_{60}Cl_{24} \cdot VOCl_3$	$C_{60}Cl_{30} \cdot 2CS_2$	$C_{60}Cl_{30}O_{1.22} \cdot 0.05Cl_2$
Molecular weight	1744.69	1936.36	1805.28
Crystal symmetry	Trigonal	Tetragonal	Monoclinic
Space group	$R\overline{3}$	$P4_2/m$	$P2_1/n$
a/Å	12.4934(4)	13.4450(4)	12.780(2)
b/Å	12.4934(4)	13.4450(4)	13.572(2)
c/Å	31.669(2)	17.1008(6)	16.969(3)
Angle/deg	120 (γ)	90 ($\alpha = \beta = \gamma$)	99.71(2) (β)
V/Å^3	4280.8(3)	3091.3(2)	2901.1(8)
Z	3	2	2
d_{calc}/g cm^{-3}	2.030	2.080	2.067
Crystal dimensions/mm	0.03×0.03×0.03	0.32×0.21×0.08	0.60×0.25×0.04
T/K	100	100	170
θ_{max}/deg (λ/Å)	36.7 (0.9100)	30.0 (0.71073)	27.5 (0.71073)
Number of measured/independent reflections	7588/2043	28832/4415	26467/6652
Number of reflections with $F^2 > 2\sigma(F^2)$	1788	4318	4996
Number of reflections/parameters in refinement	2104/142	4392/226	6639/473
R_1/wR_2	0.0532/0.1497	0.0232/0.0523	0.0253/0.0529
$\Delta\rho$/e $\cdot$ Å^{-3}	1.094/–1.081	0.788/–0.735	0.362/–0.475

Table 2. Conditions of formation of chlorofullerenes using different chlorinating reagents

Entry	Starting compound	Chlorinating reagents	T/°C	τ*/day	Reaction products
1	C_{60}	$SbCl_5$	25	14—180	Mixture of chlorofullerenes**
2	$C_{60}Br_{24}$	$SbCl_5$	140	7	$C_{60}Cl_{24}$, $C_{60}Br_{24}$
3	$C_{60}Br_{24}$	$SbCl_5$	140	14	$C_{60}Cl_{24}$
4	C_{60}	$SbCl_5$	170	1	$C_{60}Cl_{24}$, $C_{60}Cl_{28}$, C_2-$C_{60}Cl_{30}$**
5	$C_{60}Cl_{24}$	$SbCl_5$	300	2	D_{3d}-$C_{60}Cl_{30}$
6	C_2-$C_{60}Cl_{30}$	$SbCl_5$	300	2	D_{3d}-$C_{60}Cl_{30}$
7	C_{60}	$SbCl_5$	280	1	D_{3d}-$C_{60}Cl_{30}$
8	C_{60}	VCl_4	160	7	$C_{60}Cl_{24}$
9	C_{60}	VCl_4	160	40	$C_{60}Cl_{24}$, $C_{60}Cl_{28}$, C_2-$C_{60}Cl_{30}$
10	C_{60}	VCl_4	160	60	C_2-$C_{60}Cl_{30}$
11	C_{60}	VCl_4	280	2	$C_{60}Cl_{24}$, $C_{60}Cl_{28}$, C_2-$C_{60}Cl_{30}$**
12	$C_{60}Br_{24}$	$KICl_4$	150	30	$C_{60}Cl_{24}$, $C_{60}Br_{24}$
13	$C_{60}Br_{24}$	$KICl_4$	150	90	$C_{60}Cl_{24}$
14	$C_{60}Br_{24}$	$KICl_4$	210	6	$C_{60}Cl_{24}$
15	C_{60}	ICl	120	30	$C_{60}Cl_{28}$
16	C_{60}	$MoCl_5$	210	11	$C_{60}Cl_{24}$, C_{60}
17	C_{60}	$MoCl_5$	225	1	$C_{60}Cl_{24}$, C_{60}
18	C_{60}	$MoCl_5$	300	3	D_{3d}-$C_{60}Cl_{30}$, C_{60}
19	C_{60}	$VOCl_3$	150	4	$C_{60}Cl_{24}$ **

* The reaction time.

** Samples were characterized by broad absorption bands in IR spectra.

proposed to employ inorganic chlorides of elements with variable oxidation states, such as $SbCl_5$ and VCl_4, as new chlorinating agents for selective chlorination of fullerenes. In the present study, we carried out systematic investigation of the reaction of C_{60} with these chlorinating agents and examined reactions with a number of other reagents, such as $MoCl_5$, $VOCl_3$, and $KICl_4$. The reaction products were identified primarily by IR spectroscopy, because several chlorofullerenes have already been reliably characterized by this method. For several samples, valuable information on the composition was obtained by MALDI mass spectrometry (for more detail, see Refs 28 and 29). Thermogravimetric studies and elemental analysis provided additional information on the compositions of chlorination products. The principal results obtained in the study of the reactions of C_{60} with chlorinating reagents at different temperatures and different reaction times are given in Table 2.

Experiments with $SbCl_5$ as the chlorinating agent were carried out for 1—24 weeks at both room temperature and 100—300 °C. The reaction of C_{60} with $SbCl_5$ at room temperature for 2—4 weeks produced a mixture of chlorofullerenes with composition $C_{60}Cl_n$ (n = 12—28),[28] no individual compound was obtained even after 24 weeks (see Table 2, entry *1*). Heating of C_{60} and antimony pentachloride at 140—160 °C led to simplification of the IR spectra of the reaction products. An analogous situation was observed when the reaction was carried out with bromide $C_{60}Br_{24}$ instead of C_{60}. The reaction with $C_{60}Br_{24}$ at 140 °C for 14 days afforded a compound whose IR spectrum had a small number of sharp bands (see Table 2, entry *3*, Fig. 1, spectrum *1*) and was very similar to the spectrum of bromide $C_{60}Br_{24}$ studied earlier.[20] This fact together with elemental analysis data led us to conclude that the resulting chloride has the composition $C_{60}Cl_{24}$

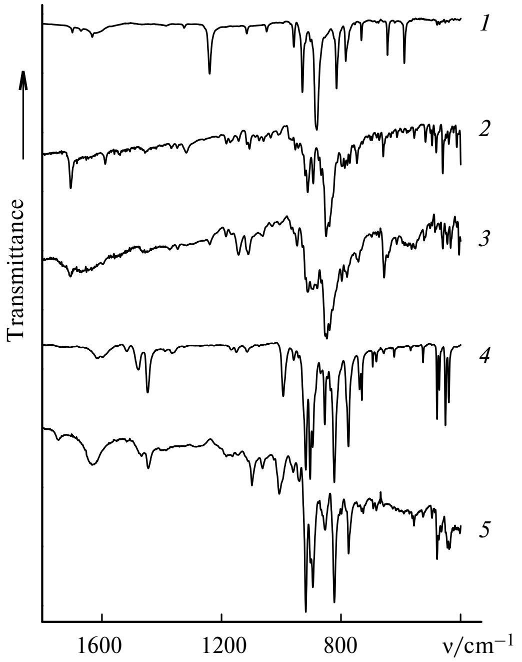

Fig. 1. IR spectra of $C_{60}Cl_{24}$ (*1*), $C_{60}Cl_{28}$ (*2*), C_2-$C_{60}Cl_{30}$ (*3*), D_{3d}-$C_{60}Cl_{30}$ (*4*), and a mixture of $C_{60}Cl_{30}O_2$ (61%) and D_{3d}-$C_{60}Cl_{30}$ (39%) (*5*).

and is isostructural with bromofullerene. When the time of the reaction of $C_{60}Br_{24}$ with antimony pentachloride was reduced to 7 days, the IR spectra of the samples corresponded to a superposition of the spectra of chloride $C_{60}Cl_{24}$ and unconsumed fullerene bromide, which indicates that chlorination occurs selectively under these conditions (see Table 2, entry *2*). The reaction of C_{60} with VCl_4 at 160 °C within only 1 week afforded a product, whose IR spectrum was characteristic of $C_{60}Cl_{24}$ (see Table 2, entry *8*).

In a series of experiments, chlorination of C_{60} with vanadium tetrachloride performed at 160—180 °C but for a longer period of time (40—50 days) afforded samples whose IR spectra were totally different. Thus the absorption bands corresponding to $C_{60}Cl_{24}$ were absent, and the spectrum showed the strongest absorption band at 850 cm^{-1}, which was observed as a shoulder in the IR spectra of products containing $C_{60}Cl_{24}$ as the major component (see Fig. 1, spectrum *2*).[28] Chemical analysis of these samples gave the C : Cl ratio of 60 : 28 (±0.5). Later on, this ratio was confirmed by determining the molecular structure of the adduct $C_{60}Cl_{28} \cdot ICl$, which was characterized by an analogous IR spectrum and was prepared by the reaction of C_{60} with iodine monochloride (see Table 2, entry *15*). Apparently, it is the presence of $C_{60}Cl_{28}$ as an impurity in samples containing $C_{60}Cl_{24}$ as the major component that masked the presence of the latter in the MALDI mass spectra.[29]

Chlorination of C_{60} with vanadium tetrachloride for 60 days afforded a product with composition $C_{60}Cl_{29\pm1.0}$ (see Table 2, entry *10*) whose IR spectrum was on the whole very similar to that of $C_{60}Cl_{28}$, except for a substantial decrease in the intensity of absorption bands at 1705 and 1589 cm^{-1} (see Fig. 1, spectrum *3*). X-ray diffraction study allowed us to refine the composition of the major component of this product as $C_{60}Cl_{30}$ (molecular symmetry C_2, the notation C_2-$C_{60}Cl_{30}$), which is structurally similar to $C_{60}Cl_{28}$. Taking into account that the IR spectrum of the sample contained weak absorption bands at 1589 and 1704 cm^{-1} characteristic of the spectrum of $C_{60}Cl_{28}$, it can be concluded that the latter was present as a minor admixture to chloride C_2-$C_{60}Cl_{30}$.

Study of the dynamics of chlorination of fullerene C_{60} with antimony pentachloride at 250 °C demonstrated that $C_{60}Cl_{24}$ with an admixture of chloride $C_{60}Cl_{28}$ or C_2-$C_{60}Cl_{30}$ was formed in 1 h, whereas an increase in the reaction time to 24 h led to an increase in the percentage of the latter in the mixture. At lower temperatures (170 and 225 °C), analogous changes in the composition of the chlorination products occurred in longer periods of time. For example, IR spectroscopic studies demonstrated that the samples prepared at 170 °C in 100 h and at 250 °C in 2 h were very similar in composition.

The time of high-temperature syntheses (280—300 °C) using C_{60} and $SbCl_5$ was varied from 1 to 5 days. However, chlorination of fullerene C_{60} at 280 °C afforded chloride $C_{60}Cl_{30}$ with molecular symmetry D_{3d} (D_{3d}-$C_{60}Cl_{30}$) in 1 day (see Table 2, entry *7*). The IR spectrum of this product is shown in Fig. 1 (spectrum *4*). However, no pure chloride D_{3d}-$C_{60}Cl_{30}$ could be obtained by chlorination of fullerene C_{60} with vanadium tetrachloride at the same temperature for 2 days. In the latter experiment, a mixture of fullerene chlorides $C_{60}Cl_{24}$, $C_{60}Cl_{28}$, and/or C_2-$C_{60}Cl_{30}$ was obtained (see Table 2, entry *11*).

Thus, systematic study of the reactions of C_{60} with $SbCl_5$ and VCl_4 revealed substantial differences in their chlorinating activity. For example, the reaction of fullerene C_{60} with vanadium tetrachloride at 160—170 °C afforded $C_{60}Cl_{24}$ as the major product after 7 days, whereas the reactions with $SbCl_5$ as the chlorinating reagent at the same temperature afforded higher chlorofullerenes with composition $C_{60}Cl_n$ (n = 24, 28, or 30) in 1 day. An analogous tendency was observed at higher temperatures. The reaction of C_{60} with $SbCl_5$ at 280 °C produced individual chloride D_{3d}-$C_{60}Cl_{30}$ in 1 day, whereas only a mixture of chlorofullerenes $C_{60}Cl_{24}$ and $C_{60}Cl_{28}/C_2$-$C_{60}Cl_{30}$ was obtained after 2 days in the synthesis with vanadium tetrachloride. These results led us to conclude that the chlorinating activity of $SbCl_5$ is higher than that of VCl_4.

In the present study, we also examined the possibility of performing chlorination of fullerene C_{60} with other inorganic chlorides and oxochlorides. Pure chloride $C_{60}Cl_{24}$ can be prepared with the use of $KICl_4$ or $MoCl_5$ (see Table 2). The advantage of $KICl_4$ is that unconsumed inorganic chlorides can be easily and completely removed after completion of the reaction by washing with aqueous HCl, whereas the drawback is a rather high pressure in the tube due to formation of ICl and Cl_2. After 7—30 days, the reaction of potassium tetrachloroiodate with $C_{60}Br_{24}$ at 150 °C afforded the reaction product $C_{60}Cl_{24}$ contaminated with the starting bromide $C_{60}Br_{24}$. Pure chlorofullerene $C_{60}Cl_{24}$ was obtained only after 90 days (see Table 2, entry *13*). An increase in the temperature to 200 °C resulted in the formation of pure chlorofullerene $C_{60}Cl_{24}$ after 6 days (see Table 2, entry *14*), whereas an increase in the reaction time to 45 days was not accompanied by changes in the composition of the product.

The reaction of molybdenum pentachloride with C_{60} at 210 and 225 °C produced chloride $C_{60}Cl_{24}$ (see Table 2, entries *16* and *17*), whereas the reaction at higher temperature (300 °C) afforded D_{3d}-$C_{60}Cl_{30}$ (see Table 2, entry *18*), both chlorides containing an admixture of C_{60}. The presence of unconsumed fullerene can be attributed to an inefficient contact of C_{60} with liquid molybdenum pentachloride because of high viscosity of the melt containing dinuclear rather than mononuclear molecules. In addition, the reduction product of $MoCl_5$ or chlorofullerene formed during the reaction can be poorly soluble in the melt and prevent further interactions with C_{60}.

Chlorination of fullerene C_{60} with $VOCl_3$ at 150 °C for 4 days afforded a product, in the spectrum of which the main absorption bands corresponded to chlorofullerene $C_{60}Cl_{24}$. However, this product was not an individual compound, because the IR spectrum of the sample contained not only absorption bands belonging to chloride $C_{60}Cl_{24}$ but also several additional broad bands. The reaction afforded the major product (orange powder) along with hygroscopic crystals, whose composition as $C_{60}Cl_{24} \cdot VOCl_3$ was determined by X-ray diffraction study (see below). Thus, the reaction of fullerene C_{60} with $VOCl_3$ under these conditions did not produce pure $C_{60}Cl_{24}$, although crystal growth of the solvate $C_{60}Cl_{24} \cdot VOCl_3$ started in some grains.

Thermoanalytical studies of $C_{60}Cl_{24}$ and $C_{60}Cl_{30}$ ($C_{60}Cl_{28}$) showed that thermal stability of chlorofullerenes is much higher than that of bromofullerenes. Their thermal decomposition occurs with elimination of chlorine to form C_{60}, as evidenced by the results of mass-spectrometric monitoring of the gas phase and IR spectroscopy of the residue. Thermal decomposition of the individual chlorides occurs in the temperature range of 280—390 °C for $C_{60}Cl_{24}$ [28] and 400—550 °C for D_{3d}-$C_{60}Cl_{30}$,[19] whereas this range for bromides is 100—220 °C.[30]

Thus, systematic study of chlorination of fullerene C_{60} with inorganic chlorides revealed the following main trends.

1. At 140—180 °C, individual compounds $C_{60}Cl_{24}$, $C_{60}Cl_{28}$, and C_2-$C_{60}Cl_{30}$ can be prepared. Chlorination of fullerene C_{60} at temperatures higher than 250 °C afforded chloride D_{3d}-$C_{60}Cl_{30}$.
2. In a wide temperature range, antimony pentachloride has higher chlorinating activity than vanadium tetrachloride.
3. The time and/or temperature of the reaction with the same chlorinating reagents can be substantially reduced if bromide $C_{60}Br_{24}$ is used instead of fullerene C_{60}.
4. Due to high selectivity of molybdenum pentachloride as the chlorinating reagent, T_h-$C_{60}Cl_{24}$ or D_{3d}-$C_{60}Cl_{30}$ are produced without formation of chlorofullerenes of intermediate compositions, although with an admixture of fullerene C_{60}.
5. Taking into account the ease and completeness of removal of unconsumed inorganic chlorides after the reaction of $C_{60}Br_{24}$ with potassium tetrachloroiodate, the latter can be considered as a promising chlorinating reagent for the preparation of pure $C_{60}Cl_{24}$.

Molecular and crystal structure

Data on the molecular structure of chlorofullerene containing the smallest known number of chlorine atoms per molecule, *viz.*, C_s-$C_{60}Cl_6$, which has been synthesized more than a decade ago, are limited to the addition pattern of six chlorine atoms (Fig. 2, *a*). These data have been obtained from the analysis of the ^{13}C NMR spectrum and were later confirmed by isolation and characterization of the products of complete or partial replacement of chlorine atoms by methyl or phenyl groups.[13,31] An analogous addition pattern is observed in the $C_{60}Br_6$ molecule, which was established by X-ray diffraction study of crystals of both $C_{60}Br_6$ [32] and its solvates.[4] It has been hypothesized that $C_{60}Cl_8$ can be prepared and its structure should be analogous to that of $C_{60}Br_8$ (symmetry C_{2v}).[33]

Until recently, data on the molecular structure of $C_{60}Cl_{24}$ have been based only on the close similarity of the IR spectra of this compound and $C_{60}Br_{24}$, the relative shifts of the bands in the spectra being well reproduced by calculations.[28] It should be noted that the condition of the absence of atoms X in the adjacent (1,2) positions in the $C_{60}X_{24}$ molecule (which is energetically unfavorable) results in the only possible addition pattern with the point symmetry T_h (see Fig. 2, *b*). The molecular structure with idealized symmetry T_h was confirmed[17] by X-ray diffraction study of the crystal solvate $C_{60}Cl_{24} \cdot 2Br_2$, the crystallographic symmetry of the molecule including only the inversion center (C_i). In the present study, we determined the crystal structure of $C_{60}Cl_{24} \cdot VOCl_3$, which was isolated from the reaction products of C_{60} with $VOCl_3$. In this adduct, the $C_{60}Cl_{24}$ molecule has the higher S_6 symmetry (Fig. 3, *a*), *i.e.*, it is characterized, on the whole, by smaller deviations from the T_h symmetry. For three types of single and two types of double C—C bonds presented in the Schlegel diagram, the following average values were obtained (the calculated values are given in parentheses): a = 1.508 (1.516) Å, b = 1.490 (1.495) Å, c = 1.515 (1.514) Å, d = 1.336 (1.338) Å, and e = 1.345 (1.349) Å, which agree well with the experimental data for $C_{60}Cl_{24} \cdot 2Br_2$.[17] The average C—Cl bond length (1.822 Å) in $C_{60}Cl_{24} \cdot VOCl_3$ is somewhat smaller than that in $C_{60}Cl_{24} \cdot 2Br_2$ (1.841 Å) (the calculated bond length is 1.846 Å) and is apparently more reliable because calculations by the density functional theory[18,19] systematically overestimate C—Cl bond lengths.

Interestingly, the adducts $C_{60}Cl_{24} \cdot 2Br_2$ and $C_{60}Cl_{24} \cdot VOCl_3$ are isostructural with the $C_{60}Br_{24} \cdot 2Br_2$ [4] and $C_{60}Br_{24} \cdot Br_2$ solvates,[20] which crystallize in the same space groups $P\bar{1}$ and $R\bar{3}$, respectively. The fact that the $C_{60}X_{24} \cdot 2Br_2$ solvates are isostructural is quite expected. In both structures, the bromine molecules occupy tetrahedral holes in the packing of halofullerene molecules. The close similarity of the packings in the solvates with one bromine molecule and $VOCl_3$ (Fig. 4) deserves more detailed consideration. In these solvates, the inorganic molecules occupy octahedral holes in the cubic closest packing of $C_{60}X_{24}$ molecules. The distances between the centers of the molecules in the layers perpendicular to the z axis are 12.5 and 12.9 Å for the chloro- and bromofullerenes, respectively, whereas the shortest distances

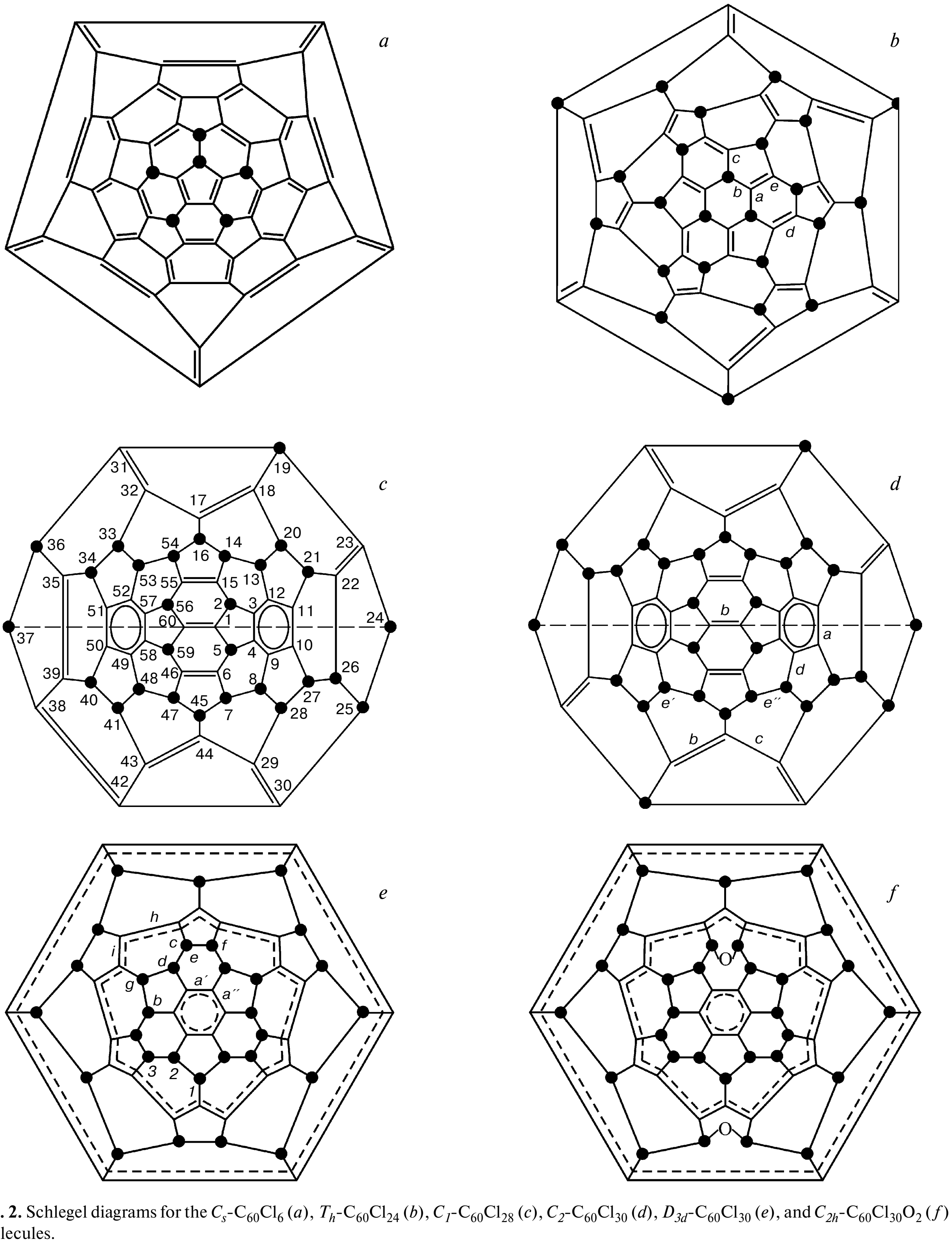

Fig. 2. Schlegel diagrams for the C_s-$C_{60}Cl_6$ (*a*), T_h-$C_{60}Cl_{24}$ (*b*), C_1-$C_{60}Cl_{28}$ (*c*), C_2-$C_{60}Cl_{30}$ (*d*), D_{3d}-$C_{60}Cl_{30}$ (*e*), and C_{2h}-$C_{60}Cl_{30}O_2$ (*f*) molecules.

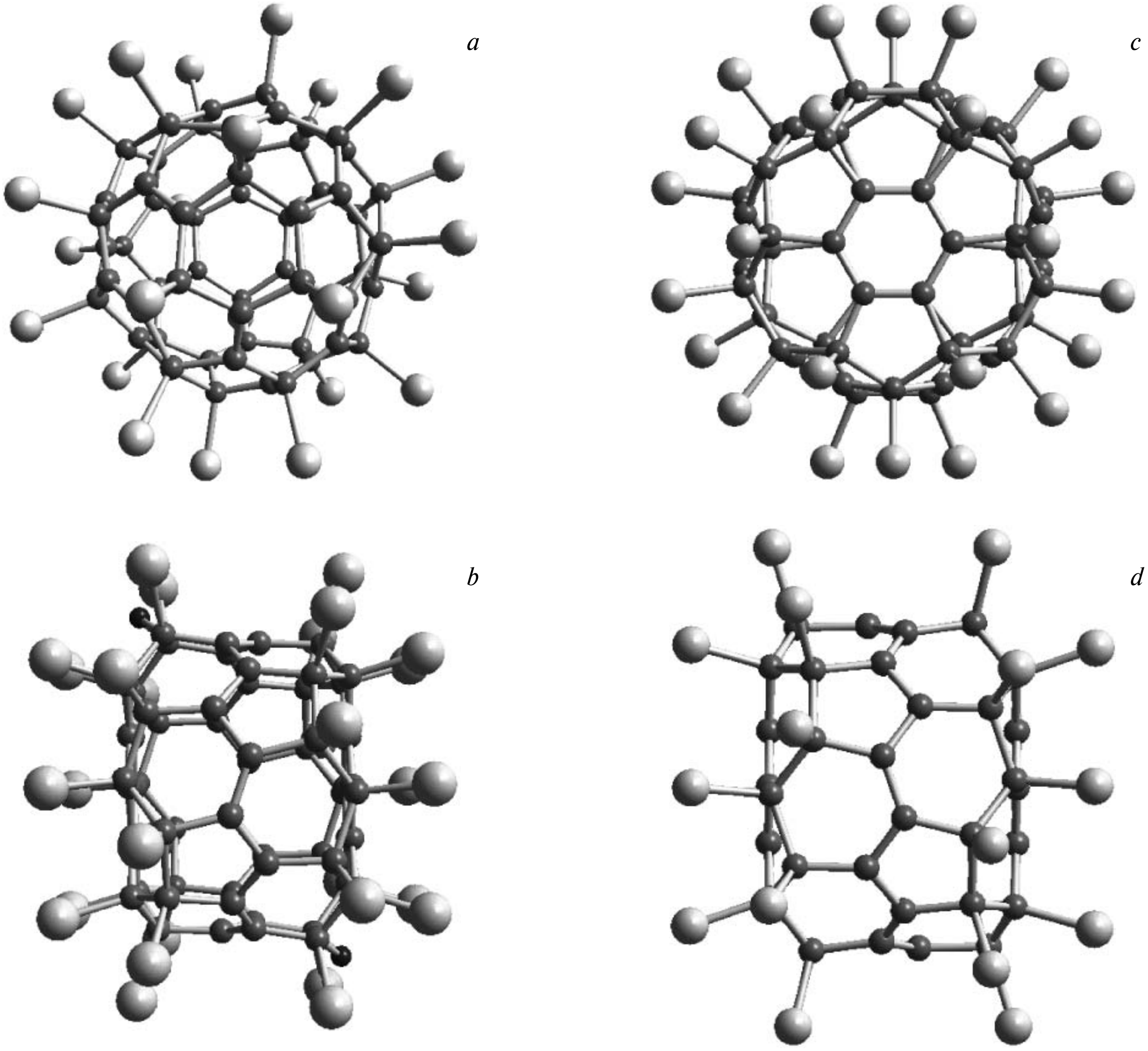

Fig. 3. Molecular structures of T_h-$C_{60}Cl_{24}$ (*a*), C_{2h}-$C_{60}Cl_{30}O_2$ (*b*), and D_{3d}-$C_{60}Cl_{30}$ (two projections, *c* and *d*).

between the molecules from the adjacent layers are somewhat larger (12.8 and 13.2 Å, respectively). The size of octahedral holes in the structure of $C_{60}Br_{24} \cdot Br_2$ is too large to fix a bromine molecule, which results in strong disorder of the latter, so that the bromine atoms of the solvate molecule are distributed over 14 different positions.[20] The bulkier $VOCl_3$ molecule matches well with the size of the octahedral hole, and its disorder is reduced to the presence of these molecules in only two opposite orientations.

Both related structures, C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$, are characterized by the presence of Cl···Cl 1,2-contacts, whose destabilizing effect is compensated by the presence of two aromatic rings inclined with respect to one another (see Fig. 2, *c* and *d*).[18] In both structures, five main types of C—C bonds can be distinguished (these types are denoted by letters *a—e*; see Fig. 2, *d*): delocalized bonds in the aromatic rings (*a*, 1.37—1.40 Å; aver., 1.385 Å); isolated double bonds (*b*, 1.33—1.37 Å; aver., 1.344 Å); single bonds between two double bonds (*c*, 1.43—1.45 Å); single sp^2—sp^3 bonds (*d*, 1.46—1.53 Å), and single sp^3—sp^3 bonds (*e*, 1.58—1.66 Å). The individual C—C bond lengths differ from the calculated values by at most 0.02 Å, and the average experimental lengths for each type of bonds differ from the corresponding calculated values by at most 0.01 Å. An interesting feature of the considerably elongated single bonds of type *e* is that longer and shorter bonds alternate in the chains of sp^3-carbon atoms. For example, the average (taking into account C_2 symmetry) C(Cl)—C(Cl) bond lengths in the C(36)—C(21) and C(25)—C(40) chains in the C_2-$C_{60}Cl_{30}$ molecule are 1.616, 1.637, 1.595, 1.603, 1.660, 1.588, 1.592, 1.649, 1.583, and 1.638 Å. An analogous alternation of the bond lengths is observed in the chains of

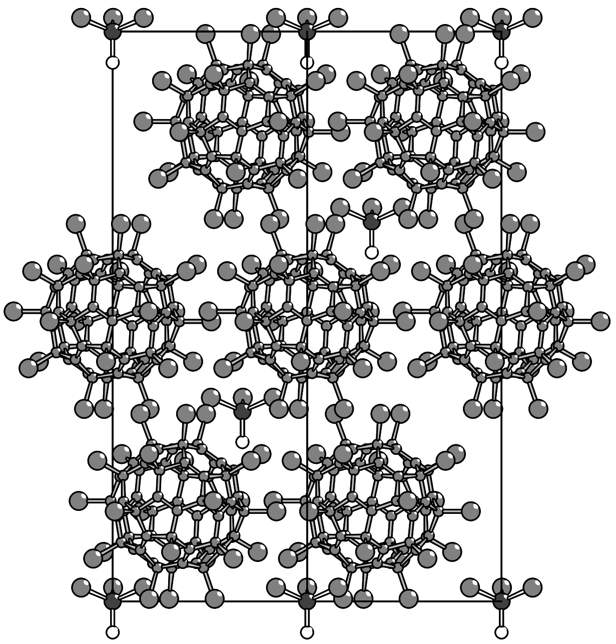

Fig. 4. Packing of the $C_{60}Cl_{24}$ and $VOCl_3$ molecules in the crystal structure of $C_{60}Cl_{24} \cdot VOCl_3$ projected onto the (110) plane. Only one of two orientations of the disordered $VOCl_3$ molecules is shown.

sp^3-carbon atoms in the C_1-$C_{60}Cl_{28}$ molecule. Apparently, these differences should be associated with the mutual arrangement of the adjacent sp^3-carbon atoms rather than with the types of the adjacent rings (5/6 or 6/6).[19] Analysis of these differences demonstrated that the shorter C—C bonds in the chains (*e*´, 1.59—1.60 Å) correspond to the *trans* arrangement of the adjacent sp^3-C atoms, whereas the longer C—C bonds (*e*″, 1.62—1.66 Å) occur in the case of the *cis* arrangement of the adjacent sp^3-carbon atoms.

A comparison of the Schlegel diagrams (see Fig. 2, *c*, *d*) shows that the C_1-$C_{60}Cl_{28}$ molecule is transformed into the C_2-$C_{60}Cl_{30}$ molecule upon the addition of two chlorine atoms to the C(35) and C(42) atoms. The fact that these positions are far apart suggests that chlorination of C_1-$C_{60}Cl_{28}$ to C_2-$C_{60}Cl_{30}$ occurs not as a simple addition of two chlorine atoms at the adjacent positions, but is accompanied by a simultaneous rearrangement of the larger fragment of the molecule. In the C(35)—C(39)—C(38)—C(42) chains, the experimental C—C distances are 1.37, 1.44, and 1.36 Å in C_1-$C_{60}Cl_{28}$ and 1.53, 1.33, and 1.44 Å in C_2-$C_{60}Cl_{30}$, which adequately reflects the character of redistribution of the single and double bonds in this fragment caused by the transformation (simultaneously, the molecular symmetry becomes higher).

At higher temperature, chlorination with $SbCl_5$ or ICl affords chlorofullerene $C_{60}Cl_{30}$ with another structure (see Fig. 2, *e*). The D_{3d}-$C_{60}Cl_{30}$ molecule also contains two six-membered benzenoid rings, but they are parallel to each other. The 15-membered closed chains consisting of sp^3-carbon atoms separate the benzenoid rings from the central 18-membered annulene ring (18-π all-*trans* annulene, the so-called trannulene ring). This arrangement of the structural fragments gives rise to a unique cylindrical shape of the carbon cage as a squirrel cage (see Fig. 3, *c*, *d*). In the previous publication,[19] the molecular structure of D_{3d}-$C_{60}Cl_{30}$ has been established by X-ray diffraction study of the crystals of $C_{60}Cl_{30} \cdot 0.1Cl_2$ and $C_{60}Cl_{30} \cdot 2ICl$. Both structures were solved with good accuracy, due to which reliable data on the molecular geometry were obtained. A slight decrease in the accuracy of determination of the $C_{60}Cl_{30} \cdot 0.1Cl_2$ structure is a result of a relativey low crystallographic symmetry of the molecule (C_i), due to which a larger number of distances of the same type were averaged and is also associated with the presence of chlorine molecules in a nonstoichiometric ratio with respect to the major component. In the structure of $C_{60}Cl_{30} \cdot 2ICl$, in which the $C_{60}Cl_{30}$ molecules have a higher point symmetry (C_{2h}), both iodine monochloride solvate molecules are disordered over several positions, which substantially decreased the accuracy of C—C interatomic distance determination. In the present study, we carried out X-ray diffraction investigation of the solvate $C_{60}Cl_{30} \cdot 2CS_2$, which is isostructural with the solvate with iodine monochloride. It should be noted that the CS_2 solvate molecules are completely ordered (Fig. 5). This fact, combined with a rather high crystallographic symmetry, allowed us to obtain more reliable structural data for the $C_{60}Cl_{30}$ molecule.

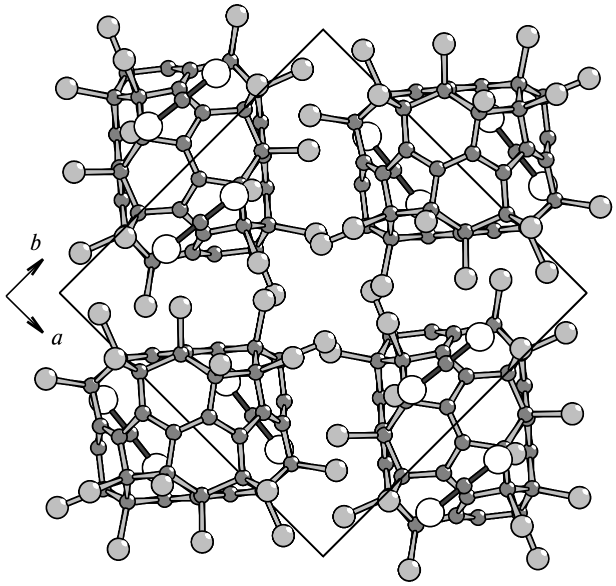

Fig. 5. The structure of $C_{60}Cl_{30} \cdot 2CS_2$ projected along the *c* axis. In layers perpendicular to the *c* axis, the holes in the packing of the $C_{60}Cl_{30}$ molecules are occupied by pairs of CS_2 molecules.

The average interatomic C—C distances (*a—i*, see Fig. 2, *e*) agree well with the experimental data**19** and the results of calculations. The fact that the C—C bond lengths in the benzenoid rings *a*´ (1.368 Å, the calculated value is 1.372 Å) are similar to those in the rings *a*″ (1.375/1.380 Å) provides convincing evidence for the aromatic character of the bonds due to delocalization. The same conclusion can be drawn by comparing the distances of types *h* (1.383/1.381 Å) and *i* (1.392/1.391 Å) in the 18-membered trannulene ring. In the D_{3d}-$C_{60}Cl_{30}$ molecule, this ring is virtually isolated from other fragments containing π bonds, resulting in a high degree of aromaticity, as in the trannulene rings present in the derivatives $C_{60}F_{15}[CX(COOR)_2]_3$.**34** As expected, the sp^2-C—sp^3-C bonds of types *b* (1.475/1.479 Å), *f* (1.509/1.509 Å), and *g* (1.494/1.496 Å) are substantially shorter than the sp^3-C—sp^3-C bonds of types *c* (1.574/1.582 Å), *d* (1.620/1.628 Å), and *e* (1.694/1.699 Å). As in the structures of C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$, the maximum sp^3-C—sp^3-C bond length is observed in the fragments containing the adjacent chlorine atoms in *cis* positions (type *e*). The average C—Cl bond lengths of types *1*, *2*, and *3* are 1.769, 1.784, and 1.782 Å, which are approximately 0.02 Å smaller that the calculated values. The distortion of the shape of the carbon cage in D_{3d}-$C_{60}Cl_{30}$ compared to fullerene C_{60} (the radius of the sphere is 3.53 Å) can be illustrated by comparing the distances from the center of the molecule to the planes of the benzenoid rings (2.61 Å) and to the atoms of the trannulene ring (3.45—3.48 Å). Apparently, it is the presence of π-electron density localized only on the aromatic rings in the D_{3d}-$C_{60}Cl_{30}$ molecule that is responsible for much higher thermal stability of this chlorofullerene (the temperature of decomposition with elimination of chlorine is 450—500 °C)**19** as compared with other known C_{60} fullerene chlorides (300—350 °C).**28**

Earlier studies of fluorofullerenes $C_{60}F_{18}$ and $C_{60}F_{36}$ have demonstrated**35—38** that the insertion of oxygen atoms between carbon atoms to form intramolecular ether becomes possible due to substantial weakening of the *e*-type bonds (which are also present in molecules of these compounds). Structural changes upon the formation of ethers are accompanied by a substantial increase in the distances between the corresponding carbon atoms (and between the halogen atoms bound to these carbon atoms). Analogous structural changes have been observed earlier in the study of the crystals of $C_{60}Cl_{30}$ prepared with the use of a chlorinating reagent that has been insufficiently carefully purified from oxygen-containing impurities. The percentage of $C_{60}Cl_{30}O_2$ in these crystals was 7—8%. In one experiment on chlorination of C_{60} with vanadium tetrachloride, where air entered the reaction system, crystals of chlorofullerene containing a much larger amount of oxochloride were formed. In fact, there is a superposition of the $C_{60}Cl_{30}O_2$ (61%) and $C_{60}Cl_{30}$ (39%) molecules in the crystals. Study of these crystals allowed us to refine the structural characteristics of intramolecular ether $C_{60}Cl_{30}O_2$. The IR spectrum of a mixture of $C_{60}Cl_{30}O_2$ and $C_{60}Cl_{30}$ has new absorption bands at 1063 and 1098 cm^{-1} (see Fig. 1, spectrum *5*) in comparison with the spectrum of pure $C_{60}Cl_{30}$. Calculations confirmed that this region of the spectrum has vibrations of the $C_{60}Cl_{30}O_2$ molecule associated primarily with the ether fragments.

The symmetry of the $C_{60}Cl_{30}O_2$ molecule in the crystal (C_i) is lower than the idealized symmetry C_{2h} (see Fig. 3, *b*). The oxygen atoms are inserted at the bonds *e* of the starting $C_{60}Cl_{30}$ molecule (*cf.* Figs 2, *e* and 2, *f*). The C—O distances are in the range of 1.29—1.34 Å, and the C—O—C bond angle is 106°. However, these values are substantially underestimated due to overlap with the fragment of the unoxidized $C_{60}Cl_{30}$ molecule. The effective C···C distance in the ether fragment is 2.1 Å. In analogous compounds, which contain a much smaller percentage of an oxidized component (~10% $C_{60}F_{18}O$ **36** or $C_{60}Cl_{30}O_2$ **19**), an elongation of the C—C bonds as compared with those in the unoxidized molecule is less pronounced (1.71—1.72 Å). The largest changes in the molecular geometry associated with the insertion of oxygen atoms are as follows: shortening of the nearest bonds of type *c* (1.560 Å as opposed to 1.574 Å for other bonds of the same type) and elongation of the bonds of types *b* (1.493 Å as opposed to 1.481 Å) and *a*´ (1.388 Å; 1.370 Å for two other bonds). Other C—C bond lengths differ only slightly from those in the unoxidized chloride. In particular, the average bond lengths of types *h* and *i* in the trannulene ring are 1.385 and 1.392 Å, respectively, which is indicative of retention of delocalization. The average C—Cl distances (1.776, 1.788, and 1.780 Å) for bonds *1—3* (except for the bonds with chlorine atoms disordered due to superposition of two strongly different fragments of two molecules) differ only slightly from those in the starting chloride. An increase in the volume per molecule for $C_{60}Cl_{30}O_2$ by ~40 Å^3 compared to that for $C_{60}Cl_{30}$ agrees well with the addition of two oxygen atoms.

Thermodynamic and kinetic stability of chlorofullerenes

Data on the formation and molecular structures of chlorofullerenes allow a comparative analysis of their stabilities. Of lower chlorides of C_{60}, only $C_{60}Cl_6$ is known so far. The formation of this compound was rationalized by quantum chemical calculations from both the relative energies of different isomers**39** and consideration of the possible mechanism of the addition of chlorine to C_{60}.**40** High stability of the C_s isomer (Fig. 2, *a*) is apparently associated with the formation of the cyclopentadiene fragment containing two conjugated double bonds.

The T_h isomer of $C_{60}Cl_{24}$ studied earlier[17] and in the present work contains the maximum number of the attached chlorine atoms provided that no Cl···Cl 1,2-contacts are present. It is believed that it is this isomer of chlorofullerene of composition $C_{60}Cl_{24}$ that has the lowest energy. Further addition of chlorine atoms should be accompanied by the appearance of Cl···Cl 1,2-contacts. In the case of chlorides (but not bromides), the formation of higher chlorinated fullerenes occurs due to a relatively high energy of the C—Cl bond. The presence of Cl···Cl 1,2-contacts is partially compensated by the formation of isolated benzenoid rings. In the presence of more than 24 chlorine atoms and in the absence of triple Cl···Cl contacts, the molecule cannot contain more than two such rings.[19] The above-considered C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$ molecules each contain two benzenoid rings inclined with respect to each other. The D_{3d}-$C_{60}Cl_{30}$ molecule also contains two benzenoid rings, which are parallel to each other. Calculations of the energy by the B3LYP method with the extended basis set cc-pVTZ(-f) demonstrated that the D_{3d} isomer of chlorofullerene with composition $C_{60}Cl_{30}$ is 78 kJ mol^{-1} more stable than the C_2 isomer. Hence, the latter is formed only as a result of a particular series of structural rearrangements during chlorination. This isomer can be isolated due to a high potential barrier for the transformation of C_2-$C_{60}Cl_{30}$ into D_{3d}-$C_{60}Cl_{30}$, which is not overcome at moderate reaction temperatures (160—180 °C).

The same is true for the C_1 isomer of $C_{60}Cl_{28}$, which is 6 kJ mol^{-1} less stable (according to calculations) than the hypothetical isomer $C_{60}Cl_{28}$ having the symmetry C_s. This isomer could be prepared from the D_{3d}-$C_{60}Cl_{30}$ isomer by removal of two adjacent chlorine atoms from the carbon atoms involved in the bond of type *e* (see Fig. 2, *e*). We found experimentally that the potential barriers for the structural rearrangements of chlorofullerenes giving rise to the thermodynamically most stable chloride are overcome at temperatures above 250 °C. For example, chlorination of C_{60} or $C_{60}Cl_{24}$ with $SbCl_5$ at 280—300 °C afforded the same product, *viz.*, D_{3d}-$C_{60}Cl_{30}$ (see Table 2, entries *7* and *5*). Heating of C_2-$C_{60}Cl_{30}$ at 300 °C in the presence of $SbCl_5$ (see Table 2, entry *6*) is also accompanied by its transformation into D_{3d}-$C_{60}Cl_{30}$.

It should be emphasized that, due to similarity of the molecular structures of C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$, C_2-$C_{60}Cl_{30}$ can be prepared from chlorofullerene C_1-$C_{60}Cl_{28}$ by the addition of two chlorine atoms. At the same time, a substantial difference in the structures of T_h-$C_{60}Cl_{24}$ (the absence of aromatic rings and the presence of only isolated double bonds), C_2-$C_{60}Cl_{28}$ or C_2-$C_{60}Cl_{30}$ (two nonparallel aromatic rings), and D_{3d}-$C_{60}Cl_{30}$ (two parallel aromatic rings) prevents the transformation of less chlorinated fullerene into more chlorinated fullerene by mere addition of chlorine atoms. Consequently, the transformation of T_h-$C_{60}Cl_{24}$ and C_2-$C_{60}Cl_{30}$ into D_{3d}-$C_{60}Cl_{30}$ should be accompanied by redistribution of a large number of chlorine atoms over the fullerene cage. For example, the rearrangement of T_h-$C_{60}Cl_{24}$ into D_{3d}-$C_{60}Cl_{30}$ requires that 18 Cl atoms were placed to new positions. The thermally induced redistribution of chlorine atoms over the fullerene cage ("chlorine dance") in the case of formation of C_2-$C_{60}Cl_{30}$ from T_h-$C_{60}Cl_{24}$ occurs at moderate temperatures (180—200 °C), whereas higher temperatures (higher than 250 °C) are required for the transformation into the thermodynamically most stable D_{3d}-$C_{60}Cl_{30}$. For fluorofullerenes, redistributions of fluorine atoms over the fullerene cage ("fluorine dance") occur at both high temperatures[41] and room temperature.[42]

* * *

Systematic investigation of chlorination of fullerene C_{60} with inorganic chlorides showed that individual chlorofullerenes $C_{60}Cl_{24}$, C_1-$C_{60}Cl_{28}$, and C_2-$C_{60}Cl_{30}$ can be synthesized at 140—180 °C, the latter two compounds being only kinetically stable. High-temperature chlorination (at a temperature higher than 250 °C) of fullerene C_{60} or chlorofullerenes ($C_{60}Cl_{24}$ and C_1-$C_{60}Cl_{28}$) and heating of C_2-$C_{60}Cl_{30}$ in the presence of a chlorinating reagent afforded thermodynamically stable chlorofullerene D_{3d}-$C_{60}Cl_{30}$.

Investigations into the synthesis and molecular structures of chlorofullerenes demonstrated that these compounds occupy intermediate position between fluoro- and bromofullerenes and are not completely analogous to the latter, as has been hypothesized earlier. A comparatively high C—Cl bond energy makes it possible to prepare chlorofullerenes containing up to 30 chlorine atoms, whereas the limiting compositions for bromo- and fluorofullerenes are $C_{60}Br_{24}$ and $C_{60}F_{48}$, respectively. The fact that chlorination affords the thermodynamically unstable isomers C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$ demonstrates that other kinetically stable chlorofullerenes can, in principle, be synthesized.

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